The role of mother earth, water, air and fire in the development of new polymer materials

Cor Koning

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The role of mother earth, water, air and fire in the development of new polymer materials

or

‘The elements’ and materials development

Four examples
Novel bio-based polyesters: Synthesis, characterization and evaluation

TA Coating Technology, DPI project # 451

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Renewable thermoset powder coatings

- **general characteristics**
  - solvent-free coating systems
  - mixing of components (i.e. resin, cross-linker and additives) by extrusion
  - powder applied to substrate using electrostatic interactions
  - subsequent thermally induced flow and curing

- **resin requirements**
  - storage stability and mechanical performance: $T_g > 45 \, ^\circ C$
    already for moderate $M_n$, 2000 – 6000 g/mol
  - functionality $f \geq 2$ (often: carboxylic acid or hydroxyl functionalities)
  - amorphous and colorless
  - appropriate flow properties at $T_{cure}$
  - UV stability $\rightarrow$ aliphatic rather than aromatic polyesters
Why use renewables?

- building blocks with high functionality available from nature, suitable for polymer network formation
- decreasing fossil feedstock (and increasing oil prices)
- rigid, high Tg providing aliphatic monomers readily available for example: dianhydrohexitols

- available feedstock: starch (corn, potatoes etc.), cellulose, vegetable oils etc. ‘From corn to coatings’

Synthesis of 1,4:3,6-dianhydro-D-sorbitol (isosorbide) from sorbitol
Monomers from biomass

- Isosorbide (IS)
- Isomannide (IM)
- Isoide (II)
- 2,3-butanediol (BD)
- 1,3-propanediol (PD)
- Glycerol (GLY)
- Sorbitol
- Citric acid (CA)
- Tartaric acid
- Succinic acid (SA)
- Adipic acid (AA)
Melt polycondensation

polyesterification under inert gas flux, followed by vacuum processing

- typical temperatures: 180 – 230 °C (not too long at 230 °C !!!)
- typical pressures (2nd stage): 1-5 mbar
Succinic anhydride + Isosorbide + second diol

Diol 2
▲ = 2,3-butanediol
▲ = 1,3-propanediol

Molar mass can be controlled (2000-6000 g/mol)
Enhancing OH functionality with glycerol

OH groups can easily be transformed into COOH groups by reaction with citric acid

Curing with petrochemical-based curing agents

OH-functional

COOH-functional

urethane

ester
## Appearance, toughness and UV-stability

<table>
<thead>
<tr>
<th>COOH functional, cured with tri-isocyanate</th>
<th>COOH functional, cured with tri-epoxide</th>
<th>COOH functional, cured with Tetra-hydroxy</th>
<th>No yellowing under high intensity mercury lamp</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Reference coating" /></td>
<td><img src="image" alt="Weathered coating" /></td>
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</tbody>
</table>

**OH functional, cured with triisocyanate**

**COOH functional, cured with tri-epoxide**

**COOH functional, cured with Tetra-hydroxy**
Fully biobased polycondensate resins

Branched polyesters and polycarbonates based on the 1,4:3,6-dianhydrohexitols (notably: isosorbide and isoidide)
Functionality enhanced by incorporation of, e.g., glycerol, citric acid

OH-functional polyesters / polycarbonates
(based on isosorbide / isoidide)

COOH-functional polyesters
(obtained by citric acid modification of linear OH-functional polymers)

fully biobased resins with \( F_n > 2 \)

conventional curing agents:
- OH-functional polymers: polyfunctional isocyanate compounds
- COOH-functional polymers: epoxy / activated OH compounds
Three novel, biobased, blocked diisocyanate compounds were developed by A&F for curing OH-functional polymers (I – III).

A biobased bis(glycidyl ether) was prepared by A&F to cure COOH-functional polymers (IV).

\[ \text{I} = \text{bl-IPDFI}, \quad \text{II} = \text{bl-IIIDI}, \quad \text{III} = \text{bl-FDEDI}, \quad \text{IV} = \text{ISBGE} \]
**Glycerol-branched biobased resin + blocked diisocyanates**  
**Citric acid-modified polyester + ISBGE**

<table>
<thead>
<tr>
<th>Coating results:</th>
<th></th>
</tr>
</thead>
</table>
| bl-IIDI:         | - good solvent resistance  
|                   | - good impact resistance  
|                   | - some discoloration  |
| bl-IPDFI/:       | - moderate to good solvent resistance  |
| bl-FDEDI         | - moderate impact resistance  
|                   | - strong discoloration  |
| ISBGE:           | - moderate to good solvent and impact resistance  
|                   | - some discoloration  |
From bio-feedstock provided by mother earth high quality performance products can be developed
Using enzymes for developing novel polymer materials

Core program DPI project #381, continued within TA-BI, project #608, Inge v.d. Meulen

M. de Geus, B. van As, J. Peeters, A.R.A. Palmans, A. Heise, C.E. Koning

Laboratory of Polymer Chemistry
Laboratory of Macromolecular and Organic Chemistry
Technische Universiteit Eindhoven
Advantages of Enzymes

• Enzymes are very efficient catalysts.
• Enzymes act under mild conditions.
• Enzymes are environmentally acceptable and metal-free.
• Enzymes are not bound to their natural role.
• Enzymes can catalyze a broad spectrum of reactions.
• Enzymes are selective (chemo-, regio-, enantioselective).

These advantages can be utilized to make materials especially for biomedical applications in view of absence of metal residues, not easily available from conventional techniques.
Two questions

1. Can enzymes be used in combination with chemical catalysts e.g. for the synthesis of block copolymers, and can this be realized in one pot?

2. Can enzymes result in materials that cannot be made using chemical catalysts?
Two questions

1. Can enzymes be used in combination with chemical catalysts e.g. for the synthesis of block copolymers, and can this be realized in one pot?

   Yes

2. Can enzymes result in materials that cannot be made using chemical catalysts?

   Yes
• Chemoenzymatic block copolymer synthesis was achieved in one pot.
• Method to synthesize block copolymers in a metal free fashion.

First example of a one-pot chemo-enzymatic cascade polymerization!
Polypentadecalactone: biodegradable polyethylene?

Polycaprolactone - PCL

Polypentadecalactone – PPDL (100% linear)

Polyethylene
## Properties ‘enzymatic’ PPDL ($M_w = 190$ kg/mol)

<table>
<thead>
<tr>
<th>Non-oriented samples</th>
<th>$T_g$ [°C]</th>
<th>$T_m$ [°C]</th>
<th>$T_c$ [°C]</th>
<th>$E$ [MPa]</th>
<th>$\varepsilon_{\text{break}}$ [%]</th>
<th>$\sigma_{\text{yield}}$ [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPDL</td>
<td>-20</td>
<td>95</td>
<td>81</td>
<td>420</td>
<td>$&gt;1200$</td>
<td>18</td>
</tr>
<tr>
<td>PCL</td>
<td>-60</td>
<td>54</td>
<td>42</td>
<td>350</td>
<td>60</td>
<td>16</td>
</tr>
</tbody>
</table>

Chemically catalyzed synthesis of PPDL: $M_{w,\text{max}} = 40.000$ g/mol
Enzymatically (literature) : $M_{w,\text{max}} = 80.000$ g/mol
After careful drying the enzyme (this study): $M_{w,\text{max}} = 190.000$ g/mol
→ (Biomedical) fiber applications come within reach (Evaluation with Bert Joosten, Marco Marcus and Ronald Deumens of AZM Maastricht)
First results fiber spinning from melt

Melt spinning of highest molecular weight PPDL, followed by drawing/elongation results in fibers with strength of 0.6-0.7 GPa (Commercial Nylon fibers: ca. 1 GPa)

Solution spinning is expected to yield even higher strength (experiments in progress in collaboration with Lemstra)


Degradability needs optimization if biomedical applications are targeted (copolymers with more hydrophilic comonomers and reduced crystallinity)

Inge van der Meulen (DPI #)
Chiral polyester particles for drug release

racemic mixture

1: poly((S)-4-methyl caprolactone)
2: poly((R,S)-4-methyl caprolactone)
3: poly((R)-4-methyl caprolactone)

Jenny Xiao, Andreas Heise, Anja Palmans 'Biomade'
Novozym 435 catalyzed degradation of chiral and racemic PMCL
UV-cured poly(4-Methyl CL) particles
Mother earth provides bio-catalysts suitable for development of high quality performance products
Carbon-Nanotube/Polymer Composites: Starting Wetter, Conducting Better

A latex-based concept to develop electrically conductive Polymer/carbon nanotube composites

TAs EP/RT + FPS, projects 416 and 529
• Nadia Grossiord, Marie-Claire Hermant, Bert Klumperman, Junrong Yu, Kangbo Lu, Joachim Loos, Jan Meuldijk, Alex van Herk, Paul van der Schoot
  
  *Eindhoven University of Technology, The Netherlands*

• Oren Regev
  
  *Ben-Gurion University of the Negev, Israel*

• Hans Miltner, Bruno Van Mele
  
  *Free University of Brussels, Belgium*
Single vs. Multi-Wall Nanotube vs.
Promising fillers for polymer composites

- Low loading can give percolation because of high aspect ratio
- Strong and stiff
- Good electrical conductivity
A bundle of nanotubes

Thess et al. Science 1996
Production of the composite

1st step Make stable aqueous CNT dispersion

1. Bring the NTs in contact with SDS (sodium dodecyl sulphate) surfactant solution

2. Sonication for debundling (15 min, 20W, 20kHz)

3. Centrifugation of catalyst residues (30 min, 4000 rpm) and continue with supernatant
2\textsuperscript{nd} step: Mixing of the NTs solution with the polymer latex

3\textsuperscript{rd} step: Freeze drying of the mixture

4\textsuperscript{th} step: Melt Processing of the powder obtained
Step 2

Mix NTs and latex

Both NTs and PS latex particles stabilized by SDS

$\Phi_{av,latex} = 70 \text{ nm}$
PS-SWNT composite

Conductivity (S/cm) vs. Concentration nanotubes (wt%)

Percolation threshold ~ 0.3wt%
4-point measurements. Addition of 2-3 wt% ‘PS’ with DP=5 to nanocomposite PS-2 with 1 wt% SWNT roughly raises conductivity by a factor 10 (2-point)
Question

How versatile is the latex concept?
Question

How versatile is the latex concept?

It works for PS, ABS, PMMA, PP, PE, PUR, PS/PPE, and PVC latexes.

So, virtually all polymer latex particles can be applied.
Polypropylene/CNT nanocomposites (semi-crystalline)

2-point conductivity measurements of Priex 801 + HiPCO SWNTs and Priex 801 + thin MWNTs of Nanocyl.
Four-point conductivity measurements as a function of the SWCNT concentration for: (●) SWCNT/Priex®801 and (□) SWCNT/PS nanocomposites.
Crystallization peak and onset temperatures for various Priex 701 / MWNT samples after non-isothermal crystallization from the melt (cooling at 2.5°C/min, temperature modulation of ± 0.5°C/60s)
Where and what can we improve?

Improving dispersion is difficult or even impossible.

Therefore we focused on
- Quality of the tubes
- Reduction of amount of CNTs by making foams
- Reduction contact resistivity by replacing surfactant SDS by conducting surfactants

as methods to reduce percolation thresholds.
Vertically grown MWNTs (John Hart, MIT)

Scale bars: (a): 250 μm; (b): 50 μm
(a): picture of a vertically-grown MWNT (MIT)

(b): commercially available MWNT (Nanocyl)

Scale bar valid for both photos: 20 nm
Long NTs vertically grown

Four-point conductivity of MWNT-PS composite as a function of MWNT concentration.
CNTs dispersed in the same PS matrix, under similar conditions.

NOTE: extremely high conductivity (>1000 S/m) for 1.5-2.0 wt% MWNT

Blue: Nanocyl MWNTs
Pink/green: vertically grown MWNTs

Vertically grown tubes are longer after incorporation into PS, and contain less amorphous carbon
Reduction of required wt% CNTs by ‘foaming’

Continuous styrene/divinyl benzene phase is polymerized
SWNTs are dispersed in water droplets
High internal phase emulsion derived PS foam
SWNTs embedded in polyHipe walls
Percolation threshold reduced by factor 3 - 4

![Graph showing conductivity vs. SWNT loading (wt%) in PS phase.]

- polyHIPE - SWNT foam: 75/25 (w/o)
- polyHIPE - SWNT foam 84/16 (w/o)
- PS - SWNT films
Conductive surfactants replacing SDS and lowering contact resistivity
Water plays a crucial role in the development of polymer/carbon nanotubes nano-composites with well-dispersed CNTs.
New coating resins based on the copolymerization of epoxides with carbon dioxide

TA-CT, DPI projects # 451 and 607

Rob Duchateau  Wouter van Meerendonk
Saskia Huijser   Maurice Frijns
Bart Noordover  Wieb Kingma
Marion van Straten
Co-polymerization of CO$_2$ and oxiranes

First discovery in 1969 by Inoue.

Most frequently used catalysts are based on Zn, Al and Cr.

Frequently used monomers: cyclohexene oxide (CHO), propylene oxide (PO) and ethylene oxide (EO).

![Diagram of co-polymerization reaction]

Aliphatic polycarbonates

C2 bridge

O=C=O + \[\text{Oxirane} \] \[\text{[cat]}\] \[\text{Polycarbonate}\]
Development of catalysts

1969
ZnEt₂ + H₂O

1995
M = Zn, Y, La

1998
M = Al, Cr, Mn, Co

2002
M = Al, Cr, Mn, Co

2004
M = Zn, Mg
Typical reaction kinetics of β-diiminate zinc catalysts

Properties of polycyclohexene carbonate

Thermal stability

Thermal stability is significantly increased by end-capping

![Diagram showing chemical structures and thermal stability curves]
Properties of polycyclohexene carbonate (PCHC)

Glass Transition temperature PCHC: $T_g = 116 \, ^\circ\text{C}$ – rather low
Tg prevents broad application as engineering plastic

Compression molding tests on high MW PCHC

Too brittle for engineering plastic applications, but
low molar mass PCHC might be suitable for coatings
→ controlled breakdown
(Tg high enough for powder coating applications)
Controlled breakdown of high MW PCHC

TMP-mediated break-down of high MW PCHC through alcoholysis affords OH-functional polycarbonate, curable with trifunctional isocyanate (glycerol also possible). R1 and R2 are polymer chain fragments.
This works, but:
Preferred route: chain transfer agents furnishing OH end groups in living polymerization
The resins obtained after hydrolysis of high Mw polycarbonates using TMP afford highly glossy, chemically inert and tough coatings after cross-linking.
Catalytic routes to renewable (biodegradable) polymers

An example of fully renewable, biodegradable polymers.

Maurice Frijns, Saskia Huijser

One of the components of the air is a promising raw material for the manufacturing of novel, high performance coating materials.
One of the components of the air is a promising raw material for the manufacturing of novel, high performance coating materials

But we cannot solve the ‘greenhouse’ problem by polymerizing all carbon dioxide present in the air!
All four examples illustrate DPI ‘chain-of-knowledge’ philosophy and have a flavor of important aspects of DPI’s future strategy

- **Sustainability**
  Where possible use biomass as feedstock
  Enhance lifetime by e.g. enhancing coatings UV stability

- **Alternative (bio)catalytic routes to existing bulk and new specialty polymers.** Full understanding of catalysis mechanisms is required. Join forces with modelling groups

- **Upgrade existing polymers with ‘smart additives’**

- **Environment deserves priority #1**
  Cleaner processes (in water or carbon dioxide). More focus on process development is required.
  Compostable, CO$_2$-neutral polymers
The elements help making the DPI dream to come true

- Natural resources for new polymers
- Biocatalysts from nature furnishing new materials
- ‘Greenhouse’ gas from the air as feedstock for new polymers
- Water as an environmentally benign medium for the manufacturing of nanocomposites
- Fire (heat) for taking the chemistry ‘over the top’
DPI, congratulations with your 10th anniversary!