Photo-initiated Cationic Polymerization of Sustainable Epoxy Materials

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Applications of Epoxy


Motivation

Develop green and sustainable alternatives to the highly polluting and energy-intensive epoxy resin chemistry.

1. Substrates should be readily available in substantial quantities with minimum chemical modification.

2. Polymerization reaction should be rapid, energy efficient and solvent-free.
Approach

Vegetable oils
Ester-based Monomer Source with Unsaturated Bonds (Triglycerides with unsaturated fat)

- **Soybean oil**
- **Linseed oil**

![Chemical structures of soybean and linseed oils](image)
Epoxidation by Phase Transfer Catalyst

- No byproduct other than water
- High conversion (>60%)
- Easy workup

Photo-initiated Cationic Polymerization

\[
\text{MtX}_n^+ \quad \text{Diarylodonium salts}
\]

\[
\text{MtX}_n^- \quad \text{Triarylsulfonium salts}
\]

\[
\text{Ar}_2\text{I}^+ \text{MtX}_n^- \xrightarrow{\text{hv}} \text{Ar}^+ \text{MtX}_n^- + \text{Ar}.
\]

\[
\text{H-donor} \quad \text{Ar}^+ \text{MtX}_n^- + \text{ArI} \rightarrow \text{HMtX}_n
\]

\[
\text{MtX}_n^- = \text{SbF}_6^-, \text{PF}_6^-, \text{AsF}_6^-, \text{BF}_4^-, (\text{C}_6\text{F}_5)_4\text{F}_6^- \text{ etc}
\]

Drawbacks to Epoxidized Vegetable Oils as Monomers

- Low glass transition temperatures limit use to non-structural applications
- Relatively slow photopolymerization rates

**Photoinitiator:**

![Chemical structure of Photoinitiator]

**Epoxidized linseed oil (ELO)** $T_g = 50 \, ^\circ C$

**Epoxidized soybean oil (ESO)**

![Graph showing temperature change over irradiation time]

**Optical Pyrometry Apparatus**
Butadiene-based comonomer

- Cyclohexene, 4-ethenyl
- 1,5-cyclooctadiene
- 1,3-Butadiene
- Cyclohexane, 1,2,4-triethenyl-
- 1,5,9-cyclododecatriene
- Poly-butadiene
Photoinitiator:

Light Intensity:

2354 mJ/cm$^2$/min

100 wt% CODD

CODD: 

- 100 wt% CODD

- 2 wt% Photoinitiator:

- Light Intensity:
  - 2354 mJ/cm$^2$/min
- **Photoinitiator:**
  \[
  \text{CODD:} \quad \text{O} \quad \text{O}
  \]
  
  \[
  \begin{align*}
  \text{Photoinitiator:} & \quad \text{C}_{6}H_{8} \quad \text{O}_{8}H_{17} \\
  & \quad 2 \text{ wt}\% \\
  \text{Light Intensity:} & \quad 2354 \text{ mJ/cm}^{2}\text{min}
  \end{align*}
  \]

- **Temperature (°C):**

- **Irradiation Time (s):**

- **Sample Compositions:**
  - 100 wt% CODD
  - 70 wt% ELO 30 wt% CODD
  - 80 wt% ELO 20 wt% CODD
  - 90 wt% ELO 10 wt% CODD
  - 95 wt% ELO 5 wt% CODD
  - 100 wt% ELO
100% wt TVCHT

- Photoinitiator:
  \[
  \text{Phenyl}^4 \text{C}_{4}H_{4}^{+} \text{C}_{17}H_{35}^{8-bF_{6}}^{-}
  \]
  2 wt%

- Light Intensity:
  2354 mJ/cm²/min

Temperature (°C)

- 100 wt% ELO
- 80 wt% ELO 20 wt% TVCHT
- 60 wt% ELO 40 wt% TVCHT

Irradiation time (s)
• Photoinitiator:

\[
\text{C}_{6}H_{17}^\text{O} \quad \text{(2 wt%)}
\]

• Light Intensity:

2354 mJ/cm² min

- 100 wt% CODD
- 100% wt TVCHT
- 60 wt% ELO 40 wt% TVCHT
- 80 wt% ELO 20 wt% TVCHT
- 100 wt% ELO
$T_{\text{substrate}} = 90 \, ^\circ \text{C}$

Sample: 100%

Threshold temperature of autoacceleration

Photoinitiator:

Light Intensity:
- 2354 mJ/cm$^2$min
- 2 wt%
<table>
<thead>
<tr>
<th>Monomer</th>
<th>Temperature (°C)</th>
<th>Viscosity (Pa•S)</th>
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<tr>
<td><strong>TVCHT</strong></td>
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<tr>
<td><strong>ELO</strong></td>
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<td>2.10</td>
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</tbody>
</table>
Glass transition Temp (°C)

VCHD:

Glass transition Temp (°C) vs. VCHD content (wt%)

* Error bar using t test (95%)

VCHD:

- Photoinitiator: ![Chemical Structure]
- Light intensity: 3336 mJ/cm² min
- Irradiation time: 15s
- Sample Thickness: 100-120 µm
- Samples were postbaked at 80°C for 2h

100% ELO
90 wt% ELO / 10 wt% VCHD
80 wt% ELO / 20 wt% VCHD
70 wt% ELO / 30 wt% VCHD
Conclusions

- Unsaturated vegetable oils can be epoxidized and polymerized into epoxy thermoset. However, their reactivity and thermal properties need to be improved. (e.g. Tg (ELO) = 50 °C)

- Butadiene-based epoxy comonomers show a good enhancement of reactivity and glass transition temperature (Tg to 110°C for a blend of 70 wt.% ELO/30 wt% VCHD, for example).

- A critical threshold temperature (~80°C) exists for autoacceleration of photopolymerization of trivinyl cyclohexane triepoxide (TVCHT) and viscosity plays an important role in control the induction period.
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