Creating markets for recycled resources

R&D Report: Plastics

EVALUATION OF WEATHERING IN MIXED POLYETHYLENE AND POLYPROPYLENE PRODUCTS

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1. Executive Summary

This report covers the investigation of the weathering behaviour of mixed waste plastics which is identified as Sub-Project 1 of the WRAP programme (Project Code PLA0007 – 008). The second part of this project, identified as Sub-Project 2 has been reported in a separate document. The work began with a detailed review of the literature on polymer degradation mechanisms with particular emphasis on environmental degradation. This makes up the first part of the enclosed document. The second contains the details of the test methods, results and analysis of the performance of the various materials studied.

The study addresses primary 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, identical products that were subjected to simulated weathering according to a regime of UV and moisture exposure.

The literature review had shown that 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 peroxyl radicals, which further propagate to more stable alkoxy radicals that remain present in the polymer sample.

Competing reactions of chain scission and cross–linking are expected to occur in polyethylene samples, where at high temperatures, chain scission 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. Subsequent addition of stabilisers to aged polymer material (restabilisation) 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.

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 estimated that 1000 hours of UV/moisture exposure corresponds to 1 year of exposure in the natural environment. However, 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.

The results of the study produced the following main conclusions:

- All the materials tested show that the mechanical strength is not significantly affected during continuous exposure equivalent to five or more equivalent years in the field. The results also show that UV degradation has not affected the onset of failure significantly.
- Some changes occur when the materials are taken all the way to failure. In particular the scatter in the results increases. This is consistent with the fact surface damage does occur, especially beyond about 1000 hours of exposure. However, this is not enough to influence design.
- The flow characteristics as measured by the melt flow index (MFI), shows little change in most cases. This is not unexpected for these thick section applications as any UV degradation is limited to the surface.
- The viscosity as measured by rotational oscillating viscometry also shows little variation with exposure to at least 3000 hours.
- The gel permeation chromatography (GPC) measurements show that the molecular weight profile is only changed slightly.
- The variation in field-aged materials and the artificially aged materials shows that in practice, it is difficult to control the composition of the mix coming from the waste

suppliers. This is much more significant for the properties of the materials than any UV exposure.

- Equally, the thermal and shear damage during processing appear to be more significant than subsequent exposure to UV.
- For the above reasons it is 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.

2. Acknowledgements

The study has been made possible with the cooperation of Centriforce Products Limited and British Polythene Industries plc who supplied products which were granulated and converted into test pieces for the study. Further products that had been in use were also supplied. Used wheelie bins made by Plastic Omnium, were also procured from Magpie Recycling. Polypropylene car bumpers were extracted from end-of-life vehicles.

The project was also dependent on the effective cooperation between two separate organisations, RAPRA Technology and the University of Brighton. The willing support of personnel in both organisations is gratefully acknowledged.

Overall funding and sponsorship of the project by WRAP is also gratefully acknowledged.

3. Background

Polyolefin degradation has been reasonably well studied. 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 peroxyl radicals, which further propagate to more stable alkoxy radicals that remain present in the polymer sample.

Heat ageing or weathering brings about the onset of further modification of the polymer, resulting in irreversible changes to the chemical and physical properties of the polymer. Predominantly polyethylene samples experience cross–linking, leading to increases in molecular weight, although this is catalyst dependent. Competing reactions of chain scission and cross–linking occur in polyethylene samples, this is temperature dependent as at high temperatures chain scission is dominant owing to faster movement of the polymer chains. Chain scission of polypropylene samples is the predominant degradation mechanism owing to the higher reactivity of the tertiary carbon based radical.

Regardless of the mechanism of degradation of the polymer, these irreversible changes affect the overall properties of the polymer including melt flow, molecular weight, viscosity and mechanical strength. Reduction in molecular weight (chain scission) leads to shorter polymer chains and decreases in all mechanical properties. Increase in molecular weight (cross–linking) yields stiffer materials; a slight increase in impact strength is also observed, although all the other mechanical properties diminish.

Addition of small quantities of virgin polymer to recyclate can help to maintain most of the mechanical properties, but this is likely due to the presence of stabilisers and additives in the virgin polymer. Subsequent addition of stabilisers to aged polymer material ('restabilisation') can help to recover mechanical performance comparable with the virgin material. Blends of polyethylene and polypropylene usually suffer from more or less limited miscibility [49] A misconception that the properties of a blend will have intermediate properties of the individual components has been shown. Chain scission in polypropylene and cross–linking in polyethylene in mixed blends could counterbalance each other and lead to non–degradative effects. The degradation products from the initial thermal processing step can often act as compatibilisers for the system, especially in very different polymer species. For blends of polyolefins, under thermal reprocessing conditions, the antagonistic effect of individual polymers is not counterbalanced as the two polymers exist in different domains.

Under natural and accelerated weathering conditions many different factors need to be considered. The external conditions the polymer experiences during natural weathering, such as humidity, rain, wind and atmospheric pollutants, need to be known as they affect the rate of polymer degradation. Accelerated weathering has been shown to able to match the polymer degradation of a naturally aged sample, but this is polymer test dependent. 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. Recent development of exposure models to account for the variability of degradation with light intensity, temperature and humidity are noted; these models can also account for variability in a given test on a material and between different tests.

4. Introduction to Weathering

The stability of polymers is essential, especially for outside use, and has attracted much research into degradation reactions and mechanisms.[1-8] 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.[9]

One particular aspect of polymer ageing is degradation of the material in question; in particular this degradation usually affects both the chemical and physical properties of the polymer.[2, 6] 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.[3, 4, 6, 10-22] 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.[10, 23-27]

Two different aspects of polymer ageing have been studied in great detail: thermal degradation and photochemical degradation. This review intends to provide an overview of work that has been carried out in these areas in the past, specifically those related to polyolefins, and to summarise best practice criteria for research and development studies in these areas. It is by no means a comprehensive review of either ageing process, rather it is intended to provide the reader with prior art information of the complex, and often frustrating, area of polymer ageing correlations between natural 'in–field' samples and those studied through artificial methods.

This review is intended to highlight the prior art known in the area of polymer ageing and testing. Whilst it would be ideal for all literature samples to contain no additives or UV stabilisers this is not actually possible. Most materials tested in previous studies have some amount of stabiliser or 'restabiliser' added during the processing stages; very few examples of 'pure' polyolefin polymers have been found to be tested via accelerated or natural ageing methodologies[27-32]. Even the materials that initially have no additives/stabilisers added usually have a percentage of restabiliser added to the recyclate. This review also intends to assess the applicability of accelerated weathering techniques to blended polyolefins, as would be found in plastic products supplied by Centriforce and BPI/Plaswood. Studies on mixed blends of polyolefins (HDPE and PP) are rare, especially without some additive or compatibiliser being employed to assist in the preparation of mouldable samples. In both cases, homopolymer or blended polymers, most of the weathering data has been acquired using thin film samples of 2–250 μm (0.02 – 0.25 mm) in thickness, thus comparison of every variable is not always possible. However, there are some examples of products that have been examined,[24, 25, 33-35] but these usually have stabilisers added to them to upgrade the material for reuse in the same application.

5. Thermal Degradation

There are many papers in the literature concerned with the thermal degradation of polyolefin materials.[4, 36-44] It is well documented that the degradation of polymers begins during the initial heat processing stage during product manufacture.[1, 41, 44-46] If the molecular bond forces are exceeded then chain rupture will occur, this leads to the formation of chain radicals which are well known to initiate degradation (Figure 1).[44]

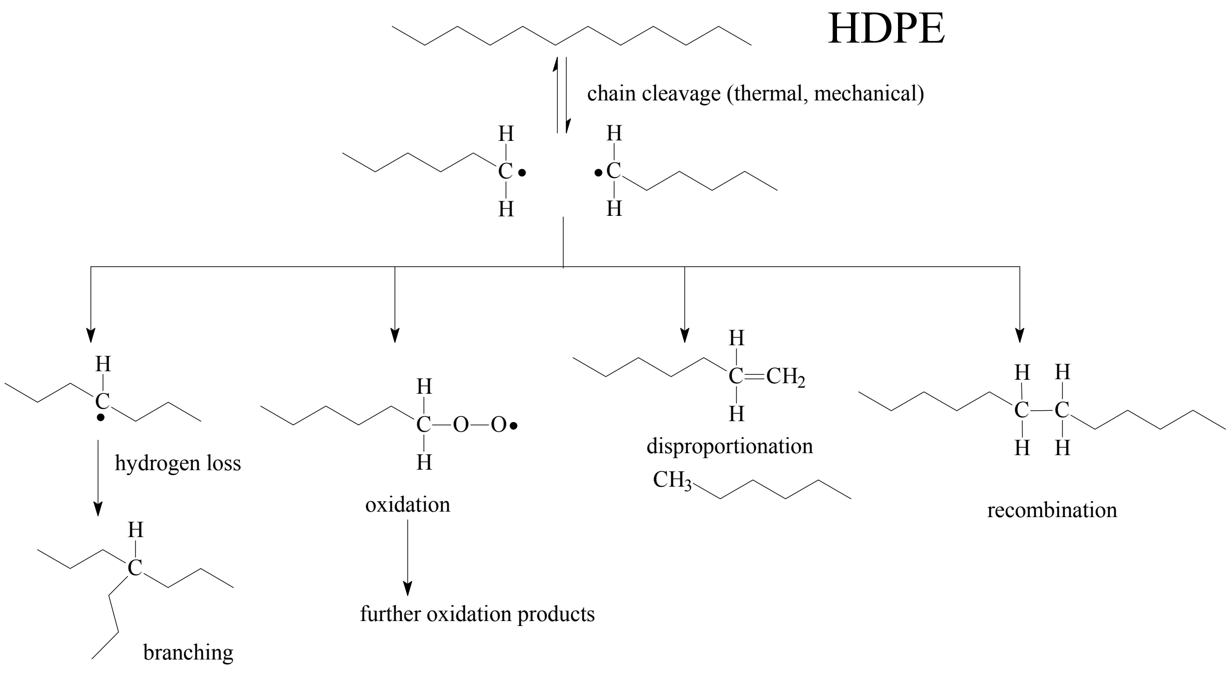


Figure 1: Reactions after thermal processing of polyethylene

As the polymers are organic materials, they 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.[47-49] Figure 1 shows the formation of a radical from chain scission.

Other reactions that polymers can undergo include cross linking and the formation of double bonds.[4, 50] It is also well documented that extrusion is the most severe form of processing that a polymer can undergo.[24] 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 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.[47, 51] This is because of the more reactive tertiary carbon in polypropylene as shown in Figure 2.

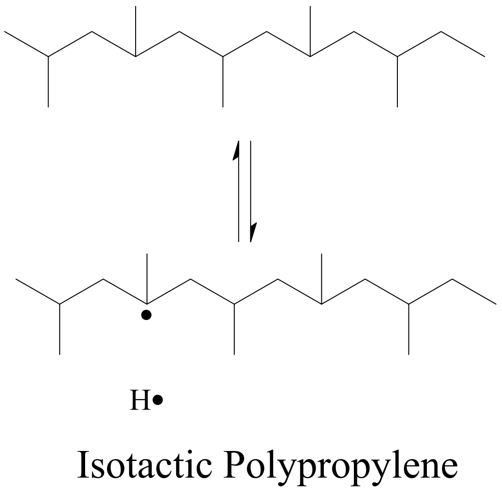


Figure 2: Radical formation of polypropylene

Studies on the repeated recycling of polyolefin materials are available in the literature.[52-54] These experiments analysed the rheological and mechanical properties of a polypropylene recycled up to seven times, using the following reprocessing scheme (Figure 3).[52, 53]

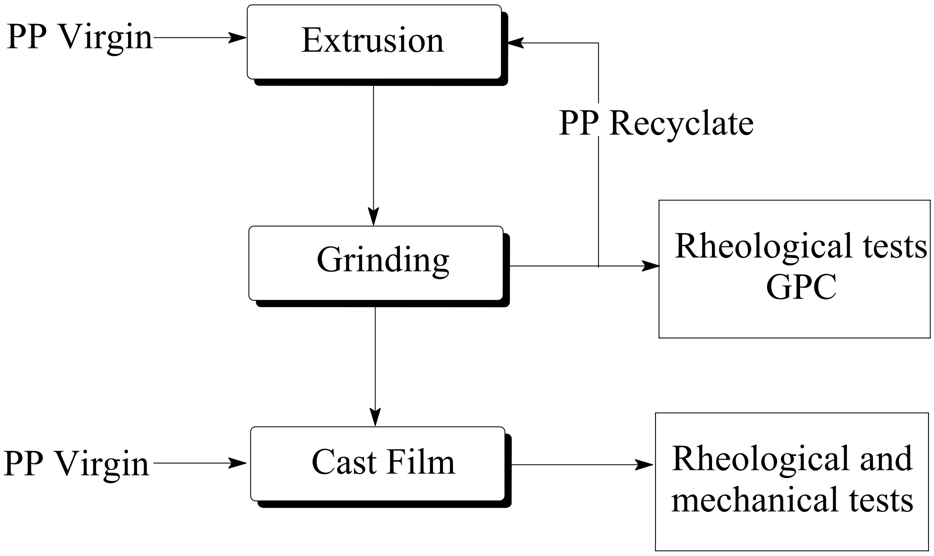


Figure 3: Continual reprocessing scheme

As with so many reports in the literature, the tests are completed on thin films of materials rather than thick specimens. This complicates matters, as samples that are in 'use' are not always film materials, for example plastic crates. Even the literature that discusses the closed–loop recycling of plastic crates uses a 'restabilisation' technique in order to improve the long term stability of the recyclate for re-use in the original application. [24, 25, 33, 34]

During the first processing stage of a polymer, it is likely that the moulding process will be carried out in the presence of air, this means that oxygen will be present and as the polymer is in a molten form this oxygen can diffuse into the 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 1).[1, 5, 55] 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) $R^{\cdot} + O_2 \rightarrow R\text{–}OO^{\cdot}$

2) $R\text{–}OO^{\cdot} + RH \rightarrow ROOH + R^{\cdot}$

3) $ROOH \rightarrow RO^{\cdot} + HO^{\cdot}$

Chain Branching

1) $RO^{\cdot} + RH \rightarrow ROH + R^{\cdot}$

2) $HO^{\cdot} + RH \rightarrow HOH + R^{\cdot}$

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 progressively, the polymer is either modified by 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.[44] 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 polymeric 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; it has regions of high crystallinity and regions that are amorphous.[28] 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 slip through 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 glass like and brittle. Polypropylene crystallinity can vary depending on the polymer's tacticity (Figure 4).

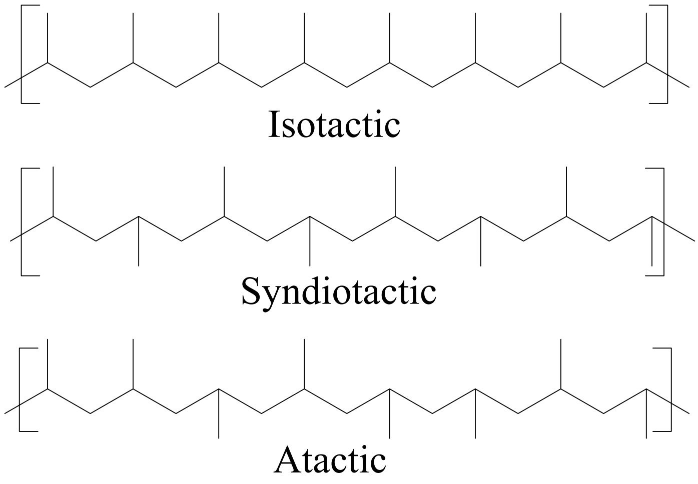


Figure 4: Tacticity of polypropylene

Isotactic and syndiotactic polypropylene are highly stereoregular polymers, unlike atactic polypropylene. Of these, the isotactic form is the most commercially important. The higher the stereoregularity of a polymer, with little or no chain branching, the more likely it is 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).[10] One of the most studied areas of polymer degradation during closed–loop continuous recycling is changes in molecular weight distribution.[4-6, 12, 17, 18, 24, 27, 28, 34, 35, 39, 41, 42, 44, 46, 47, 50-54, 56-71] 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.[52] 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.[24, 51] For example Table 1 shows the physical data for unstabilised high density polyethylenes prepared using different catalysts.[51]

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

Table 1: Physical data for unstabilised 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.

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

Table 2: Molecular weights of virgin HDPE after multiple extrusions [51]

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 a 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.[51] However, crosslinkage 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 stabilisers present, so that experimental observations can be recorded correctly.

Melt flow of the reprocessed polymer is another important characteristic that is often required by manufacturers so they have an idea of how 'well' the recyclate can be moulded. 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.[51] 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,[28] i.e. similar to the results seen for the Philips type catalyst previously.[51]

Another study examined post–use high density polyethylene bottle crates.[24] Although this study was aimed at a restabilisation technique, by the addition of different amounts of stabiliser, a non–stabilised sample was reprocessed at the same time for comparison. This work took 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.[33] 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.[24] 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.[24]

Another study looked at the melt flow properties of recycled HDPE and PP, together with addition of small amounts of virgin polymer into the recyclate.[54] This work only concentrated on a sample of polypropylene with mixtures of virgin and recycled polymer (0.1 and 0.3) 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 undesirable 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.[54] This implies that the properties of the melt flow can remain fairly constant in comparison with 100% recyclate in a closed–loop processing.

Blends of polypropylene and polyethylene, with small additions of PE (10%) to PP shows an improvement of the flow properties, i.e. a decrease in viscosity, but these materials were not examined for further mechanical characteristics.[72] 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.[73] 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 interact with each other 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'.[73]

6. 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 5).[10, 20]

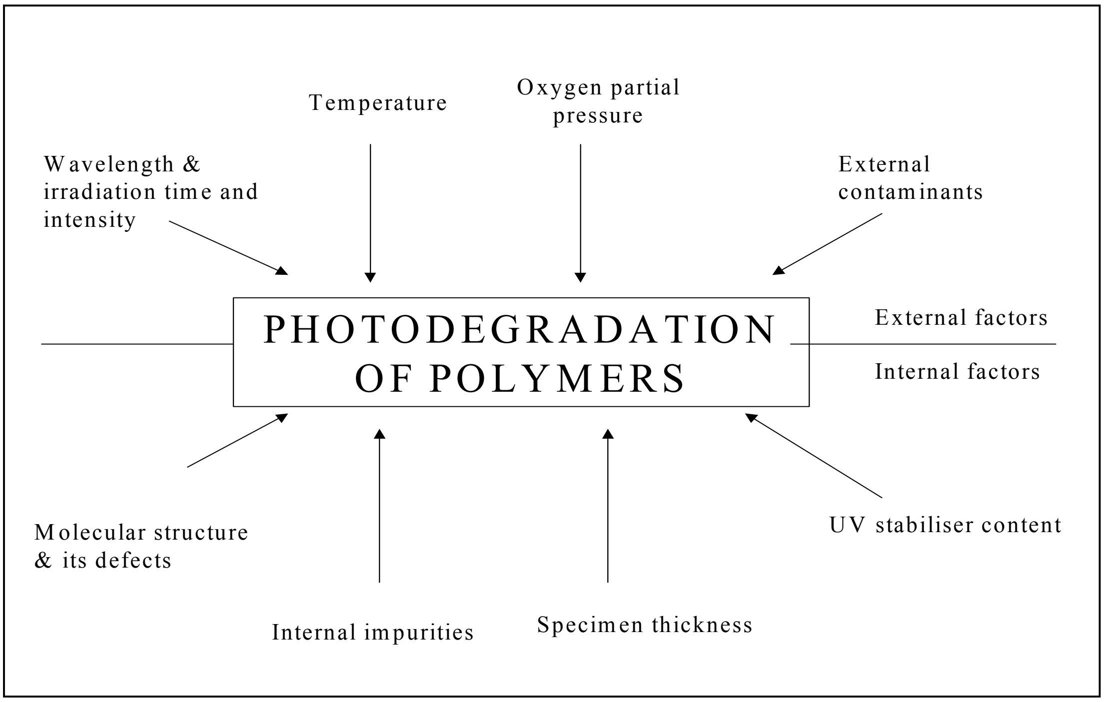


Figure 5: Factors affecting the oxidative photodegradation of polymers

It has been well documented that the ultraviolet (UV) contribution from solar radiation is believed to be a major factor in polymer degradation. The portion of UV light with high enough energy (290–400 nm, an energy of between 412–300 kJ/mol) to break chemical bonds is only about 4–6 % of the mean annual radiation on Earth.[74] 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.[10, 44, 46] 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.

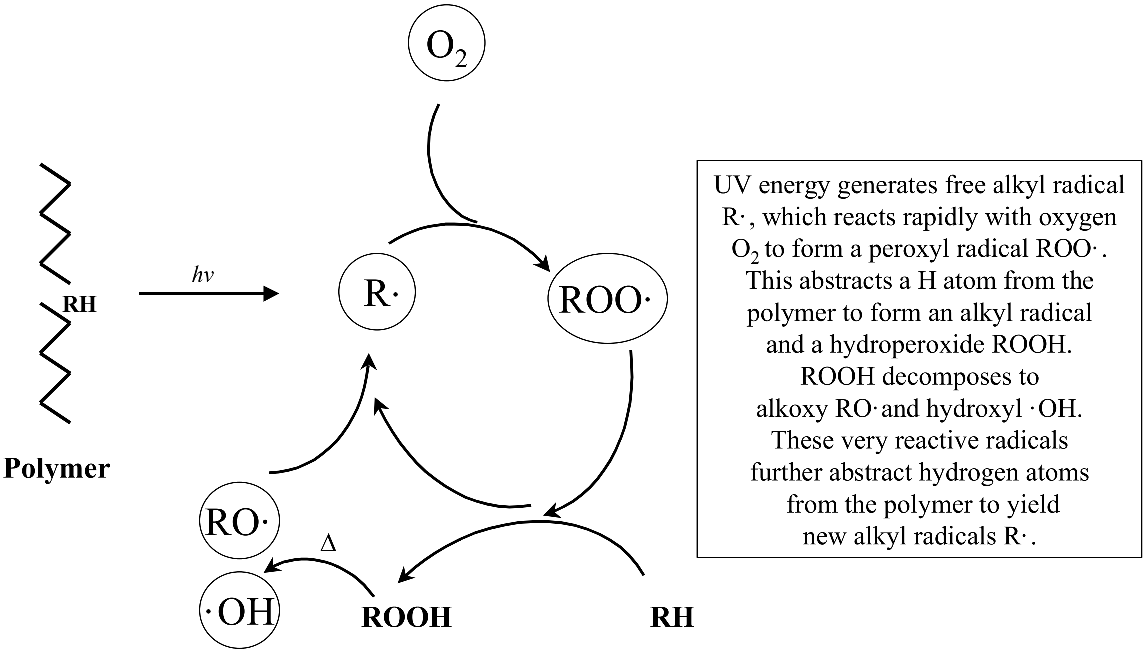
During processing, manufacturing, the polymer can undergo some fundamental, irreversible, changes to the polymer structure. Cross–linking, chain scission, or the formation of double bonds, have been observed in materials manufactured from virgin polyolefin.[1-6, 11, 13, 14, 21, 24, 25, 28, 31, 34, 45, 46, 52, 54, 55, 60, 62, 67, 70, 75] 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.[24, 25, 51]

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.[44, 45] A full synopsis of photochemically initiated degradation of polyolefins now follows.

It has been well documented in the literature that polyolefin materials will degrade through a photo–oxidative reaction path, as shown in Figure 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 susceptibility of polypropylene to these oxidation processes is augmented by the extra branch point, evenly distributed along the polymer backbone, which owing to its tertiary carbon atom renders the hydrogen atom highly reactive.

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.[44, 45]

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.



UV energy generates free alkyl radical R·, which reacts rapidly with oxygen O_2 to form a peroxyl radical ROO·. This abstracts a H atom from the polymer to form an alkyl radical and a hydroperoxide ROOH. ROOH decomposes to alkoxy RO· and hydroxyl ·OH. These very reactive radicals further abstract hydrogen atoms from the polymer to yield new alkyl radicals R·.

Figure 6. Photo oxidative mechanism and radical formation

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).[76] As would also be expected the temperature at which the photo–oxidation occurs is also important; it is often cited that a 10ºC rise in temperature doubles the rate of decomposition.[44] 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.[23, 44] 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.[77] 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.

7. Comparison of Natural and Accelerated Weathering

7.1 Irradiation (Natural)

Only about 4–6 % of the mean solar radiation has enough energy to break carbon–carbon bonds (~400–300 kJ/mol).[74] However, this implies that 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 will ultimately see. 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.[22] 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.[45] This is of course a reasonably apparent observation to make, but of more interest is the observation by Satoto et al[74] 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.[17, 18, 78, 79] 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 stabiliser of polyolefins. Hence, the majority of studies tend to employ pure, light coloured polymer samples.

7.2 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.[59, 80] In 1993, Tidjani et al studied the natural and accelerated ageing of LLDPE films; the former had an average ambient temperature of 25–32 ºC whilst the latter had an average temperature of 60 ºC, 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.[59] 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.[59] To show this effect, Tidjani studied the photooxidation 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. .[20] 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.[20] 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.[59, 81] The work by Shaner[33] 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. 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 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.

7.3 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.[78] It has been observed by Gijsman et al that this increase is enhanced only at elevated temperatures (40–50ºC), although the actual amount of oxygenated degraded products is only slightly higher than those observed at 29ºC. In outdoor tests at lower temperatures it is stated that since the rate of oxygen uptake has decreased, more oxygen is necessary than in accelerated tests at 40-50°C to obtain the same value for carbonyl absorbance or decline in elongation at break. This is attributed to two different degradation mechanisms of oxygen uptake by the polymers.[79] Without going into great detail about these different mechanisms, it is noted that the oxygen uptake by polymers undergoing natural outdoor weathering, the 'normal' oxidation mechanism, occurs at higher temperatures (30-35°C). Therefore oxygen pressure in accelerated testing should be kept to as near that at ambient temperature as possible.[79]

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 sees, and can also play very active roles in the photodegradation of polymers,[82, 83] unfortunately a detailed synopsis of these factors is not possible within this review. 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.[22] 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.[22]

7.4 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.[20, 23, 29, 59, 81] 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.[84] 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 25μm thickness, the same as 3mm).[84] 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.[84] 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 Carlsson et al, which examined the surface and bulk phase oxidation of polyolefins.[32] 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 photodegraded products, because the plate prevented the entry of oxygen through the rear surface. [84]

The role of melt flow index 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.[24, 25, 52, 53, 55, 70, 72] 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,[85, 86] 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.[85]

Degradation studies of blended plastics are also not as well covered as those of their homopolymers. This area is of interest due to the products to be studied that will be supplied by Centriforce and BPI/Plaswood. 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.[87] The compatibility of blends is an important issue, and frequently the degradation products formed upon thermal processing can often act as a compatibiliser 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 compatibiliser. Also, it has been shown that low density polyethylene acts as a stabiliser for isotactic polypropylene by retarding the autocatalytic propagation of tertiary carbon radicals, probably by crosslinking.[64, 88] A simple assumption is often 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.[37, 42, 64]

The work by Camacho et al, uses a variety of different techniques to assess the degradation of the homopolymers as well as the blends prepared.[37] 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.[66, 89] 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. [57] This is even more apparent when an excess of PP is present; the apparent 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,[52, 54, 71, 72] but the actual effect of final lifetime and possible reprocessing has many unanswered questions.[42] 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.[37]

8. 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 and photostabilisers) and metal compounds. [100] In the case of stabilisers, the susceptibility of a polymer to weathering is dependent to a degree on the type and concentration of stabiliser 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.

This review shows clearly that degradation during thermal processing and weathering significantly affect the properties of these materials. 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 effect of degradation is diminished, if at all, by the addition of recycled polymer in blends with virgin material, particularly for products other than film. Thirdly, there is little understanding of the correlation between artificial ageing and natural weathering. 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 many researchers[90-93]. 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.[51] 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.[20, 59, 94]

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 'restabilisers', although some work has shown that addition of virgin polymer to a recyclate can also improve the mechanical properties.[52, 53]

Blends of polypropylene and polyethylene have also been studied. The results of these studies vary in the depth of analysis of the polymer blends.[37, 54, 64, 71-73, 95] There is a lack of information about the mechanical properties for these blended materials. Most investigations have only studied molecular weight distributions or viscosity measurements. It is noted that polypropylene can be stabilised by the addition of polyethylene, in small amounts, and is attributed to the 'dilution' of the tertiary alkyl radicals in polyethylene 'domains'.[64] However, as polypropylene is known to degrade faster than polyethylene, and via chain scission rather than cross–linking, the degradation of polypropylene enhances the oxidation of polyethylene and causes chain scission reactions to dominate the degradation.[37] More work is required to establish and quantify the potential adverse affects of incorporating photochemically degraded recyclate such as polypropylene into virgin polypropylene material.

As all polymers experience thermal processing during product manufacture,[1] 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 5). More recently, exposure models have been developed to account for the variations in photo–oxidation rate observed in different outdoor locations.[91, 96-99] 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.[97, 98] They can also account for the variability that is observed in a given test with different materials and from test to test.

9. Summary of Research Objectives

Sub-Project 1: Weathering of recycled plastics.

Weathering programme to certify recycled products from four different waste streams including mixed plastics waste compound from Centriforce Products Ltd, HDPE wheelie bin granulate from Plastics Omnium Urban Systems Ltd, mixed plastics waste compound from British Polythene Industries plc (BPI) and PP taken from end of life vehicle bumpers.

10. Detailed Objectives:

- To establish a distinct and rapid assessment of stabilisation of recycled plastics from a series of waste streams and certify these for future reuse, that is preferably closed loop.
- To simulate a comprehensive weathering profile, using standard QUV cabinet exposures, with intermittent analysis and data assessment.
- To produce moulded components for testing, both in Brighton and Shawbury, on these recycled materials and to complete full physical testing.
- To investigate closed loop applications for mixed plastics waste.

11. Materials

The work carried out describes the study of materials from four different sources. They are as follows:

- Centriforce - three sets of extruded samples identified by the their colour as blue, brown and black;
- BPI – two sets of extruded samples identified by the product shape as square and rectangular sections;
- Plastic Omnium Wheelie bins – two bins identified by their colour as green and black;
- PP bumper – PP taken from end of life vehicle bumpers.

The PP bumper material was supplied granulated, by Brighton University from a previous research project. This material was added to the original project proposal as it was felt to be a good representative of the kind of recyclate that may be used in outdoor applications. The granules were blended together and injection moulded into test specimens, then exposed to the accelerated weathering cycle.

HDPE wheelie bins were sourced from Magpie Recycling by the University of Brighton. Two bins were supplied; one green and one black. Both were 330 litre bins manufactured by Plastic Omnium in 1991 (these were the only identification marks that could be found to give an idea of the history of the material). As such they have undergone approximately 104,000 hours in the environment. Assuming 12 hours of UV exposure per day, this gives an upper limit of 52000 hours of UV exposure. The bins were chopped into suitable sized chunks and granulated. It was decided that the two colours would be run as separate streams since the different colours could respond differently to UV radiation. Test specimens were injection moulded from the granules before being subjected to UV exposure and testing according to the test schedule.

Samples supplied by Centriforce Products Ltd comprised a range of recycled HDPE from "jazz" to natural bottle scrap. According to the supplier, the recyclate could contain a nominal percentage of PP. The material also contains 4% polyethylene encapsulated pigments and 1% Hydrocerol BIN as a blowing agent. It also contains Northern European UV 10 stabiliser. Nine forms of extrudate were supplied, in solid and hollow form. They were grouped according to colour for the subsequent tests. Field-aged material was supplied by Centriforce in July 2003. This material had been in the field for approximately 1 year. This represents UV exposure of approximately 4500 hours assuming that exposure is limited to 12 hours per day.

Samples supplied by British Polythene Industries plc (BPI) comprised black pigmented polyethylene recyclate, which, according to the supplier, could include waste from agricultural applications. Three types of samples were provided, two of which comprised unused "Plaswood" sections, which were used in the accelerated weathering tests. The field-aged BPI samples had been in the field for approximately 3-4 years, representing 13000 to 17000 hours of real-time UV exposure. In terms of composition of the material, it was not possible to obtain exact quantities as the blend varied in accordance with the material available. However, an approximation was given as follows:

Polymer	Typical source
60% LDPE	Industrial waste, bottle tops
20% HDPE	Plastic cores, crates, bottles
10% Carbon Black Masterbatch	Masterbatch supplier
10% PP	Bins, cores, crates

The material is processed using an extruder in line with a bank of steel moulds. This process is better called intrusion. The processing temperature range is 190-240 °C.

All the materials in Sub-Project 1 were acquired in product form. They were prepared by cutting, granulating, washing and drying and then converting into test pieces without further additions. The wheelie bins and PP bumper materials were prepared and fully tested at RAPRA. The Centriforce and BPI samples were prepared at the University of

Brighton. The tensile and MFI tests on these materials were carried out at the University of Brighton and the remaining tests at RAPRA. The UV exposure tests consisted of a programme of alternating UV and moisture exposure according to manufacturer's guidelines. The number of specimens exposed at any time was restricted only by the capacity of the UV cabinets.

It was decided at the December 2002 meeting that exposure to 9000 hours or longer would be unnecessary, as the new UV test method was an improvement on the original specifications. Whereas, in the older cabinets, UV lamps would progressively deteriorate and therefore deliver a decreasing UV intensity during tests, the new cabinets provide constant intensity by compensating for the degradation of the lamps. Therefore, the total cumulative UV dose received by the samples is achieved in a shorter time period. With traditional fluorescent UV tubes, the radiation intensity drops off rapidly with time. Therefore, it was difficult to determine the total UV dose.

12. Experimentation - Physical Methods

12.1 Test specimen injection moulding

The sample material was cut into small sections initially to enable granulation. After granulation, the material was washed and oven dried at 60°C. The granules were stored in desiccators ready for moulding. Test specimens were produced at Rapra and Brighton by injection moulding to type 1A tensile dumbbell configuration (BS 2782-9) using the following conditions:

Shot size:	42mm
Injection Pressure:	75 bar
Hold Pressure:	25 bar for 5 seconds
Temperature:	180° C nozzle (generally)
	190° C barrel (generally)

12.2 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^2 @ 340 nm. This is considered a good match with noon summer sunlight. 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 4500 hours, with some continuing up to 6000 hours.

UV and Sunlight simulation

The QUV uses fluorescent UV lamps because they are more stable than other types of lamp and provide more reproducible test results. The UVA-340 lamp gives a good simulation of sunlight in the critical short wavelength region from 365 nm down to the solar cut-off of 295 nm. This lamp type produces only those UV wavelengths found in sunlight.

The Solar Eye irradiance control system on the QUV is a precision light control system, which continuously monitors the irradiance from the UVA-340 lamps. Any change in UV intensity (brightness) is detected via four sensors at the sample plane. The Solar Eye compensates for lamp ageing or any other variability by adjusting power to the lamps. The fluorescent tubes were calibrated every 400 hours.

12.3 Tensile Test

The tests are carried out using a Shimadzu tensile tester at Brighton and an Instron universal tester at Rapra in accordance with BS 2782, Method 320A to 320F. It was expected that as materials degrade, key 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 therefore dependent on the following factors:

- rate of loading and therefore strain-rate
- time of application of load
- Previous loading history
- temperature

The tensile test is a constant strain-rate test. In this case, the specimen is clamped between platens (Figure 6) and one platen is allowed to move at constant speed relative to the second. In addition to the strain-rate, the temperature must also be kept constant.

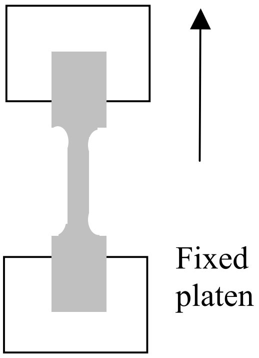


Figure 6: Tensile Test

The behaviour of solid polymers can be classified into a few different types where the mechanisms by which they deform are similar and independent of the nature of the material. Figure 7 below is a generic representation, where the critical 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.

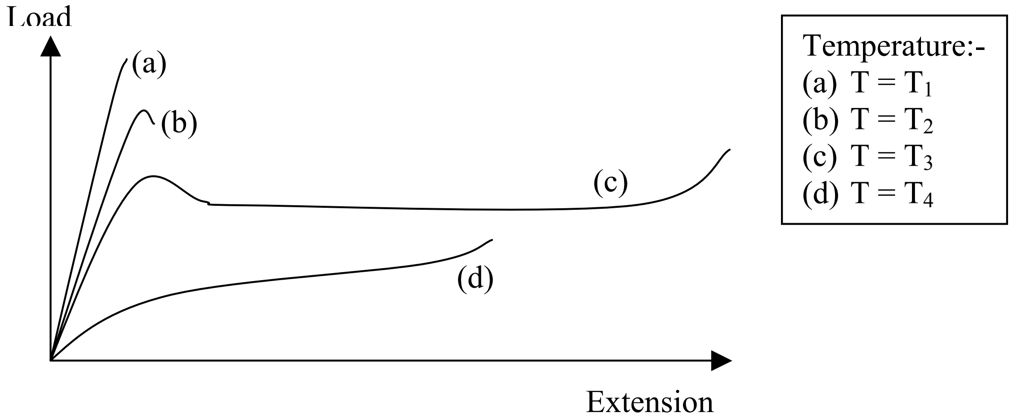


Figure 7: Typical Test results for solid polymers

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

Curve (b) - 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. This is true for semicrystalline polymers.

Curve (c) - At T_3 ($>> T_G$), necking is followed by cold drawing. This is only possible with semicrystalline thermoplastics and so is indicative of significant crystallinity. High Density polyethylene, which is more than 90 % crystalline, and syndiotactic and isotactic polypropylene, which are over 80 % crystalline, will show such behaviour. However, low density polyethylene, which is about 50 % crystalline, will not.

Curve (d) - 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. Low density polyethylene should show such behaviour.

The behaviour can be explained with reference to curve (c) in Figure 7 which contains all the features seen in curves (a), (b) and (d). Hence this curve is reproduced below as Figure 8:

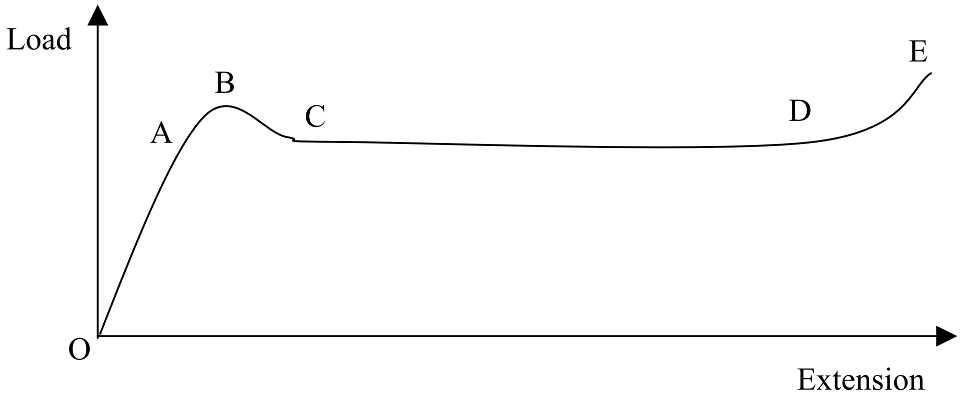


Figure 8: Tensile test behaviour incorporating cold drawing

As the specimen is forced to extend at a constant velocity, the load increases and the material deforms in an elastic manner. The limit of this behaviour cannot be determined easily but has been identified with point A in the graph above. The load eventually reaches a maximum at point B. Until this point is reached, the specimen would have deformed uniformly and so changes in the shape of the specimen are hardly noticeable. However, at point B, the deformation becomes localised. The load drops quickly to point C as the cross-sectional area at a point along the specimen reduces. This is described as necking. Between points C and D, three regions are clearly defined. 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.

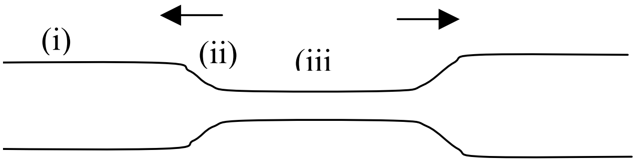


Figure 9: Development of a neck at the onset of cold drawing

The stress calculated from the load at C is regarded as the Yield Stress of the original material. This is also referred to as the 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. A true stress – true strain graph may be obtained by applying the Considere construction.

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. This quantity is regularly used at Brighton as a measure of the failure characteristics although not required in industry. In the RAPRA-based tests, a measure of the failure stress is given in terms of the load at failure and the initial cross-sectional area. This will be referred to as "Tensile Strength at Break".

The behaviour described for curve (c) is generally seen for semicrystalline polymers when the test temperature is significantly greater than the glass transition temperature, T_G. In the case of high density polyethylene (T_G = -12 ^oC) and polypropylene (T_G = -10 ^oC), tests at ambient temperature will produce this result. It is also important to maintain the strain-rate at a low level. On increasing the strain-rate, the behaviour observed becomes more like curve (b). At very high strain-rates, brittle failure as indicated by curve (a) will be seen.

12.4 Impact Test

Izod impact tests are being carried out on notched samples in general accordance with BS2782. The specimen is held at one end and struck close to the free end with the notch at the fixed end. Thus at impact the specimen resembles a cantilever beam under bending, set up to open up the notch. The impact test is an extreme example of the tensile test as the notch tip will be under high tensile stress at impact and the rate of strain would also be very high. It is a measure of the toughness of the material as the test measures the energy required to completely fracture the sample. As such, any flaws in the material now dominate the behaviour observed. It is therefore expected that as the material degrades, lower impact strength should result.

12.5 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. 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 are 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.

13. Experimentation - Analytical Methods

Measurement of physical properties of the materials gives an indication of degradation and the bulk behaviour of the material. Analytical techniques are being used to investigate how the polymer is changing during the ageing process. The three techniques being used are Infrared spectroscopy, Gel Permeation Chromatography and Rotational oscillating viscometry.

13.1 Microhardness

Surface hardness of the exposed samples is measured using a Denison-Matsuzawa microhardness machine in general accordance with the manufacturers guidelines. Microhardness measures the surface hardness on the Vickers hardness scale. Typically a 10g force is used by the diamond indentor.

13.2 Gloss and colour

During degradation, the chemical changes in the polymer result in changes in 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. Therefore the changes in colour and gloss are being measured using a Minolta colour and gloss meter.

13.3 Gel permeation chromatography (GPC) Method

Sample Preparation

A single solution of each sample was prepared 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.

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.

Interpretation of GPC results.

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.

GPC gives the molecular weight distribution of a polymer in the form of the following data. The number average molecular weight (M_n) which is the average molecular weight calculated from the common average weights of the individual molecules. The weight average molecular weight (M_w) is calculated by weighing a number of molecules. The sum of the square of the weights is then divided by the total mass of all of the sampled molecules. The polydispersity is the ratio M_w/M_n and this gives an indication of the spread of molecular weight distribution. A high polydispersity means 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. A highly degraded material will show a narrow distribution of low molecular weight material (i.e. curve will have a narrow peak, over to the left of the graph as shown in Figure 10).

Crosslinking 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.

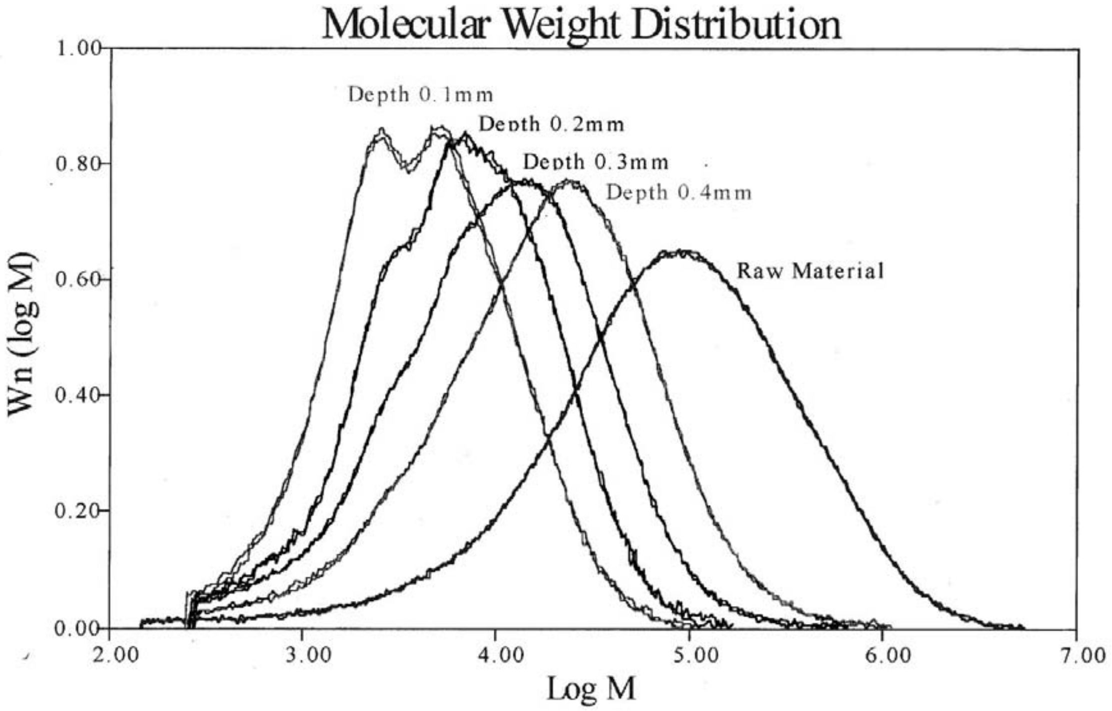


Figure 10 Molecular weight of a PP exposed to UV radiation.

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.

13.4 Infra-Red Spectroscopy

The end product of a chain scission degradation reaction is the oxidation of a polymer group, leading to the production of a carbonyl molecule. The presence of carbonyl groups show up as absorption peaks in the range of 1690-1760 cm^{-1}. The absorption peak height gives an indication of the degree of oxidative degradation.

Other termination reactions can produce different molecular groups in the polymer. Therefore, the changing molecular structure can be shown during degradation.

13.5 Rotational oscillating viscometry

The oscillation technique involves applying a sinusoidal oscillating stress wave to the polymer melt and measuring the resulting strain wave. Figure 11 below indicates how the test is run.

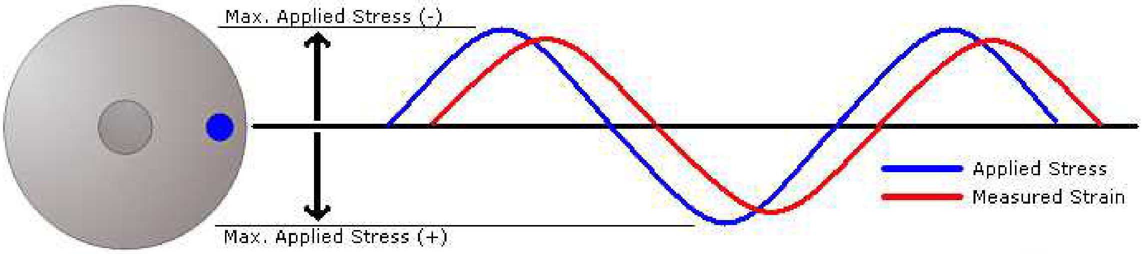


Figure 11 Schematic of the oscillatory measurement method.

A purely elastic (hookean) material will retain all of the deformation energy applied to it and therefore have a phase difference (phase angle) of 0 degrees (Figure 12a). Conversely, a purely Newtonian viscous fluid will have a phase angle of 90 degrees. Most polymeric materials are visco-elastic and demonstrate a response that falls somewhere between the two extremes (Figure 12c).

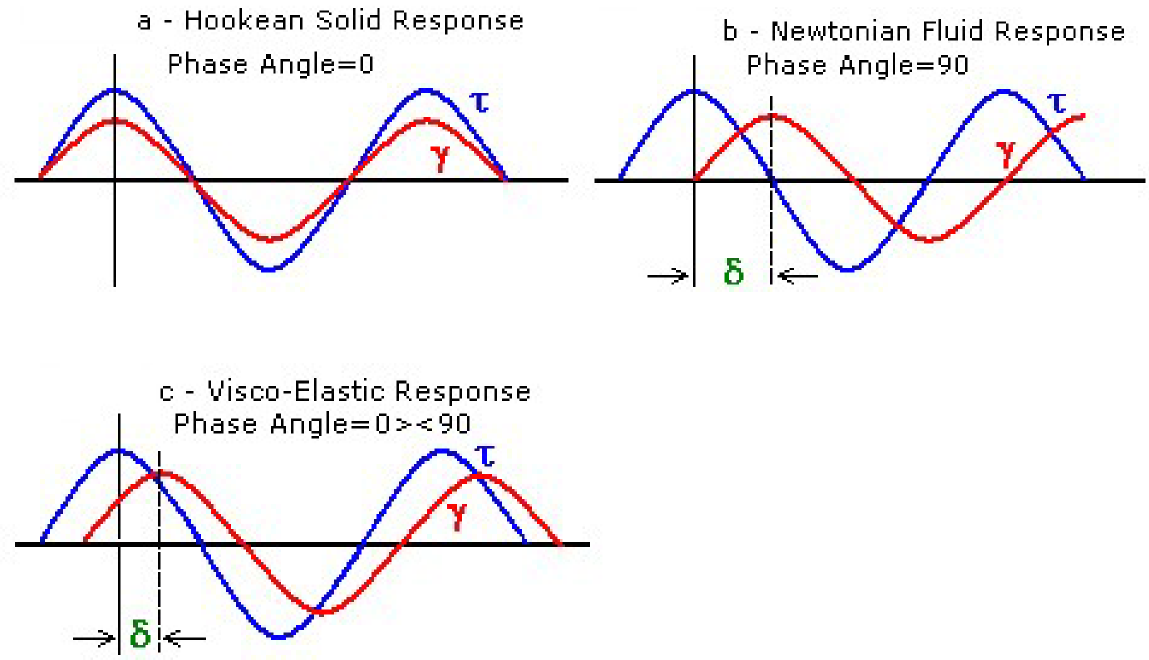


Figure 12 Phase response of fluids under oscillating stress.

Measurements are made over a range of frequencies at constant temperature and a family of curves generated. Data of most interest derived from these oscillation strain control measurements are the complex viscosity (η^*), the phase angle (^{o}) and the storage and loss modulus (G' and G"), as a function of frequency. An example of such results is given in Figure 13 for acetal.

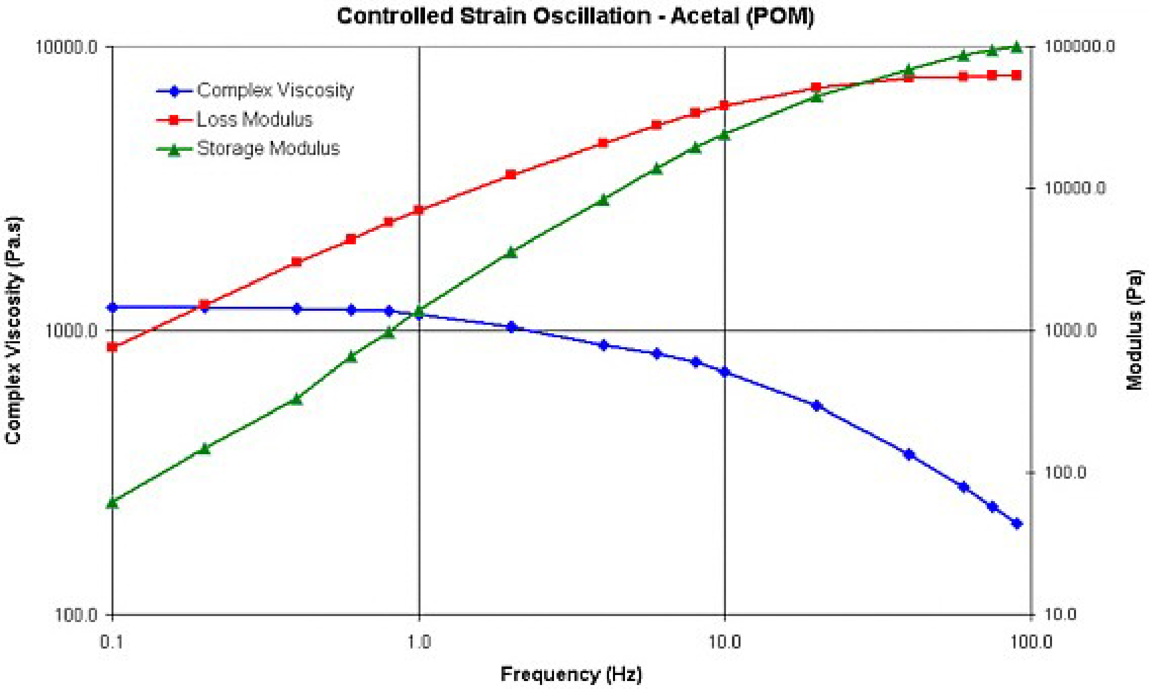


Figure 13 Typical results generated for an acetal.

The point at which the storage modulus (G′) and the loss modulus (G″) cross can give a good indication of the magnitude of the molecular weight of a polymer and the molecular weight, as shown in Figure 14.

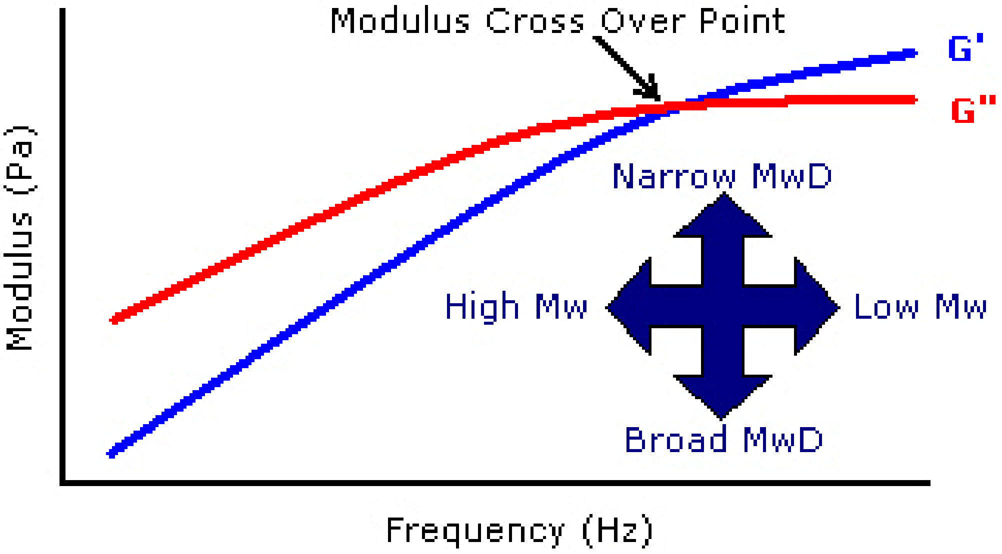


Figure 14 Change in position of the G′/G″ crossover point with molecular weight.

Work done at Rapra has shown that the correlation between crossover frequency and molecular weight is good in HDPE (as shown in Figure 15). The advantage of measuring molecular weight using rotational rheometry techniques is that samples can be compared directly from batch to batch and the test procedure is easier to set up and quicker than GPC since there is no need to use solvents to dissolve the polymer. Therefore, it is likely that the use of rotational viscometry will increase in the future as a quality tool for thermoplastics.

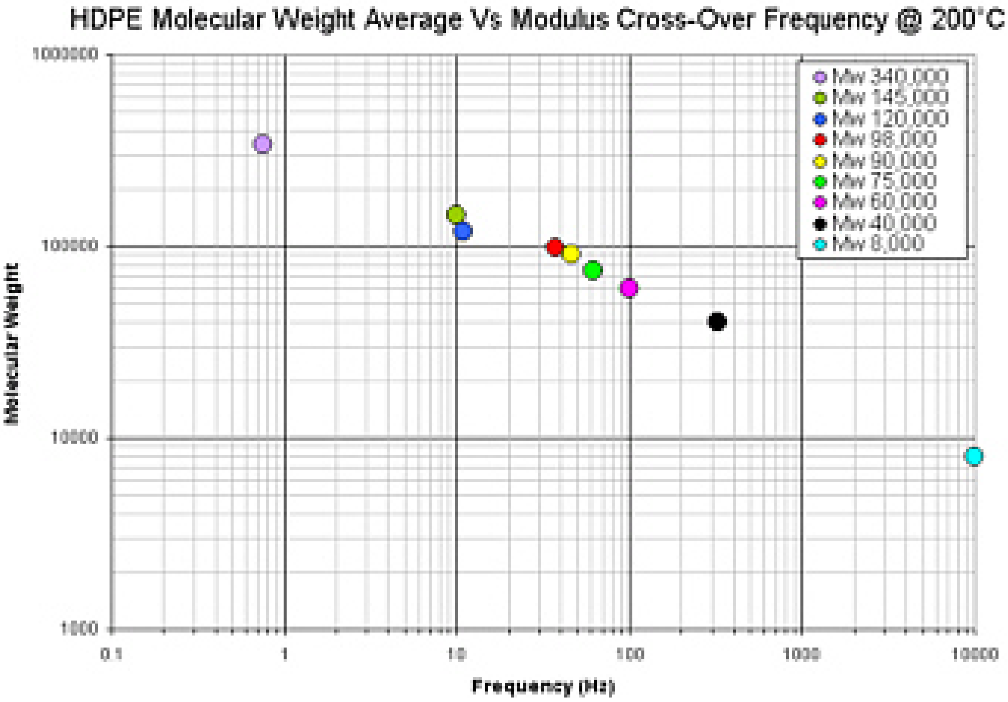


Figure 15: G′ and G″ crossover frequency vs molecular weight for HDPE.

14. Effects of UV Degradation

Results for all the tests are displayed graphically in Appendix A1. As tests were carried out for time periods ranging from 100 hours up to 6000 hours, it was deemed more appropriate to present the results against log exposure time. For comparison, the results for samples that were not exposed to UV radiation have been presented nominally at 10 hours of exposure.

14.1 Tensile properties

The green and black wheelie bin materials give yield stress or tensile strength of approximately 27 MPa and remain constant for tests up to 5000 hours (Appendix A1.1). The Strength at Break in both cases is much lower at around 5 MPa. This measure is likely to be variable as it is dependent on the presence of microscopic flaws within the structure and represents the moment when the lasts strands of material give way. The results however show that UV degradation has not affected the onset of failure significantly. The strain at yield is approximately 10 % and shows a slight increase with UV exposure. As the yield stress does not change, this may suggest that many flaws created at the surface, are now enabling deformation. The strain at failure is much more variable as would be expected. However, the values of 200 % to 400 % would suggest that the material is significantly ductile. The green material does not show any loss of ductility although the black material, with the lower strain to failure, shows further decrease from around 1000 hours of UV exposure. Since yielding is a property of the amorphous / crystalline interface it is not expected to change as much as the behaviour at failure, which is dependent on flaws in the material. Hence it is not surprising that significant damage is beginning by 1000 hours of exposure. The tensile modulus, being dependent on the resistance to elastic deformation and therefore primarily the amorphous network, was not expected to change with UV exposure.

The polypropylene bumper materials show virtually no change in static tensile properties with exposure except for a slight increase in the strain at yield beyond 1000 hours. This material has experienced natural degradation in use and had been subjected to UV exposure to 6000 hours. Clearly, the product is deemed to withstand such severe UV exposure.

The Centriforce materials show tensile strengths of about 25 MPa which remain constant with exposure. The Failure stress remains reasonably constant between 70 and 90 MPa although in the case of the blue material, the value drops considerably after 1000 hours of exposure. In the case of the black material, there is a great deal of scatter and again the failure stress seems to fall beyond 1000 hours. The Field-aged materials show similar tensile strengths to the UV aged materials. Hence it appears that UV degradation, being a surface effect, does not damage the mechanical integrity of the material from a design point of view. The failure stress of the field-aged materials remains within the error band for brown and black materials although the value is much lower for blue. In this case, the strain measurement shows that the material failed in a brittle manner at about the yield point. The strain at yield is again very similar for the three grades at a value of 20 % but the elongation to failure varies form 120 % for Brown to over 400 % for the Blue and Black grades. All three grades show a decrease in elongation to failure with UV exposure and significantly at above 1000 hours in the case of the blue and to a certain extent for the brown.

The BPI samples are virtually identical in mechanical terms. Their tensile strength of 12.5 MPa is expected, for a grade of mixed polyolefins. The Failure stress is twice as high and the Field-aged samples show slightly higher corresponding limiting stresses. These materials possess the highest strain to yield, which is virtually identical to the elongation to failure. This reflects the predominance of LDPE, which is significantly amorphous and also rubbery in character.

14.2 Microhardness

Surface hardness measurements (Appendix A1.2) carried out on the wheelie bin materials show no change up to 1000 hours of UV exposure after which the black material seems to show a huge rise. The green material shows a small rise. This is unexpected and may suggest a localised effect. The PP bumper materials show some variability but there is little net change. The Centriforce materials display small changes with the brown and the blue tending to increase after 1000 hours and the black tending to fall after the same length of exposure. The changes are of the order of 10 %.

14.3 Impact behaviour

The impact behaviour (Appendix A1.3) of the wheelie bin materials remains reasonably constant at approximately 10 kJ/m^2, although there is significant scatter in the results. The scatter is an indication in part of the presence of flaws in the material and so it would have been expected that any degradation should increase the scatter. This is not evident except possibly in the black material at 5000 hours. Polypropylene bumper materials give a much higher impact strength of 42 kJ/m^2 which would be expected for the application. There is significant scatter but, following a slight rise on first exposure, the average value remains constant for exposure from 100 hours to 3000 hours. The Centriforce materials show significant variation. There is a suggestion that the brown grade might in fact have become tougher by 3000 hours of exposure. Starting with the lowest impact strength of 16 kJ/m^2, the figure jumps to 23 kJ/m^2, which is nearer the value for the black grade. The black grade shows a decrease from 27 kJ/m^2 to 23 kJ/m^2. The blue grade shows the greatest scatter although averaging at 35 kJ/m^2. For the BPI materials, it is seen that at the onset of UV exposure there is a large decrease in impact strength for both grades. Thus at 100 hours of exposure, the first point of testing, there has already been a decrease of about 30 % in the rectangular sections and nearly 45 % in the square sections. By 1000 hours of exposure, the drop is about 50 % in both cases after which there is a suggestion that the value becomes constant. The rectangular sections show the higher impact strength before UV exposure and maintain that higher value at all stages.

14.4 Melt Flow Index

The melt flow index (Appendix A1.4) shows little change in most cases. The highest value of 8 g/10 min is measured for the PP bumper materials. This is followed by a value of 3.5 g /10 min for the wheelie bin materials. The values for the green show no change but the black shows a 30 % increase beyond 1000 hours. The BPI samples have values of about 1.5 g/10 min, decreasing by about 5 % in the case of the square sections and about 12 % in the case of the rectangular sections. In both cases, the MFI of the field-aged samples is much less than that of the UV exposed samples. The Centriforce samples have the lowest

MFI values, which also confirm that they are extrusion grades. In the case of the Blue grade, the MFI appears to be decreasing especially beyond 750 hours of UV exposure. The MFI values for field-aged materials in the case of the blue and brown grades are very different from the UV exposed results, suggesting significantly different materials. The Black grade however gives a value of about 0.45 with little variation even for the field-aged sample.

14.5 Rotational Oscillating Viscometry

The viscosity as measured by rotation oscillating viscometry (Appendix A1.6) show little variation with UV exposure for the PP bumper material up to 5000 hours. The wheelie bin grades however, show a significant drop in viscosity at 3000 hours after showing little change up to 1000 hours. There is no further change to 5000 hours. This indicates the onset of significant degradation with increased exposure. The BPI samples show higher viscosity in the field-aged samples than the UV aged samples. The square section samples also show the greatest variability from one level of exposure to another. The Centriforce blue samples also show some variability with UV exposure. In the case of the blue grade, the field-aged samples show greater viscosity whereas the other two grades show lower viscosity in the field-aged samples.

The BPI and Centriforce show a fair degree of scatter and this is probably due to the variability of the material rather than degradation effects. Factors that will effect the viscosity will include filler content, the localised polymer blend for the test sample (different melting points and molecular weight), degree of degradation and plasticisers. Overall it does not look like a good test for mixed plastic materials as there are too many variables that cloud the behaviour.

14.6 Gel Permeation Chromatography

The molecular weight distribution (Appendix A1.7) of the wheelie bin materials are similar and show little change with UV exposure. However, the drop in values of the number-averaged molecular weight, M_n and the weight-averaged molecular weight, M_w is significant, suggesting that chain scission is taking place. The PP bumper materials show a slight decrease in M_n while M_w remains constant up to 1000 hours. Beyond 1000 hours, both values fall. The results for the Centriforce grades show significant fluctuation in values although there is a trend to narrower distribution in the blue and black grades. The brown grade indicates a widening distribution. The BPI grades show slight decrease in both M_n and M_w. This leads to a slightly widening distribution of molecular weights.

14.7 Colour and Gloss Change

There is considerable scatter in the measurements of gloss and colour change as might be expected. However as can be seen in Appendix A1.5, there are clear trends that can be identified. In the case of the PP bumper material, there is a small initial colour change with UV exposure, but then there is little change with exposure from 100 hours to 6000 hours. The gloss levels appear to increase with exposure.

In the case of the green wheelie bin material, there is little change in the gloss levels with exposure whereas the colour change shows a stepwise rise at initial exposure and then a progressive increase beyond about 750 hours. The black material shows almost exactly the same colour change although the gloss levels in this case fall beyond about 1000 hours.

The Centriforce materials show quite different levels of colour change, being greatest in the case of the blue, by a factor of 10. In all cases, there is a stepwise change with exposure. In the case of the black grade, there is then a small increase up to 1000 hours followed by a large increase to 3000 hours. In the case of the blue and the brown grades, there is a large degree of scatter, but not necessarily an increase with exposure. The gloss levels seem to drop on initial exposure to UV in the case of the brown and the blue grades, then remain approximately constant up to about 1000 hours before falling. In the case of the black grade, there seems to be little change in the gloss levels with exposure.

The BPI samples indicated a stepwise increase on initial UV exposure and then remained constant up to about 750 hours before increasing sharply with further exposure. This is confirmed by the gloss levels that show an initial decrease, then little variation up to 750 hours and then a sharp drop.

15. Implications for Products

15.1 Polypropylene Bumper

The results show that the polypropylene bumper material is very stable over the long period of artificial UV exposure, as might have been expected. The tensile strength, failure strength and modulus all remain constant over the whole period. Specific property changes include a slight increase in toughness as measured by the Izod impact test at very low levels of UV exposure. The level remains constant with further exposure. This is related to a slight increase in the yield strain well beyond 1000 hours of UV exposure. As previously explained, this level of exposure is equivalent to approximately one year in the normal, northern European environment. There is little change in colour beyond that with the first exposure to UV. The flow characteristics do not seem to change with increased expose to UV according to the MFI and the molecular weight distribution. However, the average molecular weights decrease, indicating a reduction in chain length and therefore chain scission.

The PP bumper material shows an increase in gloss. It could be argued that the surface degrades to some degree with uv exposure. Chain scission then leads to shorter molecules and the elevated temperature could cause some long term recrystallisation at the surface. This could be aided by the long-term stress relaxation at the surface. Recrystallisation would imply closer packing of molecules at the surface, effectively pulling the surface tighter, giving higher gloss reading. Once significant degradation takes place, the surface will eventually become chalky and the gloss will drop. There appears also to be slight colour change with the material tending towards grey. Grey reflects more light so the amount reflected will be measured higher. This would explain why black is such a difficult colour to measure.

Overall therefore, the study has shown that this material can be used with reasonable confidence,, in future recycled products likely to be exposed to the normal environment.

15.2 Wheelie Bins

The tensile strength and strain to yield of both grades remains the same and independent of the UV exposure up to 6000 hours. Similarly, the tensile modulus remains constant. This is not unexpected as both are bulk properties and the contribution from surface degradation is likely to be small. The characteristics at break show small decreases, especially in the case of the black grade for exposures greater than 1000 hours. The toughness of the materials is also unaffected by the exposure to UV. The melt flow characteristics do not change as measured by the MFI and polydispersity although both M_n and M_w decrease with UV exposure, suggesting chain scission. The surface characteristics are affected as seen in the colour change especially after about 750 hours of exposure. The gloss levels are unaffected although in the case of the black grade again, there seems to be a fall beyond about 750 hours of UV exposure. The microhardness measurements do not indicate any changes although there does seem to be an apparent increase in hardness in the black grade beyond 1000 hours. This might indicate the effect of degradative products on the surface. Surprisingly, it is the black grade that begins to degrade and thus influence the failure characteristics.

Both black and green wheelie bins seem to be affected in a similar way in terms of molecular weight and viscosity. After 300 hours the viscosity drops, indicating the onset of degradation. Changes in viscosity profile like this are more indicative of a degradation effect rather than general scatter. There does not seem to be such a step change in the molecular weight graphs. Although the oscillating viscometer is very sensitive, the change in molecular weight may be at the limit of its sensitivity. However, it is more repeatable than GPC. It may be possible to plot the G' and G'' cross over frequency against molecular weight to obtain a good correlation although the cross-over frequency is not easily identified.

The sudden onset of degradation could be due to residual stabilisers being consumed. When the part was recycled, the remaining hindered amine light stabilisers (HAL) in the bulk, are redistributed bringing stabiliser to the surface but more dilute. Therefore, recyclers may be able to reduce UV stabiliser when recycling. However determining the correct level is difficult and could be considered in a further study.

15.3 Centriforce Products

The tensile strength of the brown, blue and black grades remains unaffected by UV exposure and in fact might be increasing slightly. The strain at yield however shows a small decrease beyond 1000 hours although the black grade is unaffected. The impact properties are also largely unaffected although there was an apparent increase beyond 1000 hours in the brown samples. These results suggest that the bulk solid properties are not detrimentally affected by UV exposure. The melt flow characteristics again remain unaffected by the length of UV exposure although the blue grade shows a decrease in MFI beyond 1000 hours. This is confirmed by the polydispersity measure, which decreases in the case of the blue grade. The black grade also shows a smaller decrease in polydispersity. In both cases, M_w decreases significantly, suggesting chain scission. The brown grade shows a greater fall in M_n than in M_w and hence the polydispersity increases.

If the composition of the materials is effectively the same then crystalinity effects are 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 crystalinity is higher than expected, the crystal structure is very fine. Hence a brittle material may result.

15.4 BPI Products

The tensile strength of the square and rectangular components, referred to as square and rectangular grades for convenience, remain constant with UV exposure and virtually identical. Similarly the strength at break remains similar and seems to increase with UV exposure. The strain to yield and the strain to failure are identical for both grades. This suggests that the there is little difference in the grade of material and their properties are largely unaffected by UV exposure. The impact strength definitely decreases with the degree of UV exposure up to about 750 hours, after which the value levels off. In this case, the rectangular grade is significantly tougher than the square grade. The MFI for both grades shows a slight decrease with UV exposure, while both M_n and M_w also decrease very slightly, giving little change in polydispersity. Both grades were found to be too soft for the microhardness tests. In addition, there is great colour change beyond about 500 hours of UV exposure. Gloss levels fell significantly with initial exposure and again seem to drop further beyond about 750 hours of exposure.

15.5 Comparison between Aged-in-Field and Artificial UV Exposure tests

In the case of Centriforce and BPI samples of materials were provided both after use in the field and also before first use. The samples had all undergone the same processing into identical shapes. However given the time span between field-aged samples and those made available for laboratory studies, it was impossible to check for any changes that may have happened to the composition in the intervening time. The manufacturers keep records of materials. However, they are dependent to a certain extent, on suppliers of materials and the changing sources of materials. The results for field-aged samples were plotted onto corresponding graphs at an exposure time of 2000 hours. This was done merely for convenience.

In the case of the Centriforce materials, the tensile strength and strain at yield are virtually identical with the zero UV exposure with the exception of the strain at yield in the black grade. This last result is higher than expected. In general the suggestion is that the artificial UV exposure does not compare with the effect of the natural environment. The MFI values for the blue and the brown grades were also significantly different from that for the materials artificially exposed to UV radiation. The complex viscosity of the materials is slighty lower for the black and brown grades and slightly higher for the blue grade at any frequency than the corresponding set of values for the UV exposed materials.

In the case of the BPI materials The MFI is significantly lower in the case of the Field aged materials and the complex viscosity higher than the corresponding UV exposed materials. The tensile properties are therefore slightly different.

In the case of the PP bumper materials and the Wheelie bins, field-aged materials became the start materials for the UV exposure regime. Hence these materials had already undergone UV/moisture exposure in the field.

16. Conclusions

The work in this project has shown that the effect of UV exposure, whether in the field or in the artificial environments, is not significant as far as the mechanical properties of the materials are concerned. There is some change in the surface characteristics that are primarily in the colour and gloss levels. For most recyclers this will not be much of an issue since products tend to be of large wall thickness and so a surface effect would not compromise the mechanical integrity of the product. Surface appearance may be an issue though. In the example of a decking board, the surface degradation by UV may lead to accelerated wear with pedestrian use.

However, on reprocessing of the materials during recycling, it is likely that stabiliser is brought to the surface of any new moulding, thus renewing the surface characteristics. Hence damaged or end-of-life products should not be discounted from recycling. In any case, the stabilisers being used currently in these materials are effective in negating any likely effects of UV radiation.

For the mixed waste materials it is expected that there will be considerable variability in the test results because the source materials are so variable. This has already been demonstrated from the molecular weight and viscosity analysis of the BPI new and field aged material. The field-aged material has a higher overall molecular weight in comparison with the new material. It could be that this increase is due to degradative cross-linking. However, it is more likely to be due to variability in the batches of raw material. Most recyclers manufacturing using mixed plastic streams will 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.

Overall, the study has shown that all the materials tested have generally maintained their mechanical properties with little change under accelerated UV exposure. The significant exception was the impact strength of the BPI materials, expected because of the nature of the source materials. All materials will show the surface effects of ageing eventually but this does not seem to affect the mechanical integrity. Thus it can be argued with reasonable confidence that all the materials meet fitness for purpose criteria.

17. Recommendations

- The work shows that the materials currently used in outdoor applications can continue to be used without significant detrimental effects.
- To reduce shear damage during the reprocessing of materials, the temperature of the process should be kept near the upper end of the working range.
- The MFI test seems a very appropriate method for quality checks in industry. A comparison of the MFI of the materials before and after processing should be carried out to see how stable materials are.
- The use of colour should be considered carefully as the study suggests that different pigments can influence the crystallisation process to a greater or lesser degree and thus influence properties.

18. 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 level of restabilisation required should be examined in the light of levels of stabilisers remaining in the material. This is important as the net increase in stabiliser content with repeated recycling will significantly affect the material 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.

- No work has been done on materials without any stabilisers and very little has been done in the past. Hence a long-term study should be undertaken with materials without stabilisers in order to understand the mechanism of UV degradation fully.

References

[1] O. Cicchetti, *Advances in Polymer Science* **1970**, *7*, 70.

[2] A. L. Bhuiyan, *Advances in Polymer Science* **1982**, *47*, 43.

[3] J. R. McCallum, *Macromolecular Chemistry* **1982**, 296.

[4] W. W. Wright, *Macromolecular Chemistry* **1982**, *2*, 305.

[5] C. Vasile, in *Handbook of Polyolefins: Synthesis and Properties* (Ed.: R. B. Seymour), Marcel Dekker, New York, **1993**, pp. 479.

[6] J. M. Hutchinson, *Progress in Polymer Science* **1995**, *20*, 703.

[7] G. Scott, *Polymers and the Environment*, 1 ed., Royal Society of Chemistry, Cambridge, **1999**.

[8] M. P. Stevens, *Polymer Chemistry: an introduction*, 3 ed., Oxford University Press, Oxford, **1999**.

[9] J. K. Lynch, T. J. Nosker, R. W. Renfree, P. Krishnaswamy, R. Francini, in *ANTEC*, Dallas Texas, **2001**, p. Paper 392.

[10] B. Baum, in *Predicting Plastics Performance*, Downington, PA, **1973**, pp. 180.

[11] A. B. Mathur, G. N. Mathur, *Popular Plastics* **1977**, 17.

[12] F. Severini, R. Gallo, S. Ipsale, *Polymer Degradation and Stability* **1988**, *22*, 185.

[13] M. E. Austin, J. H. O'Donnell, in *18th Australian Polymer Symposium*, **1990**, p. Paper 68.

[14] F. Severini, R. Gallo, S. Ipsale, *Die Angewandte Makromolekulare Chemie* **1991**, *189*, 117.

[15] F. Yoshii, G. Meligi, T. Sasaki, K. Makuuchi, A. M. Rabie, S.-i. Nishimoto, *Polymer Degradation and Stability* **1995**, *49*, 315.

[16] P. Pagès, F. Carrasco, J. Saurina, X. Colom, *Journal of Applied Polymer Science* **1996**, *60*, 153.

[17] G. Yanai, A. Ram, J. Miltz, *Journal of Applied Polymer Science* **1995**, *57*, 303.

[18] G. Yanai, A. Ram, J. Miltz, *Journal of Applied Polymer Science* **1996**, *59*, 1145.

[19] N. M. Livanova, G. E. Zaikov, *Polymer Degradation and Stability* **1997**, *57*, 1.

[20] A. Tidjani, *Journal of Applied Polymer Science* **1997**, *64*, 2497.

[21] F. Carrasco, P. Pagès, S. Pascual, X. Colom, *Polymer Degradation and Stability* **2001**, *37*, 1457.

[22] J. Sampers, *Polymer Degradation and Stability* **2002**, *76*, 455.

[23] M. S. Rabello, J. R. White, *Polymer Degradation and Stability* **1997**, *56*, 55.

[24] C. N. Kartalis, C. D. Papaspyrides, R. Pfaendner, K. Hoffmann, H. Herbst, *Journal of Applied Polymer Science* **1999**, *73*, 1775.

[25] C. N. Kartalis, C. D. Papaspyrides, R. Pfaendner, K. Hoffmann, H. Herbst, *Journal of Applied Polymer Science* **2000**, *77*, 1118.

[26] F. R. Mayo, in *ACS, Div. of Organic Coatings & Plastics Chemistry Coatings, Vol. 34(2)*, **1974**, pp. 117.

[27] P. Gijsman, J. Hennekens, J. Vincent, *Polymer Degradation and Stability* **1993**, *39*, 271.

[28] A. T. P. Zahavich, B. Latto, E. Takacs, J. Vlachopoulos, *Advances in Polymer Technology* **1997**, *16*, 11.

[29] A. V. Shyichuk, D. Y. Stavychna, J. R. White, *Polymer Degradation and Stability* **2001**, *72*, 279.

[30] R. Broska, J. Rychlý, *Polymer Degradation and Stability* **2001**, *72*, 271.

[31] P. Gijsman, G. Meijers, G. Vitarelli, *Polymer Degradation and Stability* **1999**, *65*, 433.

[32] J. Lacoste, Y. Deslandes, P. Black, D. J. Carlsson, *Polymer Degradation and Stability* **1995**, *49*, 21.

[33] B. E. Shaner, in *ANTEC, Vol. III*, Boston MA, **1995**, pp. 4218.

[34] M. Kostadinova Loultcheva, M. Proietto, N. Jilov, F. P. La Mantia, *Polymer Degradation and Stability* **1997**, *57*, 77.

[35] M. Clauss, H. Herbst, J. H. Botkin, in *GPEC 2002: Plastics Impact on the Environment*, Detroit MI, **2002**, pp. 341.

[36] J. Boxhammer, *Polymer Testing* **2001**, *20*, 719.

[37] W. Camacho, S. Karlsson, *Polymer Degradation and Stability* **2002**, *78*, 385.

[38] R. M. Fischer, W. P. Murray, W. D. Ketola, *Progress in Organic Coatings* **1991**, *19*, 151.

[39] F. Gugumus, *Polymer Degradation and Stability* **2002**, *77*, 147.

[40] A. R. Horrocks, J. Mwila, M. Miraftab, M. Liu, S. S. Choban, *Polymer Degradation and Stability* **1999**, *65*, 25.

[41] M. Iring, S. Laszlo-Hedvig, K. Barabas, T. Kelen, F. Tudos, *European Polymer Journal* **1978**, *44*, 439.

[42] J. Pospíšil, Z. Horák, Z. Kruliš, S. Nešpurek, S. Kuroda, *Polymer Degradation and Stability* **1999**, *65*, 405.

[43] L. M. Rincon-Rubio, B. Fayolle, L. Audouin, J. Verdu, *Polymer Degradation and Stability* **2001**, *74*, 177.

[44] R. Schaaf, in *Recycling of Thermoplastic Wastes* (Ed.: V. D. Ingenieure), Dusseldorf, **1979**, pp. 153.

[45] A. Wojtala, *International Polymer Science and Technology* **2001**, *28*, T85.

[46] J. R. Dunn, *Rubber Chemistry and Technology* **1978**, *51*, 686.

[47] W. G. Drake, J. R. Pauquet, R. V. Todesco, H. Zweifel, *Die Angewandte Makromolekulare Chemie* **1990**, *176/177*, 215.

[48] R. Pfaendner, K. Hoffmann, B. Klingert, F. Sitek, T. Cooper, *Kunststoffe-Plast Europe* **1995**, *85*, 81.

[49] J. Pospíšil, F. Sitek, R. Pfaendner, *Polymer Degradation and Stability* **1995**, *48*, 351.

[50] H. Herbst, K. Hoffmann, R. Pfaendner, F. Sitek, *Improving the quality of recyclates with additives*, Hanser, Munich, **1995**.

[51] S. Moss, H. Zweifel, *Polymer Degradation and Stability* **1989**, *25*, 217.

[52] L. Incarnato, P. Scarfato, D. Acierno, *Polymer Engineering and Science* **1999**, *39*, 749.

[53] L. Incarnato, P. Scarfato, G. Gorrasi, V. Vittoria, D. Acierno, *Polymer Engineering and Science* **1999**, *39*, 1661.

[54] C. A. Bernardo, A. M. Cunha, M. J. Oliveira, *Polymer Engineering and Science* **1996**, *36*, 511.

[55] H. Hinsken, S. Moss, J. R. Pauquet, H. Zweifel, *Polymer Degradation and Stability* **1991**, *34*, 279.

[56] N. C. Billingham, P. D. Calvert, in *Degradation and Stabilisation of Polyolefins*, Applied Science Publishers Ltd, Barking, **1983**, pp. 1.

[57] F. P. La Mantia, A. Valenza, D. Acierno, *Polymer Degradation and Stability* **1985**, *13*, 1.

[58] S. M. Chua, P. J. Henderson, *Journal of Materials Science Letters* **1991**, *10*, 1379.

[59] A. Tidjani, R. Arnaud, A. O. Dasilva, *Journal of Applied Polymer Science* **1993**, *47*, 211.

[60] J.-F. Doyon, P. G. Lafleur, P. J. Carreau, B. Vergnes, in *ANTEC*, **1994**, pp. 2876.

[61] A. Boldizar, T. Gevert, M. Markinger, *Polymer Recycling* **1995**, *1*, 249.

[62] J. Pospíšil, S. Nešpurek, R. Pfaendner, H. Zweifel, *Trends in Polymer Science* **1997**, *5*, 294.

[63] C. M. C. Bonelli, A. F. Martins, E. B. Mano, C. L. Beatty, in *ANTEC, Vol. III*, Atlanta GA, **1998**, pp. 2901.

[64] W. R. Waldman, M. A. De Paoli, *Polymer Degradation and Stability* **1998**, *60*, 301.

[65] E. Epacher, E. Fekete, M. Gahleitner, B. Pukanszky, *Polymer Degradation and Stability* **1999**, *63*, 499.

[66] E. Epacher, J. Tolveth, K. Stoll, B. Pukanszky, *Journal of Applied Polymer Science* **1999**, *74*, 1596.

[67] G. Teteris, *Macromolecular Symposia* **1999**, *144*, 471.

[68] T. Yukino, M. Fukushima, in *Polyolefins XI*, Huston, TX, **1999**, pp. 505.

[69] A. A. Edidin, C. W. Jewett, A. Kalinowski, K. Kwarteng, S. M. Kurtz, *Biomaterials* **2000**, *21*, 1451.

[70] C. N. Kartalis, C. D. Papaspyrides, R. Pfaendner, K. Hoffmann, H. Herbst, *Polymer Engineering and Science* **2001**, *41*, 771.

[71] A. S. F. Santos, R. C. Santana, J. A. M. Agnelli, S. Manrich, *Polymer Recycling* **2001**, *6*, 57.

[72] J. Z. Liang, J. N. Ness, *Polymer Testing* **1997**, *16*, 379.

[73] D. Braun, S. Ritcher, G. P. Hellmann, M. Ratzsch, *Journal of Applied Polymer Science* **1998**, *68*, 2019.

[74] R. Satoto, W. S. Subowo, R. Yusiasih, Y. Takane, Y. Watanabe, Hatakeyama, *Polymer Degradation and Stability* **1997**, *56*, 275.

[75] V. G. Barkhudaryan, *Polymer* **2000**, *41*, 5787.

[76] H. Al-Madfa, Z. Mohamed, M. E. Kassem, *Polymer Degradation and Stability* **1998**, *62*, 105.

[77] Y. Kato, D. J. Carlsson, D. M. Wiles, *Journal of Applied Polymer Science* **1969**, *13*, 1447.

[78] P. Gijsman, J. Sampers, *Polymer Degradation and Stability* **1997**, *58*, 55.

[79] P. Gijsman, J. Sampers, *Die Angewandte Makromolekulare Chemie* **1998**, *261/262*, 77.

[80] J. N. Patel, J. R. B. Westwood, *Journal of the Oil and Colour Chemists' Association* **1990**, *73*, 484.

[81] H. D. Hoekstra, J. L. Spoormaker, J. Breen, L. Audouin, J. Verdu, *Polymer Degradation and Stability* **1995**, *49*, 251.

[82] H. G. Jellinek, *Journal of Applied Polymer Science - Applied Polymer Symposia* **1967**, *4*, 41.

[83] H. Kaczmarek, *Polimery* **1997**, *42*, 521.

[84] G. C. Furneaux, K. J. Ledbury, A. Davis, *Polymer Degradation and Stability* **1981**, *3*, 431.

[85] Z. Zhenfeng, H. Xingzhou, L. Zubo, *Polymer Degradation and Stability* **1996**, *51*, 93.

[86] J.-L. Philippart, C. Sinturel, J.-L. Gardette, *Polymer Degradation and Stability* **1997**, *58*, 261.

[87] F. P. La Mantia, D. Curto, *Polymer Degradation and Stability* **1992**, *36*, 131.

[88] F. P. La Mantia, C. Mongiovi, *Polymer Degradation and Stability* **1999**, *66*, 337.

[89] E. Epacher, E. Fekete, M. Gahleitner, B. Pukanszky, *Polymer Degradation and Stability* **1999**, *63*, 489.

[90] T. Tomiita, *Construction and Building Materials* **1994**, *8*, 223.

[91] S. H. Hamid, M. B. Amin, *Journal of Applied Polymer Science* **1995**, *55*, 1385.

[92] W. K. Busfield, P. Taba, *Polymer Degradation and Stability* **1996**, *51*, 185.

[93] A. Boldizar, A. Jansson, T. Gevert, K. Möller, *Polymer Degradation and Stability* **2000**, *68*, 317.

[94] A. Tidjani, A. O. Dasilva, E. Fanton, R. Arnaud, *JMS - Pure Applied Chemistry* **1999**, *A36*, 633.

[95] C. Albano, E. de Freitas, *Polymer Degradation and Stability* **1998**, *61*, 289.

[96] L. F. E. Jacques, *Progress in Polymer Science* **2000**, *25*, 1337.

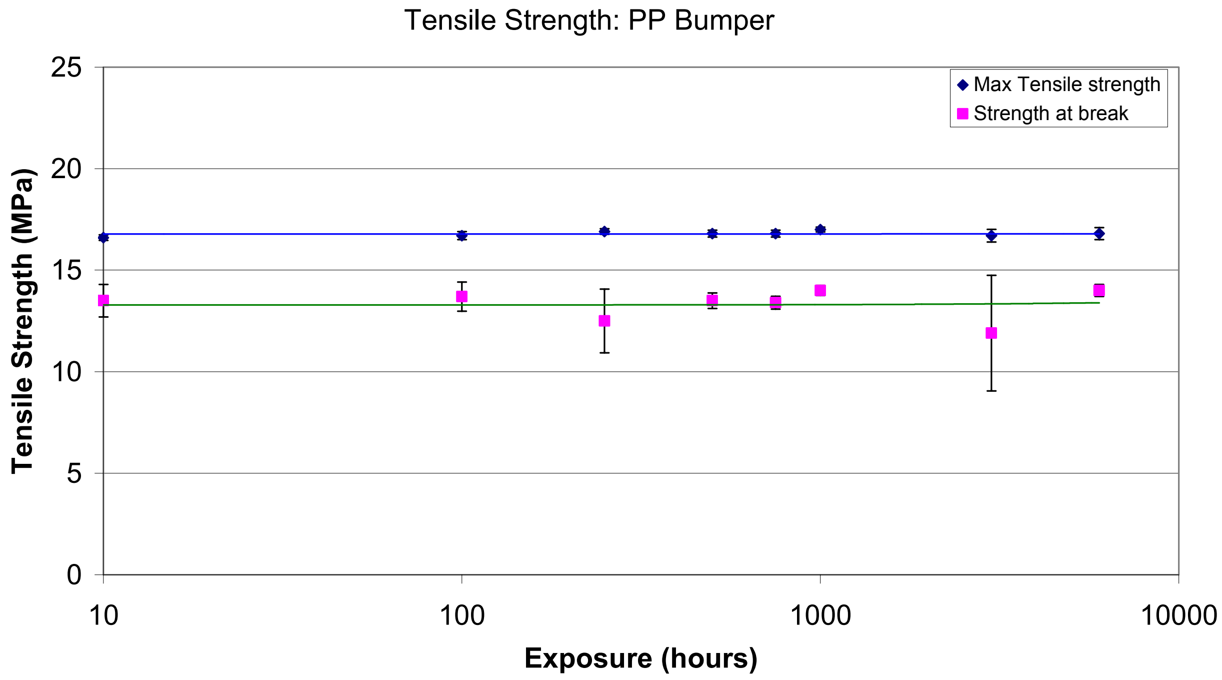
[97] D. R. Bauer, *Polymer Degradation and Stability* **2000**, *69*, 297.

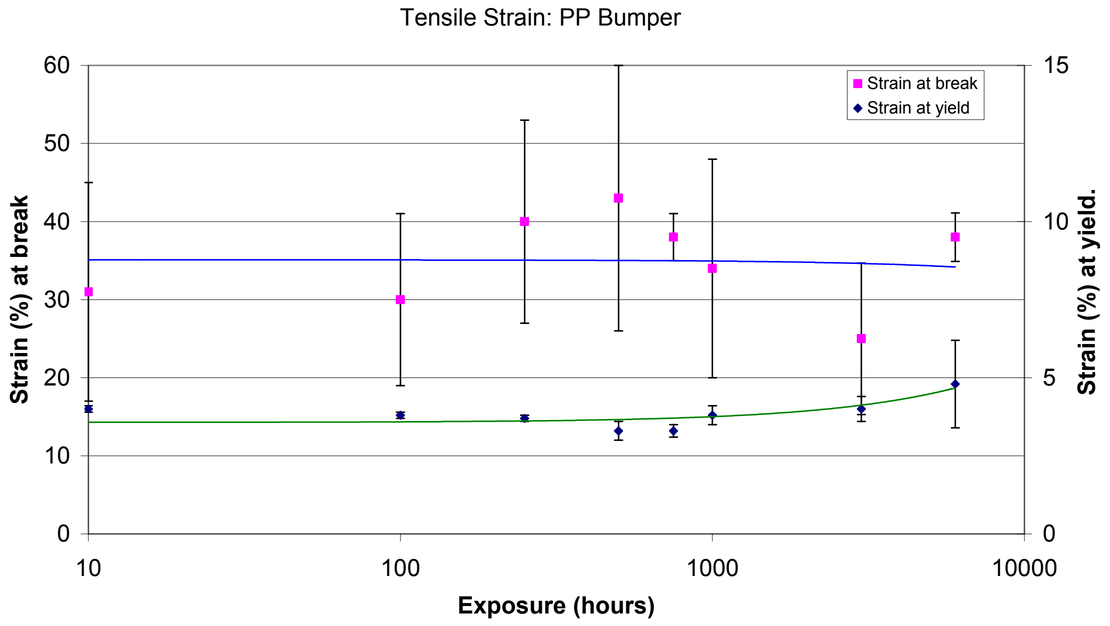
[98] D. R. Bauer, *Polymer Degradation and Stability* **2000**, *69*, 307.

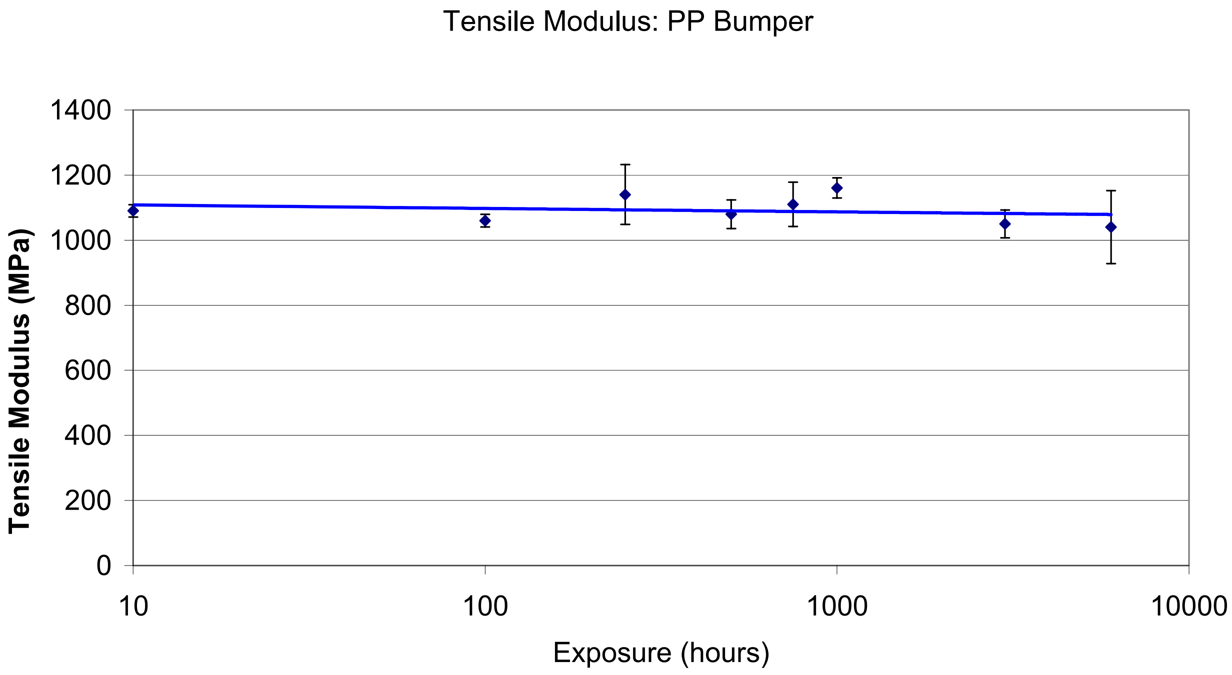
[99] J.-L. Philippart, C. Sinturel, R. Arnaud, J.-L. Gardette, *Polymer Degradation and Stability* **1999**, *64*, 213.

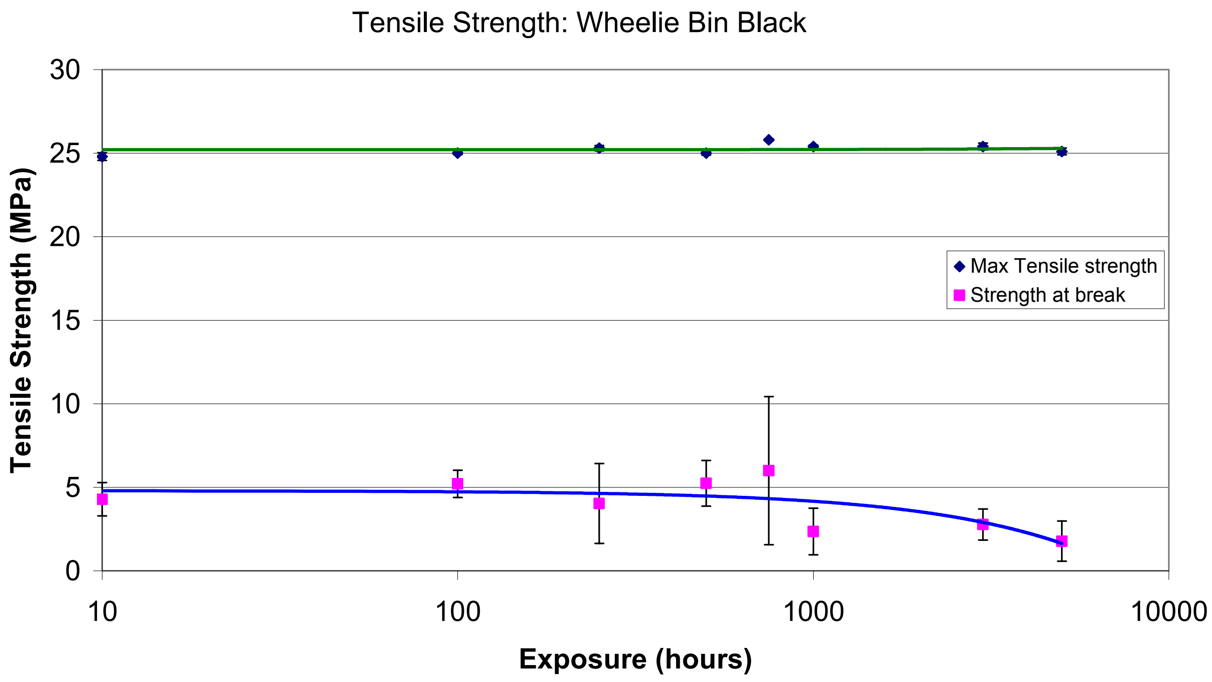
[100] Rabek J.F, *Polymer Photodegradation,* Chapman & Hall 1995,

A1.1 Tensile Testing

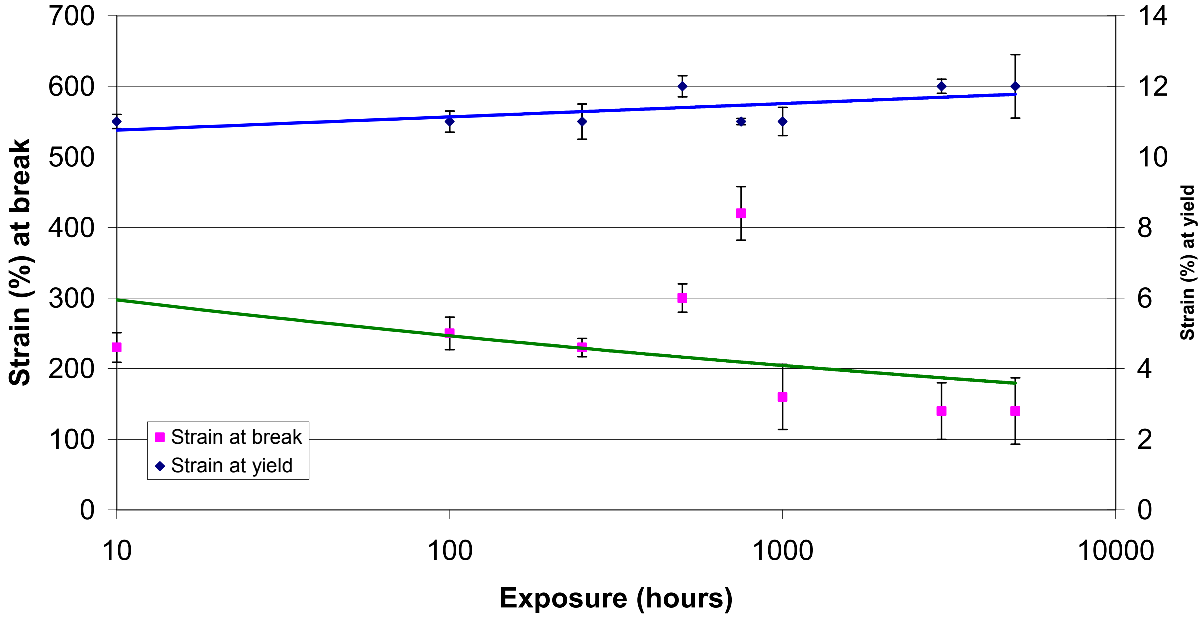




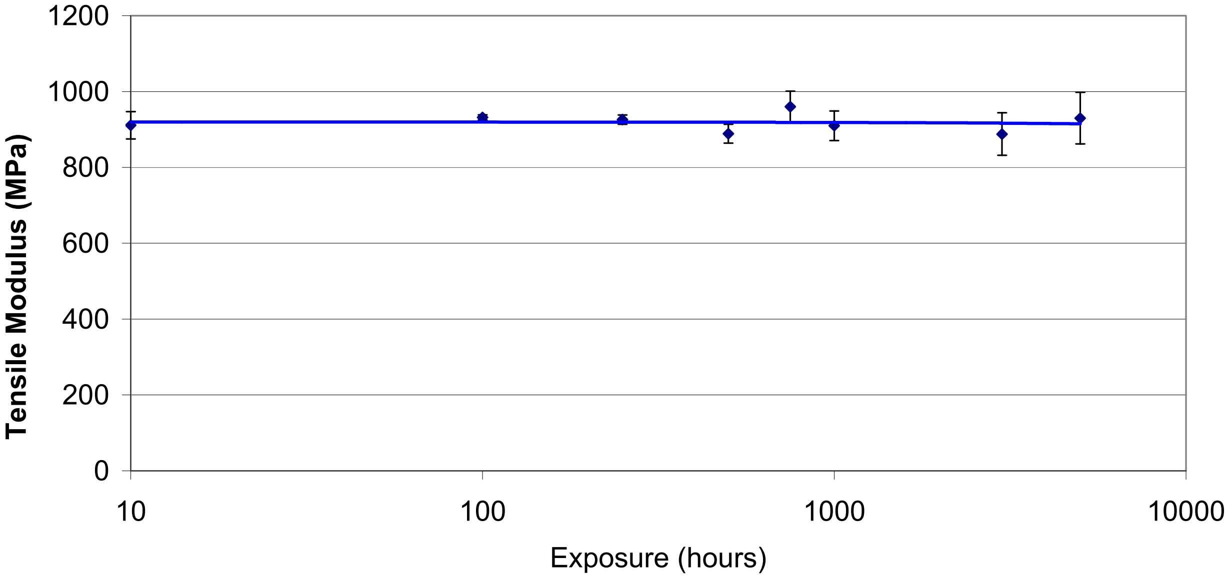

Tensile Modulus: PP Bumper
Tensile Modulus (MPa)
1400
1200
1000
800
600
400
200
0
10
100
1000
10000
Exposure (hours)

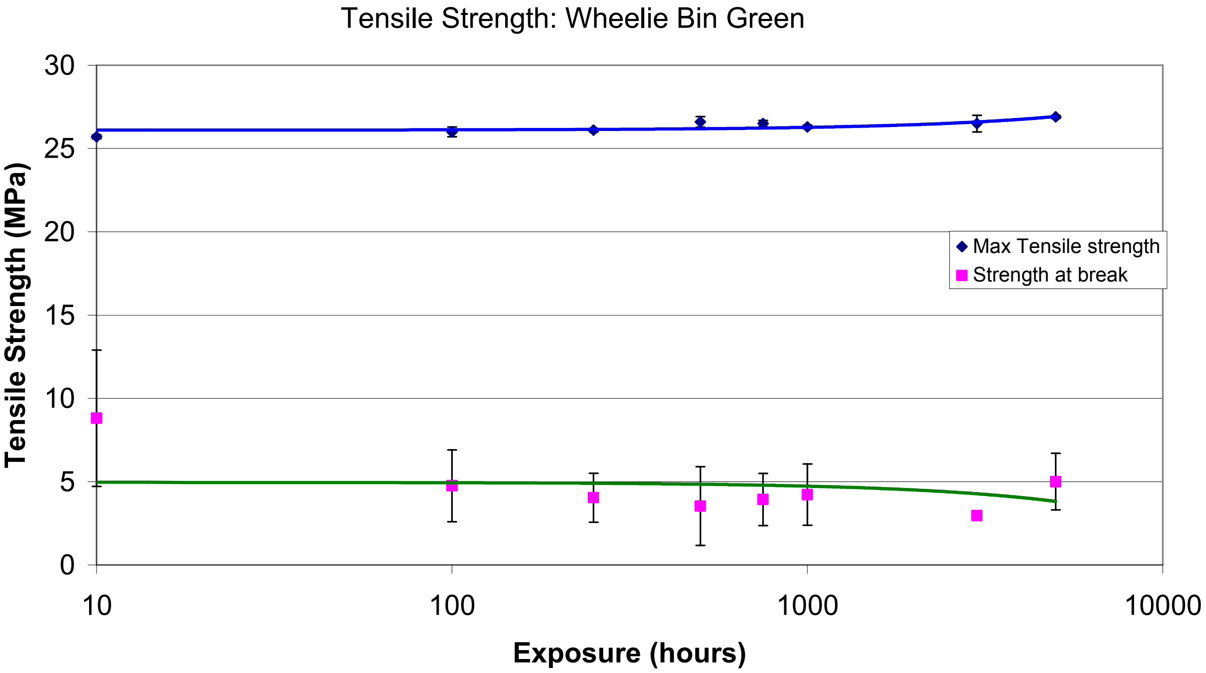

Tensile Strength: Wheelie Bin Black
Tensile Strength (MPa)
30
25
20
15
10
5
0
◆ Max Tensile strength
■ Strength at break
10
100
1000
10000
Exposure (hours)

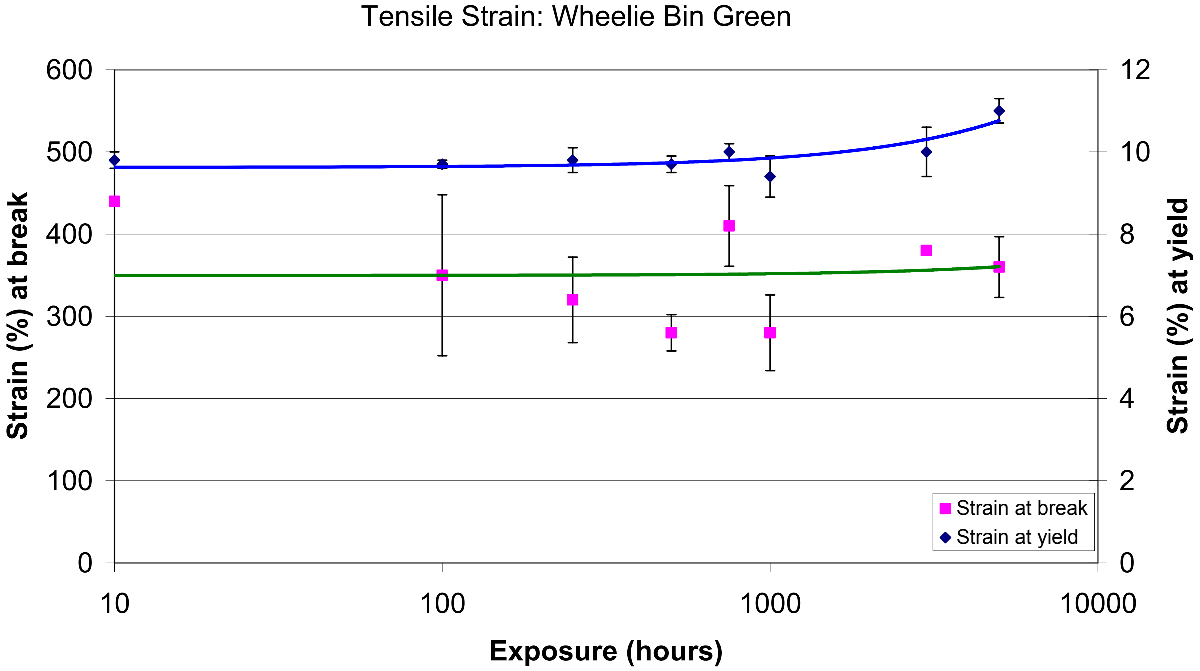
Tensile Strain: Wheelie Bin Black



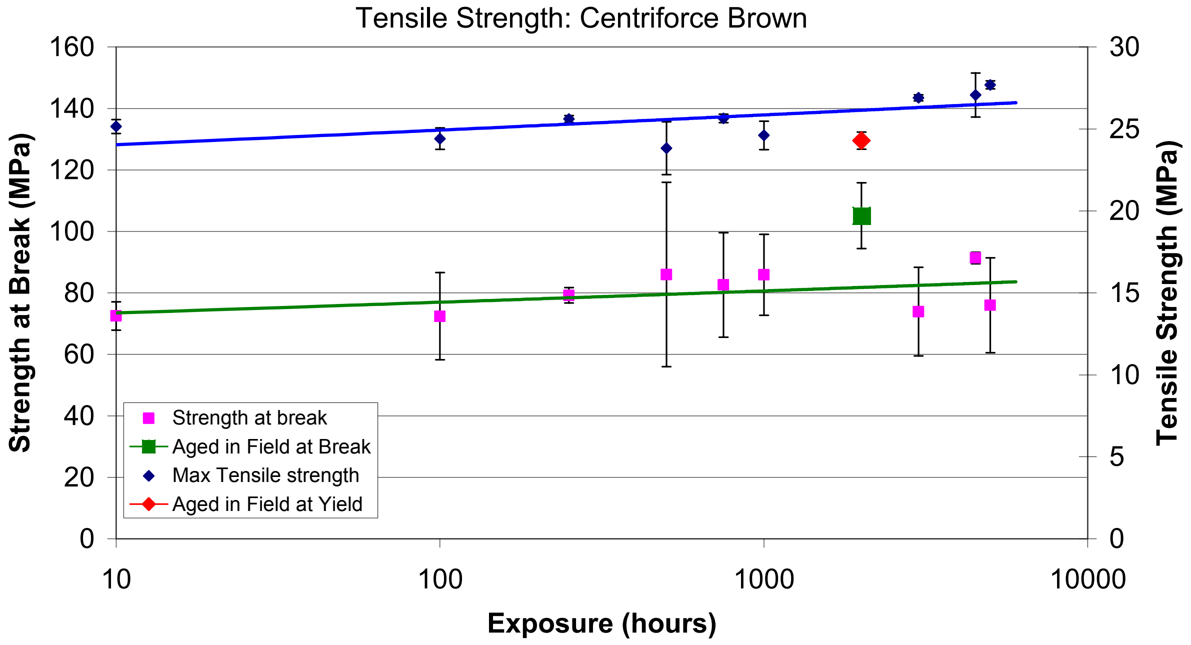
Tensile Modulus: Wheelie Bin Black

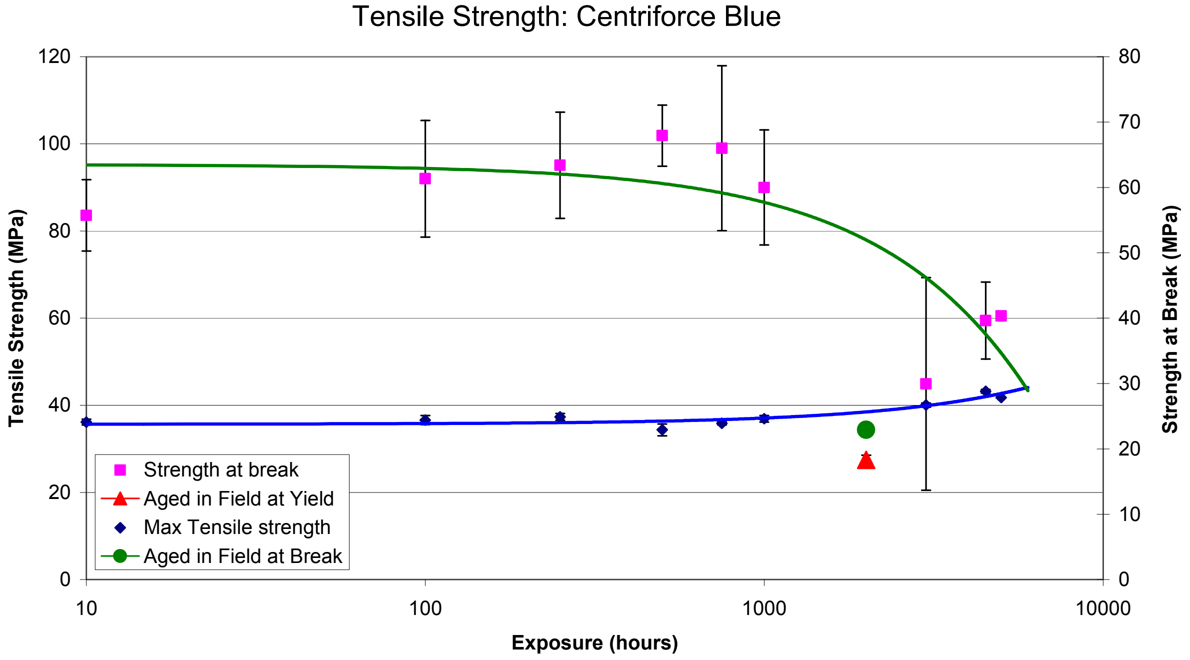


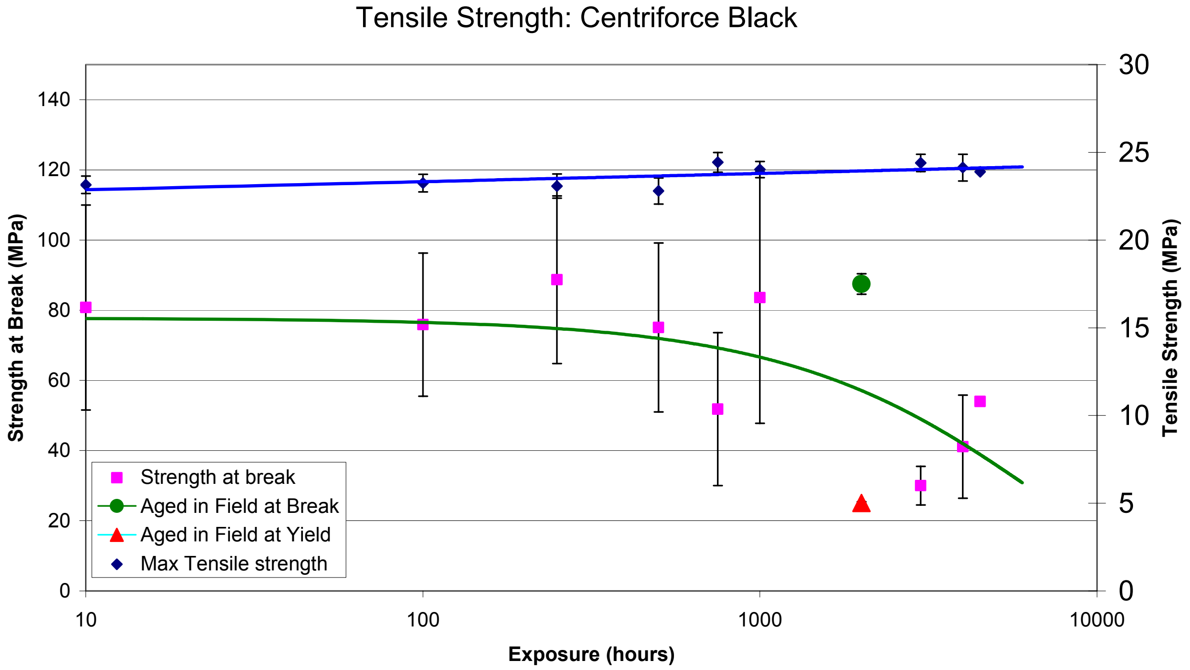

Tensile Strength: Wheelie Bin Green
Tensile Strength (MPa)
30
25
20
15
10
5
0
10
100
1000
10000
Exposure (hours)
◆ Max Tensile strength
■ Strength at break

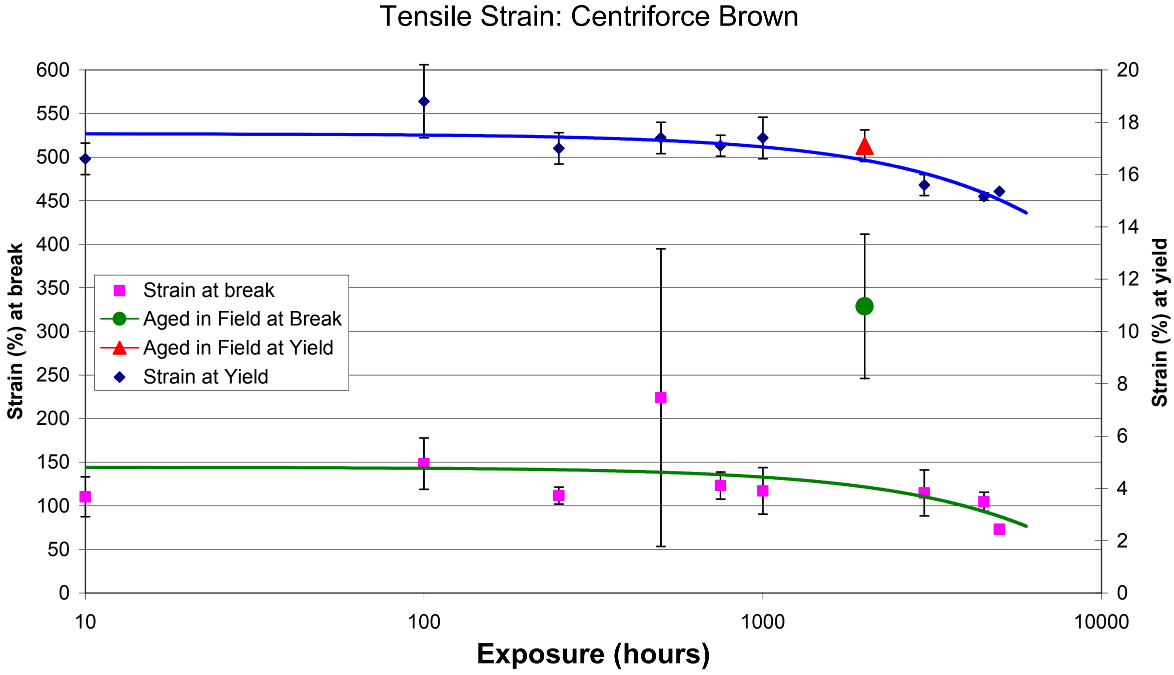

Tensile Strain: Wheelie Bin Green
Strain (%) at break
600
500
400
300
200
100
0
Strain (%) at yield
12
10
8
6
4
2
0
10
100
1000
10000
Exposure (hours)
■ Strain at break
◆ Strain at yield

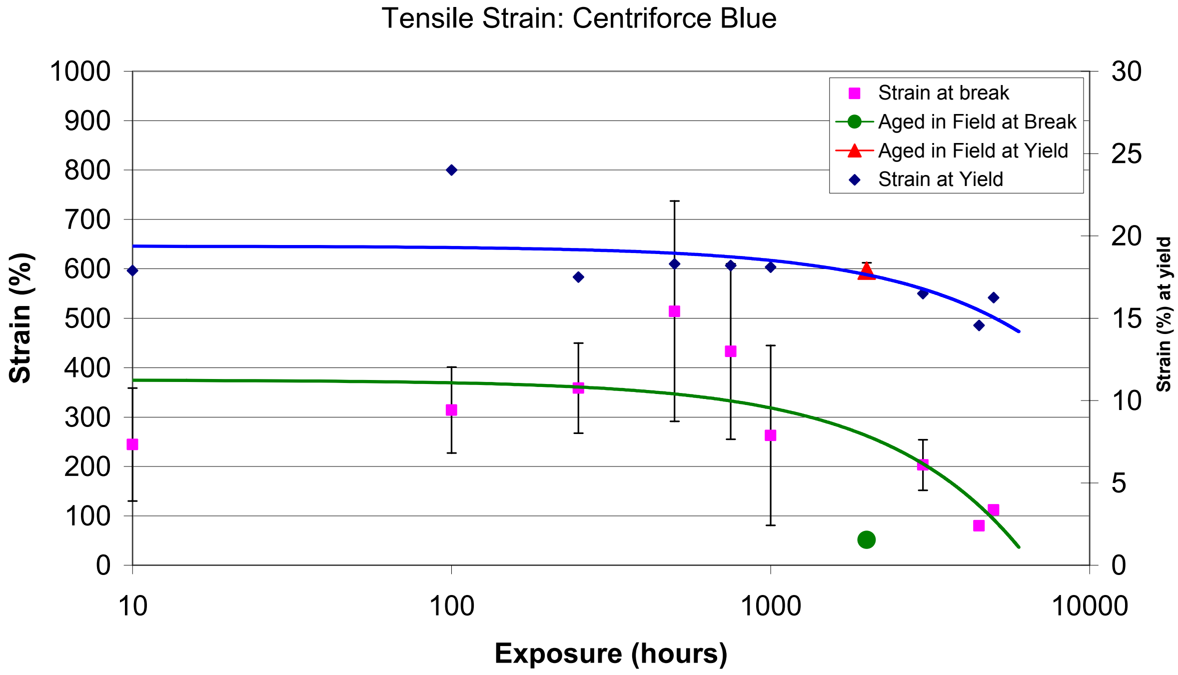

Tensile Modulus: Wheelie Bin Green
Tensile Modulus (MPa)
1400
1200
1000
800
600
400
200
0
10
100
1000
10000
Exposure (hours)

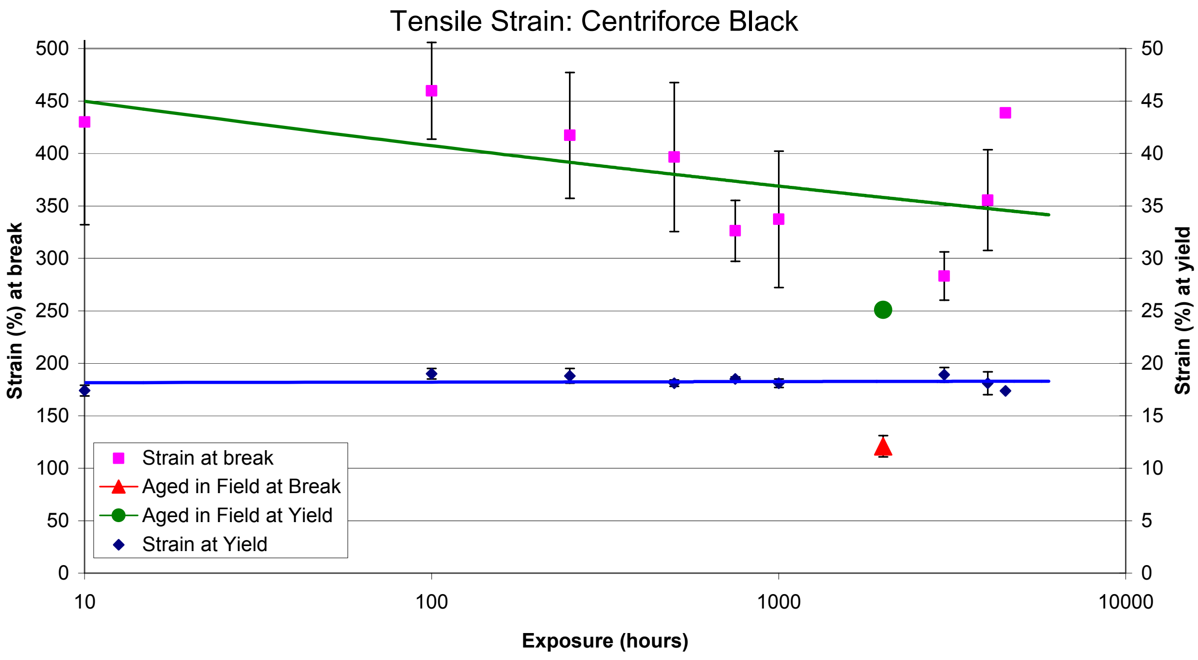

Tensile Strength: Centriforce Brown
Strength at Break (MPa)
160
140
120
100
80
60
40
20
0
Tensile Strength (MPa)
30
25
20
15
10
5
0
Strength at break
Aged in Field at Break
Max Tensile strength
Aged in Field at Yield
10
100
1000
10000
Exposure (hours)

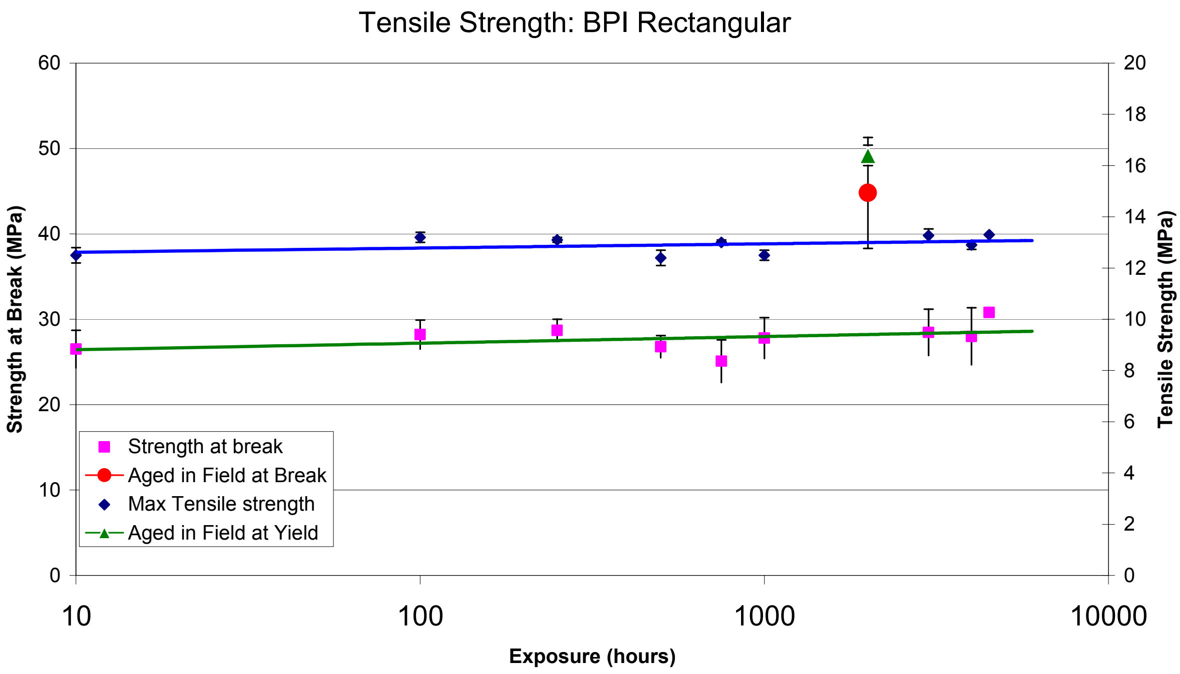

Tensile Strength: Centriforce Blue
Tensile Strength (MPa)
0
20
40
60
80
100
120
Strength at Break (MPa)
0
10
20
30
40
50
60
70
80
10
100
1000
10000
Exposure (hours)
Strength at break
Aged in Field at Yield
Max Tensile strength
Aged in Field at Break

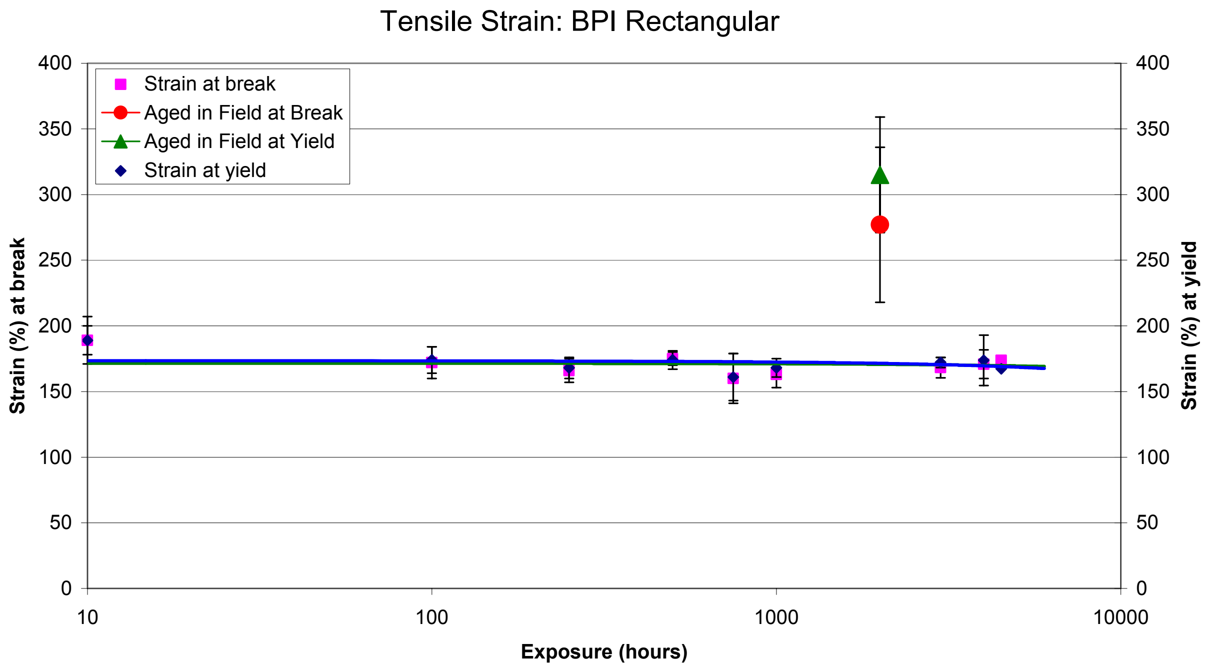

Tensile Strength: Centriforce Black
Strength at Break (MPa)
0
20
40
60
80
100
120
140
Tensile Strength (MPa)
0
5
10
15
20
25
30
10
100
1000
10000
Exposure (hours)
Strength at break
Aged in Field at Break
Aged in Field at Yield
Max Tensile strength

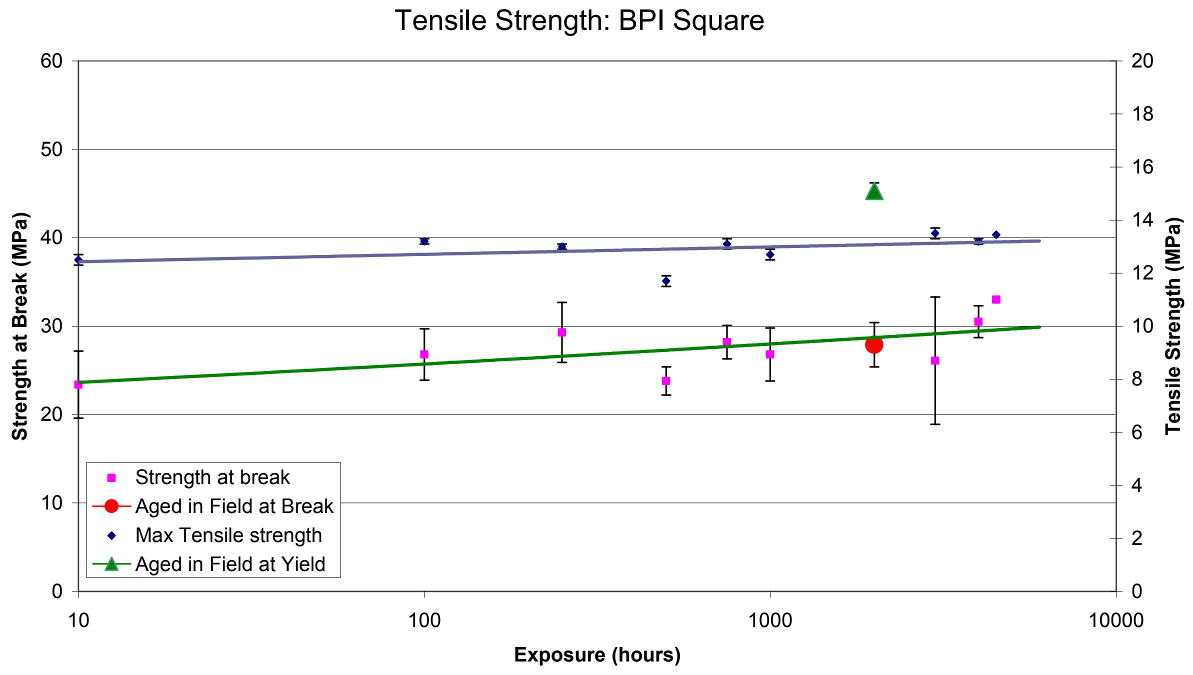

Tensile Strain: Centriforce Brown
Strain (%) at break
Strain (%) at yield
Exposure (hours)
Strain at break
Aged in Field at Break
Aged in Field at Yield
Strain at Yield
0
50
100
150
200
250
300
350
400
450
500
550
600
0
2
4
6
8
10
12
14
16
18
20
10
100
1000
10000

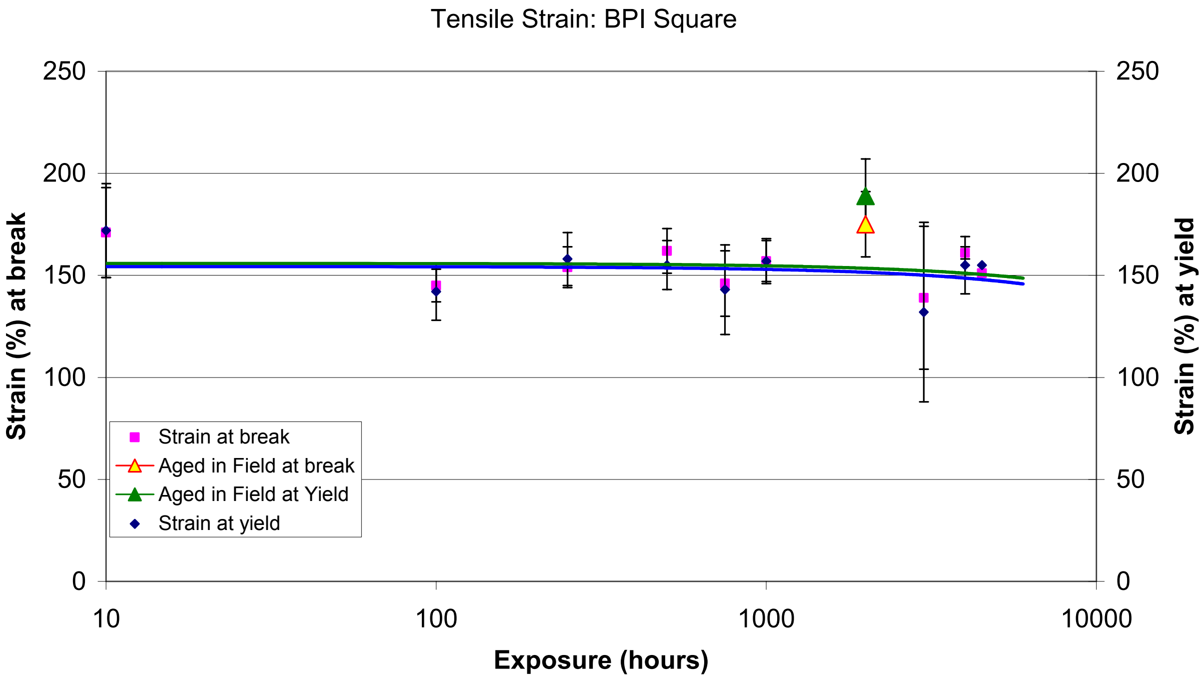

Tensile Strain: Centriforce Blue
Strain (%)
Strain (%) at yield
Exposure (hours)
Strain at break
Aged in Field at Break
Aged in Field at Yield
Strain at Yield
0
100
200
300
400
500
600
700
800
900
1000
0
5
10
15
20
25
30
10
100
1000
10000


Tensile Strain: Centriforce Black
Strain (%) at break
Strain (%) at yield
Exposure (hours)
0
50
100
150
200
250
300
350
400
450
500
0
5
10
15
20
25
30
35
40
45
50
10
100
1000
10000
Strain at break
Aged in Field at Break
Aged in Field at Yield
Strain at Yield

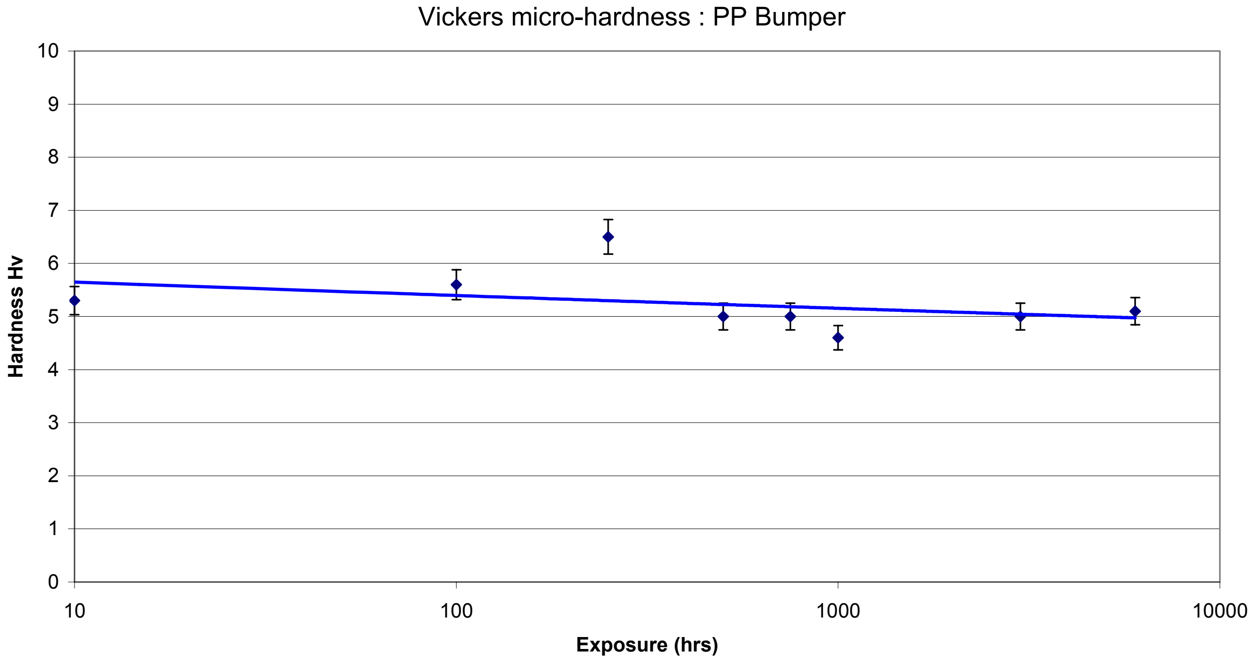

Tensile Strength: BPI Rectangular
Strength at Break (MPa)
Tensile Strength (MPa)
Exposure (hours)
0
10
20
30
40
50
60
0
2
4
6
8
10
12
14
16
18
20
10
100
1000
10000
Strength at break
Aged in Field at Break
Max Tensile strength
Aged in Field at Yield

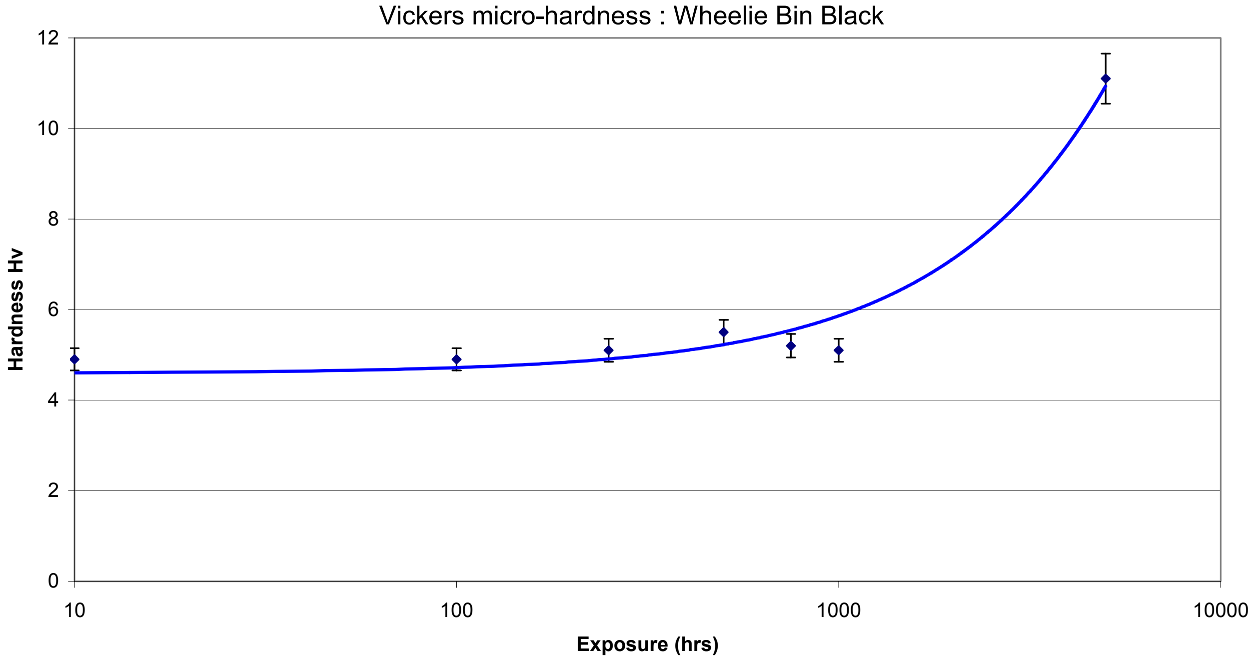

Tensile Strain: BPI Rectangular
Strain at break
Aged in Field at Break
Aged in Field at Yield
Strain at yield
Strain (%) at break
Strain (%) at yield
Exposure (hours)
0
50
100
150
200
250
300
350
400
10
100
1000
10000

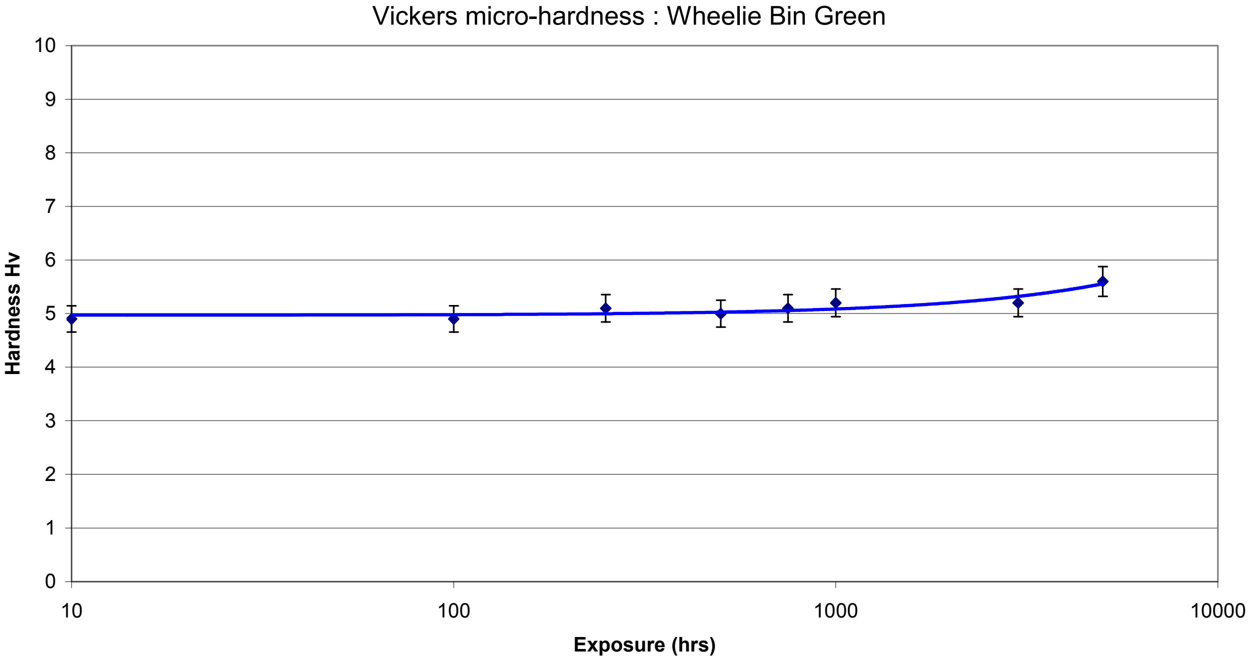

Tensile Strength: BPI Square
Strength at break
Aged in Field at Break
Max Tensile strength
Aged in Field at Yield
Strength at Break (MPa)
Tensile Strength (MPa)
Exposure (hours)
0
10
20
30
40
50
60
2
4
6
8
10
12
14
16
18
20
10
100
1000
10000

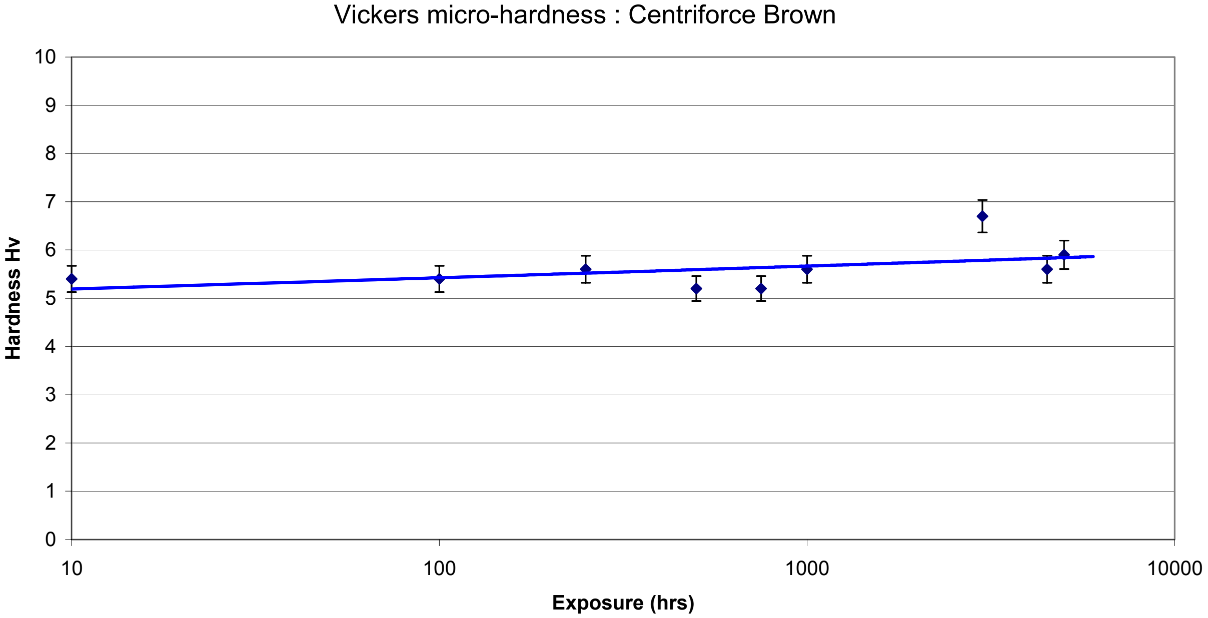

Tensile Strain: BPI Square
Strain (%) at break
Strain (%) at yield
Exposure (hours)
250
200
150
100
50
0
10
100
1000
10000
Strain at break
Aged in Field at break
Aged in Field at Yield
Strain at yield

A1.2 Microhardness

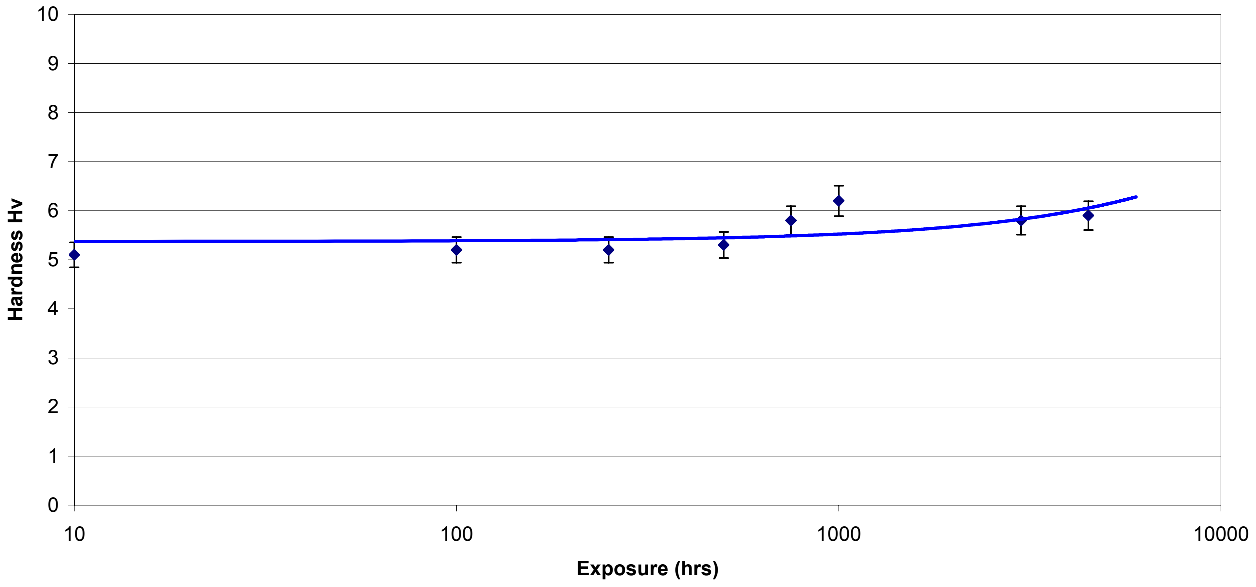




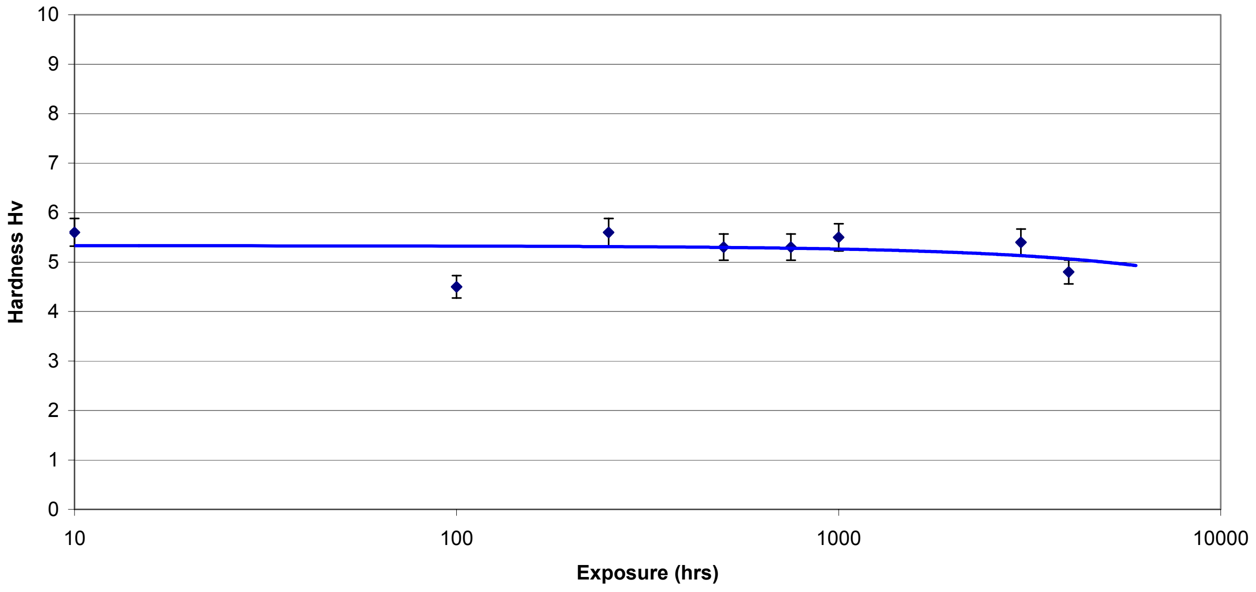

Vickers micro-hardness : Wheelie Bin Green
Hardness Hv
Exposure (hrs)
0
1
2
3
4
5
6
7
8
9
10
10
100
1000
10000


Vickers micro-hardness : Centriforce Brown
Hardness Hv
Exposure (hrs)
0
1
2
3
4
5
6
7
8
9
10
10
100
1000
10000

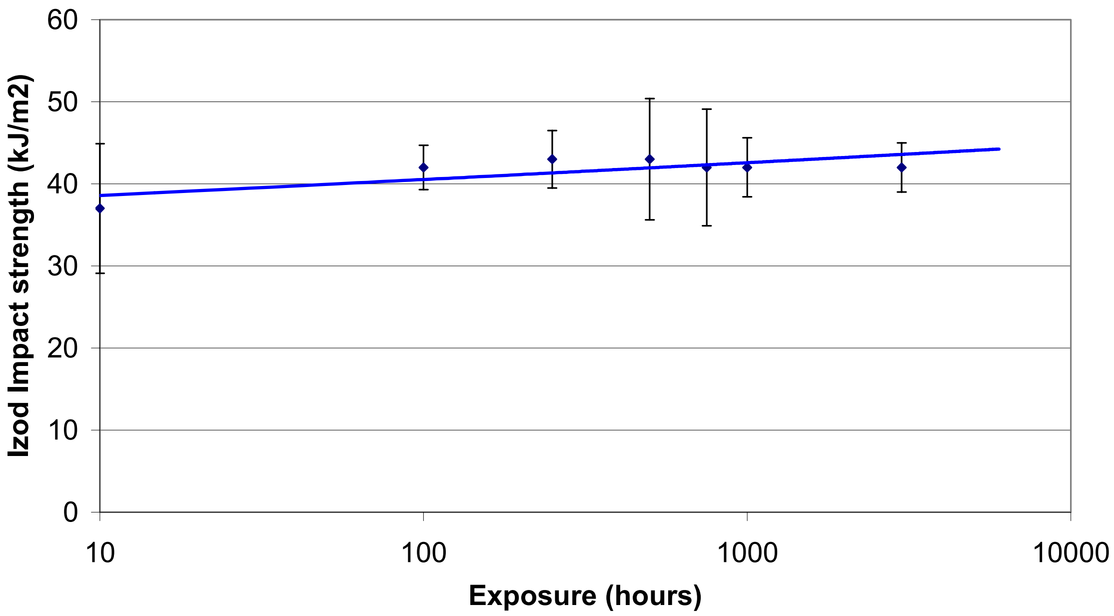
Vickers micro-hardness : Centriforce Blue

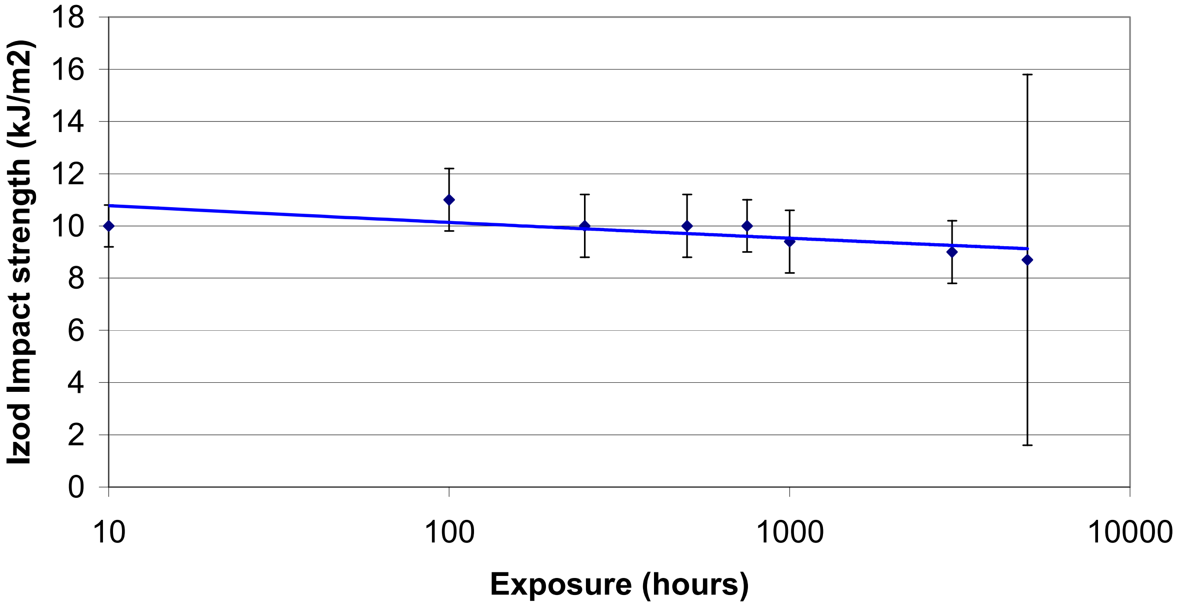


Vickers micro-hardness : Centriforce Black

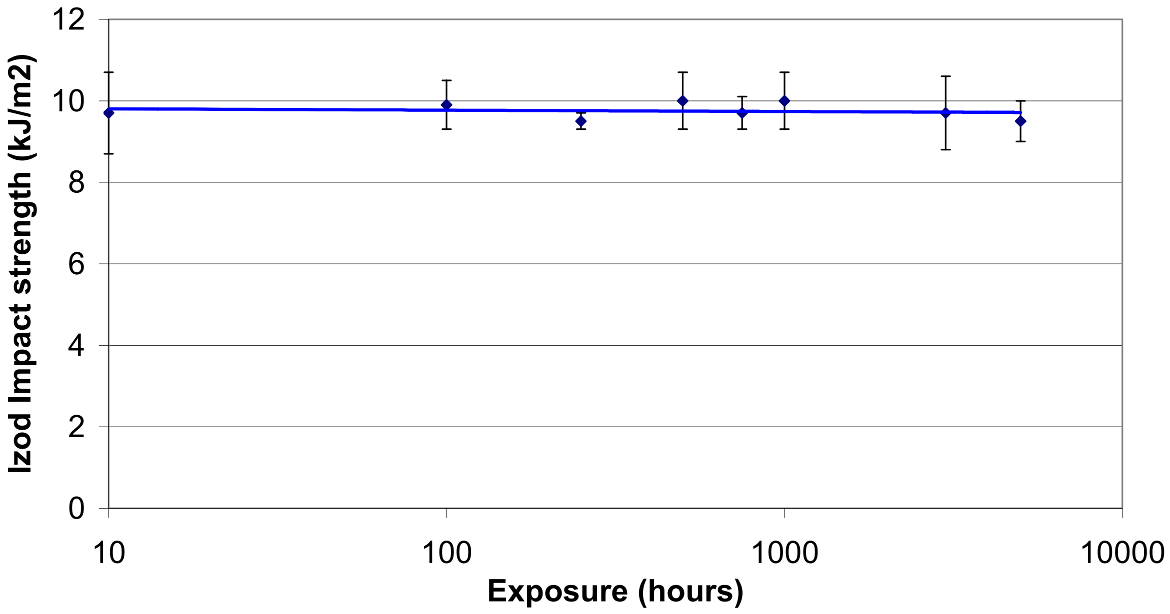


A1.3 Impact testing

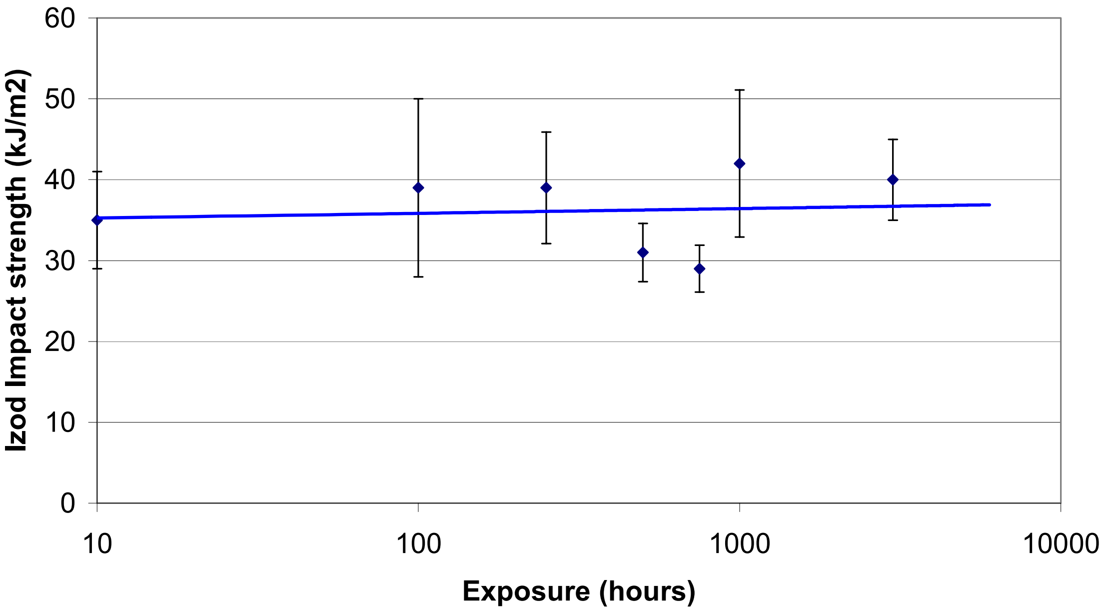

Izod Impact Strength: PP Bumper

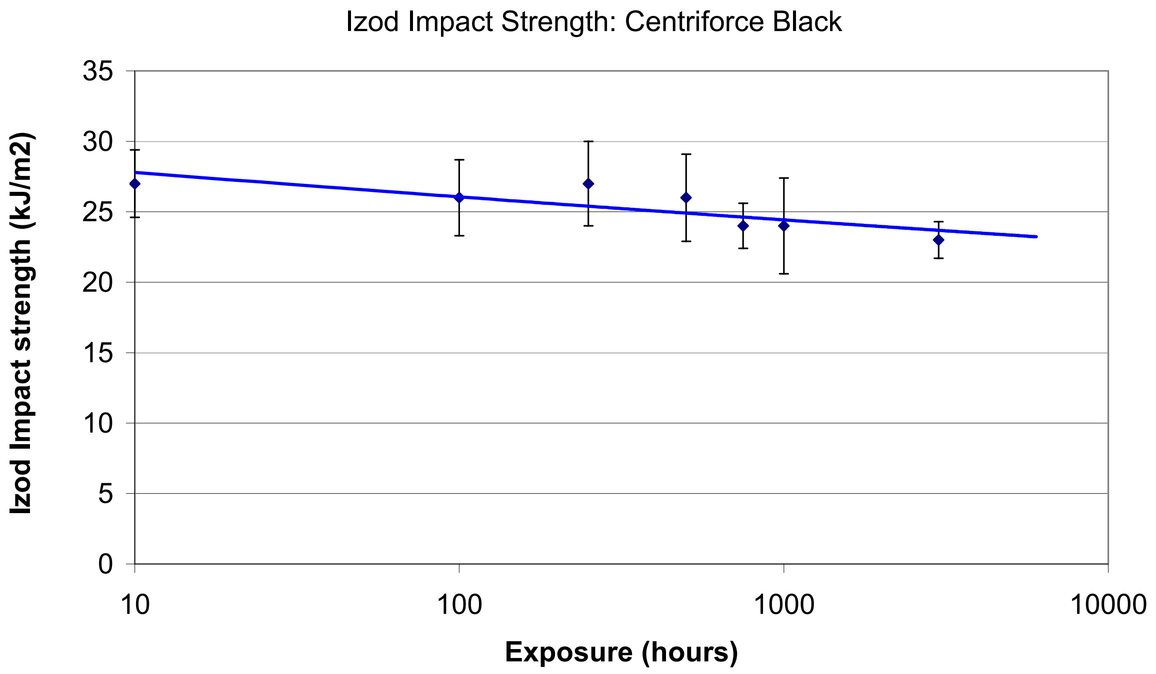

Izod Impact Strength: Wheelie Bin Black

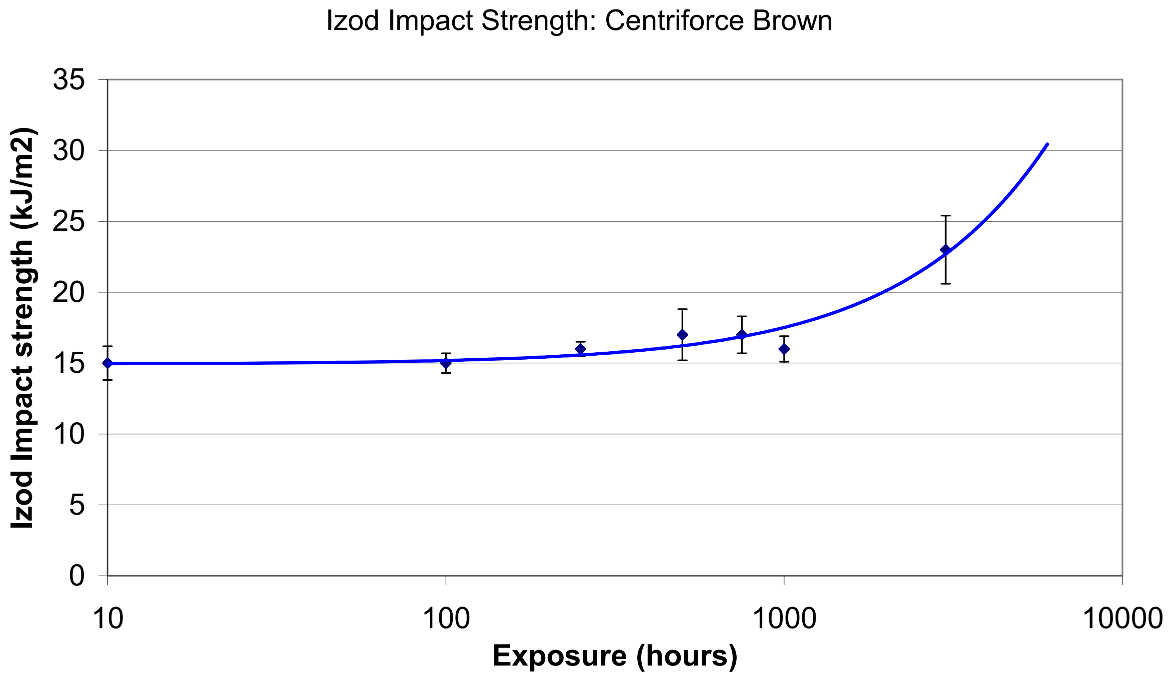
Izod Impact Strength: Wheelie Bin Green



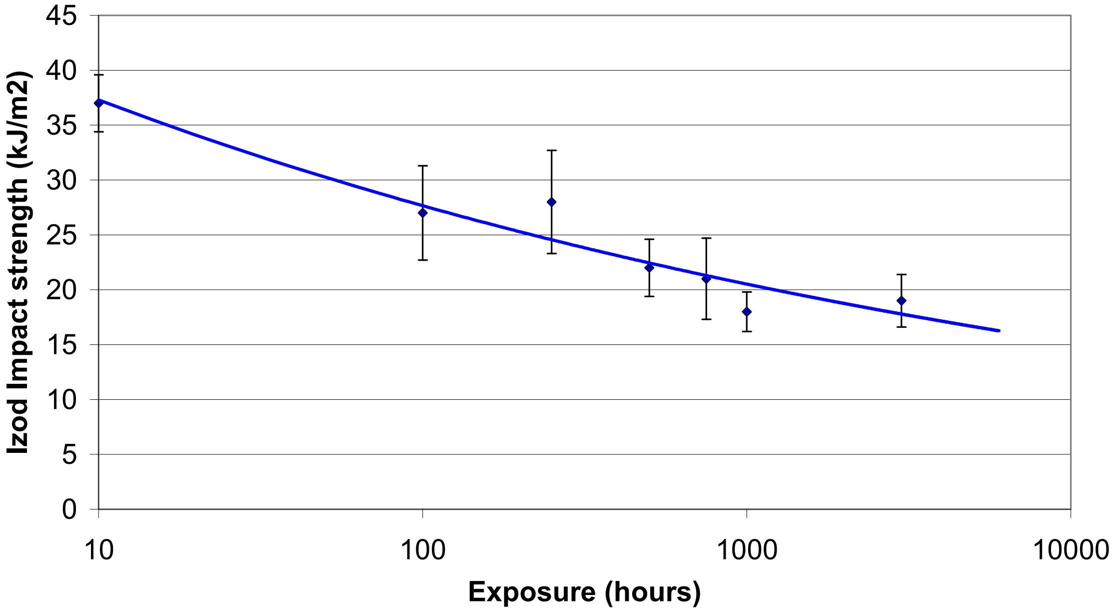
Izod Impact Strength: Centriforce Blue



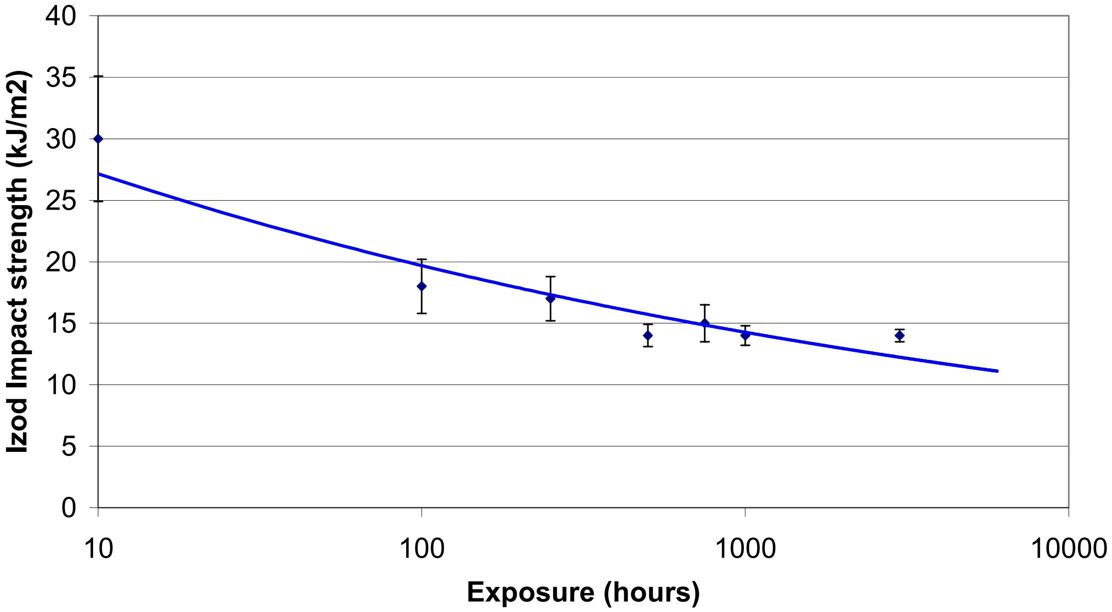

Izod Impact Strength: Centriforce Black
Izod Impact strength (kJ/m2)
35
30
25
20
15
10
5
0
10
100
1000
10000
Exposure (hours)


Izod Impact Strength: Centriforce Brown
Izod Impact strength (kJ/m2)
35
30
25
20
15
10
5
0
10
100
1000
10000
Exposure (hours)

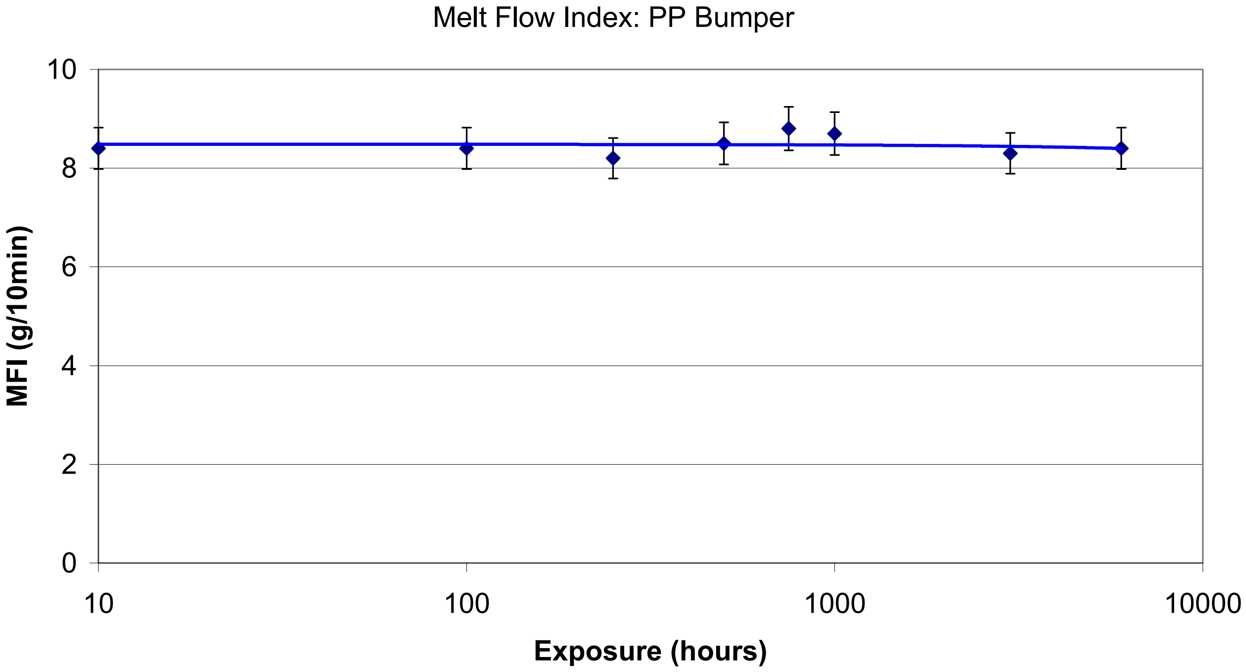
Izod Impact Strength: BPI Rectangular

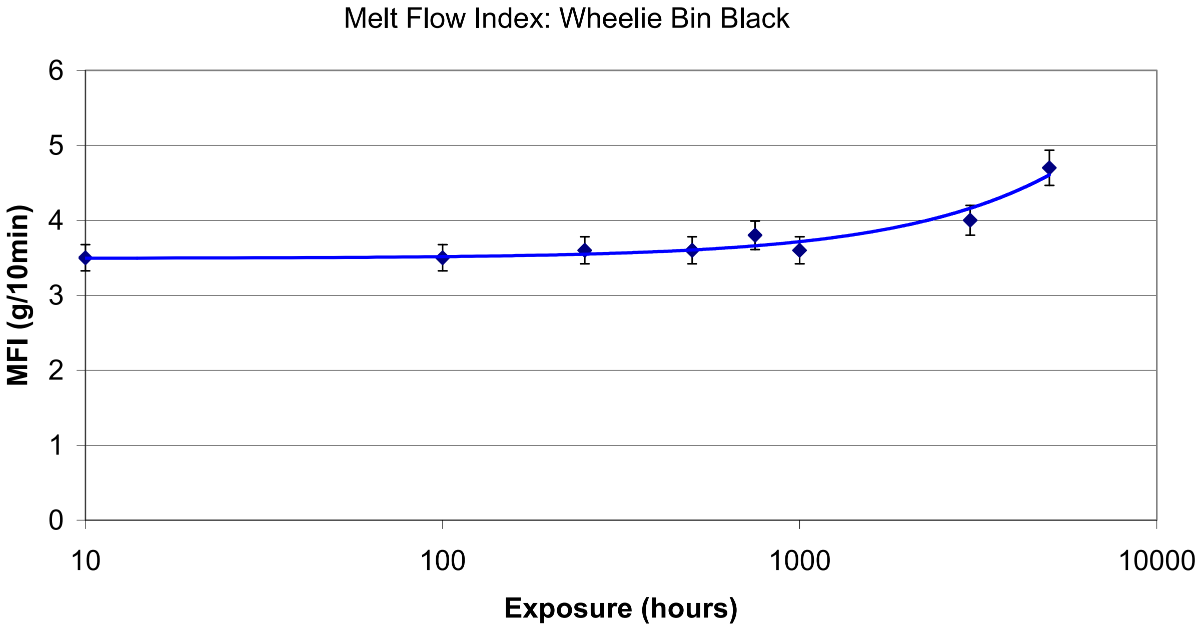


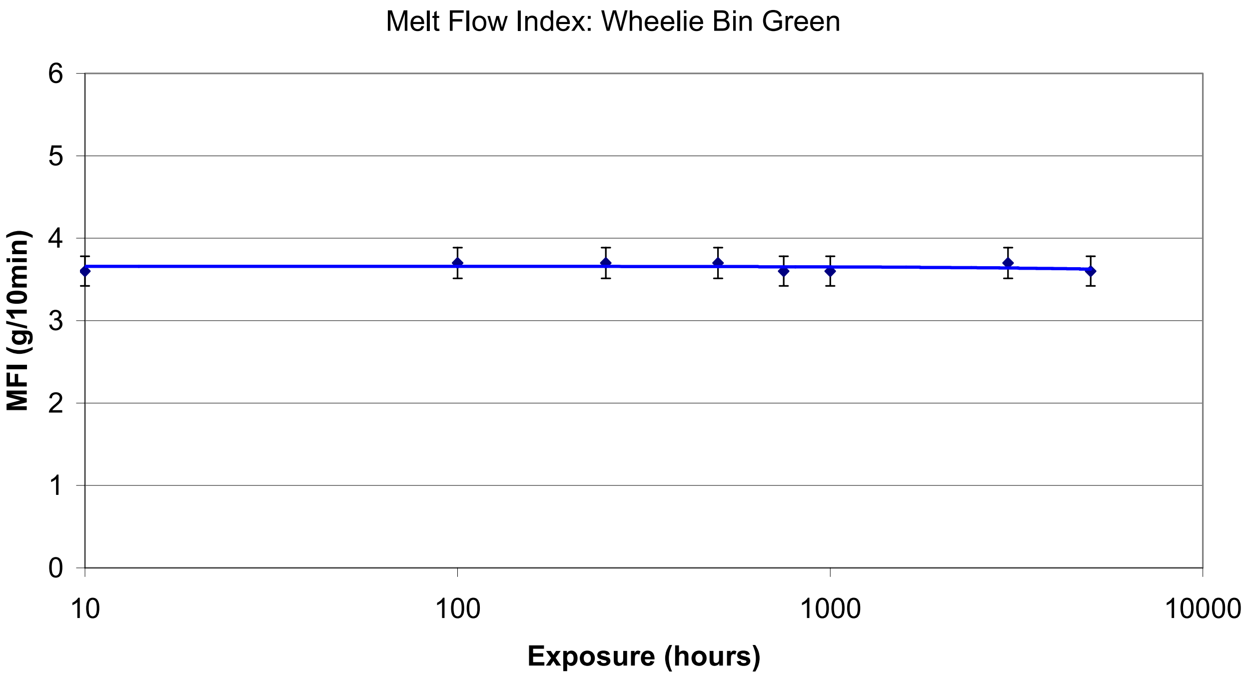
Izod Impact Strength: BPI Square

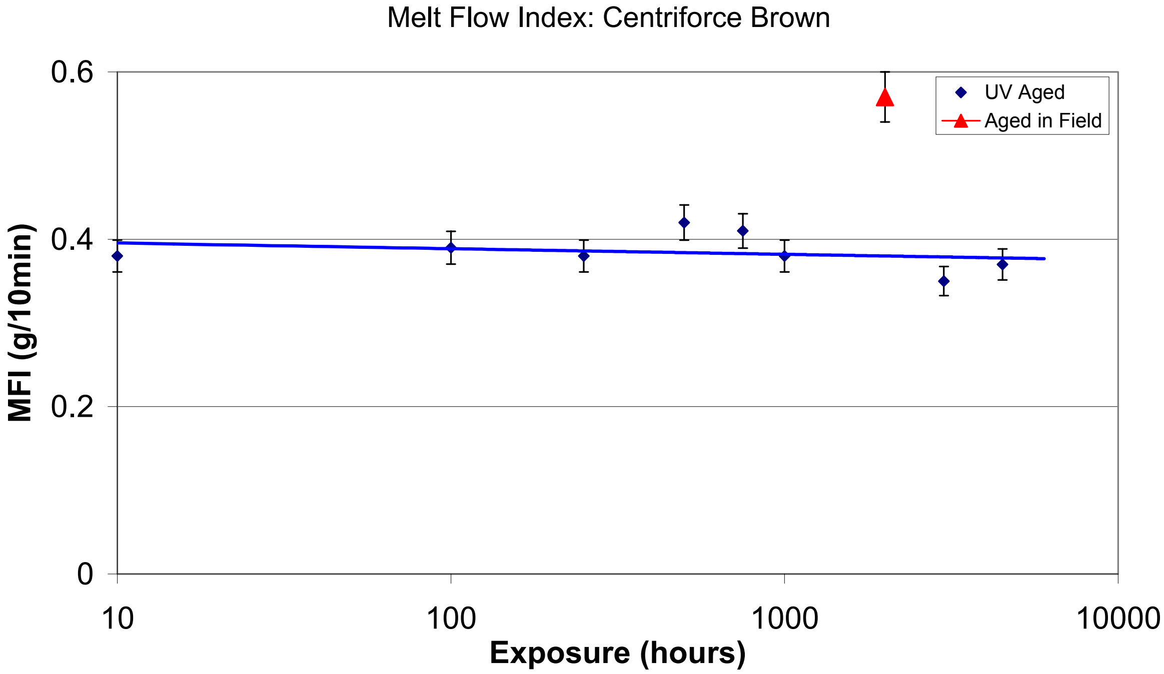


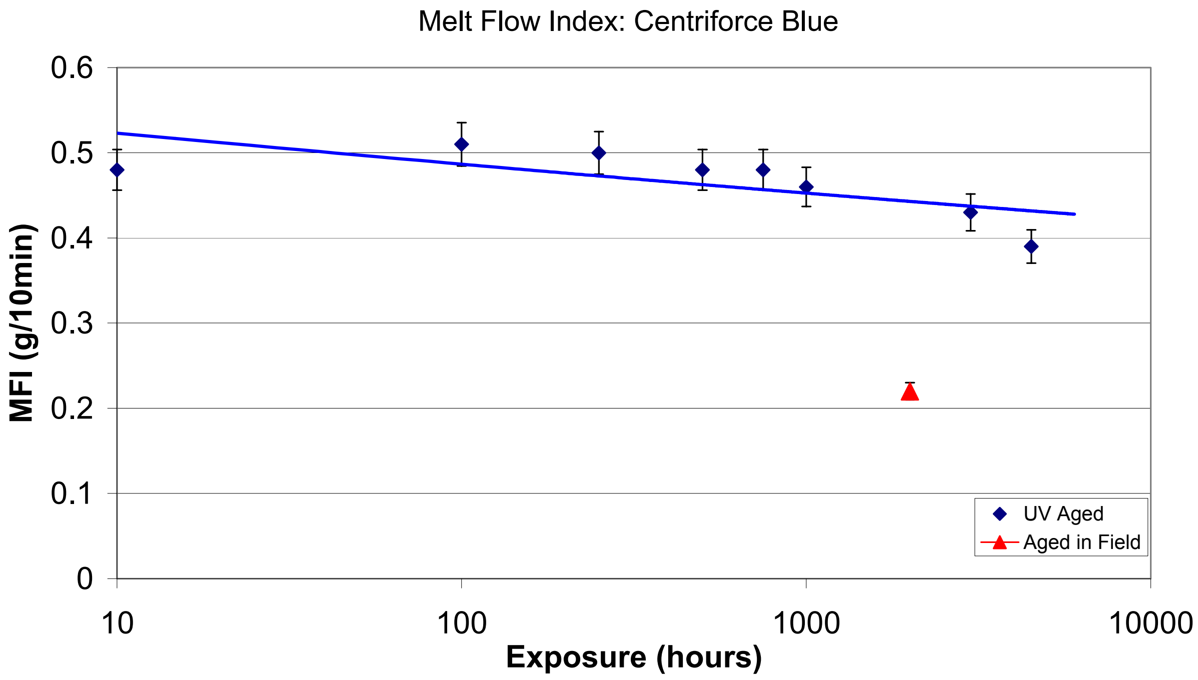
A1.4 Melt Flow Index

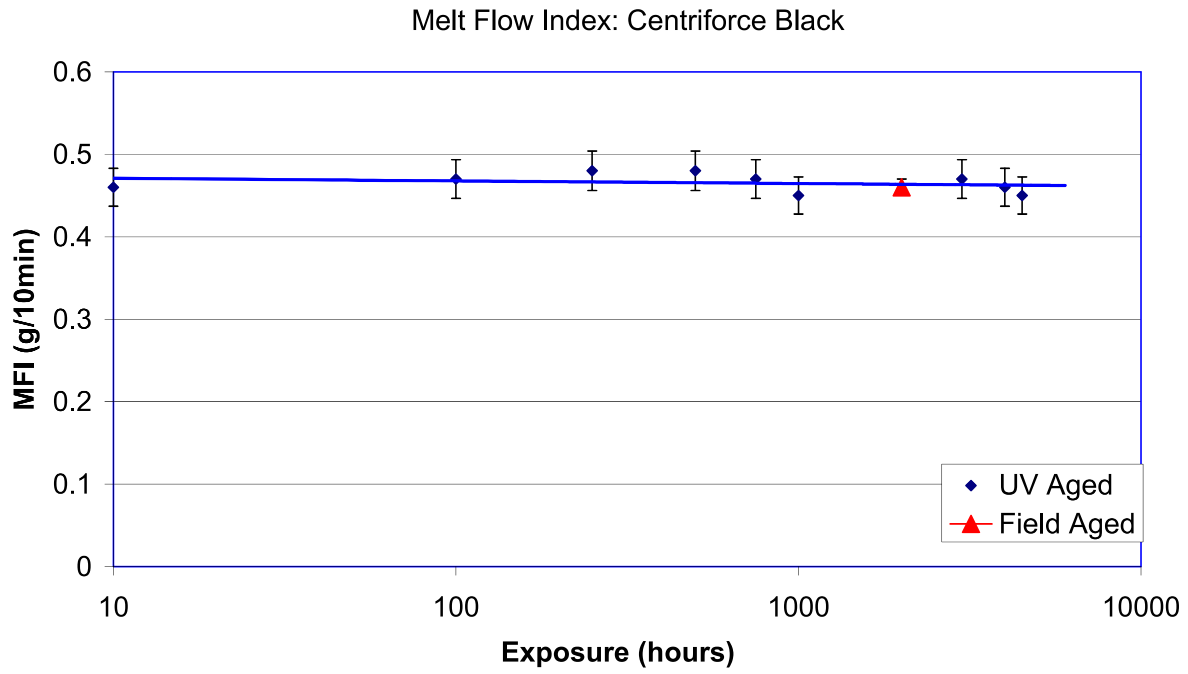


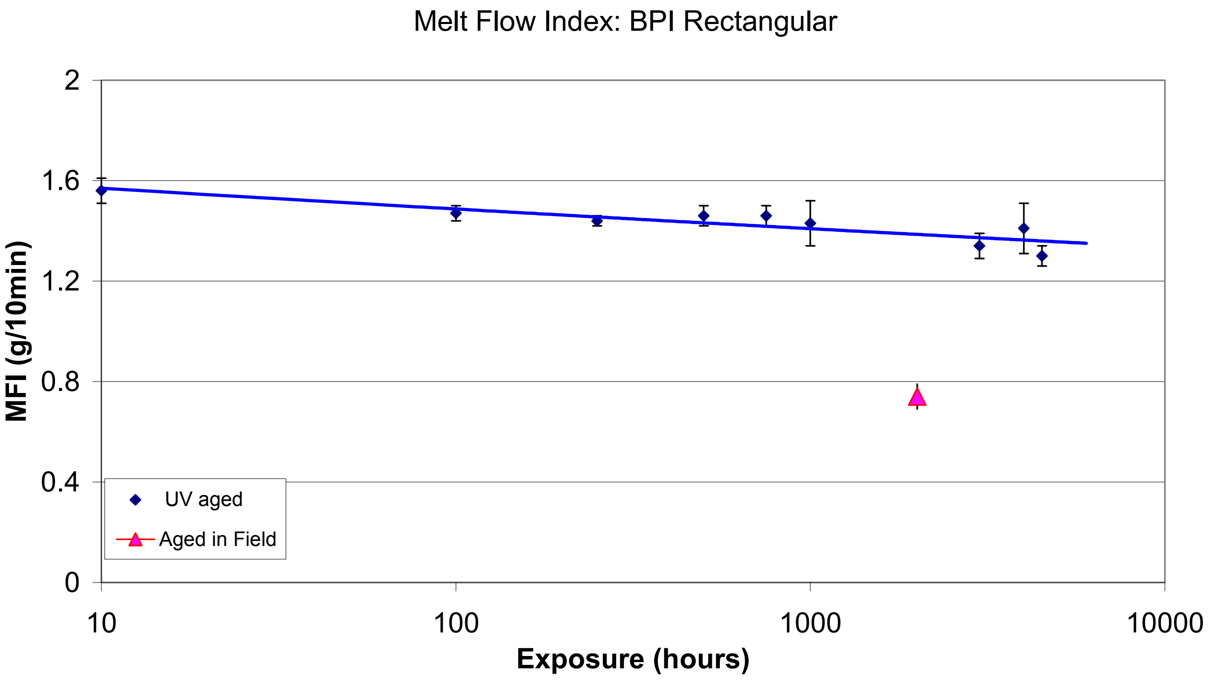


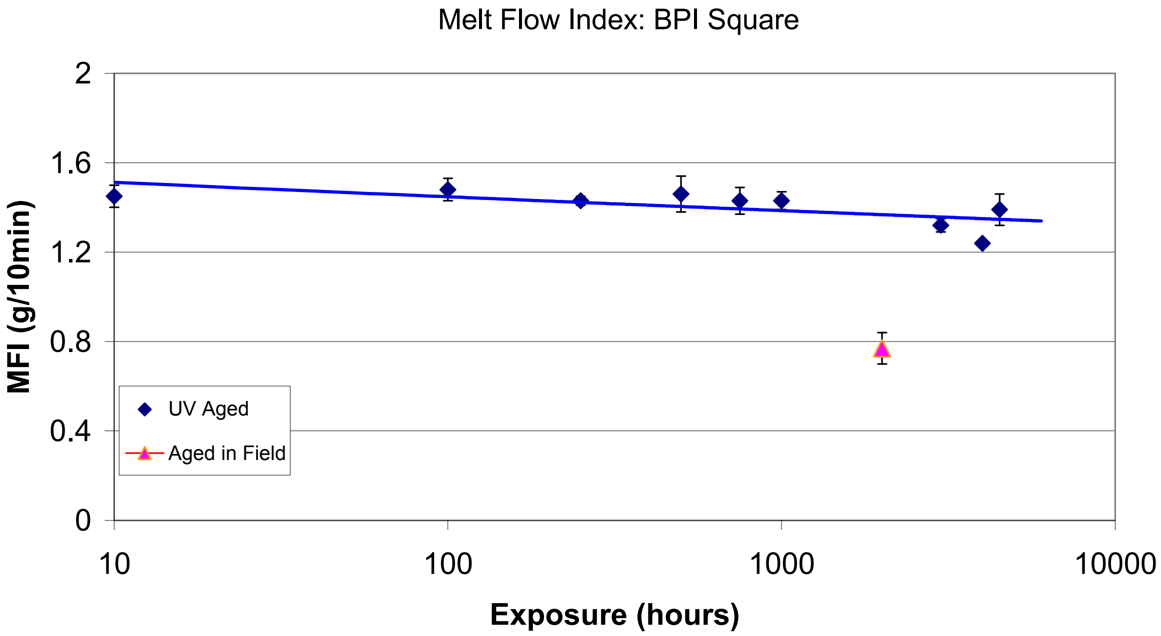

Melt Flow Index: Wheelie Bin Green
MFI (g/10min)
0
1
2
3
4
5
6
10
100
1000
10000
Exposure (hours)


Melt Flow Index: Centriforce Brown
MFI (g/10min)
0
0.2
0.4
0.6
10
100
1000
10000
Exposure (hours)
UV Aged
Aged in Field

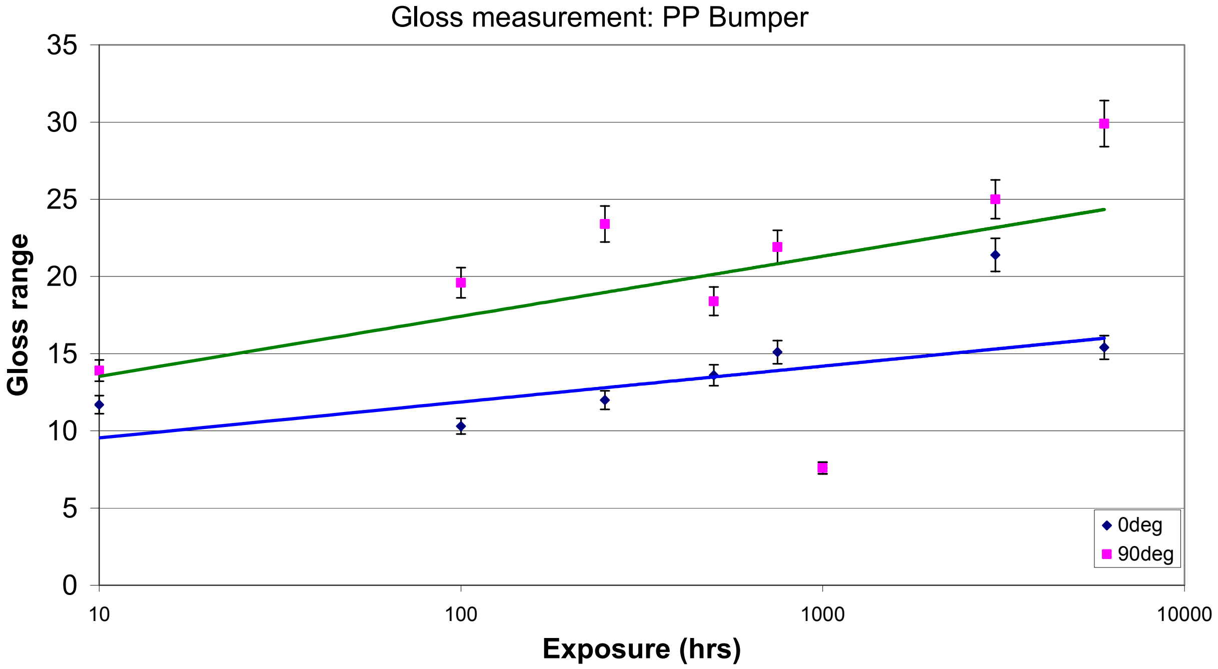

Melt Flow Index: Centriforce Blue
MFI (g/10min)
0.6
0.5
0.4
0.3
0.2
0.1
0
10
100
1000
10000
Exposure (hours)
UV Aged
Aged in Field

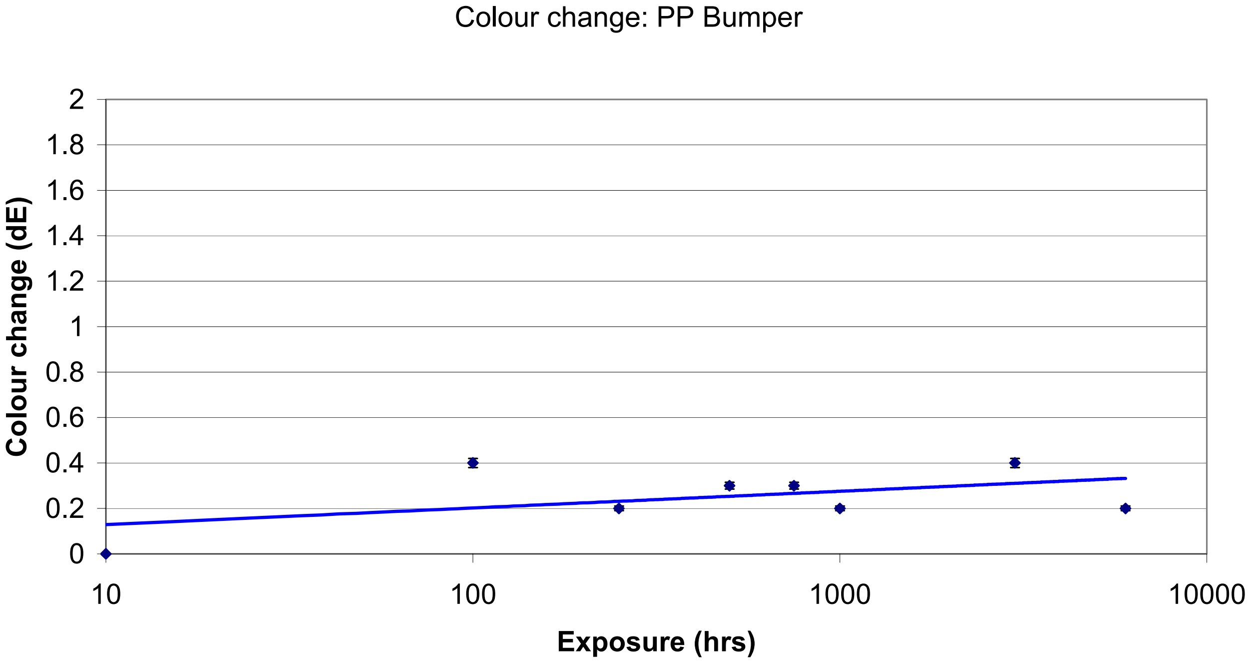

Melt Flow Index: Centriforce Black
MFI (g/10min)
0.6
0.5
0.4
0.3
0.2
0.1
0
10
100
1000
10000
Exposure (hours)
UV Aged
Field Aged

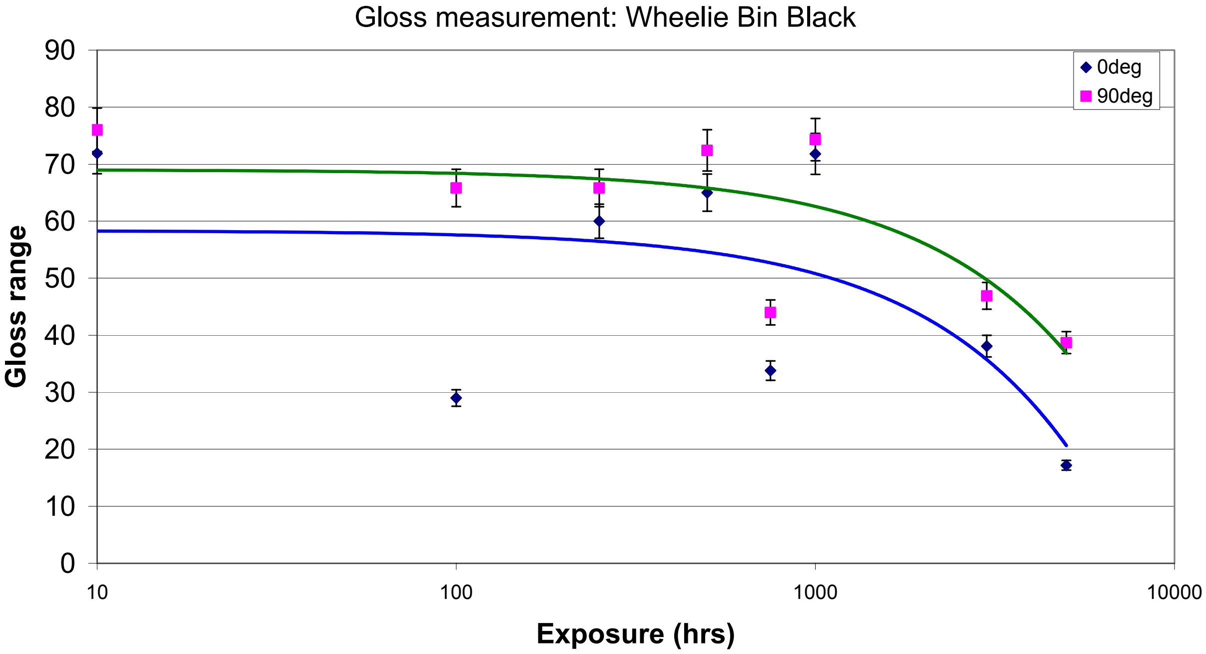

Melt Flow Index: BPI Rectangular
MFI (g/10min)
2
1.6
1.2
0.8
0.4
0
10
100
1000
10000
Exposure (hours)
UV aged
Aged in Field

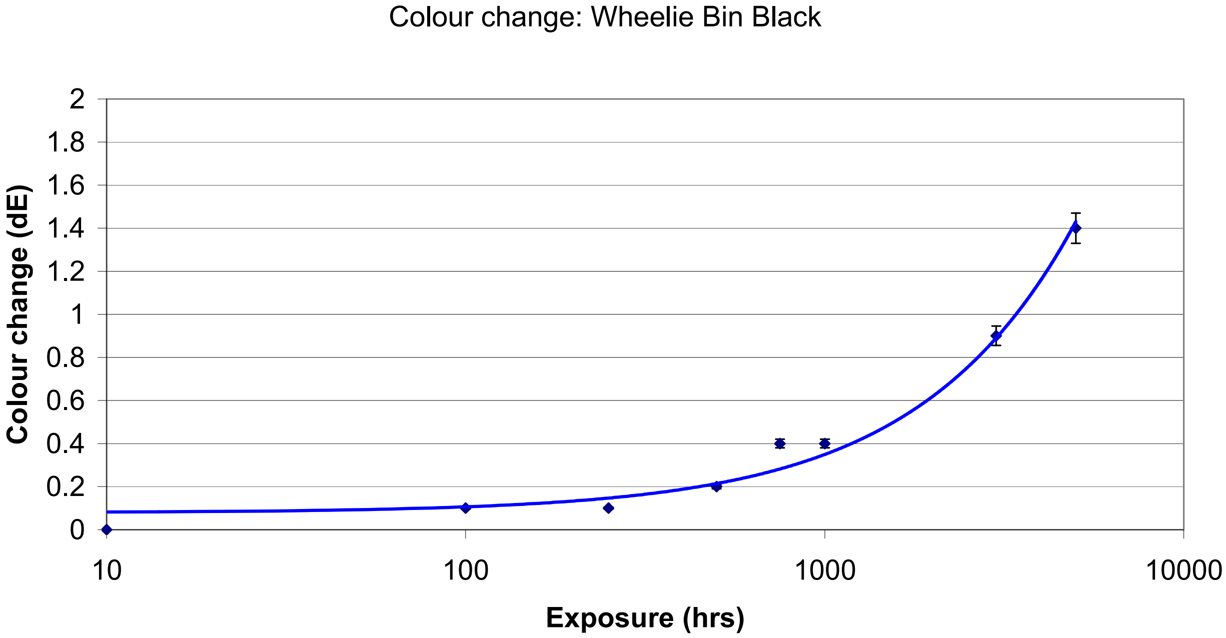

Melt Flow Index: BPI Square
MFI (g/10min)
2
1.6
1.2
0.8
0.4
0
10
100
1000
10000
Exposure (hours)
UV Aged
Aged in Field

A1.5 Colour and gloss.

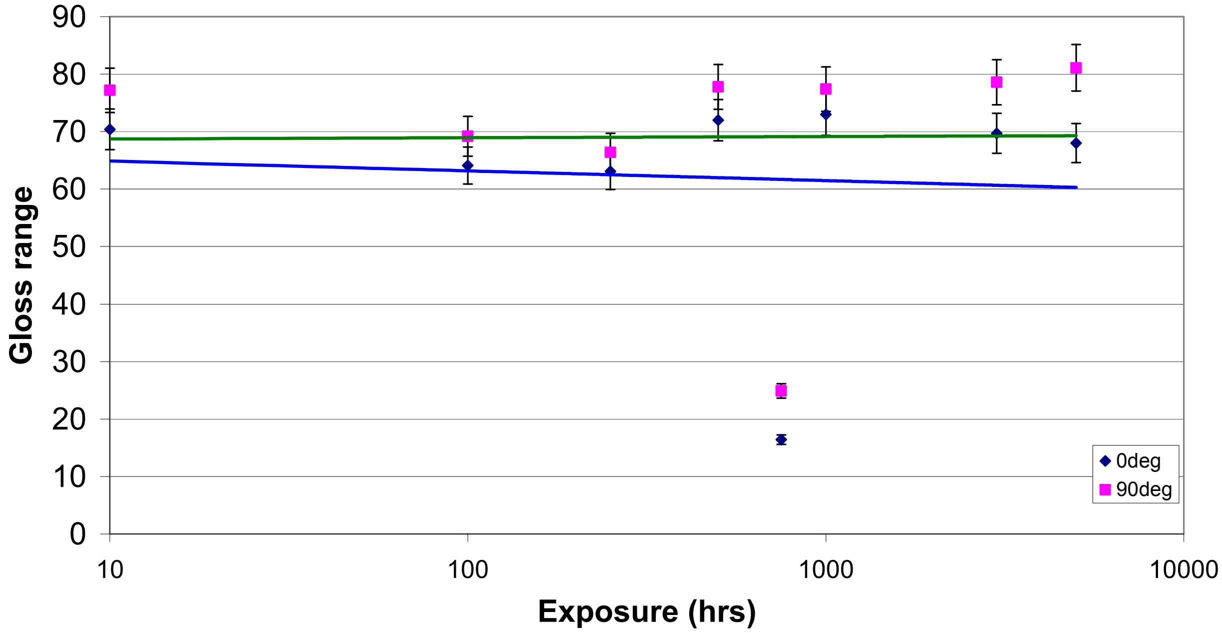




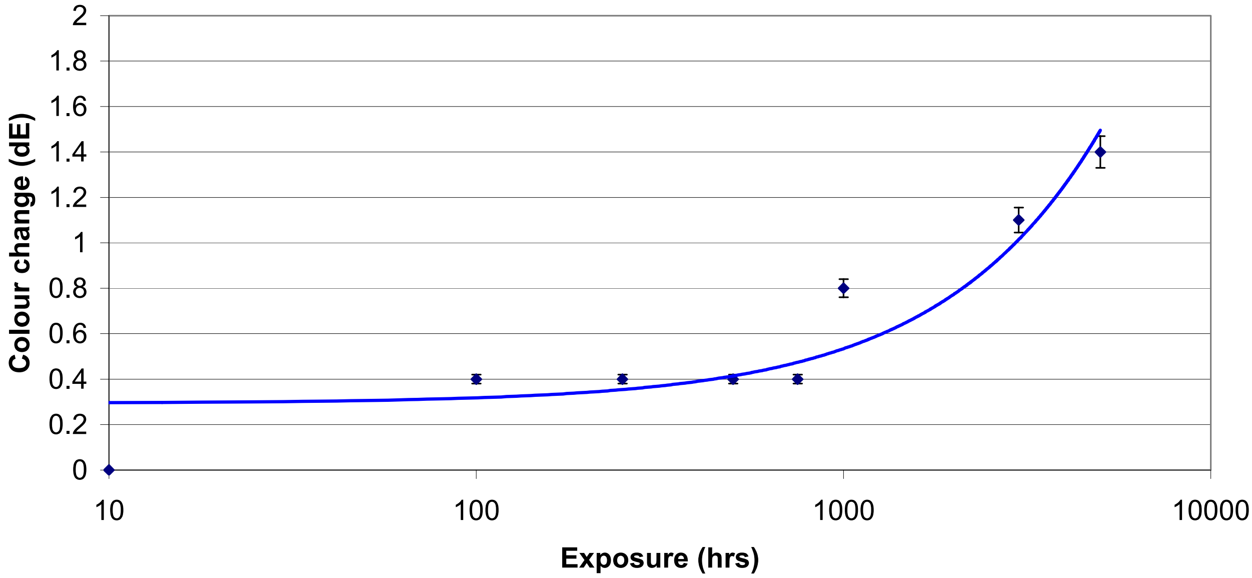

Gloss measurement: Wheelie Bin Black
Gloss range
0
10
20
30
40
50
60
70
80
90
10
100
1000
10000
Exposure (hrs)
0deg
90deg

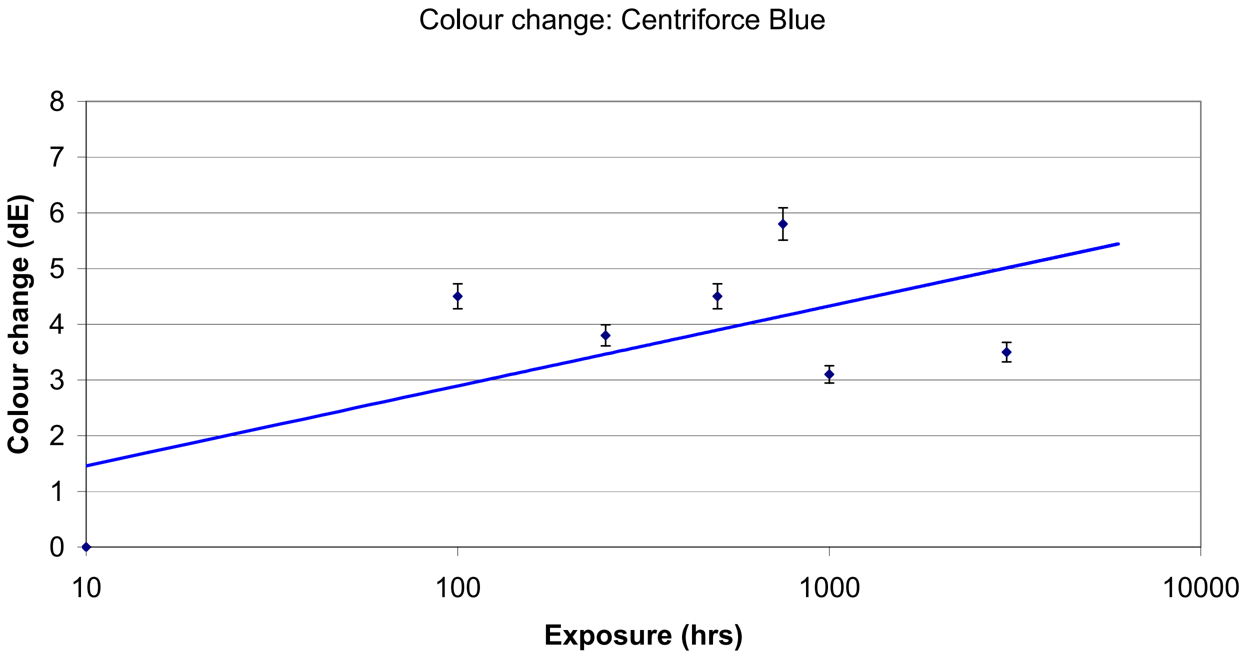

Colour change: Wheelie Bin Black
Colour change (dE)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
10
100
1000
10000
Exposure (hrs)

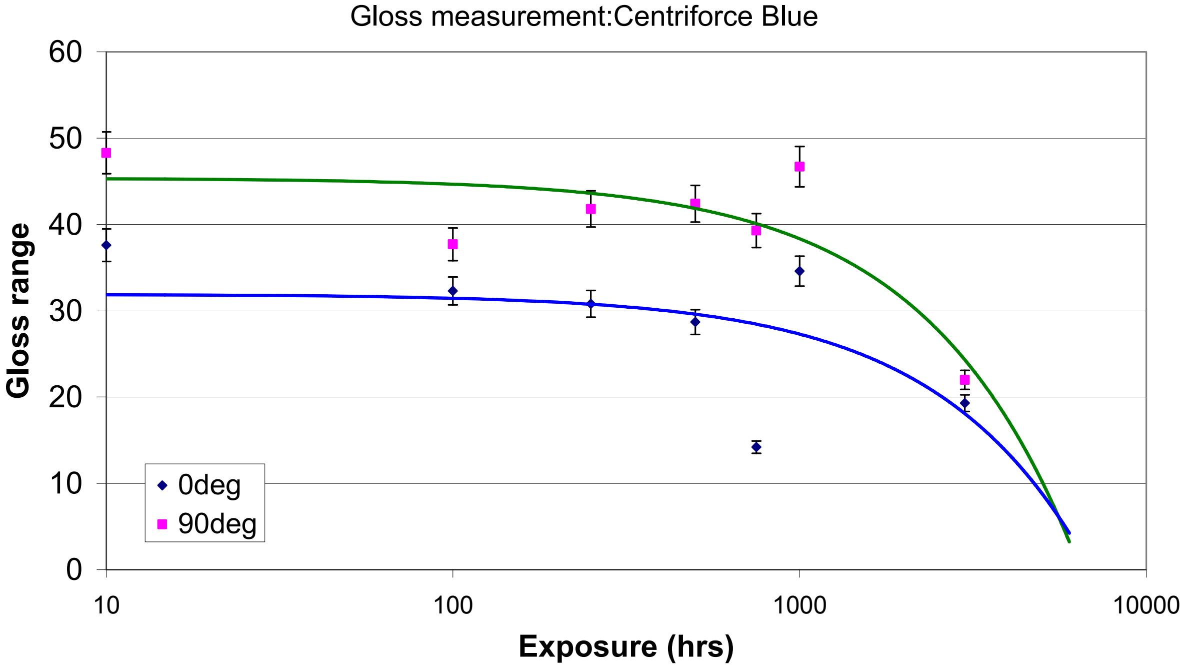
Gloss measurement: Wheelie Bin Green

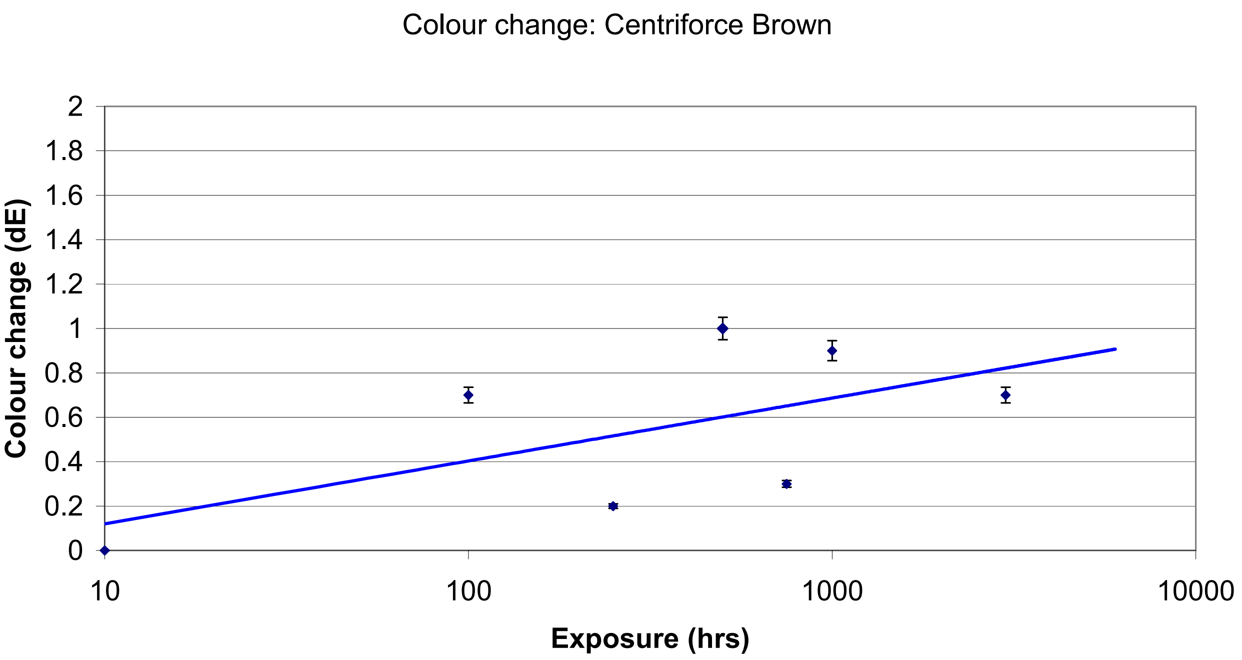


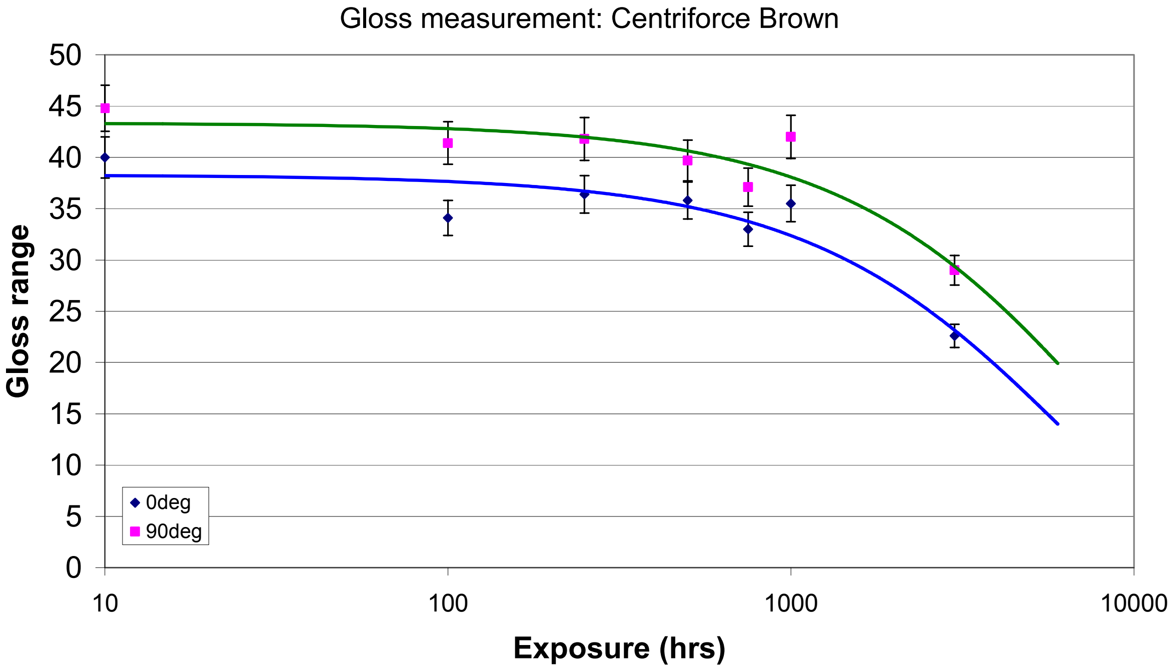
Colour change: Wheelie Bin Green

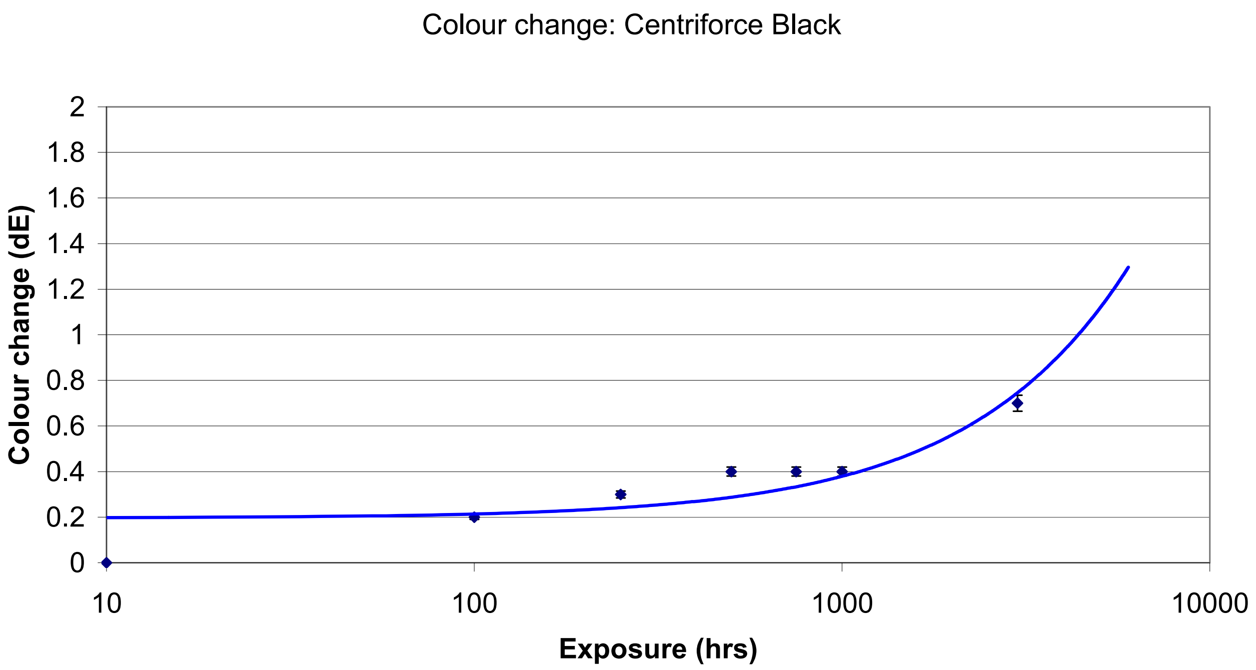


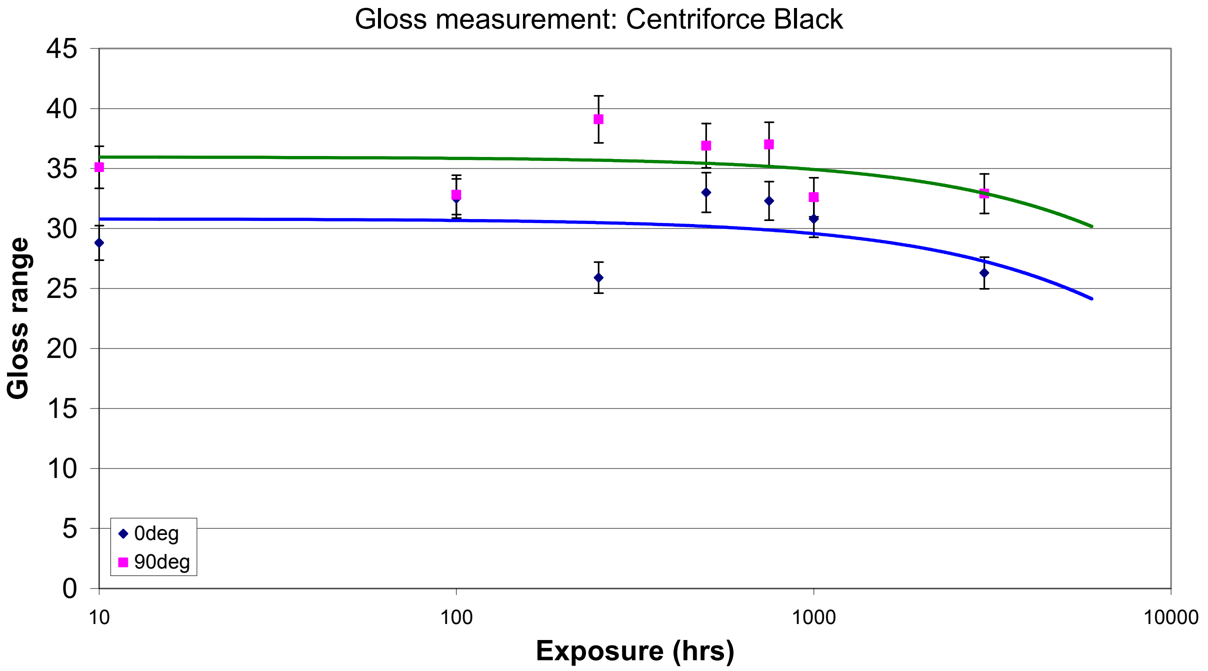

Colour change: Centriforce Blue
Colour change (dE)
0
1
2
3
4
5
6
7
8
10
100
1000
10000
Exposure (hrs)

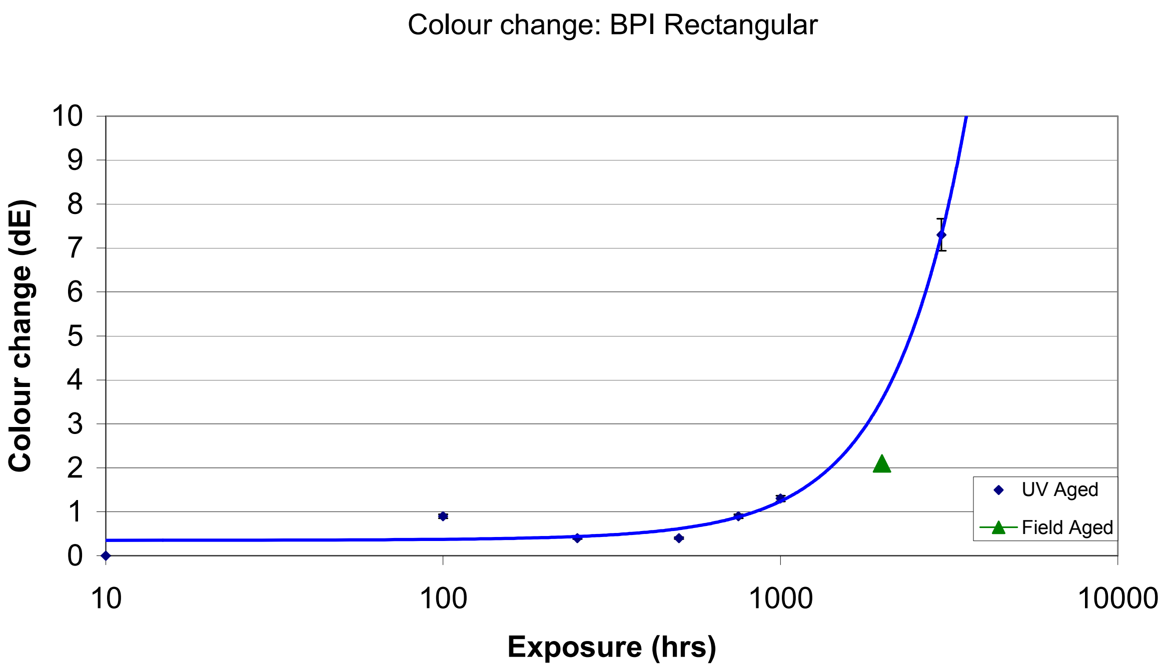

Gloss measurement:Centriforce Blue
Gloss range
0
10
20
30
40
50
60
10
100
1000
10000
Exposure (hrs)
0deg
90deg

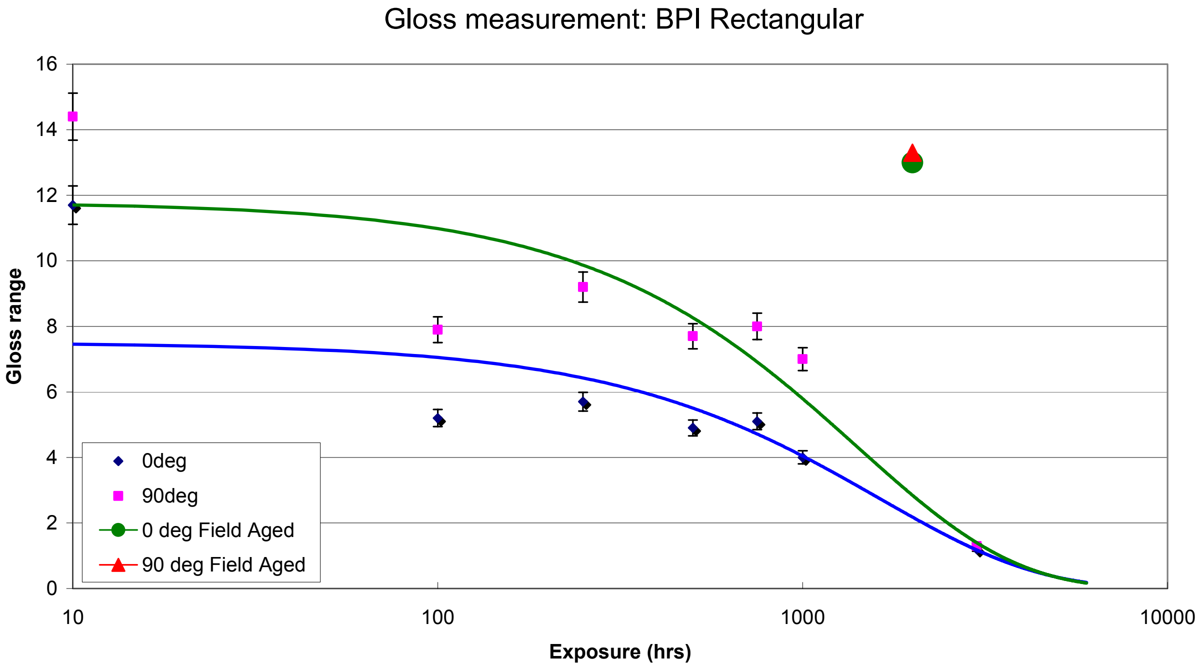

Colour change: Centriforce Brown
Colour change (dE)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
10
100
1000
10000
Exposure (hrs)

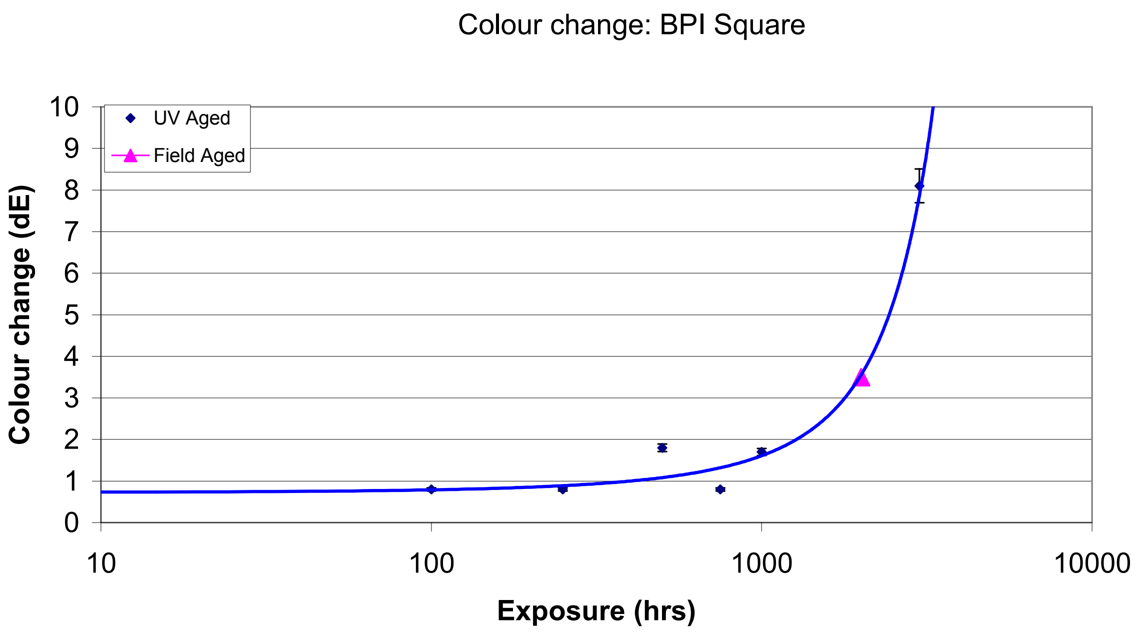

Gloss measurement: Centriforce Brown
Gloss range
0
5
10
15
20
25
30
35
40
45
50
◆ 0deg
■ 90deg
10
100
1000
10000
Exposure (hrs)

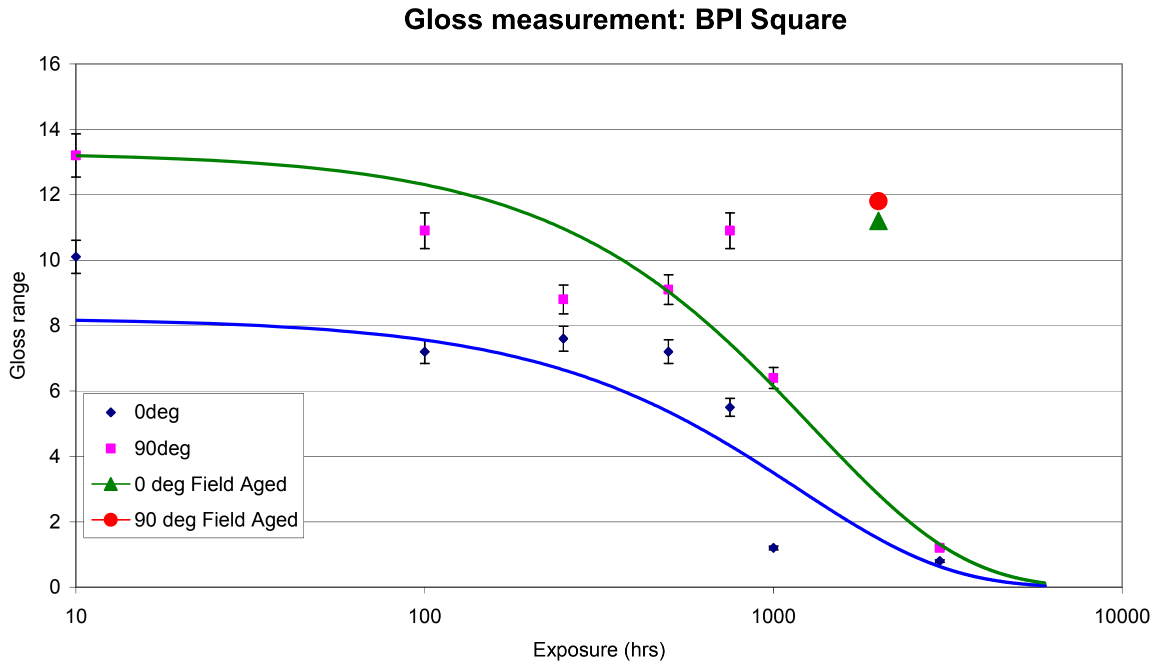

Colour change: Centriforce Black
Colour change (dE)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
10
100
1000
10000
Exposure (hrs)


Gloss measurement: Centriforce Black
Gloss range
45
40
35
30
25
20
15
10
5
0
10
100
1000
10000
Exposure (hrs)
0deg
90deg

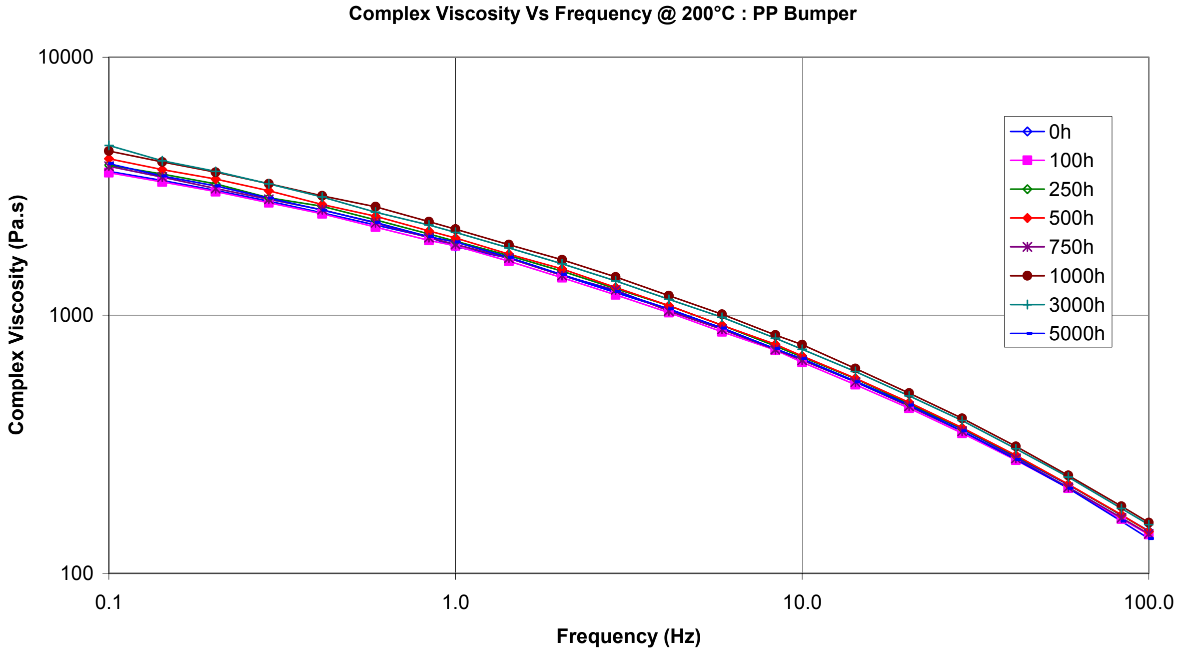

Colour change: BPI Rectangular
Colour change (dE)
10
9
8
7
6
5
4
3
2
1
0
10
100
1000
10000
Exposure (hrs)
UV Aged
Field Aged

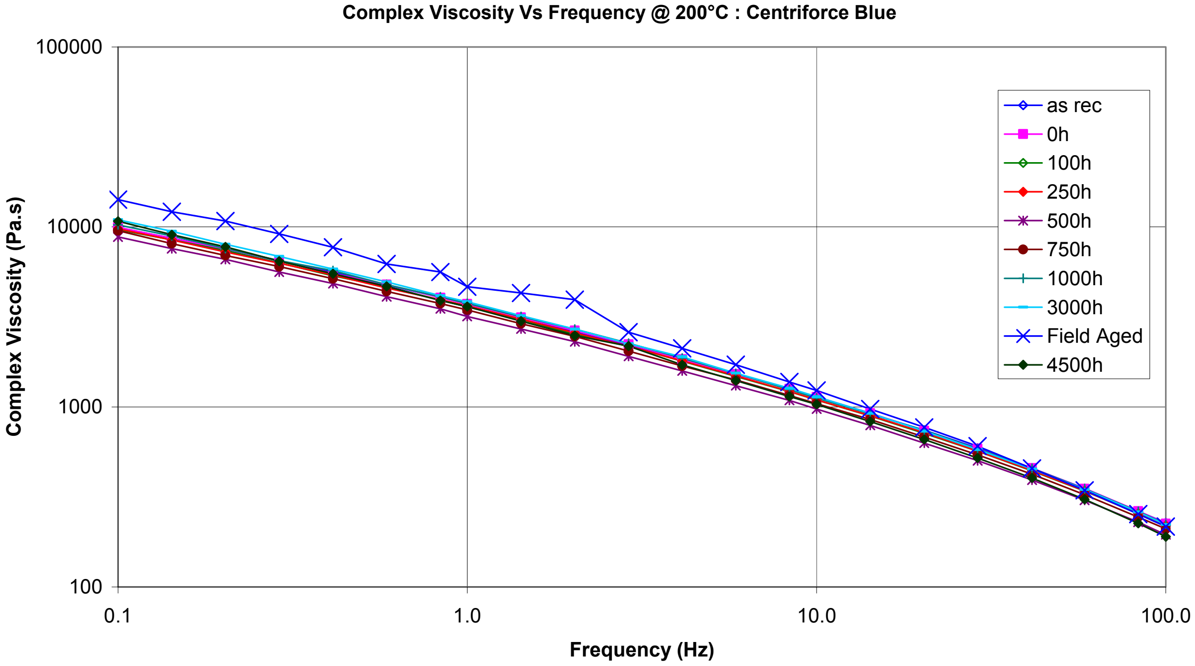

Gloss measurement: BPI Rectangular
Gloss range
16
14
12
10
8
6
4
2
0
10
100
1000
10000
Exposure (hrs)
0deg
90deg
0 deg Field Aged
90 deg Field Aged

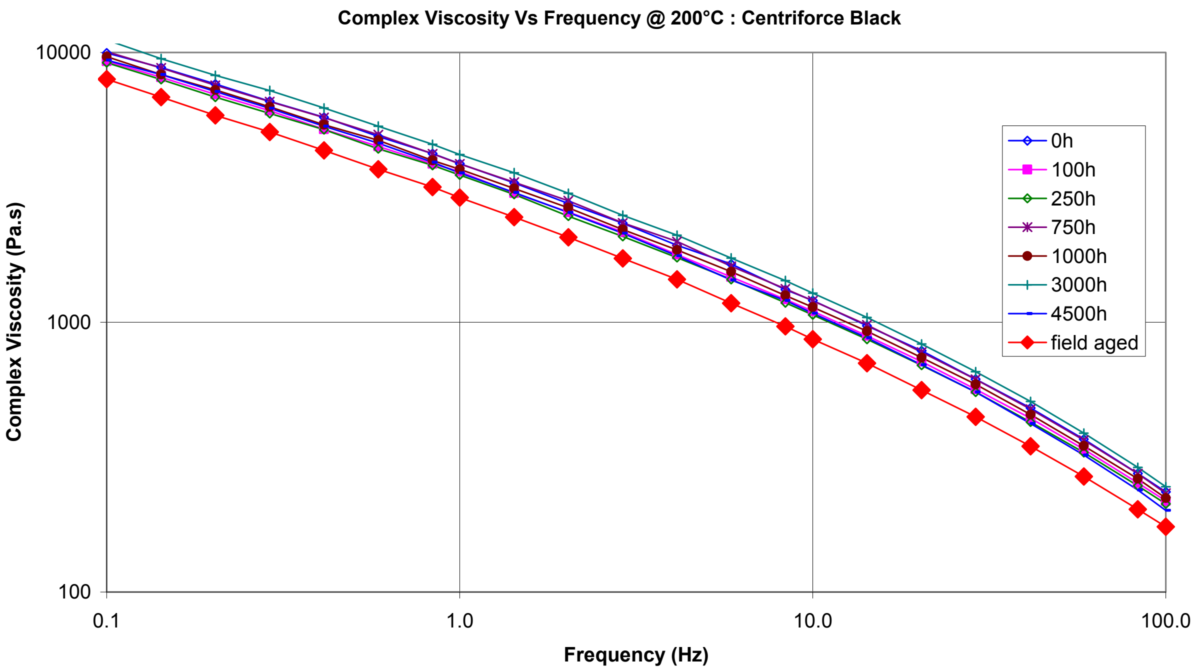

Colour change: BPI Square

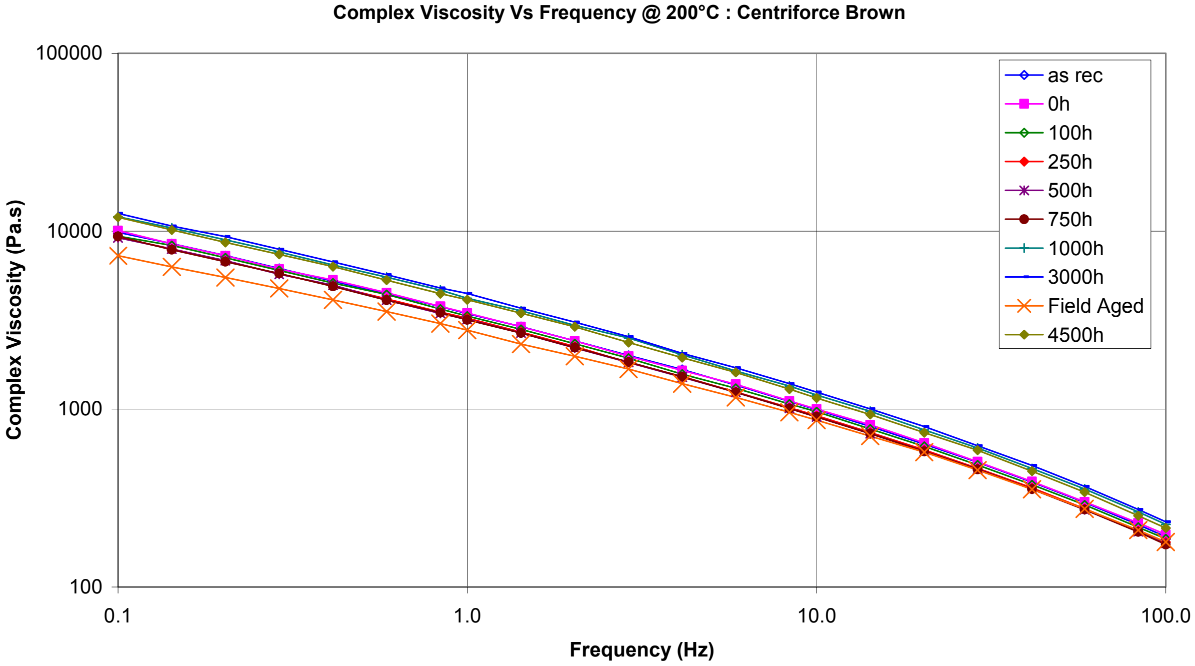

Gloss measurement: BPI Square

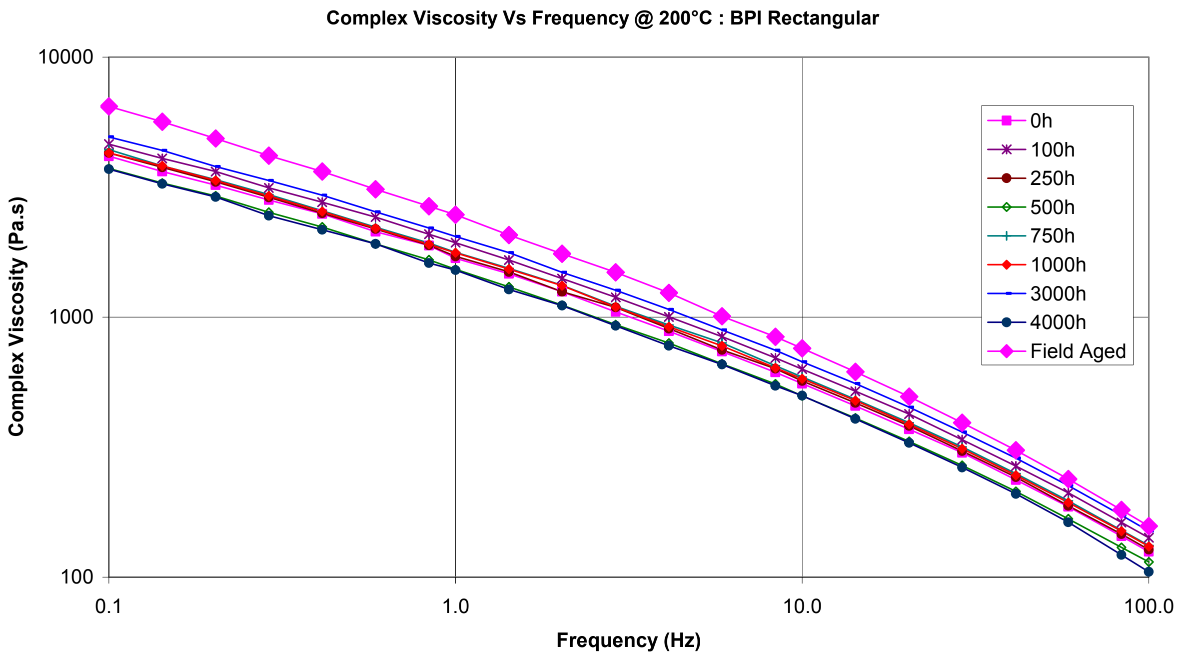
A1.6 Rotational Oscillating Viscometry

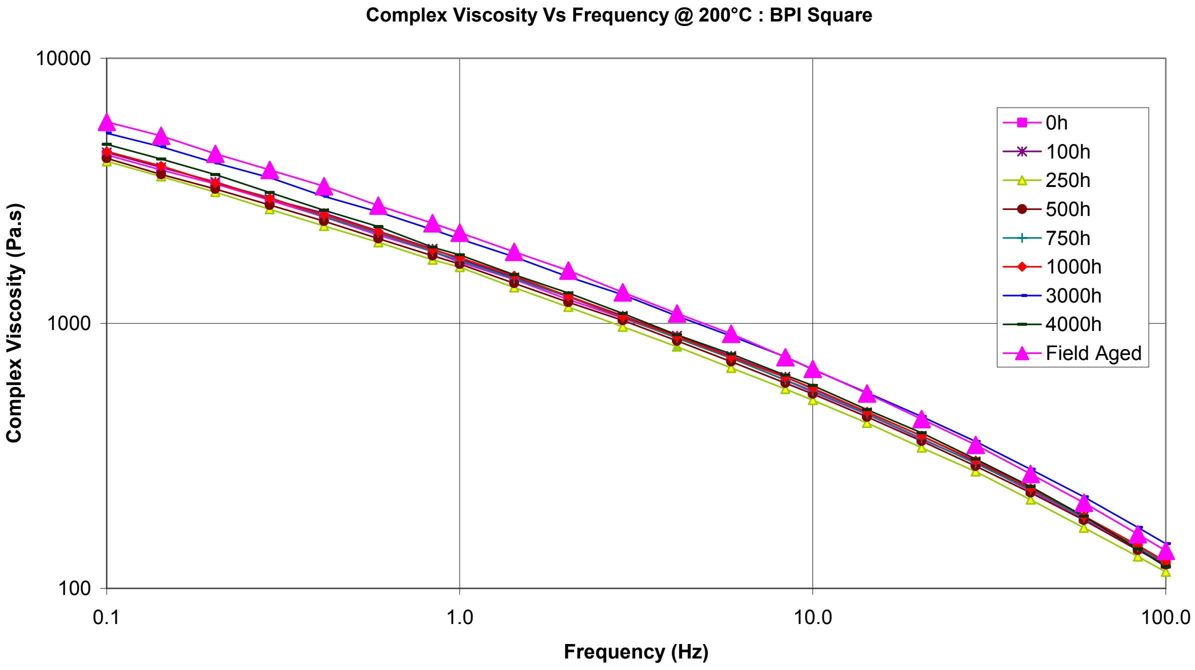


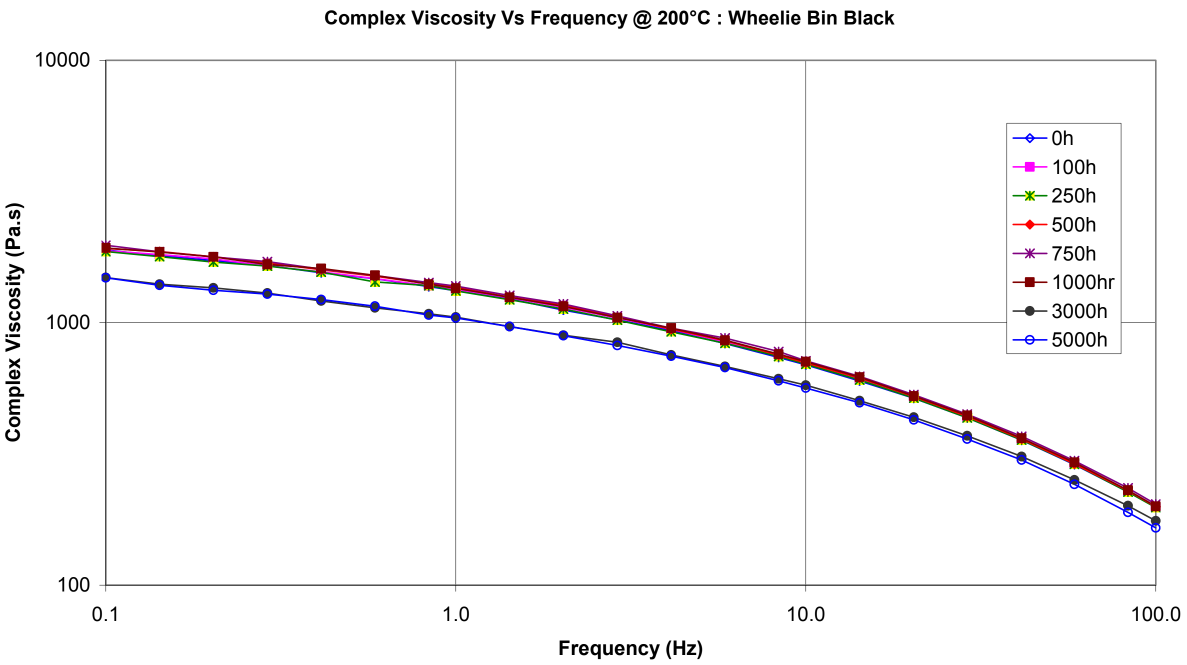



Complex Viscosity Vs Frequency @ 200°C : Centriforce Black
Complex Viscosity (Pa.s)
10000
1000
100
0.1
1.0
10.0
100.0
Frequency (Hz)
0h
100h
250h
750h
1000h
3000h
4500h
field aged

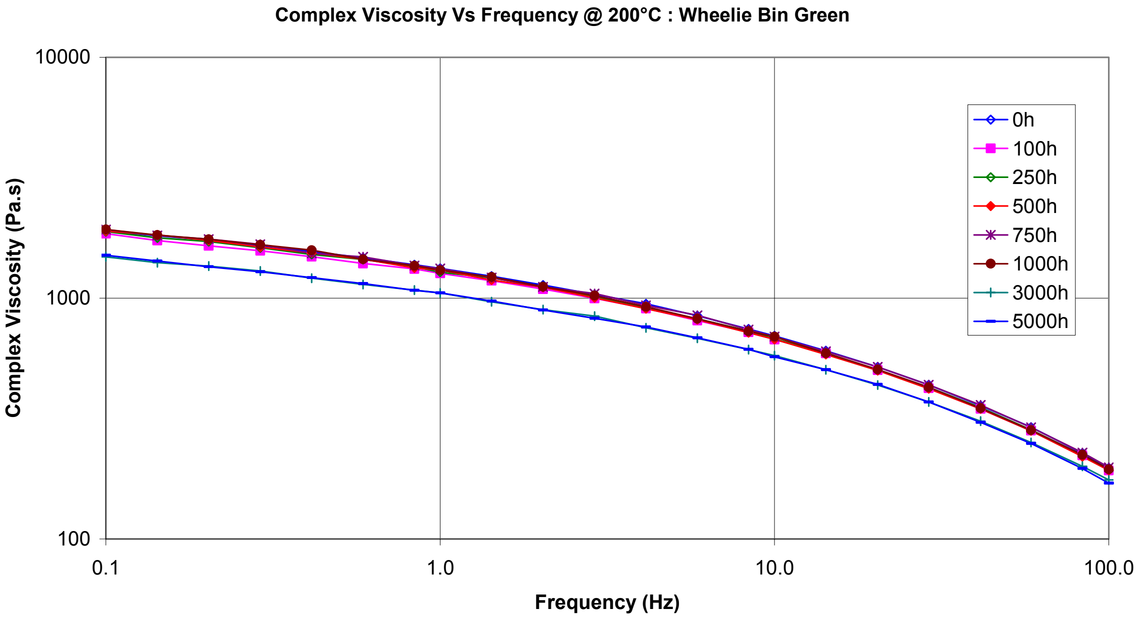

Complex Viscosity Vs Frequency @ 200°C : Centriforce Brown
Complex Viscosity (Pa.s)
100000
10000
1000
100
0.1
1.0
10.0
100.0
Frequency (Hz)
as rec
0h
100h
250h
500h
750h
1000h
3000h
Field Aged
4500h


Complex Viscosity Vs Frequency @ 200°C : BPI Rectangular
10000
1000
100
Complex Viscosity (Pa.s)
0.1
1.0
10.0
100.0
Frequency (Hz)
0h
100h
250h
500h
750h
1000h
3000h
4000h
Field Aged


Complex Viscosity Vs Frequency @ 200°C : BPI Square
10000
1000
100
Complex Viscosity (Pa.s)
0.1
1.0
10.0
100.0
Frequency (Hz)
0h
100h
250h
500h
750h
1000h
3000h
4000h
Field Aged

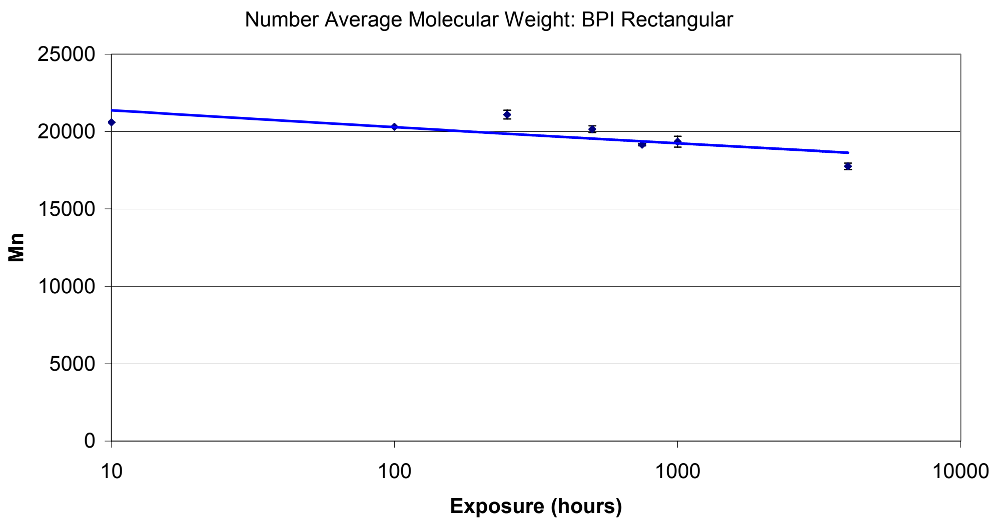


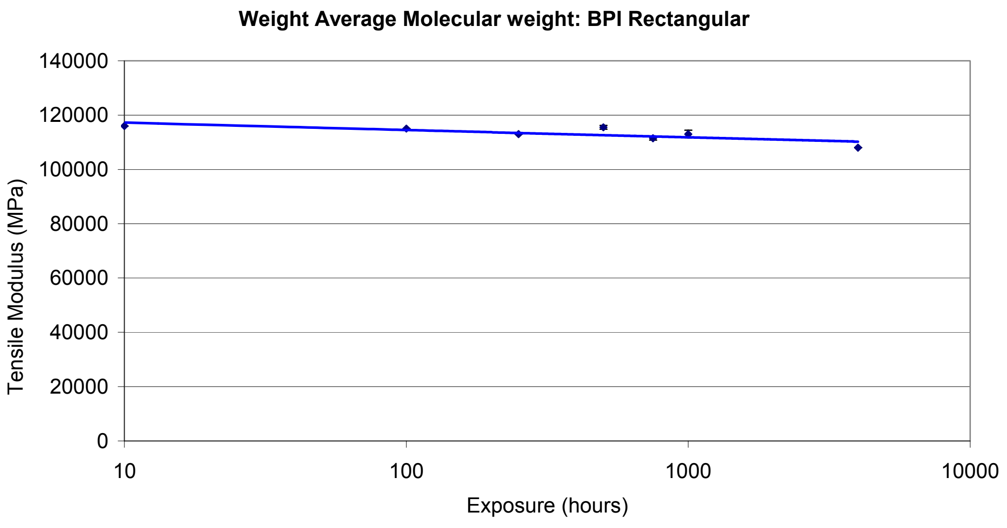
Complex Viscosity Vs Frequency @ 200°C : Wheelie Bin Black
Complex Viscosity (Pa.s)
10000
1000
100
0.1
1.0
10.0
100.0
Frequency (Hz)
0h
100h
250h
500h
750h
1000hr
3000h
5000h

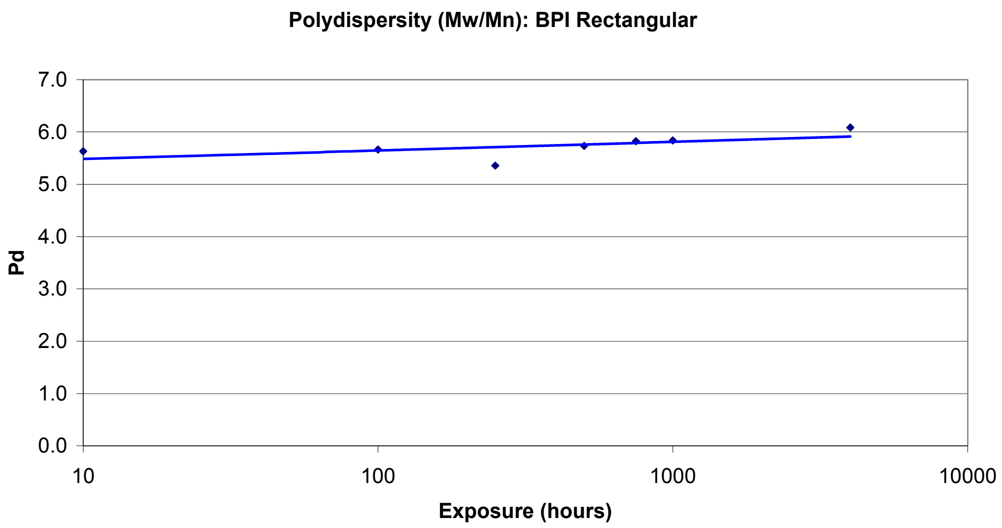


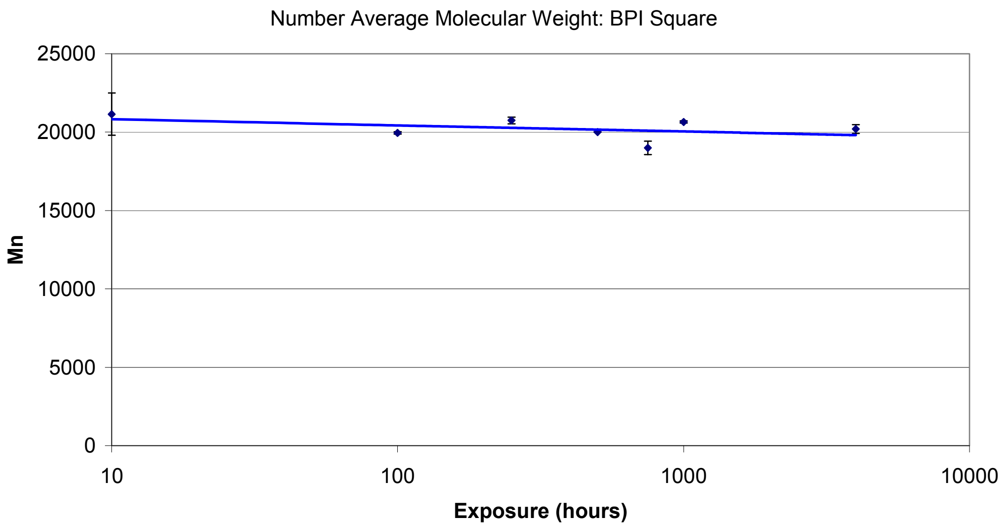
Complex Viscosity Vs Frequency @ 200°C : Wheelie Bin Green
Complex Viscosity (Pa.s)
10000
1000
100
0.1
1.0
10.0
100.0
Frequency (Hz)
0h
100h
250h
500h
750h
1000h
3000h
5000h

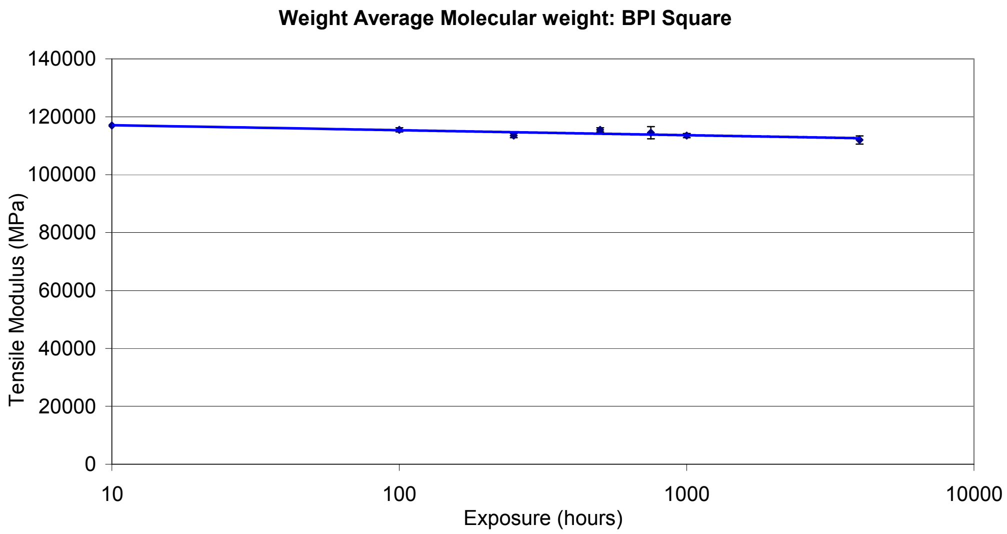
A1.7 GPC – Molecular weight measurement

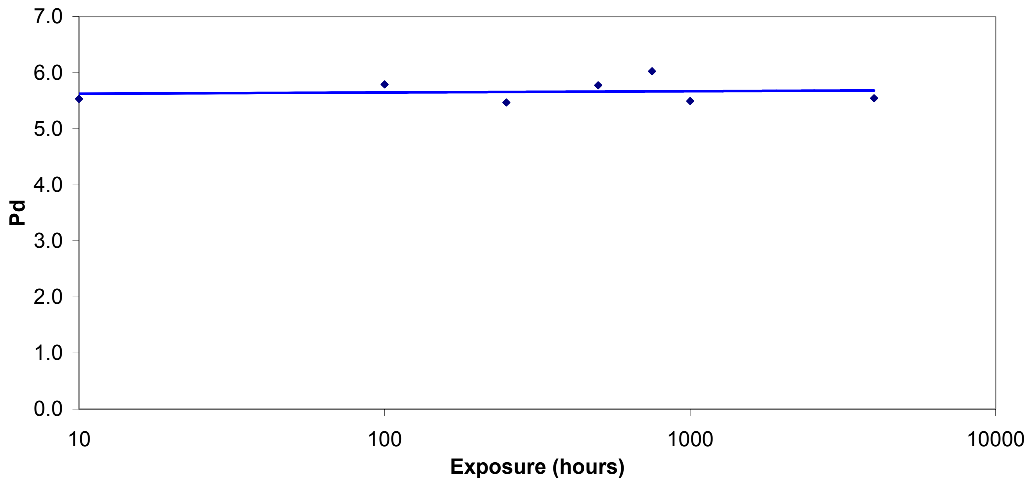




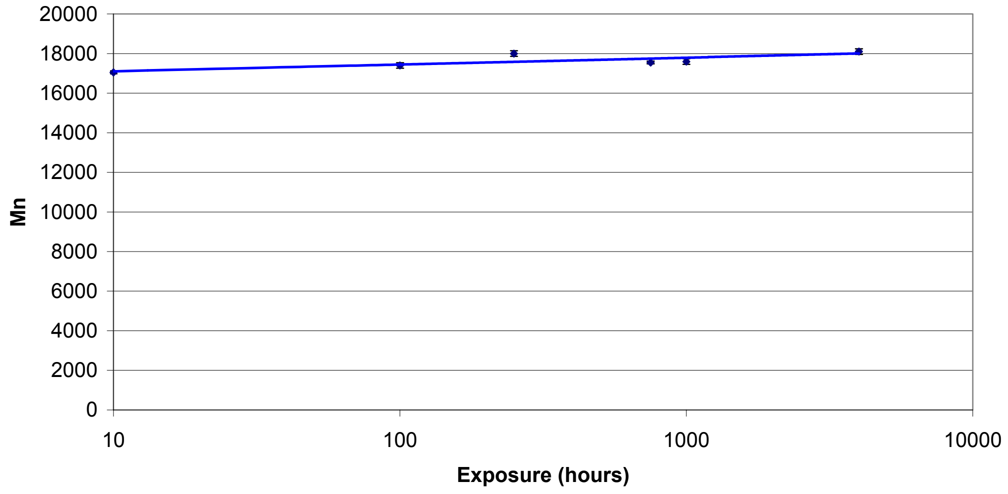

Polydispersity (Mw/Mn): BPI Rectangular
Pd
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
10
100
1000
10000
Exposure (hours)


Number Average Molecular Weight: BPI Square
Mn
25000
20000
15000
10000
5000
0
10
100
1000
10000
Exposure (hours)

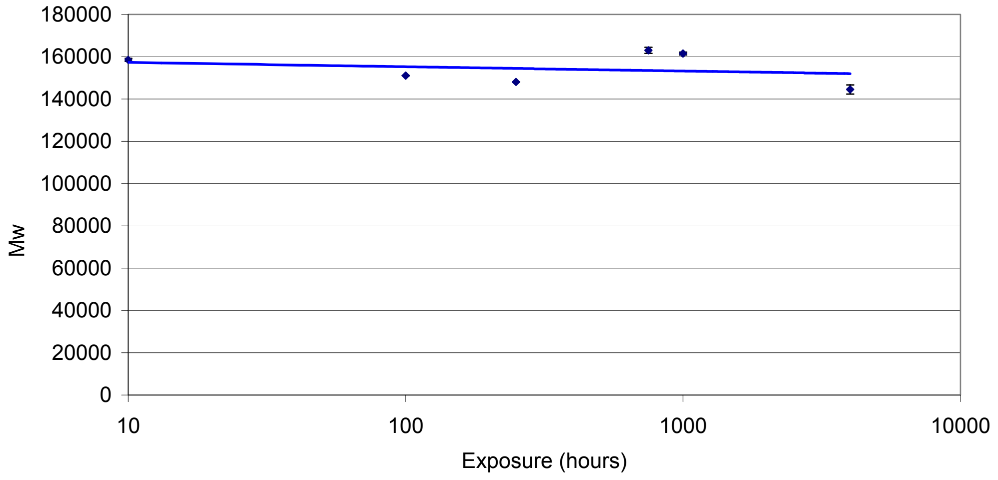

Weight Average Molecular weight: BPI Square
Tensile Modulus (MPa)
140000
120000
100000
80000
60000
40000
20000
0
10
100
1000
10000
Exposure (hours)



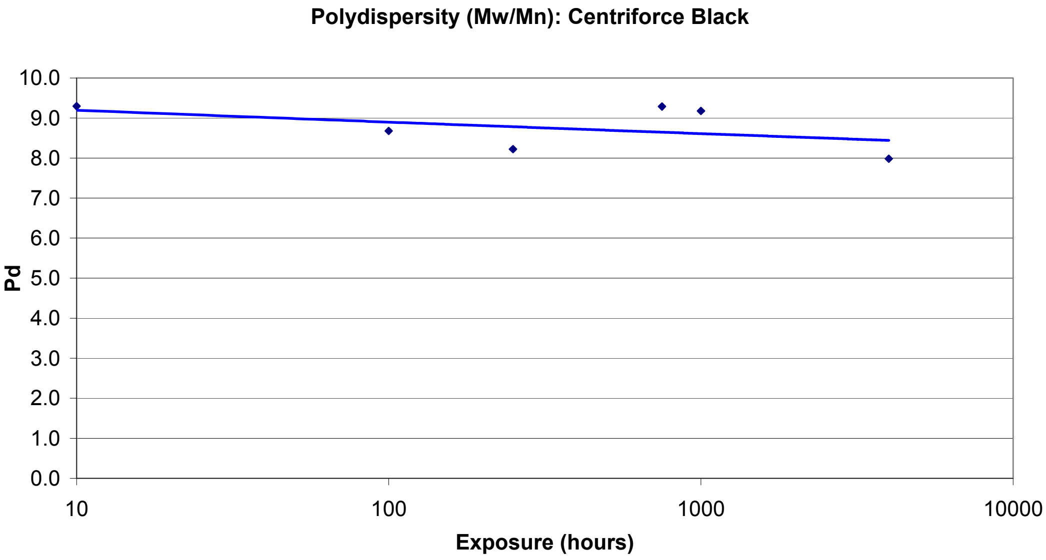
Polydispersity (Mw/Mn): BPI Square

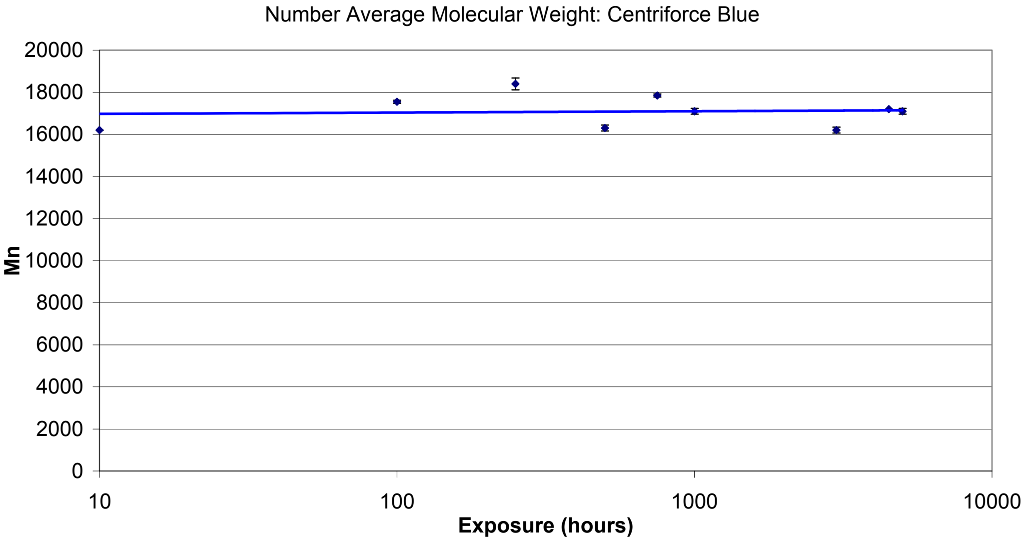


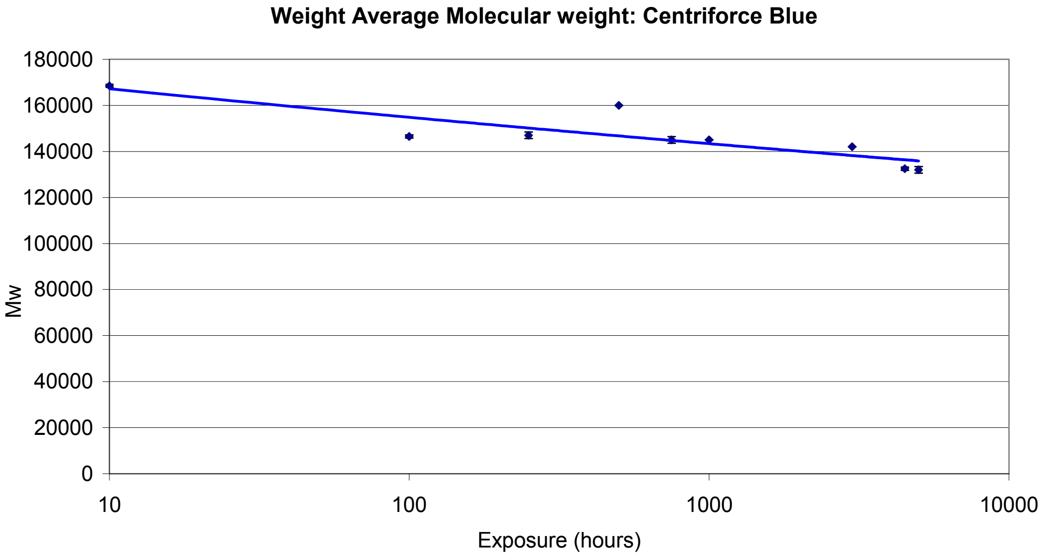
Number Average Molecular Weight: Centriforce Black

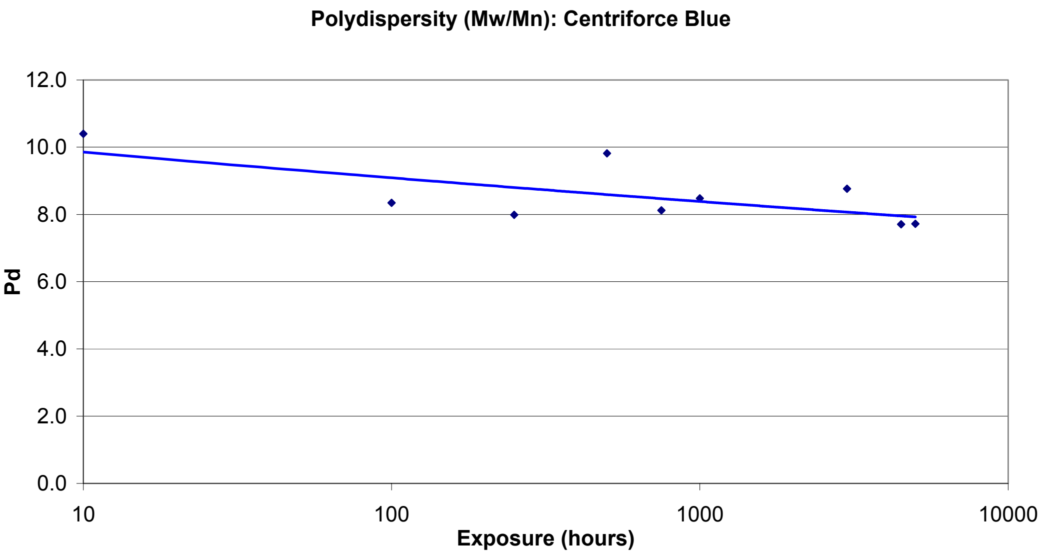


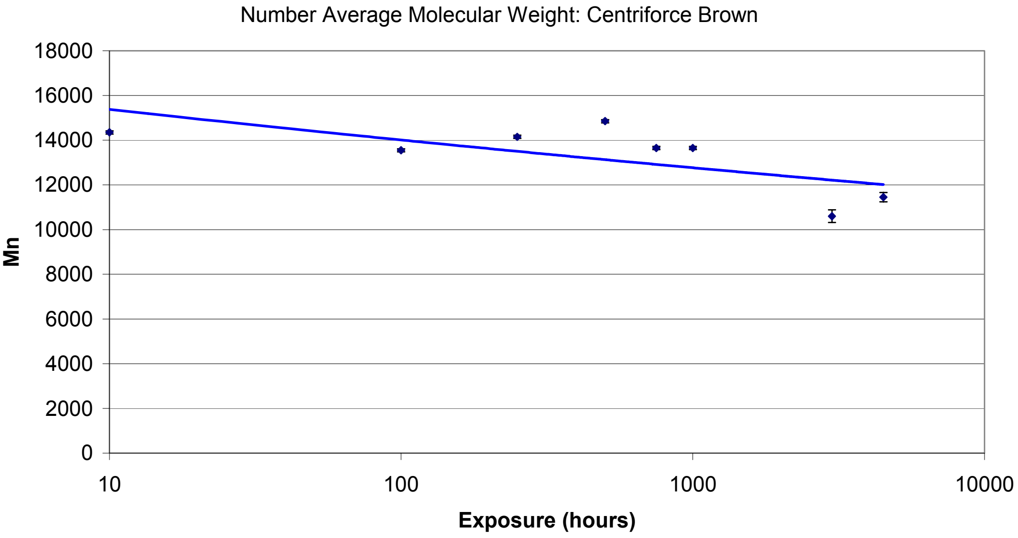
Weight Average Molecular weight: Centriforce Black

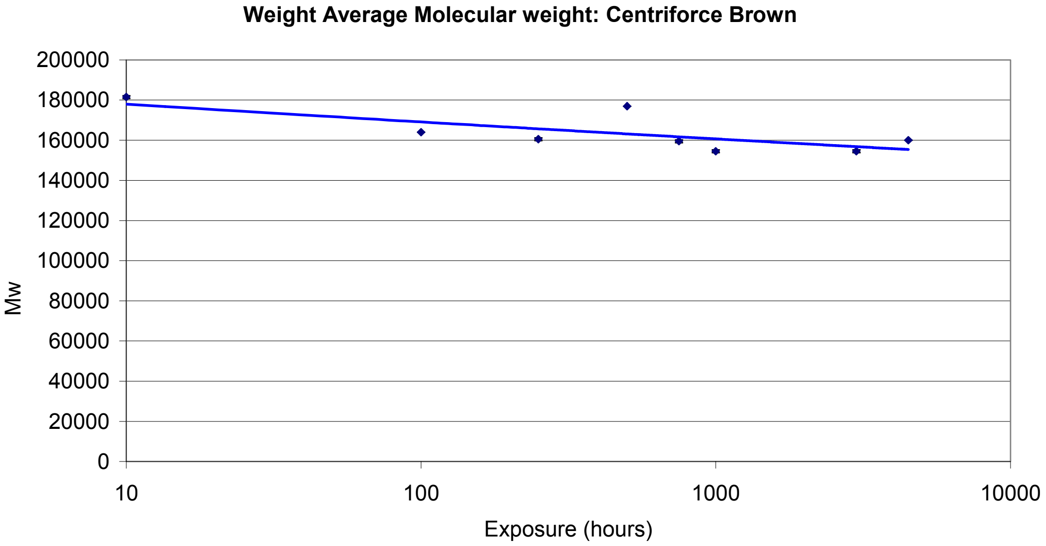

Polydispersity (Mw/Mn): Centriforce Black
Pd
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
10
100
1000
10000
Exposure (hours)

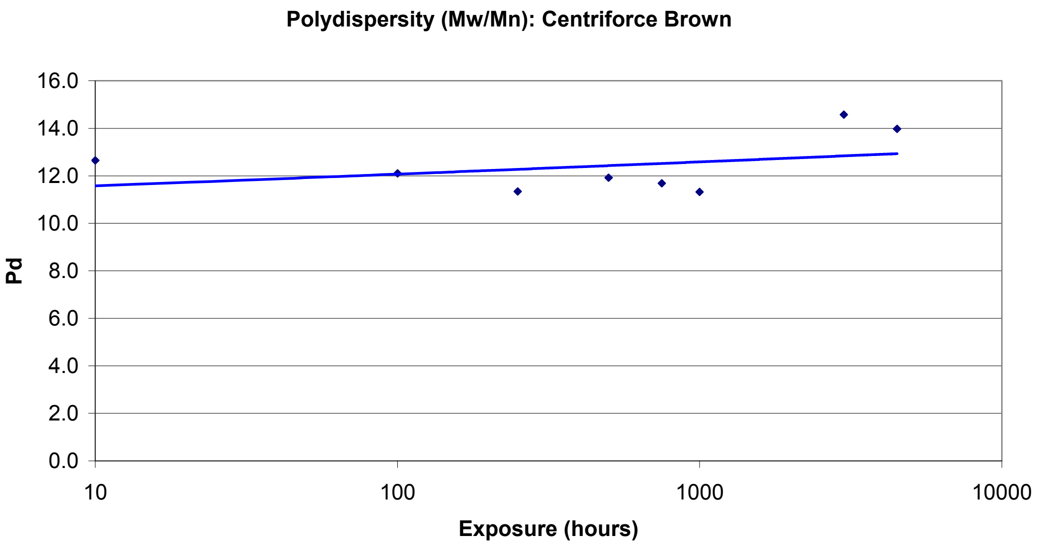

Number Average Molecular Weight: Centriforce Blue
Mn
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
10
100
1000
10000
Exposure (hours)

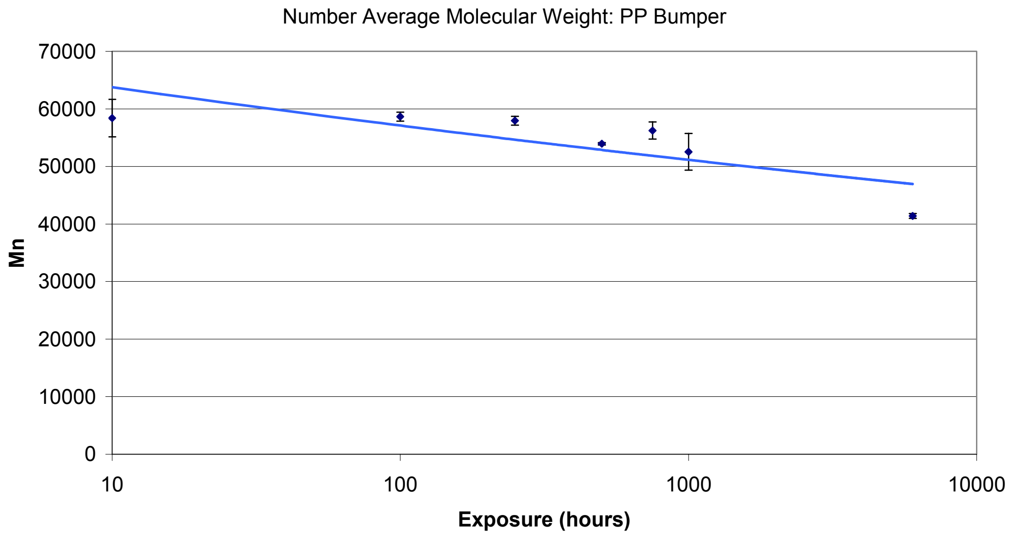

Weight Average Molecular weight: Centriforce Blue
Mw
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
10
100
1000
10000
Exposure (hours)

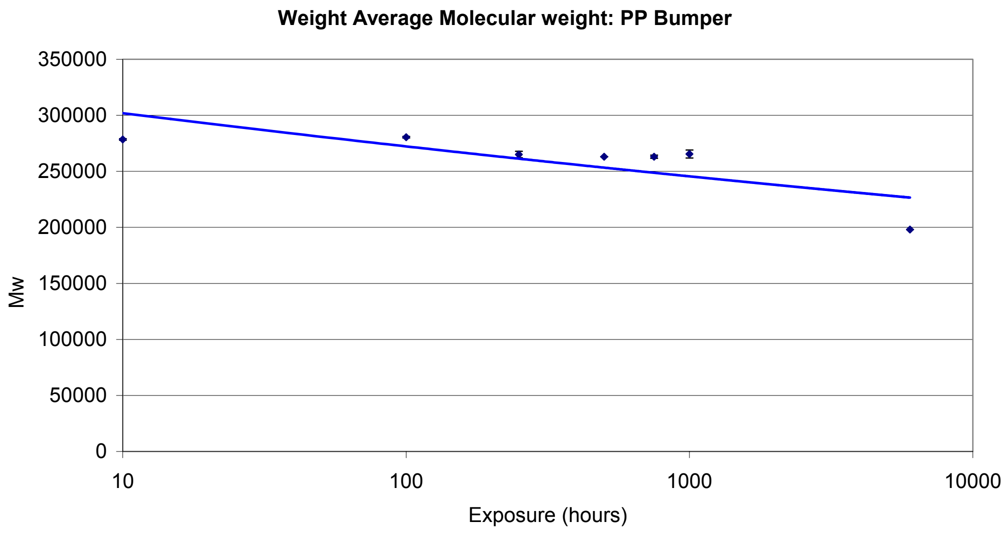

Polydispersity (Mw/Mn): Centriforce Blue
12.0
10.0
8.0
6.0
4.0
2.0
0.0
Pd
10
100
1000
10000
Exposure (hours)

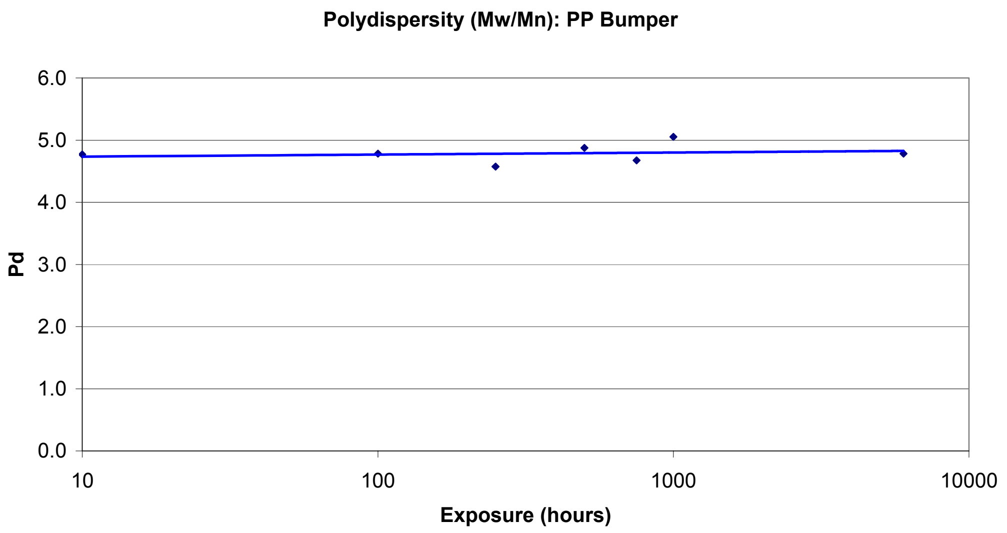

Number Average Molecular Weight: Centriforce Brown
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
Mn
10
100
1000
10000
Exposure (hours)

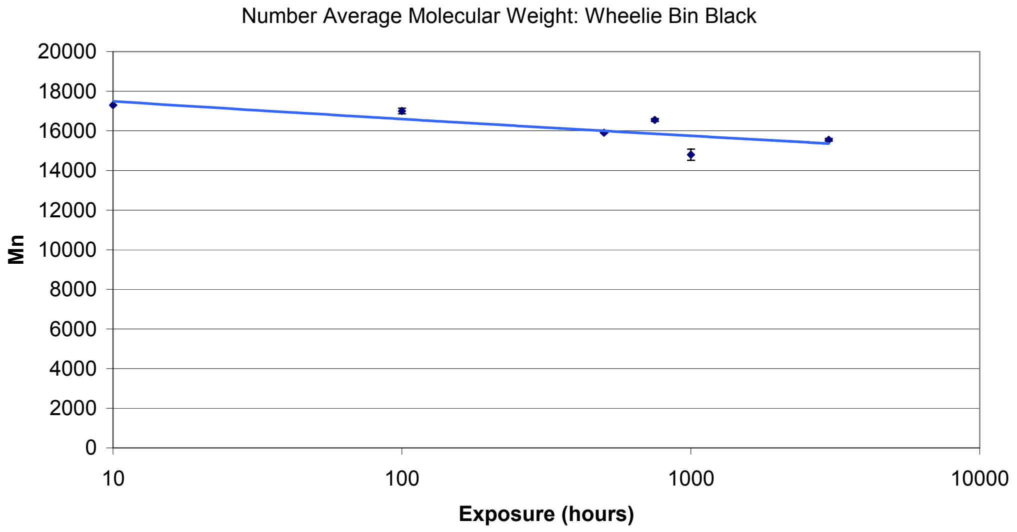

Weight Average Molecular weight: Centriforce Brown
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
Mw
10
100
1000
10000
Exposure (hours)

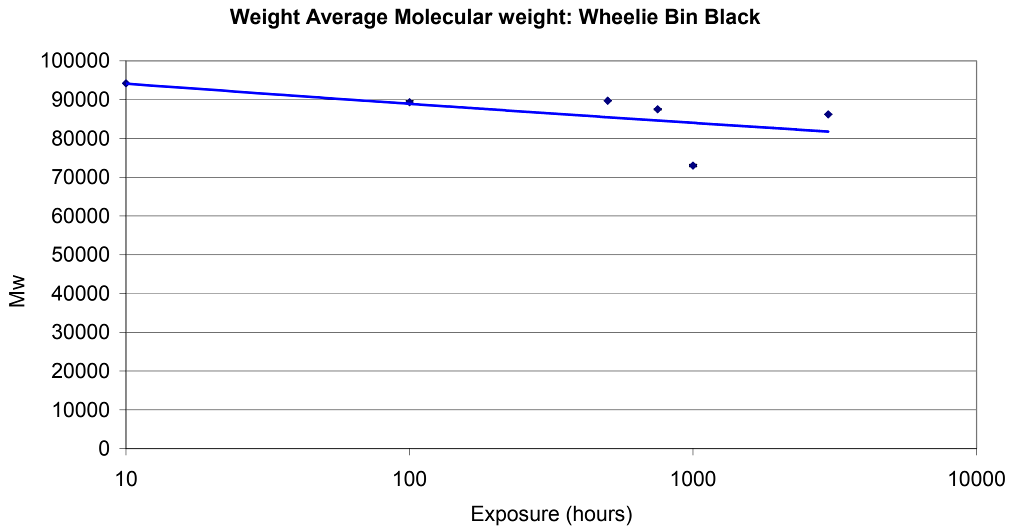

Polydispersity (Mw/Mn): Centriforce Brown
Pd
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
10
100
1000
10000
Exposure (hours)

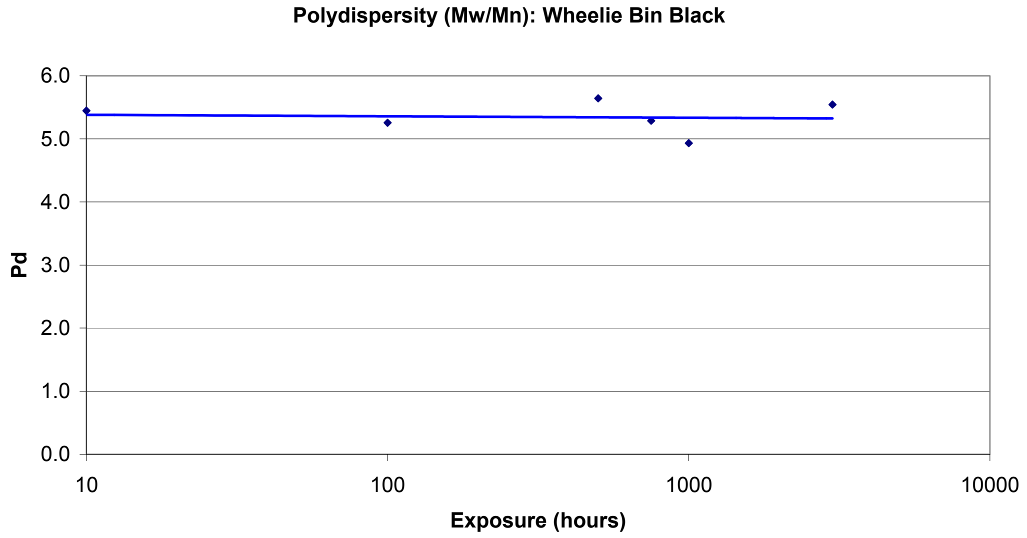

Number Average Molecular Weight: PP Bumper
Mn
70000
60000
50000
40000
30000
20000
10000
0
10
100
1000
10000
Exposure (hours)

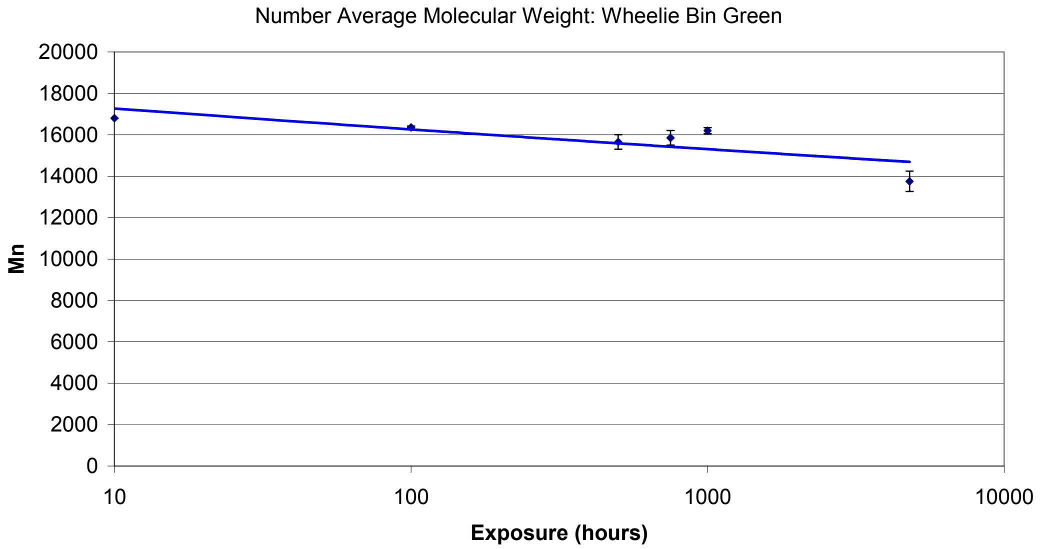

Weight Average Molecular weight: PP Bumper
Mw
350000
300000
250000
200000
150000
100000
50000
0
10
100
1000
10000
Exposure (hours)

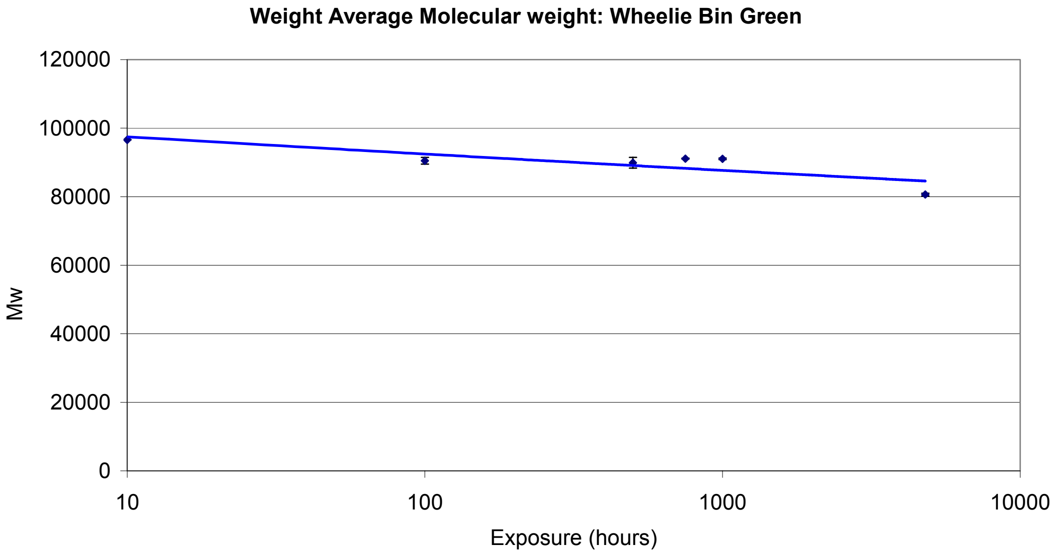

Polydispersity (Mw/Mn): PP Bumper
Pd
6.0
5.0
4.0
3.0
2.0
1.0
0.0
10
100
1000
10000
Exposure (hours)

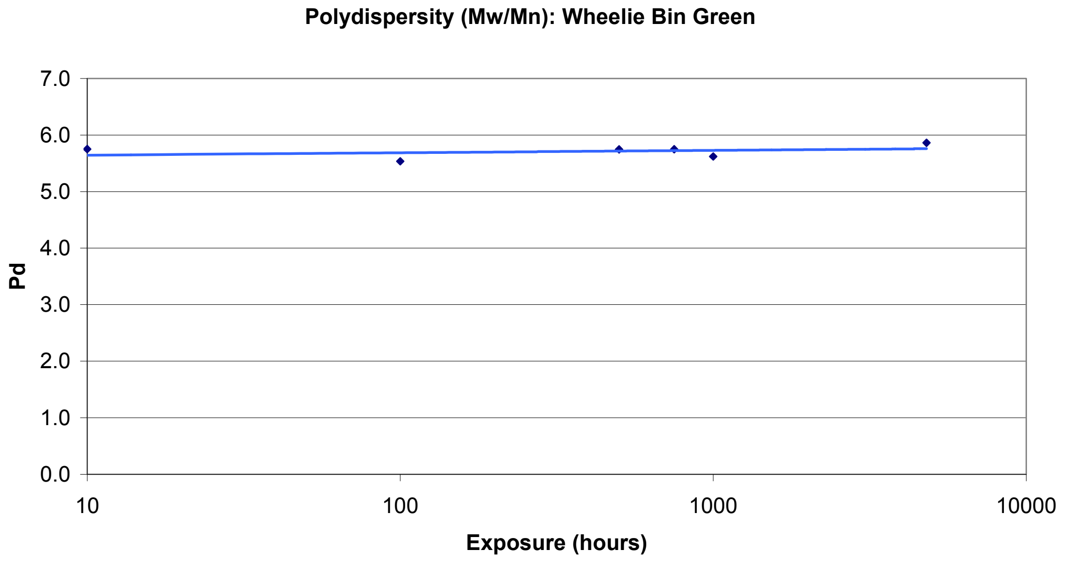

Number Average Molecular Weight: Wheelie Bin Black
Mn
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
10
100
1000
10000
Exposure (hours)


Weight Average Molecular weight: Wheelie Bin Black
Mw
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
10
100
1000
10000
Exposure (hours)


Polydispersity (Mw/Mn): Wheelie Bin Black
Pd
6.0
5.0
4.0
3.0
2.0
1.0
0.0
10
100
1000
10000
Exposure (hours)


Number Average Molecular Weight: Wheelie Bin Green
Mn
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
10
100
1000
10000
Exposure (hours)


Weight Average Molecular weight: Wheelie Bin Green
Mw
120000
100000
80000
60000
40000
20000
0
10
100
1000
10000
Exposure (hours)


Polydispersity (Mw/Mn): Wheelie Bin Green
Pd
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
10
100
1000
10000
Exposure (hours)

Project Partners

Rapra Technology Limited

www.rapra.net

Rapra Technology is the largest consultancy in the UK specialising in rubber and plastics materials, processes and products. It offers a comprehensive range of services to tackle both technical and commercial problems. Consultancy services specialising in material selection, product development, failure diagnosis, long term data prediction, Injection moulding simulation and finite element analysis. These services are backed up by extensive analytical and physical test laboratories and processing capabilities. Rapra has over 5000 clients worldwide and undertakes around 2000 technical projects each year.

University of Brighton

www.brighton.ac.uk

The University of Brighton has a fast growing reputation for research in the area of sustainable development. Within the School of Engineering, there is expertise on mechanical behaviour of recycled thermoplastics, dynamic behaviour of elastomers and product design for the construction industry. Within the School of the Environment, there is expertise in pyrolysis, waste modelling and minimisation and life cycle assessment. Our research programmes in the main concentrate on meeting commercial targets.