Abstract

The controversy surrounding some phthalate plasticizer chemistry in PVC is not based on meeting regulatory requirements alone but also an issue of meeting public expectations: addressing the one whilst ignoring the other cannot be regarded as a realistic long-term strategy for the industry.

This paper outlines how particular bio-based plasticizers increasingly have the capacity to fulfill a role as viable alternatives in terms of their use as primary plasticizers in PVC to replace current petroleum-based chemistry that is under scrutiny from the regulators and in addition satisfy many of the qualitative needs demanded by market forces.

Secondly, the use of bio-based plasticizers as auxiliaries to complete the bio-based offering is also presented in the form of a Case Study of a new generation of paste CaZn Heat Stabilizers for the Plastisol process within the European Flooring Industry to meet the needs of Internal Air Quality standards under AgBB.

A further development is advocated in the use of bio-based plasticizers as carriers for other actives to give the PVC industry the opportunity of completing the bio-based offering.

Introduction

Focus areas have been split into three sub-sections:

i) A study to determine the technical competence of selected bio-based chemistry vs general purpose plasticizers on the market

ii) A Case Study highlighting how the novel stabilizers meet the regulatory EU obligations

iii) The use of an Acetylated MonoGlyceride as a primary plasticizer and extending that use as an auxiliary within the paste stabilizer and potentially to its use as a carrier for other actives in a PVC formulation

A brief description of the current generation of bio-based plasticizers in the European market is offered and the way that the use of this chemistry has evolved from its original concept of being reserved for 'sensitive' applications to mainstream plasticization. In addition, how two companies working together are offering an option to tackle possible longer-term challenges that are not enshrined in law but that cannot be ignored if the PVC industry is to thrive and progress – adopting, if possible, a holistic approach to the substitution of some additives to make the polymer both demanded and appreciated by society as a whole.

Food Ingredient Technology as Polymer Additives

The use of Food Ingredient chemistry to replace polymer additives under the scrutiny of the regulators is not a new phenomenon within the Polyolefins, Polycarbonates and Styrenics markets where such chemistry is commonplace. Food emulsifiers similar to those used in the bakery and dairy industries have been used successfully by resin manufacturers for many years for their broad acceptance in food contact applications. Triglycerides (Vegetable Oils based on Sunflower, Rapeseed, Coconut, Palm Oil etc) are combined with glycerine in an inter-esterification process with a resultant Monoglyceride containing amounts of Di and Tri. The intermediate is subsequently distilled and the resultant molecule is the core of the technology. Chain length, degree of Saturation, Acid Esterification and Glycerol Polymerization can be adjusted to achieve particular properties whose final iteration become Anti-Stats, Anti-Fogs and Mould Release agents for the Food Contact packaging market.

Technical Competency of General-Purpose Bio-Based Plasticizers

It is only relatively recently that such chemistry has been extended into the world of PVC as plasticizers where issues of migration have kept many phthalate plasticizers in the regulatory spotlight. An Acetylated MonoGlyceride introduced to the market in 2004/5 based on Castor Oil and Glycerol and similar Food Ingredient technology has spearheaded the advance of bio-based technology into PVC as a plasticizer.

Comparisons were made between the Acetylated MonoGlyceride (AMG) ie a fat-based plasticizer, and an Isosorbide (ISO), a starch-based product, another general purpose bio-based plasticizer revealed to the market in 2010. The two renewable-resource products were also compared to the main general purpose primary plasticizers
in the US and EU markets: C₈ through C₁₀ phthalates plus DOTP (Di Octyl Tera Phthalate) and DINCH (Di Iso Nonyl Cyclo Hexane) being the principal players. Plasticizers based on Levulinic Ketals are also said to be on their way to being manufactured in quantities and their commercialization will lend further credence to the bio-based movement but their introduction to the market is too new for their consideration here.

The ‘hard’ values of Technical Competence were examined to check their suitability, and the Toxicological profile of the AMG and what many regard as the ‘softer’ value of Environmental performance, no less important if raw material suppliers are to provide the PVC industry with a positive message in terms of the additives used in a PVC formulation so that – over time - society both accepts and appreciates the polymer as opposed to the current view tainted occasionally by suspicion of the chemistry.

The Castor Oil-based AMG demonstrates good technical properties compared to C₈-C₁₀ general purpose phthalates and is a good candidate to replace phthalates in many applications and the Isosorbide offers characteristics that are similar in nature to phthalate chemistry and both appear to have the attributes to escape the general controversy over plasticizers. It is important to highlight that notable differences exist between EU and US regulators on the subject of phthalate chemistry:

Table 1: Internal comparative study of bio-based plasticizers vs C₈-C₁₀ #1 (Danisco internal data)

<table>
<thead>
<tr>
<th>Mw</th>
<th>AMG 505</th>
<th>DOP 390</th>
<th>DIDP 446</th>
<th>ISO 414</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity @ 25degC</td>
<td>113</td>
<td>66</td>
<td>97</td>
<td>55</td>
</tr>
<tr>
<td>@ 25degC</td>
<td>78</td>
<td>77</td>
<td>78</td>
<td>78</td>
</tr>
<tr>
<td>Cold Impact</td>
<td>-42.5</td>
<td>-33*</td>
<td>-29*</td>
<td>-47.5</td>
</tr>
<tr>
<td>Volatile Loss %:</td>
<td>0.8</td>
<td>9.0</td>
<td>1.6</td>
<td>4.3</td>
</tr>
<tr>
<td>Cell Oven 135°C 1 day</td>
<td>1.4</td>
<td>19.3</td>
<td>3.6</td>
<td>10.2</td>
</tr>
<tr>
<td>135°C 3 days</td>
<td>5.9</td>
<td>29.1</td>
<td>12.3</td>
<td>17.8</td>
</tr>
<tr>
<td>Elong. at Break (before Ageing)</td>
<td>794</td>
<td>763</td>
<td>727</td>
<td>676</td>
</tr>
<tr>
<td>(after Ageing 7d @ 135degC)</td>
<td>500</td>
<td>31</td>
<td>376</td>
<td>214</td>
</tr>
<tr>
<td>Retention</td>
<td>63%</td>
<td>4%</td>
<td>52%</td>
<td>32%</td>
</tr>
<tr>
<td>(* Manf. own data)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Similar Viscosities between the bio-based candidates and the general purpose phthalates are achieved in addition to good Efficiency and notable Cold Impact resistance. Extremely low VOC (Volatile Organic Solvents) emissions of the AMG (highlighted area) are also observed and are a key characteristic in the product’s rapid acceptance in the marketplace - an increasingly valuable characteristic, either as primary plasticizer or as an auxiliary for other additives that may be contained in a Flexible PVC formulation.

In addition, (see Table 2) comparable Tensile Strength, Color, reasonable Extraction Resistance are achieved with the bio-based products which suggests a short lead time between laboratory sample through to full production:

<table>
<thead>
<tr>
<th>Mw</th>
<th>AMG 505</th>
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<th>DIDP 446</th>
<th>ISO 414</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength</td>
<td>18.0</td>
<td>15.8</td>
<td>18.9</td>
<td>15.3</td>
</tr>
<tr>
<td>Mpa</td>
<td>100% Modulus</td>
<td>4.4</td>
<td>4.1</td>
<td>5.4</td>
</tr>
<tr>
<td>Volume Resistivity</td>
<td>6.6 x 10¹²</td>
<td>3.6 x 10¹³</td>
<td>4.9 x 10¹³</td>
<td>3.3 x 10¹³</td>
</tr>
<tr>
<td>Hazen (Color):</td>
<td>35</td>
<td>5</td>
<td>9</td>
<td>16</td>
</tr>
<tr>
<td>Extraction (%):</td>
<td>12.4</td>
<td>14.1</td>
<td>25.2</td>
<td>9.6</td>
</tr>
<tr>
<td>Hexane (24hrs @ 25degC)</td>
<td>0.1</td>
<td>0.1</td>
<td>&lt;0.1</td>
<td>0.7</td>
</tr>
<tr>
<td>Water (24hrs @ 60degC)</td>
<td>7.3</td>
<td>5.3</td>
<td>7.8</td>
<td>7.1</td>
</tr>
<tr>
<td>Olive Oil (24hrs @ 60degC)</td>
<td>63%</td>
<td>4%</td>
<td>52%</td>
<td>32%</td>
</tr>
</tbody>
</table>

Table 2: Internal comparative study of bio-based plasticizers vs C₈-C₁₀ #2 (Danisco internal data)

From the above internal investigation it can be concluded that the cited bio-based products appear to offer genuine options – they cannot be regarded as technical lightweights and in some cases show genuine improvements over a ‘traditional’ plasticizer. Sensible product selection according to end use, application, process and formulation is a prerequisite and industry has now built up processing experience using this new technology.

The Isosorbide is presently only available in semi-commercial quantities whereas the AMG is an established product and freely available, although capacity restraints currently exist. The initial expectation was that
this technology would find a market primarily in ‘sensitive’ areas such as Food Contact Gaskets and Medical Devices and these industries do form part of the portfolio. Nonetheless, AMG technology has moved rapidly into technical applications such as PVC Flooring, Coated Fabrics, Automotive applications, Carpet tile systems, Domestic Cabling, Films and Wallpaper, all areas where Internal Air Quality plays an important role and low VOC emissions from the plasticizer are an attractive feature to processors and brandowners.

**Safety & Environmental Profile of Bio-Based Plasticizers**

Controversy over phthalate plasticizer technology centers on the safety of the product migrating to the surface of the polymer and this issue is therefore key. The AMG has been subject to extensive Toxicological testing and a recent 2-generation combined Reproduction and Developmental Neurotoxicity Study reinforces the other test regime that has been conducted. Given that the NOAEL values exceed 1100 mg/kgbw/day (vs a recommended max of 1000 mg/kgbw/day) the results do lend credence that such bio-based chemistry offers an enviable safety profile.

The high bio content of the AMG (80%) offers an interesting Environmental profile whose prime raw material (fully Hydrogenated Castor Oil) does not compete with the food chain and the product is backed by an LCA according to ILCD EU Green Purchasing guidelines - publication is expected within the next few months.

The Isosorbide (said to be 100% bio-based) has also been REACH-registered for EU regulatory purposes but it is believed that no further data on its Safety or Environmental profile have been published formally.

**Case Study – Bio-Based Plasticizers as Auxiliaries in Novel Paste Stabilizers in EU**

Flooring is a high profile product in the eyes of the public and has a potentially large effect on Indoor Air Quality. It is perhaps not surprising that having dealt successfully with the demands of REACH the next regulation that has imposed a challenge to Flooring manufacturers using a Plastisol process is that of meeting VOC levels under AgBB. Both REACH and AgBB are regulations that are enshrined in law and AgBB has been in force from 2008 with a further revision in May 2010 when the LCI (the Lower Concentration of Interest) value of acceptable phenol levels was reduced from 78 ug/m³ to 10 ug/m³.

On the other hand, suppliers of Heat Stabilizers and Plasticizers are challenged by other external factors that are not necessarily enshrined in law and yet have a material bearing on the future health of the industry: most of these elements are currently ‘non-obligatory’ or ‘voluntary’ but the industry would be naïve to ignore them. Examples of such elements range from:

- The need to provide Architects and Specifiers the means whereby they can choose PVC over other materials at the beginning of a project
- The desire of Brand owners to create new markets with a wider appeal
- The avoidance of a poor public image and the potential de-selection of PVC
- More tangible still – and towards the end of the life cycle of the product - the need to ensure that the industry does not repeat the situation often faced by recyclers today as they battle with the trouble of keeping recycled plastics as contaminant-free as possible: Sn, Cd, Brominated Flame Retardants are typical examples of contaminants used in the 20th century but that have become a 21st century matter, although – it must be stressed - not necessarily directly related to the Flooring industry. There is a much greater awareness today of the obligations to learn from the experience of the last couple of decades of the recycling industry.

- Other market influences are the rising credibility of the Consumer and Voluntary Industry Standards.

For manufacturers using a Calendering process such regulations as AgBB are more easily met – the adoption of solid CaZn stabilizers ensures compliance in terms of Heat Stabilizers and changes from C8 to C9 meet current formal regulations in terms of Plasticizers, at least for the time being. Alternative primary plasticizers, i.e. non-phthalates, are being increasingly used and the industry has recently seen the introduction of AMGs to this sector of the Flooring industry.

However, in the Plastisol process a move from traditional Liquid Mixed Metals to the more recent REACH-compliant stabilizers – whether these are liquids, pastes or solids - (and the move away from DIHP to DINP, for example) do not solve the problem that VOC levels are exceeded under AgBB.
Novel CaZn Stabilizers

With these new AgBB limits on phenol in place an investigation was launched by a prominent stabilizer producer in the EU with the aim of reducing any negative influence of liquid stabilizers on the VOC and focused on the transparent wear layer, the most critical area. Novel, low-VOC CaZn pastes and solid stabilizers were developed specifically for this application that are unique in their composition and results indicate good performance in terms of transparency, early color, color retention and even better ultimate degradation time.

And yet, given that the EU PVC flooring industry is looking to eliminate phthalate plasticizers from their finished articles, alternative commercially-available options were tested and bio-based plasticizers have been found to be a viable techno-commercial solution. In keeping with the wider aims of the flooring industry the plasticizer used as carrier for the CaZn paste stabilizers for the wear layer was successfully replaced by the bio-based AMG. Positive results were obtained in terms of stabilizer ‘shelf-life’ without the phenomenon of separation of the solid and liquid part and in addition static heat stability (Mathis oven) tests were carried out comparing the new ‘Low VOC’ CaZn pastes containing phthalates to the bio-based product. The results obtained show no significant difference in overall performance, thus opening up new possibilities of a completely holistic approach to the elimination of phthalates if the customer so demands:

Further Use of Bio-Based Plasticizers as Carrier for Other Actives

Any approach to the elimination of phthalates as primary plasticizers may also demand the removal of such products from any microbiocides used in the formulations should the processors so desire, thus completing the bio-based offering where such additives are used.

Other areas of Flexible PVC should also further benefit from similar industry initiatives such as extending the use of bio-based products as carriers for the active ingredient: Flooring is just one industry sector where they are utilized but anywhere that such additives are employed to protect the polymer – such as Coated Fabrics or Sheeting, for example – then the same logic applies.

Fig 2 shows a standard PVC sheet attacked by Aspergillus Niger under ASTM GS21-96 using a standard test formulation with a typical result – growth formation under the test conditions:

Fig 1: CaZn paste with AMG as primary plasticizer and carrier – lower three lines (Baerlocher Italia SpA)

In keeping with the industry’s aim of promoting itself as a polymer that is ‘sustainable’ in the wider sense of the word and that continues to grow because it is recognized and appreciated by society ie ultimately good for business and good for the polymer industry in the longer term, then the adoption of plasticizers that fulfill wider functions must be acknowledged as being the logical path to follow: new raw materials that satisfy both the criteria of Technical Competency whilst introducing a positive image to the general public can only be of benefit - the achievement of sustainability cannot be the expectation of sea-changes but the consolidating of small, positive steps that move the industry towards its goals.
Fig 3: ZnP (Zinc Pyrithione or Zinc Omadine) stable emulsion (Danisco internal data)

Fig 3 demonstrates the AMG used as both primary plasticizer and as a carrier in a stable emulsion of ZnP at a rate of 500ppm under the same conditions. ZnP was used for these test purposes as it is regarded as a challenging product to offer in an emulsion suggesting that other microbiocide actives (liquids, in particular) may be more easily carried in the same manner via a bio-based carrier.

It is advocated that this approach moves the debate forward, substituting the commonly-used C₈ through C₁₀ plasticizers used as carriers in paste CaZn Heat Stabilizers, not necessarily solely for the purpose of current regulatory compliance but also to anticipate in advance any further desire of the regulators and to present the PVC Flooring industry with genuine technically-competent options that fulfill the aforementioned ‘non-obligatory’ elements.

Conclusions

Certain general purpose bio-based plasticizers can provide technically competent products for the PVC market that can meet regulatory obligations and offers some improvements over current plasticizers on the market. Furthermore, benefits to the PVC industry above and beyond obligatory regulatory requirements can accrue from incorporating bio-based plasticizers as carriers within Heat Stabilizers and as carriers for Microbiocide actives in addition to any qualitative benefits achieved through their more obvious use as primary plasticizers - their wider functionality can ensure greater public acceptance of PVC as a polymer of value to society.