Reconditioning Process Of Waste Low Density Polyethylene Using New Technique

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ABSTRACT

Reconditioning of low density polyethylene (LDPE) was examined using dissolution/reprecipitation process. Virgin LDPE material, either in the form of pellets for three different waste material (carrier bags original used (bags), laboratory pipits (pipits) and intravenous fluids containers (Int.)), are present in this paper. Petroleum ether in (90-120) °C boiling point was used as solvent for plastic dissolution and petroleum ether in boiling point (40-60), (60-80) °C were used as non-solvents for reprecipitation, washing of the material obtained and drying. The solvent mixtures involved are separated by distillation for further reuse. The recycled material was evaluated in terms of the following properties: melt flow index (MFI), intrinsic viscosity, crystallinity and mechanical performance in tensile mode.

Keywords: LDPE reconditioning, Dissolution/reprecipitation, petroleum ether
1. Introduction

The plastic resins and plastics manufacturing industry is one of the most dynamic and vibrant growth sectors within the Malaysian manufacturing sector (ISA, 2011). The Malaysian plastics industry has developed into a highly diversified sector producing an array of products. Exports of plastics products were valued at U.S. $1.83 billion in 2001 with growth rate approximately 1.5-2% and the key markets are Singapore, Japan, Hong Kong, China, Thailand, UK, U.S, and Indonesia. Besides that being an exporter, Malaysia remains a net importer of plastic resins as well. In 2002, the total market demand of plastic resins was estimated at 1.25 million metric tons (of which 60% consumed were polyethylene and polypropylene). Total local production was at around 1.4 million metric tons in 2002, of which more than 50% was exported. Thus, Malaysia imports approximately 513,000 metric tons, accounting for 43% of the total market demand. In 2002, the main import countries were Singapore, Japan, the U.S. and Thailand with market shares of 24%, 23%, 9% and 8% respectively (MPMA, 2005). The main resins produced locally are commodity resins. Therefore, approximately 55% of plastic resins imports are engineering resins. Despite the large production capacity of local producers, according to the Malaysian Plastics Manufacturers Association (MPMA), total resins consumption amounted to 1.2 million metric tons in 2001, of which 60% were polyolefin (PE &PP). In 2002, total resins consumption was estimated to be at 1.25 million metric tons. A breakdown of resins consumption in 2002: PE (46%), PP (19%), PS (15%), PVC (9%), ABS (7%), and others (4%). Moreover, imported resins totaled 570,000 metric tons (about 10% were re-exported), indicating that the use of imported resins is still high. Local production of resins increased to 1.4 million metric tons, and more than 50% were exported (MPMA, 2005).

The strategies that have been suggested for recycling of waste polymers from the consumers either domestic or industrial include the methods by which value may be regained from waste or used plastics may be divided into four categories according to two imperfectly coincident hierarchies (Harper, 2006):

- Reuse or: primary
- Mechanical recycling secondary
- Chemical recycling tertiary
- Thermal recovery quaternary

At each level the original structure, first of the article then of the polymer molecule itself, is further dismantled. Mechanical recycling may be primary or secondary, while the third and fourth categories have an exact correspondence.

Primary recycling involves process scrap, or a single clean waste type. An important sub-class of primary recycling is known as "Closed loop recycling" in which polymer from a single product or product type is collected and recycled in-to the same product. Polypropylene from battery cases is a well-established example (BPF Directory of UK Companies, 1995). Secondary recycling uses reclaimed post-consumer materials as a source of material for new products. Tertiary recycling involves chemical breakdown of materials which are then re-utilised further back in the feedstock chain. Quaternary recycling is often termed energy from waste.
There are many initiatives to be found, but for all types of recycling the question of whether it is economically worthwhile must be addressed. Either the arisings must be very abundant or they must be very valuable. The high volume plastics are polypropylene (PP), polyethylene (PE), polystyrene (PS), polyvinyl chloride (PVC), polyethylene terephthalate (PET) and acrylonitrile butadiene styrene (ABS) and naturally most work has been done on these polymers although high value polymers such as polyether ether ketone (PEEK) have also received attention (Voûte, 1994; Achilias et al., 2009; Day, 1994; Hamilton, 1995).

The dissolution of thermoplastic polymers (PE, PP, PS, PET and PVC) process plays an important role and an essential in plastics recycling which belongs to the mechanical recycling techniques. Previous studies shows that the dissolution/precipitation the thermoplastic polymers specifically polyolefin family can be separated and reprocessed using a solvent/non-solvent system. Solvent-based methods contain phases of treating plastic waste with solvents so that the polymeric materials are dissolved and then separated by reprecipitation. These methods have the benefit that they are competent to deal with mixtures of polymers, based on the principle of the selective dissolution. Besides, the dissolution/reprecipitation method appears to comprise a successions of advantages, such as: (i) the plastic waste is ultimately renewed into a form powder or small grains, (ii) additives and insoluble impurities can be separated by filtration, (iii) without heating for dissolving no further degradation, due to the recycling method itself, is anticipated, (iv) the value added through the polymerization step is sustained intact and the recycled polymers, free of any impurities, can be used for any kind of application, subsequently the final product is of viable quality compared with the virgin material. Several researchers has already been studied successfully renewed the used/waste commodity polymers used by dissolution/reprecipitation system (Arostegui et al., 2006; Kampouris et al., 1986; Kampouris et al., 1988; Mark, 1999; Poulakis & Papaspyrides, 2001).

In this paper, experiments are first presented on establishing a satisfactory solvent/non-solvent system for virgin and wastes LDPE pellets. The research was based on the satisfaction of the following criteria: precipitation of the polymer in an acceptable form grains or powder, total recovery of the polymer, and limited, as much as possible, quantities of the solvent and non-solvent employed. Characterization studies on the recycled grade were focused on melt flow rate, differential scanning calorimetry, mechanical properties.

2. Experimental

2.1 Materials

The virgin LDPE grade (LD N109X) was donated from Petlin, Malaysia Sdn Bhd. It was used together with a number of commercial waste materials made from these polymers bags, caps for water bottle, intravenous fluids containers, some laboratory materials such as pipits. Petroleum ether (PetE) were used as solvents, with boiling points (40-60) °C , (60-80) °C and (90-120) °C and notations A, B, and C, respectively. The solvents were of reagent grade purities from Sigma-Aldrich and Merck Germany.
2.2 Measurement

2.2.1 Melt Flow Index (MFI)

MFI measurements were carried out according the ASTM D1238-04 at the procedure A, which is a manual cutoff operation based on time used for materials having flow rates that fall generally between 0.15 and 50 g/10 min. The instrument are used Melt Flow Indexer LMI 4000 Model D4004 from Dynisco. The temperature was fixed at 190°C and the weight of the ram was equal to 2.16 kg. Sample weights varied from 2.5 to 3 g.

2.2.2 Differential scanning calorimetry (DSC)

Thermal properties such as melting temperature (Tm) and heat of fusion of the polymer produced after recycling, the waste samples and the model polymers was measured using the DSC Q1000 (V9.6, Build 290) from TA instrument. 10 mg samples were prefaced onto the instrument and the heat emitted was recorded at a temperature interval of 20–300 °C and a scan rate of 10 °C/min, in N₂ atmosphere.

2.2.3 Universal testing machine (UTM)

The Universal Testing Machine Shimadzu AG-X was used to improve the mechanical properties of the virgin and waste polymers before and after recycling. Stress at maximum load, strain at break, stress at yield and elasticity were noted. Five specimens were examined for each sample and the average values reported. The testing was performed according to the standard method (ASTM D638-03). The speed of the testing was 5 mm/min. A carbon steel frame (30cm x30cm x3mm) was prepared to mold the polymer as a film. Three sheets were prepared from the virgin, waste and recycled polymer, each sheet weighing approximately 240 to 260 gram. The molding temperature was fixed at 150, 190, 230 °C, for LDPE, HDPE and PP, respectively. Films were cut and shaped according to ASTM D638-03 by a manual press.

2.3 Preparation of Used Polyolefin Sample

The waste plastic containers were first rinsed with tap water and then cut with a plastic crusher machine into pieces between 2cm-4cm. The pieces were then cleaned with distilled water and placed in vacuum oven for 3-6 hours at 50 °C.

2.4 Dissolution/reprecipitation technique

The experimental procedure was performed for several rates ranging from (0.5-20) % weight/ volume polymer/solvent. The solvent and pieces of waste polymer were added to the flask with three necks; the first with a vertical condenser with tap water, the second with a mercury thermometer to measure temperature and the third with a stirrer. An oil bath was used for heating with a flask immersed and a high speed stirrer doing the mixing. The system was heated for 30 minutes and brought to the desired temperature. Once the polymer pieces had dissolved completely, the flask was removed from the oil bath and left to cool for 15-30 minutes, after which the solution was carefully poured into a non-solvent. The precipitate was then washed, filtrated and dried at 70 °C in a vacuumed oven for 10-15 hrs. The resulting
polymer was in granular (powder) form. PetE(C) was used as the solvent and another two grades of petroleum ether were used as non-solvents.

Figure 1 Experimental steps of the reconditioning process.
3. Result and discussion

In sequence of experiments on virgin LDPE pellets were employed to optimize the LDPE waste material. Xylene, toluene, turpentine and Mesitylene were tested as solvent at the temperature of 75 °C. Petroleum ether grade C (PetE (C)) as solvent, where higher concentration was achieved 20 g polymer/ 100 ml solvent. The concentration in the other solvent was higher such as 35g /dl for xylene, turpentine and mesitylene and 40 g/dl for toluene. PetE (C) was selected as a solvent throughout the rest of this study at the temperature 80 °C.

The new in this study that, petroleum ether in (90-120) °C, was a solvent for dissolve the virgin and waste LDPE. From the experiments after the dissolution process was complete and before the filtration and repricipitation process, when the solution was left 10-20 min. in the room temperature and the system was closed we are observed that there were two layers one is a precipitate in the bottom of the flask, and clear liquid on the top of the beaker. That mean the precipitation was done without using non-solvent as precipitator after the solution was filtrated using vacuum pump. Two methods to dry the products were used, the first one was by using the vacuum oven and the second was rotary evaporator. The results were same by the two methods, where the products were as grains or powder. The samples were got it from this technique was compared with samples were produces from the solvent/non-solvent technique using different solvent as mention above for dissolution, the properties of the products were almost same in the two methods. On the other hand PetE(C) was used as solvent while PetE(A, B) were used as non-solvent in the ratio 1/3 solvent/non-solvent by volume, it was gives very good products and similar with products properties from the first technique.

Selection of the most suitable solvent/non-solvent system was followed by examination of the process in terms of polymer and solvents recovery. In this study the polymer recovery was up to 97% almost in the entire sample used. while separation and recovery of solvent (PetE(C)) in the two methods, means without precipitator and with precipitator were 95% and 93% respectively. In the second method when using non-solvent (PetE(A) and PetE(B)), fractional distillation process was used to separate the solvent/non-solvent mixture where, the non-solvent recovery was 74% from PetE(A) and 88% PetE(B). From the experiments it was observed that using the big amount from the solvents and non-solvents gives recoveries of the solvents better than the small quantities.

3.1 Properties of the recycled polymer

Table 1 indicates to the MFI in g/10min and the weight average molecular weight (Mw) in g/gmol of the virgin LDPE and for the three wastes LDPE before and after recycling. The results show very slight deviation in some samples. The variations may have occurred due to the experimental conditions and the accuracy of the analytical balance; however these deviations were very small and can be neglected.

According to (Papaspyrides et al., 1994; Poulakis & Papaspyrides, 1997), melt flow index is related directly to molecular weight, however these results indicate that no degradation occurs during the reconditioning process.
Table 1 Melt flow index in (g/10min) and weight average molecular weight (Mw) in g/gmol, of virgin and three wastes LDPE before and after recycling

<table>
<thead>
<tr>
<th>Sample</th>
<th>Before recycling</th>
<th>After recycling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MFI(g/10min)</td>
<td>Mw (g/gmol)</td>
</tr>
<tr>
<td>Virgin</td>
<td>0.8496</td>
<td>94900</td>
</tr>
<tr>
<td>Bags</td>
<td>0.841</td>
<td>95146</td>
</tr>
<tr>
<td>Pipits</td>
<td>0.8416</td>
<td>95129</td>
</tr>
<tr>
<td>Int.</td>
<td>0.8472</td>
<td>94968</td>
</tr>
</tbody>
</table>

Average molecular weight was calculated from equation:

\[
\frac{1}{MFI_{g/10min}} = 3.63 \times 10^{-26} (M_w, \eta)_{mol}^{0.892}
\]

from (Seavey et al., 2003)

The weight average molecular weight (M_w) of the virgin, waste samples and the recovered polymers after the recycling procedure was obtaining using viscosimetry. The Mw are calculated based on intrinsic viscosity [\(\eta\)] at TCB as solvent. Intrinsic viscosity was measured according to standard test method for dilute solution viscosity ASTM 1601-99. Cannon-Fenske routine viscometer for transparent Liquids as mention in ASTM 446-04 with size No. 50 was used to complete this testing. The measured viscosities values and the calculated Mw’s of virgin and wastes LDPE before and after recycling are illustrated in Table 2. It can be observed that the Mw of almost all samples after the recycling procedure, are arbitrary, and some samples larger than the virgin and in some cases less. On the other hand in the case of the comparison between recovered polymers and the waste, the Mw values of recycled polymers always will be largest than waste and goes towards the original. This situation may be happen due to the solvents and materials type, testing circumstances and the additives type as well. However all the changes in the values in Mw were very small, and it is still in allowed range. The kinematic viscosity value of the TCB at 135°C was 0.85mm²/s.
Table 2 Intrinsic viscosities in (dL/g) and (Mw), in g/gmol, of virgin and three wastes LDPE before and after recycling

<table>
<thead>
<tr>
<th>Sample</th>
<th>Before recycling</th>
<th>After recycling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[η] at TCB (dL/g)</td>
<td>Mw (g/gmol)</td>
</tr>
<tr>
<td>Virgin</td>
<td>1.506</td>
<td>94226</td>
</tr>
<tr>
<td>Bags</td>
<td>1.478</td>
<td>91601</td>
</tr>
<tr>
<td>Pipits</td>
<td>1.480</td>
<td>91837</td>
</tr>
<tr>
<td>Int.</td>
<td>1.488</td>
<td>92602</td>
</tr>
</tbody>
</table>

Mw weight average molecular weight was evaluated using the equation obtained from (Strazielle & Benoît, 1971) 

\[ [\eta] = 7 \times 10^{-4} M_w^{0.67} \]

DSC used to study the fusion behavior, melting point and crystallinity of the LDPE samples before and after recycling. The heat of fusion is the quantity of energy which is required to change a polymer state from crystalline or partially crystalline to a completely disordered amorphous form. The relevant heat effects of a physicochemical process can be estimated by measuring the area under a proper thermogram peak. The percentage crystallinity (C) can be derived as follows:

\[ C = \frac{\Delta H_{\text{exp}}}{\Delta H_f} \]

Where \( \Delta H_{\text{exp}} \) is the experimental heat of fusion of the sample tested. \( \Delta H_{\text{exp}} \) is calculated by measuring the area under the thermogram peak, while \( \Delta H_f \) is taken to 293J/g for PE which represent the heat of fusion of the 100% crystalline polymer (TN 48, n.d.; Wunderlich, 1990).

The resulting crystallinity and melting point values for the virgin and waste LDPE used in this investigation before and after recycling are listed in Table 3. The melting point remained practically unchanged by the recycling procedure and stayed within the permissible limits. According to (Poulakis & Papaspyrides, 1997), the melting temperature and melting range fluctuation for the waste and recycled grades could be attributed to plasticization and additives of the polymer due to the presence of trace amounts of the solvent that would likely remain in the polymer structure. Nevertheless, the melting range of the virgin PE is much broader than that of the recycled grades since the lower the degree of crystallinity, the broader the melting range (Miller, 1966). In addition, the crystallinity of the waste samples based on LDPE before the restoring process ranged between 24-27 and after restoration procedure, the crystallinity increased to 44.1-50. This could be due to the polymer precipitating during the restoration process from the solution under very slight cooling conditions, which indicates that the recycling process itself serves as a kind of annealing treatment (Papaspyrides et al., 1994; Poulakis & Papaspyrides, 1995). The experimental conditions and the efficiency of the testing instrument could also have influenced the results.
Table 3 Melting temperature, (Tm), Heat of fusion $\Delta H_m$ and crystallinity of virgin and three wastes LDPE before and after recycling

<table>
<thead>
<tr>
<th>Samples</th>
<th>Before recycling</th>
<th>After recycling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tm (K) $\Delta H_m$ (J/mol) Crystallinity (%)</td>
<td>Tm (K) $\Delta H_m$ (J/mol) Crystallinity (%)</td>
</tr>
<tr>
<td>virgin</td>
<td>379 4266.08 52</td>
<td>379 4225.06 51.5</td>
</tr>
<tr>
<td>(bags)</td>
<td>379 1993.53 24.3</td>
<td>382.4 3626.17 44.2</td>
</tr>
<tr>
<td>(pipits)</td>
<td>386 2149.45 26.2</td>
<td>386.15 4036.37 49.2</td>
</tr>
<tr>
<td>(int.)</td>
<td>381 2223.28 27.1</td>
<td>382.0 4102 50</td>
</tr>
</tbody>
</table>

The mechanical properties of LDPE virgin and the three waste polymers before and after recycling are shown in Table 4. The tensile stress at maximum load levels and the tensile stresses at yield measurement are seen to be very close for the virgin and recycled polymers. The strain at break (elongation) it was decreased after the recycling and for the recycled from the waste it was turned to virgin. The elastic modules seem to increase after recycling, possibly due to the fractionation phenomena (i.e some lower molecular weight fractions may remain soluble in the solvents/ non-solvents phase), as well as the additives initially contained in the starting material (Papaspyrides et al., 1994; Poulakis & Papaspyrides, 1997). Due to the effects of the sample preparation methods, the tensile stress at yield for the recycled polymer fluctuates from the virgin polymer value, as is seen in Table 4 from the results quoted so far, it can be concluded that the mechanical properties of the three recycled LDPE polymer from the three wastes are almost identical or close to the virgin LDPE properties.
Table 4: Mechanical properties of virgin and waste LDPE before and after recycling

<table>
<thead>
<tr>
<th>Testing type</th>
<th>Virgin</th>
<th>Recycled</th>
<th>Bags (original use)</th>
<th>Pipits for laboratory use</th>
<th>intravenous fluids containers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Waste</td>
<td>Recycled</td>
<td>Waste</td>
<td>Recycled</td>
<td>Waste</td>
</tr>
<tr>
<td>Tensile stress at max. load (Mpa)</td>
<td>7.78</td>
<td>7.82</td>
<td>6.2</td>
<td>7.1</td>
<td>6.3</td>
</tr>
<tr>
<td>Strain at break (%)</td>
<td>39.79</td>
<td>38.4</td>
<td>97</td>
<td>70.75</td>
<td>102</td>
</tr>
<tr>
<td>Tensile stress at yield (Mpa)</td>
<td>4.88</td>
<td>5.33</td>
<td>4.855</td>
<td>5.265</td>
<td>4.98</td>
</tr>
<tr>
<td>Elastic modulus (Mpa)</td>
<td>201.4</td>
<td>205.4</td>
<td>143</td>
<td>174</td>
<td>150</td>
</tr>
</tbody>
</table>

4. Conclusions

Recycling of three wastes LDPE (carrier bags original used, laboratory pipits and intravenous fluids containers), has been investigated using two methods first dissolve the polymer and precipitate without using any precipitator and the second by using dissolution/reprecipitation process. The concentrations of the solution in PetE(C) were employed (20 g/dl) and the polymer was reprecipitated, in the form of small grains or powder. Through the addition of PetE(A or B) or only leave the solution to cool about (10-20) min. very good recoveries in polymer and solvents are achieved. The mechanical properties either remained the same or improved after recycling, as was the case with crystallinity. Thus, the two techniques are quite effective for the recovery of waste low density polyethylene.

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References


