Plastics Additives and Green Chemistry
Additives

1 tonne = 1000 kg

About 5% (wt.) of all plastic is additives

Plasticizers account for >50% of additives

Flame retardants account for about 25%
Consequences

DOTP (aka DEHP)

PBDEs

persistence, bioaccumulation, toxicity
Solutions and strategies

• Small-molecule, drop-in replacements for DOTP, PBDEs etc.
• Higher-MW additives for reduced migration
• Designing polymers with inherently desirable properties

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green design principles
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Impacts of PVC

PVC accounts for 80% of plasticizer use; the plasticizer market is 75-85% phthalates

0% plasticizer

85% plasticizer
PVC consumption is not expected to decrease in the short term.
PVC is only part of the challenge

Biopolymers based on cellulose, starch, and wheat gluten will consume plasticizers

Poly(lactic acid) \((T_g = 55 \, ^\circ C)\) is brittle like PVC \((T_g = 82 \, ^\circ C)\) and requires additives if it is to be used as a flexible plastic
Small molecule alternatives to DOTP

The literature abounds with examples. Many alternatives belong to the phthalate class (e.g. DINP). Many are also problematic (e.g. mellitate esters).

Certain bio-based feedstocks might be expected to result in less hazardous products.

Isosorbide esters of alkanoic acids are fully biodegradable and passed tests for acute toxicity, sensitization, mutagenicity, & estrogenicity.

C8 diester shows DOTP-like performance


Flame retardancy is a widespread need

*Demand is expected to increase 5%/yr*

<table>
<thead>
<tr>
<th>Non-self-extinguishing polymer</th>
<th>LOI</th>
<th>Self-extinguishing polymer</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>polyoxymethylene</td>
<td>16</td>
<td>polycarbonate</td>
<td>27</td>
</tr>
<tr>
<td>polyethylene</td>
<td>17</td>
<td>polyarylate</td>
<td>34</td>
</tr>
<tr>
<td>polypropylene</td>
<td>18</td>
<td>polyethersulfone</td>
<td>38</td>
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<tr>
<td>polystyrene</td>
<td>18</td>
<td>PEEK</td>
<td>40</td>
</tr>
<tr>
<td>PMMA</td>
<td>18</td>
<td>PVC</td>
<td>42</td>
</tr>
<tr>
<td>natural rubber</td>
<td>18</td>
<td>polyamide-imide</td>
<td>43</td>
</tr>
<tr>
<td>ABS</td>
<td>18</td>
<td>poly(phenylene sulfide)</td>
<td>44</td>
</tr>
<tr>
<td>Nylon-6,6</td>
<td>24</td>
<td>polyether-imide</td>
<td>47</td>
</tr>
<tr>
<td>PETE</td>
<td>25</td>
<td>poly(vinylidene chloride)</td>
<td>60</td>
</tr>
<tr>
<td>polychloroprene</td>
<td>26</td>
<td>PTFE</td>
<td>95</td>
</tr>
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</table>

The LOI for self-extinguishing is usually taken as 27, not 21 (the volume % of O$_2$ in air) to correct for lack of convective heating in the test method.

M. Chanda, S. K. Roy. *Industrial Polymers, Specialty Polymers, and Their Applications*
Flame retardants

Goal: compatible with plastics, effective at reasonable levels, non-leaching, non-toxic

Source: SRI Consulting / http://www.flameretardants-online.com
Non-halogenated flame retardants

• 2007 AddCon conference: no papers on halogenated chemicals, although flame retardants made up one of the largest group of submissions

• Government and industry groups have conducted extensive reviews, e.g. http://www.nonhalogenated-flameretardants.com

• Fewer examples from bio-organic feedstocks

• Solutions are often based on mechanisms specific to a polymer
Molecular Heat Eater®

- Powder or gel based on carbonate and phosphate salts and benign organic acids
  - citric
  - glutaric
  - succinic
  - oxalic
  - formic
  - acetic
  - stearic

Some are agricultural waste products

Sub-micron particles require a strong endothermic reaction to decompose
MHE in action

untreated

Dette er virkelig imponerende.

BBC WORLD
bbcworld.com

beard

beard
Solutions and strategies

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green design principles
High MW plasticizers

- Limit mobility in polymer matrix
- Prevent transport across biological membranes
- Degradation products must be considered

1,3-propanediol from glucose via glycerol (engineered E. coli)

Adipic acid from glucose (engineered microbes)

MW 1500-2500 Da

is a better plasticizer for PLA than:

MW 371

Strategies for high-MW flame retardants

- Copolymerization with special monomers, grafting reactive additives to backbone
  - Flame retardancy is “permanent”
  - Less disruption of polymer properties
  - Effective at lower loadings than low-MW additives

Multi-wall carbon nanotubes

max. heat release rate $\sim 800 \text{ kW/m}^2$

2% nanotubes

max. heat release rate $\sim 500 \text{ kW/m}^2$

- Effective in polycarbonate, polyamide, polyethylene, polypropylene, polystyrene
- Cannot stand alone— but promising
- No halogens, metals, or phosphorus

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Plasticity without additives: thermoplastic elastomers (TPEs)

• Metallocene-catalyzed polyolefins: “the threat to flexible PVC”
  – 1 million lb polymer / 1 lb catalyst / 1 hr
  – *Journal of Vinyl and Additive Technology*, 1998: potential to capture 50% of the flexible PVC market (30-40% plasticized)

TPEs from Biobased Materials

- Polyethers
- Polyamides based on canola, castor oil
- Polyurethanes from vegetable oil

Mizuno’s 2009 running shoe models contain Pebax® Rnew, a bio-based TPE (up to 94% renewable carbon)

Inherently Fire Retardant Polymers

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Challenges

- Cost, mechanical performance, processing difficulties
- Mechanistic understanding
  - Heteroatoms (N, O, P, S, halogens)
  - Aromatic rings
  - Heteroatomic rings
  - Pro-crosslinking or pro-cyclization chemical groups

Why such a significant difference in heat release?

Inspiration from nature: wool

Wool foams rather than burns. Ignition temperature is 570-600 °C (higher than rayon, nylon, polyester)

An effect of microstructure? Chemical composition? Both?

Better understanding of naturally flame retardant materials will lead to innovation in fire-safe, bio-based plastics

CSIRO, Flame Resistance of Wool
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green design principles
Use of renewable resources is to be encouraged, but it cannot be the only metric.
Conclusions

• Functional alternatives to DEHP and PBDEs are abundant

• Bio-based chemical platforms are (and will be) a source of innovation

• All green principles should be met by new materials, to avoid the problems of the past