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What is This?

Thermal degradation of polyethylene film materials due to successive recycling

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Abstract: Mechanical recycling of plastic film involves subjecting plastic materials to a series of heat cycles that can potentially degrade the material, causing brittleness and increased melt viscosity. Plastic film recycling in the UK is in its infancy, in need of an increased understanding of how the physical properties of polymeric materials change before and during the process. Reliable data are required to estimate the behaviour of such film products when recycled. Measurements were made as to the changes in physical properties of four different varieties of polyethylene (PE) film products when subjected to a series of successive simulated heat cycles and evaluated after each step. Results showed that although changes in tensile properties were fairly small, changes in processing properties such as melt-flow index for highly branched or low-density PE are substantial and could be a concern during recycling operations.

Keywords: plastic film, recycling, thermal degradation, molecular weight

1 INTRODUCTION

The article highlights the effect of successive recycling of four polyethylene (PE) packaging film materials. Plastic film products have been in use as packaging for ∼60 years [1–4] but their recycling is a fairly new practice, which is rarely performed on material arising from municipal waste sources. Plastic film is a versatile modern packaging material with a number of applications. There are six main varieties of plastic film, each from a different polymer, whose name and principal application is listed in Table 1. Also shown are the recycling symbol numbers, used to identify the constituent polymer of the product for recycling.

The UK currently produces ∼250 million tonnes of controlled (i.e. regulated by the Environment Agency) waste per year [5]. Of this ∼30 million tonnes is municipal solid waste and 80 million tonnes is commercial and industrial waste.

In terms of the amounts of plastic film waste produced, current estimations [6] put the amount of plastic film in the UK municipal waste stream at 1.2 million tonnes/annum. Environment Agency figures estimate that plastic film in the commercial and industrial sectors is of the order of 1 million tonnes/annum [7]. Therefore, in total the UK produces an average of ∼2.5 million tonnes of plastic film waste/annum. Of the total PE products, high-density polyethylene (HDPE), low-density polyethylene (LDPE) and linear low-density polyethylene, (LLDPE) make up the majority of film consumed.

Waste management practices in the UK are heavily reliant on landfill, which is a diminishing resource due to environmental issues and tightening legislation. Alternative technologies to deal with solid waste (including recycling) have been given increased attention in recent years because of this impending landfill shortage and increased disposal costs. The recycling rate of waste plastic film is currently very poor, with only 10 per cent being recycled into new products [8].

The purpose of this article is to understand how the degradative effects of successive recycling affect the material properties of a recycled PE film product. Such information is useful to recycling operations and waste managers because it gives an indication of how much of this material can be realistically diverted from landfill and its potential applications

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Table 1 Common applications of packaging films

Name	Application	Recycling symbol
High-density polyethylene	Packaging film and grocery bags	2
Polyvinyl chloride	Low oxygen permeability packaging such as frozen food bags	3
Low-density polyethylene	Food packaging, damp-proof sheeting, agricultural films, and grocery bags.	4
Linear-low density polyethylene	Stretch wrap and cling film	4
Polypropylene	Woven tarpaulin sheets. Also used as shrink wrap such as film coverings	5
Nylon	Food contact applications where strength is needed such as soup packets and sachets	7 (other)

as a recycled product. A series of mechanical and material analysis tests were used to quantify the effect of a number of heat-recycling processes on the film material.

2 RECYCLING PROCESSES

2.1 Recycling applications and products made

Waste plastic film for recycling is acquired by recyclers from a number of sources. The simplest to process and with least contamination is from post-production sources where off-cuts or batches that have failed quality control procedures are sent directly to the recycler. At the other end of the spectrum is material from a mixed source obtained from kerbside recycling schemes, where composition can be spurious and with high levels of contamination.

In terms of PE film, the recycling process requires equipment that agglomerates the bulky film into manageable chunks before it is fed into an extruder for melt processing. This process is often referred to as the continuous agglomeration or 'KAG' process. Once in the extruder, the molten material is de-gassed and filtered to remove contaminants, before being extruded and pelletized. This is often referred to as the Erema process, named after the company that produces the filtering and recycling equipment.

Some recycling equipment allows for the direct integration with film-blowing apparatus, such that the whole film-to-film recycling process can be performed at one location in a continuous process. Such processes, whether single or multi-stage, subject the material to a series of heat cycles, which this work aims to evaluate and quantify as an impact on mechanical properties.

2.2 Factors affecting recycling

The recycling market for back-of-store packaging film, i.e. wrapping material, which has been removed at warehouses and not been used by consumers is a steadily growing industry. Film recycling from post-consumer sources, i.e. packaging discarded from households, is virtually non-existent. This is mainly attributable to two factors.

1. The inability to quantify the effect of dirt and packaging tape contamination on plastic film products, such that the mechanical properties of the material feedstock can be estimated prior to the expense of recycling.
2. The lack of a system to reliably audit the history (including the heat cycles) of a material feedstock in order to trace the origins of a particular material, leading to a reluctance to recycle material with an unknown history.

It is therefore important to understand how factors such as heat cycling of PE will affect its ability to be made into new products, as this might instil more confidence in the recycling industry to work with post-consumer material.

2.3 Previous work on the effects of recycling on PE products

As for changes in the material behaviour during manufacture, work has been carried out to understand melt-flow behaviour of recycled PE, which is derived from analysing changes in molecular weight distribution (MWD) and melt-flow index (MFI). It has been shown that there is a decrease in MFI when HDPE is reprocessed, indicating an increase in the viscosity and molar mass of the polymer [9].

The effect of multiple processing and recycling steps of PE compounds has been examined to determine the effect on mechanical properties [10]. Analyses of the changes in tensile strength, maximum elongation (El%), and MFI were examined. It was found that no significant change was identified in the material's rheological properties, indicating the possibility of returning these residues of HDPE to their original manufacturing processes. However, this work did not heat cycle the material more than twice, thus more analysis was needed in the understanding of successive heat cycling.

Effects of increased recycling on rigid HDPE packaging material in other works have shown a reduction in MFI and a reduction in both El% and ultimate tensile strength (UTS) [11]. This was attributed mostly to chain-breaking and a reduction of cross-linking, which occurs due to the successive movement and re-alignment of the HDPE polymer

chains. Such work has not been carried out on LDPE or other PE film products.

3 EXPERIMENTAL METHODOLOGY

Determining the change in mechanical properties as the polymer was recycled a number of times is of importance in the recycling production route. Therefore, an understanding of the variation in properties was a key stage in the overall methodology.

The input materials used for the experiment were as follows.

1. Virgin LDPE, i.e. fresh pelletized polymer purchased from Dow Chemicals Ltd.
2. A modern recycled film product produced from a mixed waste PE source that was washed and recycled by the Erema extrusion process [12], composition mostly LDPE and HDPE. This will be called 'Erema mix' for clarity.
3. Used HDPE supermarket bags.
4. Used retail packaging film from a local supermarket (mostly LDPE).

The polymer mix in question was injection moulded into a number of standard test pieces, some of which were tested to examine the mechanical properties and some retained. The retained pieces were then reground and remoulded ready to form the next batch, as shown in Fig. 1. This process was successively repeated a number of times, and the relationship between material properties and number of cycles was examined.

The retained pieces were shredded into $5\,mm^2$ fragments, similar in size to the pellets that constituted the original material. The equipment used in the manufacture of test specimens was a Fox and Offord 'Polylab' Universal moulding machine. The

machine was capable of heating the polymer charge to 300 °C and delivering moulding pressures of up to 17 MPa. According to the user guidelines, the moulding conditions were set to 180 °C and 10 MPa moulding pressure, as this was the advised condition for PE-based material. Moulding injection cycle times were typically 15–20 s. Mould conditions were kept constant for all the materials tested.

3.1 Tensile testing

The test pieces were evaluated for tensile properties using a Testometric M500-50 series tensile testing machine. The samples were pulled apart at a speed of 500 mm/min [13]. The testometric machine was capable of displaying load/extension or stress/strain curves for any specimen, but these were not used directly because extension of plastic specimens occurs over the whole sample, rather than just the tested portion of the sample. Extension was therefore measured independently from the machine's output.

3.2 Measurement of MFI

A device capable of measuring the melt viscosity, or MFI, of polymers was employed to conform to testing standards [14]. Details for the testing of specimens are also shown in this standard. Conditions for the testing of PE samples were nominally 190 °C under a load of 2.16 kg. Figure 2 shows a schematic of the apparatus. The polymer sample was loaded into the heated barrel and a loaded shaft was placed on top to force the polymer out of the die. The mass flowrate of the polymer moving through the die was then used as a measure of its melt viscosity. Temperature control was achieved via a microprocessor controller to within $\pm 1\,°C$.
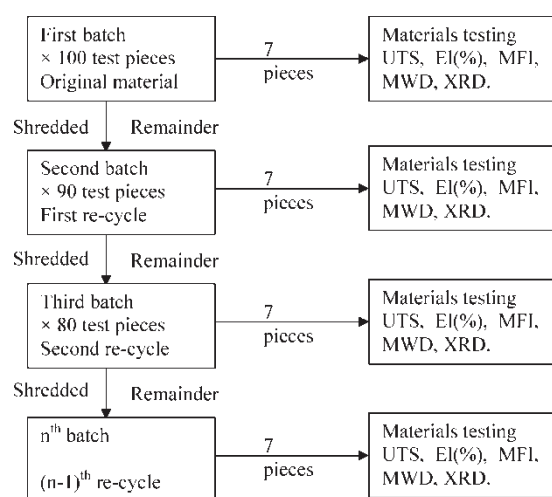

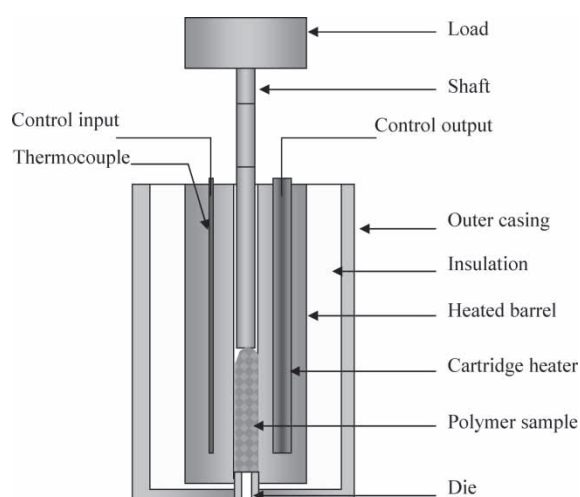**Fig. 1** Schematic of successive recycling experiment

Fig. 2 Schematic of the MFI apparatus

3.3 Measurement of crystallinity via X-ray diffraction

For this experiment, X-ray diffraction (XRD) analysis was carried out using a Philips PW 1710 Automated Powder Diffractometer. This apparatus used Copper Kα radiation, set at 35 kV and 40 mA. The software used to operate the machine was PW1877APD version 3.6, which was run on a PC for simultaneous traverse control, data collection, and storage.

The apparatus was set to traverse and gather diffraction data from 3 to 60°. An initial scan of wider diffraction angles with a variety of PE samples showed that there was no useful data outside of this interval and thus data $>60°$ or $<3°$ was not collected to save traverse times and data file size. Each scan was taken in 356 discrete steps with 8 measurements being taken per step, which were averaged for consistency. The results were then exported from the logger PC and loaded into a spreadsheet package. Initially, these results were too similar to discern quantitative changes in crystallinity, and it was decided to calculate the crystallinity based on a recognized deconvolution method [15].

3.4 Measurement of molecular weight and polydispersity index via gel permeation chromatography

The hardware used was a polymer laboratories GPC220 instrument fitted with a Viscotek differential pressure (viscosity) detector, located at Rapra Technology Ltd, Shropshire.

The polymer was first made into a gel by dissolving in Trichlorbenzene at 190 °C to a concentration of ~0.1 per cent by weight and immediately inserted into sample-injection vials. The samples were then injected into the gelpermeation chromatography (GPC) columns, where they were processed at 160 °C. The gel-phase sample was then allowed to pass through the filter columns at the rate of 1 ml/min. The columns were two 300 × 7.5 mm tubes containing 10 μm Plgel filter beads. After passing through the columns, concentrations of the gel were measured at the detector and logged into a computer. This was then used to build up a chromatograph of the polymer sample. The results were returned in electronic format and loaded into a spreadsheet package.

4 RESULTS

4.1 Tensile testing

Figure 3 shows the relationship between UTS and the number of heat processing cycles for the four types of PE. The x-axis shows the number of heat cycles that the material has undergone. The zero point on this axis represents the 'as received' case, normally pelletized feedstock, but in the case of carrier bags this refers to the untreated product. There is a steady change in UTS for each material as the number of processing cycles is increased. Each data point was made from an average of six tested samples. The range of the data around these averaged values was nominally within 15 per cent of the average.
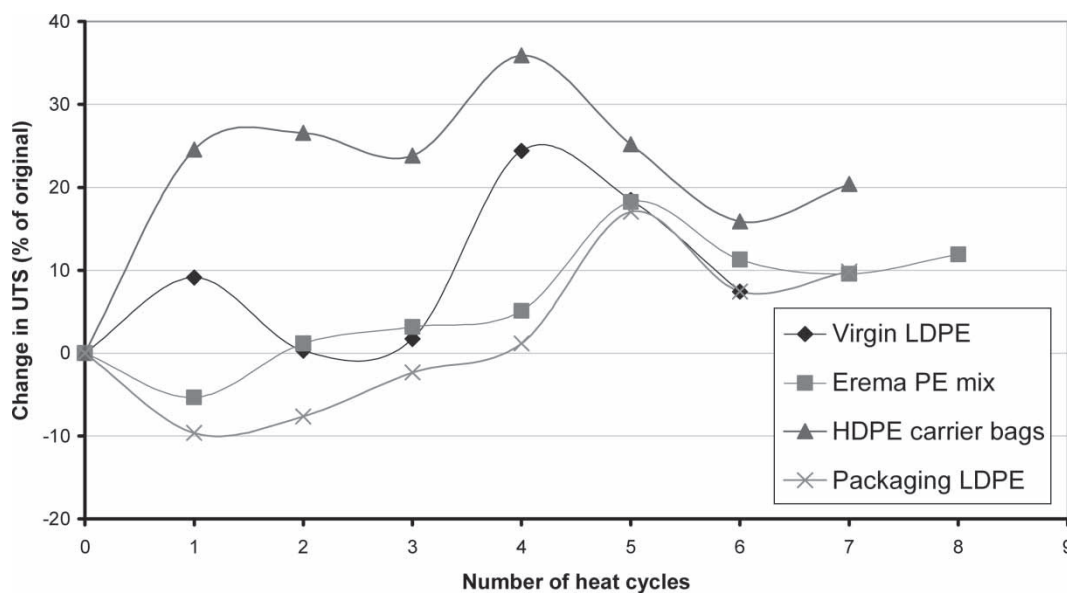

Fig. 3 UTS of different polymers with processing cycles

As the data in Fig. 3 show, the tensile strength has changed in such a way that all of the materials tested exhibit a strengthening effect, which is seen as brittleness when coupled with a decrease in El%. This would be considered detrimental in packaging applications where ductility is important.

Virgin LDPE shows an increase in UTS of ~10 per cent over six processing cycles. The Erema-processed PE also shows an increase in UTS of ~10 per cent over the same range, indicating that this material behaves similarly in recycling compared to virgin LDPE. The supermarket packing film also shows an increase in UTS of ~10 per cent over six processing cycles, however, the response curve increases less rapidly than the other LDPE-based materials discussed. The carrier bag HDPE material shows an increase in UTS of ~20 per cent over six processing cycles, although it showed a significant 30 per cent increase during the initial three heat cycles, followed by a decrease. This material produced the most amount of scatter, attributed to interference from poorly mixed printing dyes used in the labelling of the bags. The expected increases in UTS can be attributed to the chain breaking/re-alignment undergone during the processing/heat cycles, as shown later. The increase in brittleness was also linked to these effects.

Figure 4 shows the variation in percentage El% with number of heat cycles for the four materials. The initial values of the elongation at break for the four materials was virgin LDPE 97 per cent, Erema PE mix 77 per cent, HDPE 25 per cent, and packaging LDPE 37 per cent. These were based on elongations over a 25 mm portion of the test specimen, as described in the standard [13].

Each data point was made from an average of six tested samples. The range of the data around these averaged values was nominally within 20 per cent of the average, although these data were less consistent than the UTS data. It can be seen that in all cases the material becomes less ductile, thus supporting the increase in brittleness previously highlighted. It can be noted that the change in the carrier bag HDPE was the smallest in magnitude, a 10 per cent decrease in El%, which was attributed to its morphology as explained later.

The El% of virgin LDPE reduced by 35 per cent over six processing cycles from its original value, compared with the Erema material that was reduced by 15 per cent over the same range. The supermarket packing film showed a decrease in El% of 45 per cent over six heat cycles, which was the largest reduction in the El% for all the materials.

4.2 MFI measurement

Figure 5 shows the change in MFI as the materials were heat cycled. All the polymers tested show a reduction in MFI, except the HDPE carrier bag material that showed a substantial increase.

The MFI of the virgin LDPE material, being 1.5 g/10 min at zero heat cycles, reduced by 70 per cent over six heat cycles. Although the change in UTS was not significantly large, the 35 per cent reduction in El% and the 70 per cent reduction in MFI (based on original values at zero heat cycles) would be sufficiently large to raise concerns over the application and manufacture of heavily reprocessed LDPE films.
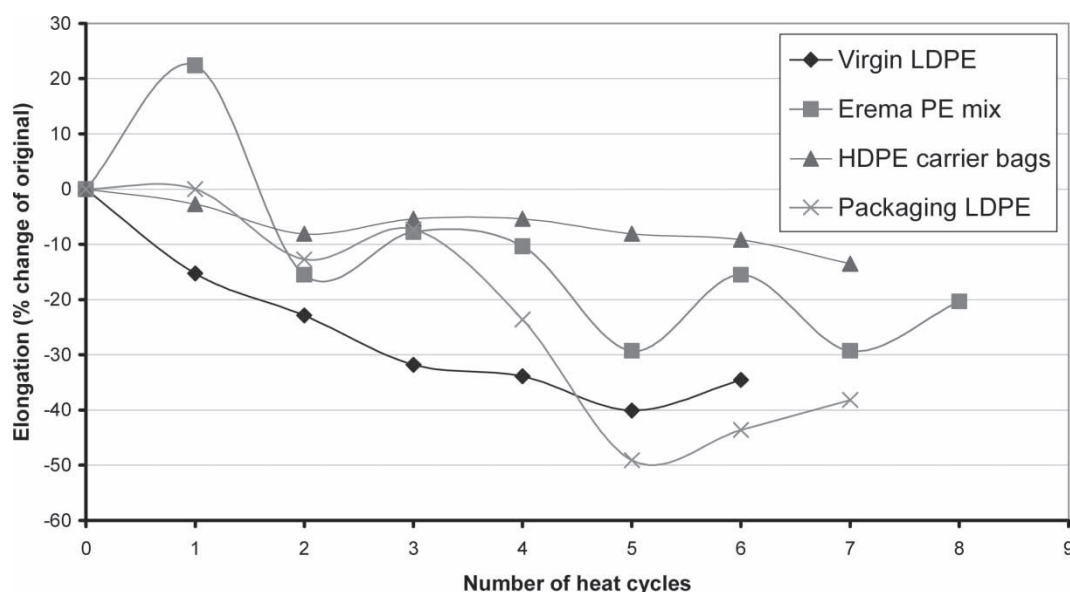

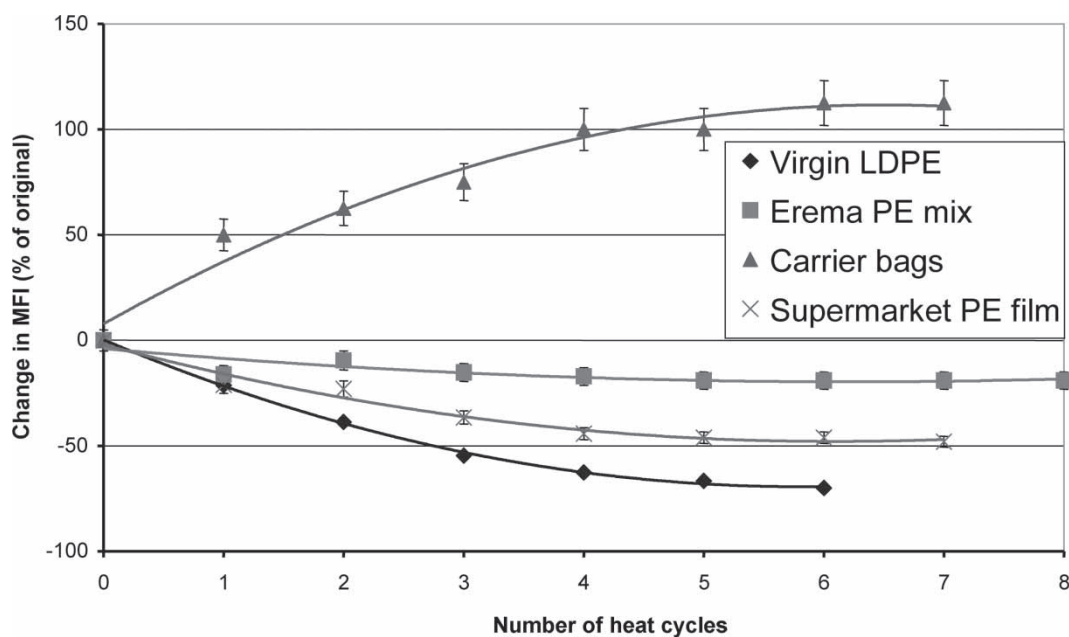**Fig. 4** Per cent El% of different polymers with processing cycles

Fig. 5 MFI of the polyethylene materials over a number of processing cycles

The MFI of the Erema material, which was 1.05 g/ 10 min at zero cycles, reduced by 19 per cent over six cycles. Although a comparatively small reduction, such a MFI could cause problems in the manufacture of small-gauge films (D. Mercer, personal communication, 2004), but in general industrial practice this material would be alloyed with a PE product of much higher MFI to produce a mixture within acceptable criteria.

The MFI of the supermarket packing film, which was 0.5 g/10 min at zero cycles, reduced by 46 per cent over six heat cycles. This reduction in MFI would probably cause problems in the manufacture of small-gauge films because the material would be more viscous and not extrude so readily, limiting the application of this material after a series of processing cycles. It is worth mentioning that the MFI of this material was still higher than that of the carrier bag material, although its UTS was lower, prompting the possibility of a potential market manufacturing this material into carrier bag-type applications. The carrier bag material, which was 0.08 g/ 10 min at zero cycles, increased by 113 per cent over six heat cycles. This was the only material in the series to show an increase in MFI after successive processing steps. This was attributed to changes in the crystallinity and molecular weight, as shown later.

4.3 XRD results

Figure 6 shows an XRD trace for the four main types of plastic used in this cycling experiment. Percentage

occurrence is shown against the scattering angle of the detector (2 theta), in degrees. It can be seen that the virgin LDPE is the most amorphous because it has a wider broadband 'hump', whereas the carrier bag film is the least amorphous (most crystalline) because it has a more defined peak structure and thus it comprises more of crystalline material than randomly arranged amorphous material.

What is also evident from the raw XRD results is that there is only a small difference in peak shape and size between the extremes of the materials tested in this work, making it difficult to quantify the differences between them. Given that changes due to heat cycling were far more subtle, results were presented in terms of percentage crystallinity.

Figure 7 shows the change in crystallinity of the PEs after a number of heat-processing cycles. The Virgin LDPE shows a 15 per cent increase in crystallinity over six heat cycles, although there is scatter evident in the data. At five heat cycles, there appears to be a sudden reduction, but this was more likely due to a spurious data point, possibly from poor mixing of the prepared sample or reduced diffraction at higher theta values. The Erema mix also shows scatter and an increase in crystallinity of 6 per cent over six heat cycles.

The carrier bag HDPE is the only material to show a consistent decrease in crystallinity over the heat cycles. Its crystallinity reduced by 5 per cent, and this change was contrary to the other PE materials tested. The packaging LDPE film behaves in a similar fashion to the virgin LDPE inasmuch as it increases in crystallinity by 15 per cent over six heat cycles, although the virgin LDPE is less consistent.
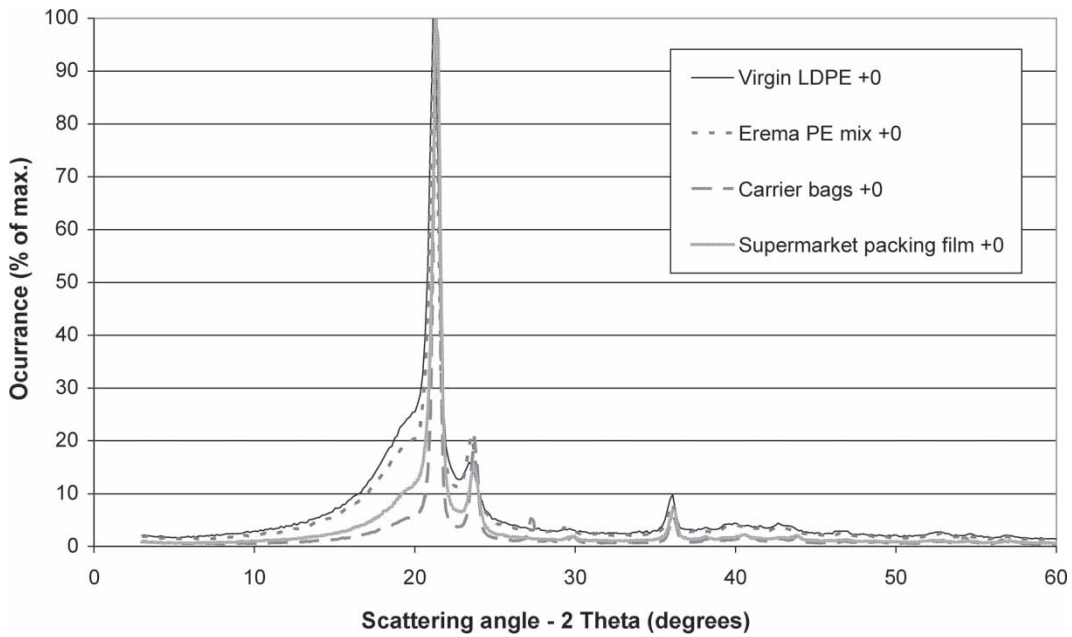
Fig. 6   XRD results for four different grades of polyethylene material

4.4   GPC results

Figure 8 shows the change in molecular weight as a function of heat-processing cycles. The results for the Erema mix are less consistent compared to that of the virgin LDPE or packaging HDPE. This was probably due to inconsistent mixing in the processing stage. Note that the '0 cycle' for carrier bags could not be achieved, because untreated carrier bags could not be analysed by the GPC hardware. The sample was therefore pelletized prior to GPC testing.

All three results point to the same general trend, that the recycling process causes the average molecular weight of the polymer to decrease, implying that the polymer chains are being broken as a result of the heat processing. For the Erema mix and virgin LDPE material, the decrease was ∼5 per cent over five heat cycles, although there was a large amount of scatter evident in the Erema sample. The data show a consistent trend, but it should be noted that a change <4 per cent is regarded as negligible. The HDPE carrier bag material decreased by 16 per cent over three cycles,
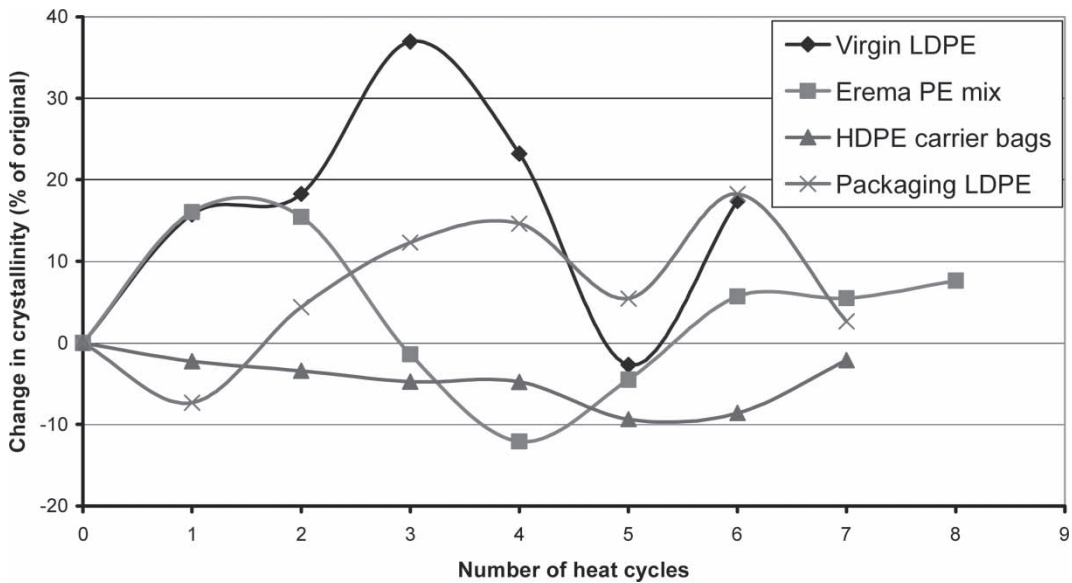

Fig. 7   XRD results of the polyethylene materials over a number of processing cycles
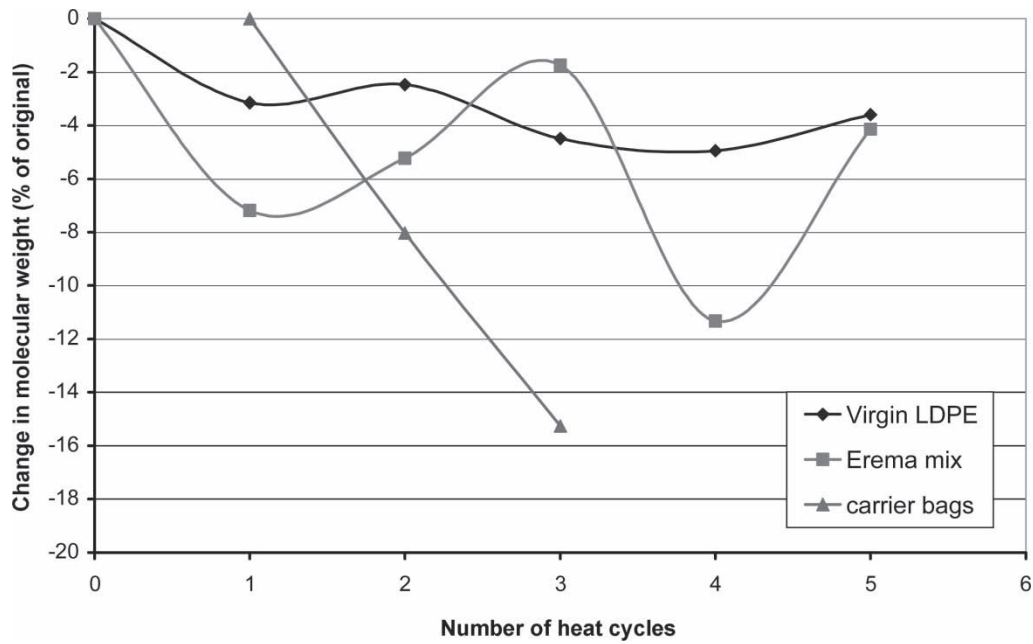
Fig. 8 Molecular weight (number average) of three polyethylene products

implying that the chain-breaking process was more pronounced in linear polymers such as HDPE. The more highly branched nature of the non-linear LDPE molecules gives them greater cohesion during the heating processes.

Figure 9 shows the effect that processing has on the polydispersity index (PI). The data show that the virgin LDPE increased by 10 per cent over five heat cycles from its original value. The Erema mix again showed large scatter, but had the potential to increase its PI

by up to 8 per cent over the range shown. The packaging HDPE sample increased its PI more readily, at 26 per cent over three heat cycles. The HDPE is, therefore, changing in molecular mass more readily than the other materials studied.

This confirms that the heat processing causes individual polymer chains to break into smaller ones, rather than combining to make larger ones. It also demonstrates that not all of the polymer chains undergo this breaking process. It appears that only
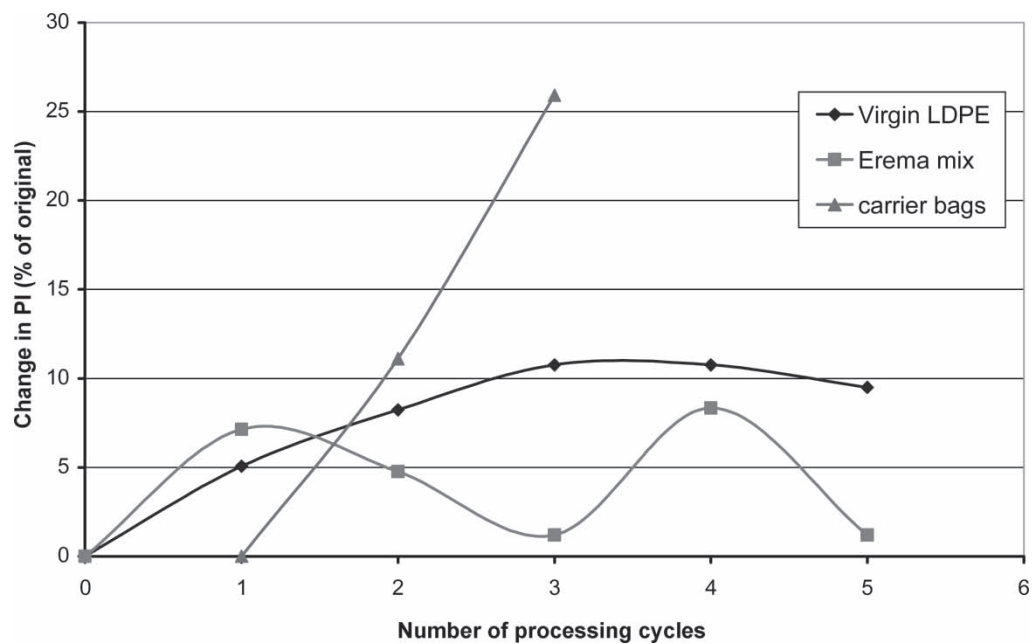

Fig. 9 Polydispersity as a function of processing cycles

a certain amount of chains are being broken per heat cycle, which seems to increase as the number of processing cycles increase. Larger molecules are more likely to retain their mass, probably due to branching and inter-linking.

These data are not consistent with the MFI results of Fig. 5. It is an accepted theory that MFI is inversely proportional to molecular weight. This is true for the case of the HDPE material, but not true for the case of LDPE materials and the HDPE/LDPE Erema mixture. It would, therefore, be logical to postulate that the reduction in MFI for the LDPE-based samples was due to something other than changes in the polymer molecular weight. It is possible that this reduction in MFI is due to products of oxidation, such as chars and other particulates, which were observed during moulding. LDPE samples were observed to discolour during the product recycling in the injection-moulding apparatus. These contaminants have potentially increased the viscosity of the resultant mixture.

5 INTERPRETATION AND DISCUSSION OF RESULTS

Processing heat cycles made all of the materials tested more brittle, except the carrier bag material, which was attributed to a reduction in HDPE crystallinity, whereas the other materials become more crystalline. These heat cycles also made all of the materials harder to process due to a decrease in MFI, with the exception of HDPE. MFI was the most significant change of all the properties tested. This implies that it was processing capability, rather than strength or ductility of recycled material, that suffers the most during recycling.

Processing heat cycles caused an increase in crystallinity in PE materials, except for the HDPE material, which becomes less crystalline. Processing cycles caused a decrease in average molecular weight and an increase in PI in all the PE materials tested. This was attributed to the breaking of molecular chains, which produces new molecular species of lower average molecular weight. This effect was seen as a broadening of the MWD towards lower molecular weights, thus reducing average molecular weight for the whole population and increasing PI.

For non-linear (branched) molecules (e.g. LDPE and the Erema mix), the heat processing probably reduces the amount of polymer chain branching as well as overall molecular weight, allowing some of the polymer chains to align more readily. This results in an increase in crystallinity. For linear (unbranched) molecules (e.g. HDPE), the decrease in molecular weight due to process cycling lowers the effectiveness of the polymers to align, therefore, decreasing the crystallinity.

Changes in MFI observed in this research have not always been attributed to changes in polymer molecular weight. There is evidence to suggest that during the thermal recycling of LDPE products, by-products are produced, which can increase melt viscosity.

6 CONCLUSIONS

The change in physical properties of four types of packaging PEs subjected to simulated recycling cycles has been demonstrated. Results have shown that successive heating cycles cause degradation to the microstructure of the materials, which was seen as an increase in polydispersity and a decrease in molecular weight. The effect and degree of this degradation was dependent on the morphology of the polymer in question, i.e. the average molecular weight and degree of side-chain branching present. Highly branched polymers become more crystalline in microstructure, whereas unbranched polymers become less crystalline.

The industrial impact of these results is that material degradation is likely to affect the processing performance of PE films (via changes in MFI). Changes greater than 50 per cent in UTS and El% (based on original values) were not observed in the tests conducted, but MFI changes were as much as 110 per cent of original values. Product applications, where consistent manufacturing properties are of greater importance, such as thin film production, would be less favourable for materials that had undergone more than two additional heat cycles.

Heavily recycled films are therefore more likely to be utilized in products where production consistency is not of prime importance. Examples of this include the manufacture of thicker profiles and plastic lumber sections. These applications can limit further recycling, but are more environmentally beneficial than directly landfilling plastic film waste.

The key findings in this article could be used to improve recycling methods as the problems often seen in recycling operations can be attributed to changes in crystallinity, molecular weight, and PI. Crystallinity can be used as an indicator as to how a material will behave in heat cycling, while PI will show the recycler how diverse the mixture is. Often in recycling operations, a material will be delivered to the recycler with little or no specification. Provided the recycler had an effective method of assessing the crystallinity and PI of the mixture, a reasonable estimation of the change in processing and mechanical properties could be made. It is also pertinent to recommend that recyclers should fully understand these molecular-scale properties.

The data have shown that the MFI of a PE material can either increase or decrease during heat cycling, based on its morphology. It is therefore possible that by alloying some PE materials together, blends can be produced to minimize the changes in MFI. This is done crudely on an industrial scale, the process could be optimized by studying input morphology and blending based on experimental data. Mixing of LDPE and HDPE waste feedstocks could then be performed to balance the processing properties of the resultant mixture, provided the mechanical properties were satisfactory for the application in mind.

As it has been shown that successive heat cycles can degrade the material properties of PE, it would be sensible to minimize the number of heating stages in recycling processes. In many operations, the material is pelletized before manufacture. If this could be undertaken as only one heating cycle, the deterioration would be minimized. Residence times would therefore be lower and the polymers would be subjected to less overall heating. Cold processes, such as shredding and crumbing, should be maximized as it is assumed that these would not degrade the material as much as hot processes such as pelletization.

Good blending on the polymers in the mixture would, therefore, be essential in achieving a consistent, homogeneous output. This implies that recycled mixtures should be well-mixed in the melt phase. However, this postulates a paradox, as excessive mixing will lead to long residence times, which will deteriorate the mixtures. A trade-off will then be in existence between well-mixed recycled mixtures and those that have been exposed to minimal heating.

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