1 Introduction

Owing to the continually increasing global population and more widespread industrialisation (particularly with respect to the developing world’s aspirations to equality of standard of living), the extraction and use of materials is constantly expanding. These materials are critical for humans to function as a society in order to construct the necessary tools and components required.

This ever-increasing demand for materials has meant that certain resources are becoming continually scarcer. This can be noticed clearly in the increasing price of commodities over the recent decades [1]. Those commodities which are in high demand, such as oil and rare earths, are prone to short term volatility in their price, irrespective of the cost of extraction or production [2, 3]. In many cases, such as those where the resource is dependent on specific geological formations or minerals, this is due to political and social instability within the few countries where these resources are found [4].

The polymer matrix composite materials sector has seen a surge in growth over the last few decades [5]. The polymer matrix within a composite is normally derived from petrochemicals with the synthetic fibre, commonly glass and carbon, requiring high amounts of energy during manufacture. As the price of raw materials for resin is heavily dependent on petrochemical price fluctuations, there has been a greater focus on deriving these resins from bio-based sources. Even though some types of synthetic fibre are not derived from petrochemicals, the energy used in the manufacturing process could ultimately be petrochemical in origin.

The development of ‘green’ composites that can be economically competitive when compared with standard synthetic fibre composites is an important area of research. Here ‘green’ is taken to mean a product that is less harmful to the environment than existing alternatives. Resin manufacturers have also been focusing on social and environmental factors during the manufacture and processing required for their resin systems. This is normally in the form of a ‘Sustainability Agenda’ [6, 7]. However, it is not always obvious how such green credentials are determined and the term sustainability has different meanings depending on the context in which it is used.

The common components for the manufacture of green composites are natural fibres and bio-based resin systems. Natural fibres come in many forms from many sources [8]. They include various plant and animal fibres, but in general there are two key features: ‘as produced’ fibres tend to be short and are lacking in the uniformity one finds in manufactured fibres. Whilst these fibres do have interesting properties that merit further attention, and whilst there is the potential to process them to a greater or lesser extent in order to produce more uniform and longer fibres, there is perhaps greater potential in the investigation of resin systems and the processes by which they can be made greener.

In a collaborative project between the University of Surrey and Scott Bader Company Ltd., both aspects
are being investigated e.g. [9-11]. In previous work by the authors, sustainability has been measured in terms of the proportion of the resin system that has been replaced by a bioderived oil, displacing fossil based petrochemicals [11]. Here, the focus is on providing a more robust assessment of the ‘green credentials’ of this class of materials. To this end, Life Cycle Analysis (LCA, sometimes referred to as Life Cycle Assessment) has been undertaken in order to assess existing options and to provide a baseline against which alternatives can be compared.

LCA is a generic term for a range of ‘inventory’ techniques: as with many concepts whose “time has come” LCA methodologies appeared independently in multiple places during the late 1960s and early 1970s [12]. Fundamentally, the purpose of such inventory techniques is to gather all available information on the production, use and disposal of a given item and hence to determine the impact of the item on the environment. (The specific methodology used in this study is outlined in section 3).

Some products are easier to assess than others. For example products which are feedstocks for multiple users are much more complex to provide an inventory for, and of course polymers and polymer matrix composites fall into this category. The important thing to carry forward is that whilst it is not always possible to provide an assessment that is perfectly accurate, usually due to the lack of good quality (or any) data when preparing the inventory. This can be perceived as a major barrier to carrying out an assessment, but even more generalised assessments can be valuable in highlighting issues within the production, use and disposal of an item. Another perceived issue is the complexity of processing and manufacturing, but streamlining methodologies have been found to be very successful in highlighting issues in production which would not be captured if LCA is reserved as a corporate strategic tool e.g. [13].

LCA of polymer resins typically used in composite systems has been carried out previously, e.g. [14-16], but whilst rigorous these studies follow typical LCA processes and limit the scope of the study quite severely, making many assumptions to simplify the case as much as possible. The current work has developed a multi-stage methodology which is much more relevant for the batch processes used to manufacture many structural thermosetting polymer systems.

The structure of the paper is as follows. In the next section the materials assessed in the current study are specified whilst, as mentioned, in section 3 the methodology used is presented in more detail. Results are presented and discussed in section 4 and the paper closes with section 5, Concluding Remarks.

2 Materials

Whilst several systems have been considered within the larger project the current work will focus on Scott Bader’s Crestapol® technology. This is a urethane methacrylate (UMa) system and a development thermosetting resin, based upon this system, has been manufactured by Scott Bader Company Ltd. This development system substitutes some of the petrochemical based raw materials with (vegetable) oils: in previous work it has been noted that the vegetable oils used in this work are active constituents not inactive fillers. This development resin system has similar production costs and shows similar mechanical performance compared to the standard thermosetting resin system [11].

As the formulation of the resin systems utilise specialist monomers, the data for some of these chemicals were not available. In some cases it was necessary to use data for another isomer of that chemical and it was thus assumed that the supply chain and production conditions for two isomers would be quite similar. Where a similar chemical could not be selected, the model still included it as a flow but not linked to any data. However, when the relevant data becomes available in the future, this information can be easily inserted into the model. This is discussed further in the Methodology.

It should be noted that the data used within this study did not describe the purity (grade) of the raw material. The purity of a chemical can be an important factor in some resin formulations, and this can be of significance if the steps required to obtain
high grade materials are energy intensive, as may be the case for components obtained through, for example, distillation or membrane filtration.

Owing to the commercial sensitivity of data used to calculate the LCA, details of specific constituents and their masses have been omitted.

3 Methodology

An environmental life cycle assessment (LCA) is carried out to assess the environmental impact of a material or product over a period of the life of the product. The “gold standard” of LCAs for a finished product is to consider the material from raw material extraction/sourcing, commonly known as the ‘cradle’ right through to the processing of a discarded item and its processing in order to produce raw materials for another product: this is referred to as a “cradle-to-cradle” assessment. In practice the item may be discarded for a variety of reasons that prohibit reuse or recycling and it may only be possible to consider disposal in a “cradle-to-grave” manner. If a product has potentially unlimited uses, usually because it is raw material for another product, the LCA is often conducted only up until the end of manufacture for the original product (in the form which it is sold to another customer). This is called a ‘cradle-to-gate’/’cradle-to-factory gate’ study.

Whatever the extent of the LCA, the aim is to account for the inputs (materials and energy) and outputs across the various stages involved in the manufacture of a product, and where possible it’s use and disposal. It is from this analysis that the environmental impact of that product (or service) can be assessed comprehensively. LCA has become the central concept for both environmental management within industry and governmental environmental policy making [17]. The international standards that cover LCA are BS EN ISO 14040 (Principles and Framework) and BS EN ISO 14044 (Requirements and Guidelines) [18, 19].

The Crestapol® system is used in a wide range of applications and therefore in the current context a ‘cradle-to-cradle’ assessment is not possible and a ‘cradle-to-grave’ LCA would not be appropriate. Instead, current work focusses on the production of the resin in a “cradle-to-gate” analysis: here ‘gate’ is taken to mean the output from the reactor, rather than the factory gate, as subsequent effects are (a) negligible and (b) the same for all systems produced.

Initially, the material flow for the LCA was broken down into five main areas, which cover ‘cradle-to-grave’. These areas are the manufacture of the raw materials and transport to site (“Wider System”), pre-processing and site distribution (“Scott Bader” from Goods In to Reactor In), the production process (“Reactor” from Reactor In to Reactor Out), post-processing (from Reactor Out to Goods Out) and Lifetime (Goods Out to End of Life). For the current ‘cradle-to-gate’ analysis, the latter two stages were not included.

Where LCAs are carried out for polymers, the production stage is usually treated as one process and various assumptions are made to account for the different steps in the manufacturing process. Here, the Reactor stage was broken down into four sub-stages in order to more accurately assess the energy used during batch production. The sensitivity of the system to changes in raw materials was investigated.

Within the model, data were not available for approximately 20 % of the final mass. Whilst this is not an ideal situation for an LCA, it is by no means unusual and is discussed in depth in the Handbook on Life Cycle Assessment [20]. It is suggested that typically one can “cut off” a flow for which there is insufficient data if it contributes less than 2.5% of the total flow. (This can be measured in economic or mass terms). Whilst no guidance is provided on what the total amount of omitted mass can be, it is acknowledged that 20% of the final mass is quite a considerable component to omit from consideration. However, these components are a) minor constituents and b) are generally found in both the commercial and developmental resins and can therefore be treated as having a comparable effect on both systems.

The analysis was carried out using GaBi software (v4.4 PE International) supported by the EcoInvent database. Site data were collected at Scott Bader’s production facility in Wollaston, UK,
The LCA considers a number of environmental impact categories:

- Acidification Potential (AP) (kg SO\textsubscript{2} equiv.)
- Eutrophication Potential (EP) (kg phosphate equiv.)
- Freshwater Aquatic Ecotoxicity Potential (FAEP) (kg DCB equiv.)
- Global Warming Potential (GWP) (100 years) (kg CO\textsubscript{2} equiv.)
- Human Toxicity Potential (HTP) (kg DCB equiv.)
- Ozone Layer Depletion Potential (OLDP) (kg R11 equiv.)
- Photochemical Ozone Creation Potential (POCP) (kg Ethene equiv.)
- Terrestrial Ecotoxicity Potential (TEP) (kg DCB equiv.)

In the next section, the findings of the LCA are presented in the light of these impact categories.

4 Results and Discussion

4.1 Results

The contributions to environmental impact of the resin system are presented in Fig. 1, where data has been normalised against the calculated total impacts of the European Union. Photochemical ozone creation potential (POCP) followed by Acidification potential (AP) and Global Warming Potential (GWP) were the categories having the highest relative impact: other contributions were at levels approximately one fifth (or lower) of those of the three main impact categories.

The Crestapol® resin system can to some extent be validated by benchmarking the quantitative results with published results for other similar resin systems. Through the Ecoinvent database there is information on the cradle-to-gate impacts of a typical unsaturated polyester resin system and a typical epoxy resin system. The selected results for comparison are the energy input and the Global Warming Potential (GWP) as these are considered key concerns in terms of cost and environmental impact respectively. The data for the three systems is presented in Table 1. Note that these quantitative results are for indicative purposes only and should not be considered as the energy or carbon footprints of these products. However it is interesting to note that the ratio of Energy Input to GWP is approximately equal for both the Crestapol® and Epoxy systems (~20 MJ/kg CO\textsubscript{2}) and that the Unsaturated Polyester is slightly smaller, at ~17 MJ/kg CO\textsubscript{2}). At this stage it is difficult to conclude anything specific from this, particularly given the issue of the mass flows that could not be incorporated into the model.

4.2 Onsite Impact vs. Constituents

POCP is attributed to the photo-oxidant formation of nitrogen oxides and volatile organic compounds. These reactive compounds can be hazardous to human health as well as causing crop damage [21]. AP is caused when acid gases are absorbed by atmospheric precipitations. As a result, this acidified rain can cause leaf damage and superacidity of soil, both of which negatively affect the growth of plants. GWP is the effect of rising average atmospheric temperature due to the absorption of solar radiation by the atmosphere due to the accumulation of particular gases such as carbon dioxide, methane and nitrous oxide in the atmosphere. This impact has been linked with increased climatic disturbance, rising sea levels and desertification [22]. HTP relates to the emission of substances, such as heavy metals, that have a negative effect on human health. The two carriers of this toxicity are air and water [22].

When the impact of the materials and processing were split it was observed that:

- POCP was mostly attributable to the materials: all of the processing for the manufacture of the resin system (the on-site input) contributed just 0.03 % to the POCP.
- AP was also significantly affected by the materials component: all of the processing for the manufacture of the resin system (onsite input) contributed just 0.06 %.
- GWP (100 years) was substantially affected by the materials. All of the processing for the manufacture of the resin system (onsite input) contributed just 0.21 % to the global warming potential.
whilst the impact of HTP was low on the list of normalised impacts (a tenth of the contribution compared with GWP, Figure 1) it is raised as a potential area of concern because this was the impact category in which the apparent dominance of the diluents in terms of contribution to the impact was not upheld.

However, whilst these impacts represent the whole “cradle-to-gate” process, the contribution from the production process itself is negligible: most issues arise from the extraction of raw materials and refinement/purification of the resin constituents.

4.3 Disproportionate impacts

Once the materials segments were broken down to the relative contribution of each of the resin components, it was found that the diluents contributed:

- 81 % of the POCP impact.
- 73.1 % of the AP impact.
- 72 % of the GWP impact.

Clearly, therefore, diluents represent an area of interest for those looking to reduce material related impacts. Whilst the role of the diluent has historically been crucial (particularly with respect to UP resin systems) in taking a material from an interesting but uneconomic material to a commercial success with widespread applications, in order to maintain this usage it is necessary to identify alternative diluents (or alternatives to diluents) with reduced impact upon the environment.

Further, when the impact of the materials and processing were split it was observed that one part of the blended system, representing around 20% of the Crestapol® resin system’s mass, was responsible for 64 % of the human toxicity potential. Further analysis showed that of this part, one monomer was the main contributor to the impact, (52.9 % of the HTP), despite contributing less than 2.5 % of the Crestapol® resin system’s mass. This too, therefore indicates a particular area for scrutiny.

The data summarised in Table 1 suggest that the model used is providing numbers that are in the right ball park for resin systems. It was expected that the Energy Input and GWP of the Crestapol® resin system would be close to the results for the unsaturated polyester and epoxy resin systems because they both manufactured from petrochemical based feedstocks. Without over interpreting the findings, especially when it is not possible to compare the system boundaries and assumptions for the LCAs of the three resins, it is worth noting that a possible explanation as to why the Crestapol® resin had a lower Energy Input and GWP is that the raw materials are different to the raw materials used in the unsaturated polyester and epoxy resins and there may be the chance that the 20% of mass of material omitted may be responsible for this difference.

4.4 Discussion

The assessment presented here has shown that for the resin system under consideration, the on-site contributions to environmental impacts are comparatively minor compared to those associated with the manufacture/collection of the primary raw materials. This analysis does not mean that resin manufacturers have no control over reducing environmental impacts. The results of the LCA suggest that there are two groups of people who have the potential to significantly reduce the environmental impact of resin systems: the polymer chemists and the purchasers of raw materials.

For example, the formulation (the monomers that make the polymer, and including the diluents that aid processability) of the resin system, can be revised with a focus on options with lower environmental impacts when developing new products. At the same time, the suppliers of the raw materials can be selected based upon the environmental impact of their product (e.g. there is usually more than one manufacturing method for a particular monomer and different manufacturers may have access to different energy sources some of which may be less carbon intensive). Even if the raw material is sourced further afield, the extra transportation environmental impact could be lower than the improved environmental impact of that particular raw material.
Interestingly, it should be noted that for the options available within the current study (i.e. oils derived from petrochemical or vegetable sources), it appears that the environmental impacts are relatively insensitive to production route. The contributions from fertilisers and harvesting are comparable to extraction from the ground. However, there is much potential for examining the choice of monomers and assessing their contribution to mechanical properties against their environmental impacts, as there can be as much as an order of magnitude difference in e.g. GWP.

As it is common practice to adjust the monomer concentrations within the formulation to form a new system, this alteration could have an effect for the environmental impacts. For example, the current analysis has shown that the majority of the human toxicity environmental impact of the resin system was attributed to a monomer that was less than 2.5 % of the formulation. Thus if the concentration of that monomer in the formulation was increased then the human toxicity potential could become an impact of concern.

To further assist in understanding the potential issue of adjustments to a formulation, Table 2 shows some of the environmental impact categories for a selection of monomers (mass of 1 kg) from the Ecoinvent database (European averages). The data within this table shows that some monomers can have greater environmental impacts than other monomers by a factor of ten.

5 Concluding Remarks

In order to understand the environmental impacts of the thermosetting resin systems manufactured by Scott Bader Company Ltd. an environmental life cycle assessment was conducted. This assessment focused on the manufacture of a urethane methacrylate resin system from the Crestapol® range and compared this with a developmental resin, which uses vegetable oils as a functional replacement for a proportion of the petrochemical feedstock.

A model for the manufacture of this resin system was created using GaBi software with data on the cradle-to-gate impacts of raw material production sourced from the Ecoinvent database.

The results from this model showed that the three environmental impact categories of interest were photochemical ozone creation potential, acidification potential and global warming potential. The results also illustrated that the on-site input within these environmental impact categories was less than 0.2 % of the impact for all impact categories. This is not to say that improvements to the production and on-site phases cannot be made.

Unusually, a full break down of the processing stage was considered: whilst the “reactor” stage will not be the same for all thermosetting polymers it is noted that this is a worthwhile exercise to undertake, and enables a manufacturer to target particular areas of their operation in order to improve efficiency and decrease harmful emissions. These are particularly associated with the energy usage and its form on site.

As a consequence of the analysis, it has been demonstrated that significant improvements to the environmental impacts of resin systems can be made through the choice of particular monomers and the choice of suppliers with access to more energy efficient and environmentally benign processes and less carbon intensive energy mixes.

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References


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**Fig.1.** Normalised environmental impacts for the resin production of Crestapol commercial resin to CML 2001 – Nov. 09, EU25+3 (6 ton batch)

**Table 1.** Quantitative energy input and GWP for the Crestapol 1212 compared with an unsaturated polyester and epoxy resin systems

<table>
<thead>
<tr>
<th>Resin Type</th>
<th>Energy Input (MJ kg⁻¹ of resin)</th>
<th>GWP (kg CO₂ kg⁻¹ of resin)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crestapol ®</td>
<td>117</td>
<td>5.7</td>
</tr>
<tr>
<td>Unsaturated Polyester</td>
<td>128</td>
<td>7.6</td>
</tr>
<tr>
<td>Epoxy</td>
<td>139</td>
<td>6.7</td>
</tr>
</tbody>
</table>
Table 2. Environmental impacts for a selection of monomers from the Eco-invent LCA database (the highest environmental impact within category marked in red)

<table>
<thead>
<tr>
<th>Monomer (1 kg)</th>
<th>Global Warming Potential (kg CO₂ equiv.) per kg of monomer</th>
<th>Acidification Potential (kg SO₂ equiv.) per kg of monomer</th>
<th>Human Toxicity Potential (kg DCB equiv.) per kg of monomer</th>
<th>Photochem. Ozone Creation Potential (kg Ethene equiv.) per kg of monomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adipic Acid</td>
<td>25.50</td>
<td>0.023</td>
<td>11.02</td>
<td>0.0041</td>
</tr>
<tr>
<td>Terephthalic Acid</td>
<td>1.85</td>
<td>0.006</td>
<td>0.67</td>
<td>0.0011</td>
</tr>
<tr>
<td>Acrylic Acid</td>
<td>2.88</td>
<td>0.005</td>
<td>0.27</td>
<td>0.0010</td>
</tr>
<tr>
<td>Diethylene Glycol</td>
<td>1.11</td>
<td>0.004</td>
<td>0.43</td>
<td>0.0008</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>1.62</td>
<td>0.005</td>
<td>0.64</td>
<td>0.0011</td>
</tr>
<tr>
<td>Propylene Glycol</td>
<td>4.24</td>
<td>0.017</td>
<td>13.54</td>
<td>0.0031</td>
</tr>
<tr>
<td>Styrene</td>
<td>3.23</td>
<td>0.010</td>
<td>0.35</td>
<td>0.0018</td>
</tr>
<tr>
<td>Methyl Methacrylate</td>
<td>6.67</td>
<td>0.034</td>
<td>0.31</td>
<td>0.0062</td>
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