Flexible Polyurethane Foams from Recycled PET

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ABSTRACT
Plastic packaging forms a significant portion of household waste, and PET soft drink bottles represent a major percentage of the waste. Consequently, PET bottle grade material makes up a significant portion of the feedstock in the recycling plant at Visy plastics. The end uses are theoretically many, however, there are few applications for less purified grades of recycled PET. This paper presents the preliminary results of an industry based collaborative research project which aims to investigate the breaking down of recycled PET into its chemical building blocks using glycolysis. The main objective is to produce a polyester polyol for the polyurethane industry from recycled PET and to compare the properties with that of a virgin resin.

INTRODUCTION
Visy Plastics is a recycling company principally dealing with post consumer bottle recycling. Recycled PET constitutes 60% of recycled plastic material at Visy Plastics and is currently shipped in flake form, and for the less purified grades of recycled PET, the end use is unclear. This paper discusses the use of chemical recycling by using glycolysis, which often investigates the depolymerisation of recycled PET into monomers and higher oligomers. The intermediates thus obtained can then be used as building blocks to synthesise other polymers with higher economical value, such as polyurethane foams and unsaturated polyesters.

Most of the literature published regarding utilisation of PET waste to yield a viable product is about unsaturated polyesters. On the other hand, little of literature concerning polyurethane synthesis from PET waste has appeared. The literature that has been cited deals with mainly rigid foams and polyurethane elastomers, made by using ethylene glycol. This paper...
investigates the likelihood of matching branched polyurethane polyol from recycled PET, which is currently being made from virgin raw materials.

Much attention has been devoted to glycolysis by ethylene glycol. In this system the effect of the reaction parameters, temperature (190°C-240°C), pressure (0.1-0.6 MPa) and PET to ethylene glycol ratio on reaction rate, has been investigated. Very few papers have been devoted to the description of the kinetics of glycolysis reaction.

Most of the past research is concerned with the process of utilisation of products obtained by using glycolysis. The PET glycolysates find application in the manufacture of unsaturated polyesters, polymer concrete resins for unsaturated polyesters, polyurethane foams, and polyisocyanurate foams.

The glycolysis process is conducted over a wide range of temperatures (180°C-250°C), during a time period of 0.5-8 hours and usually a catalyst is used, normally zinc acetate, at a level of 0.5% by weight of recycled PET used. Depending on the glycol choice, the glycolysis can be conducted either at atmospheric pressure or performed under pressure.

At least two significant advantages may be expected by use of PET degradation products for synthesis of respective unsaturated polyester. The first one is a possibility to convert the PET waste into valuable product. The other is that terephthalic acid based unsaturated polyesters can be obtained without processing difficulties encountered when virgin terephthalic acid is used.

In terms of synthesis of a polyester polyol to produce polyurethane foam, normally adipic acid is reacted with glycolysed PET oligomers at fixed hydroxyl to carboxyl ratios of about 1.2-1.5 at 170°C for the first three hours and then to 200°C for ten hours to obtain different molecular weights of polyol. The reaction is performed under nitrogen blanket until target acid value of about one is achieved. Water is removed from the reaction and some times vacuum is used to remove traces of water.

Polyester based foams are stiffer and stronger than those made from polyethers, with better resistance to oxidation and high temperatures. Polyester polyols also differ from polyether polyols in having virtually no unreactive end groups, a factor which contributes significantly to the higher strength of polyester based foams compared with those from polyethers.
Flexible Polyurethane Foams from Recycled PET

MATERIALS AND METHODS

Materials

The materials used were,

- Recycled PET Flake size 6-8 mm, Visy Plastics
- Triethylene glycol, Huntsman Chemical Company
- Diethylene glycol, Huntsman Chemical Company
- Pentarythritol, Perstop Chemicals
- Adipic acid, Dupont Chemical Company
- Toluene diisocyanate, (TDI), BASF Chemicals
- Silicon surfactant, Dow Corning
- Blowing agent, (tap water)
- Amine catalyst, Air Products Chemicals and Additives
- Tin catalyst, Witco Chemicals

Glycolysis of PET waste

PET bottle grade flake was depolymerised by using triethylene glycol. PET waste flakes, totalling 800 grams, equivalent to 4.2 mole repeating unit (molecular weight 192), were added to 1760 grams of triethylene glycol (molecular weight 150), such that the molar ratio of PET repeating unit to triethylene glycol was 1:2.8. The mixture was charged into a four-necked glass round bottom flask, which was fitted with a stirrer, reflux condenser, nitrogen inlet and a heating mantle.

Initially the stirrer was not turned on due to the high ratio of solids to liquids in the flask. The temperature was gradually increased to 180°C and the recycled PET flake started melting. It was noticeable by a decrease in size of PET particles and cloudiness in the liquid phase was observed. At this stage it was safe to turn the stirrer on and begin agitating the mixture. The temperature was slowly raised by increments of ten, until a temperature of 230°C was reached. The nitrogen flow was turned on and the recycled PET flake dissolved very easily. After about four hours at cook temperature of 230°C, all of the PET particles were visibly digested.

Samples were taken every hour for gel permeation chromatography, 25°C cone and plate viscosity and hydroxyl value to monitor the rate of depolymerisation.
Preparation of polyester polyol

The glycolysed PET was heated to 150°C and the stirrer was turned on. Adipic acid and pentaerythritol were charged into the round flask at temperature of 160°C and mixed for one hour. The glassware was modified to ensure distillation was possible and a measuring cylinder was used to collect the distillate throughout the course of the reaction. The mixture was gradually heated to 180°C and distillate was first noticed. The temperature was increased by increments of ten degrees depending on the vapour temperature until 230°C. The temperature was held at 230°C and samples were taken every hour for acid value. To increase the rate of the reaction the nitrogen flow, and stirrer speed was increased, so that more water could be removed since the temperature remained constant. The required acid value specification was between 1-5.

A polyol made from virgin raw materials (diethylene glycol and adipic acid was used as a control). The processing conditions for the virgin polyol were similar to the polyol made from recycled PET.

<table>
<thead>
<tr>
<th>Table 1 Polyester polyol samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polylol Number</td>
</tr>
<tr>
<td>POLYOL #1</td>
</tr>
<tr>
<td>POLYOL #2</td>
</tr>
<tr>
<td>POLYOL #3</td>
</tr>
</tbody>
</table>

Preparation of flexible foams

The technique used to actual produce polyurethane foams was called “box foaming”. The box foaming process simulates as close as possible a flexible slab stock production line, which is an industry standard, the dimensions of the box are 30 cm by 30 cm by 30 cm. The polyurethane foam produced is in the form of a bun.

In order to produce polyurethane foam the polylol is reacted with TDI (isocyanate), amine catalyst, tin catalyst, blowing agent (usually water) and a silicon surfactant. The polylol and the small additions like the catalysts, blowing agents and surfactants are mixed first and then mixed with the
Flexible Polyurethane Foams from Recycled PET

isocyanate, the resulting mixture is poured into a box mould and the reaction begins.

The mixture in the form of a foam begins to rise and certain observations are recorded like, rise time, cream time and gel time.

The polyurethane foam takes the shape of a bun and the bun is then cut into certain sizes and physical tests are performed to determine the quality of the foam.

The results of the physical properties and testing of the foams are presented in the results and discussion section.

RESULTS AND DISCUSSION

Glycolysis of PET waste

The glycolysis stage shows the reduction of recycled PET to lower molecular weight fragments. The major fractions of the glycolysed product by Triethylene glycol (TEG) could be represented by the following species: TEG-TPA-TEG, EG-TPA-TEG, EG-TPA-EG, free TEG and a small amount of free EG. Note: (TPA) stands for terephthalic acid and (EG) ethylene glycol.

The gel permeation chromatography results indicate initially the number average molecular weight was high at around 700. After five hours the number average molecular weight was reduced to 467. If we assume the main fraction was TEG-TPA-TEG, the theoretical value average number molecular weight is 464, which is a good correlation. The longer the reaction leads to further decrease in molecular weight, but after five hours the decrease in molecular weight is quite moderate.

In terms of 25°C cone and plate viscosity measurements, similar trends were observed. After the first hour the sample was like a paste and the cone and plate viscosity could not be measured. After three hours into the digestion a result of 7 poise was obtained. At the five hour stage a result of 2 poise was recorded and the same result of 2 poise was recorded at the six hour stage. This suggests the cone and plate viscosity remained stable hence the depolymerisation was complete somewhere between five and six hours.
Similar trends were observed for hydroxyl number initially the values were low at the start of the glycolysis, but as more glycol is exchanged the hydroxyl values begin to increase until finally when the reaction has come to completion the hydroxyl values level out and remain constant.

**Polyester polyols characterisation**

The saturated polyester polyols were made by reacting the glycolysed PET with adipic acid and a small amount of branching agent (Pentarythritol). The temperature of the reaction initially was 150°C and then was raised to 230°C until the end of reaction. Water from the reaction was removed continuously until the target acid value was achieved. The total time for the reaction was 12 hours.

<table>
<thead>
<tr>
<th>Table 2 Polyester polyol properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Properties</td>
</tr>
<tr>
<td>Viscosity</td>
</tr>
<tr>
<td>Acid Value</td>
</tr>
<tr>
<td>OH Number</td>
</tr>
</tbody>
</table>

**Foam physical properties and testing**

The two most important physical properties of a piece of polyurethane flexible foam are density and hardness. Other physical properties of flexible foam such as porosity, tensile strength, elongation and tear resistance are also important.

All three polyols were converted into urethane foam successfully, the ratio of isocyanate [NCO] to polyol [OH] was about 0.5. Polyol #2 made from purely recycled PET had a very open cell structure and even though the density of 30 kg/m³ was similar to polyol #1 the foam was very hard. The foam looked more like a rigid foam structure than a flexible arrangement. Due to the structure being a rigid arrangement the polyol was not tested for flexible physical properties.

Polyol #3 was a 50:50 blend of polyol #1 and polyol #2.
Flexible Polyurethane Foams from Recycled PET

The urethane foam made from polyol #3 resemble a flexible foam, the cell structure was closed and the foam was much softer than the foam made from recycled PET.

The urethane foam made from polyol #1 was similar to the foam made from polyol #3 in terms of cell structure and hardness. The tensile Properties differed in polyol #3 due mainly to the aromatic content in recycled PET, which made the polyol more rigid and hence lower elongation. The foaming parameters such as, cream time, gel time, blow time did not alter much when comparing polyol #1 and polyol #3.

The results of the physical properties and testings of the foams can be seen in the Table 3 and have been tested according to ASTMD 1564-71.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Polylol #1</th>
<th>Polylol #3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>34.7 kg/m³</td>
<td>30 kg/m³</td>
</tr>
<tr>
<td>Tear strength</td>
<td>882 N/m</td>
<td>687 N/m</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>117 Pa</td>
<td>70 Pa</td>
</tr>
<tr>
<td>Elongation</td>
<td>290 %</td>
<td>170 %</td>
</tr>
<tr>
<td>Cell count</td>
<td>64 (per 25 mm)</td>
<td>61 (per 25 mm)</td>
</tr>
<tr>
<td>Hardness (FID)</td>
<td>146 N</td>
<td>131 N</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.85</td>
<td>2.38</td>
</tr>
<tr>
<td>Cream time</td>
<td>26 (sec)</td>
<td>20 (sec)</td>
</tr>
<tr>
<td>Blow time</td>
<td>122 (sec)</td>
<td>140 (sec)</td>
</tr>
<tr>
<td>Rise time</td>
<td>128 (sec)</td>
<td>146 (sec)</td>
</tr>
<tr>
<td>Gel time</td>
<td>163 (sec)</td>
<td>168 (sec)</td>
</tr>
</tbody>
</table>

CONCLUSIONS

The main conclusions from this research are:

- Depolymerisation of recycled PET waste by glycolysis using triethylene was successfully performed and the digestion was complete after six hours.
A procedure was developed to produce a polyester polyol form recycled PET with a very low acid value.

Polyols made from recycled PET foam successfully, though the cell structure was too course and the foam resembled a more rigid structure.

By blending a virgin polyol with a polyol made from recycled PET it was possible to produce flexible foams with physical properties similar to the polyol made from virgin raw materials.

Figure 1 Polyurethane foam made from Polyol #2, very open cell structure resembles a rigid arrangement

Figure 2 Polyurethane foam made from Polyol #3, has a closed cell structure and resembles a flexible foam
Flexible Polyurethane Foams from Recycled PET

ACKNOWLEDGMENTS

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REFERENCES
