Polycyanurates and Polycarbonates based on Eugenol: Alternatives to Thermosetting and Thermoplastic Polymers based on Bisphenol A

14. ABSTRACT
Polycyanurate thermosetting networks, polycarbonate thermoplastics, and homogenous polycarbonate/polycyanurate network blends have been prepared from a bio-derived bisphenol. The bisphenol was prepared via a solvent-free, ruthenium-catalyzed olefin metathesis coupling reaction of eugenol followed by hydrogenation. The pure polycyanurate network exhibited a glass transition temperature (Tg) of 186 degrees Celsius and a 5% weight loss temperature above 350 degrees Celsius under nitrogen. The pure polycarbonate exhibited a Tg of 71 degrees Celsius, Mn = 8360, and a polydispersity of 1.88. No phase separation was observed in an 80:20 blend of cyanate ester: polycarbonate during or after cure; the resulting homogeneous system showed a single Tg of 132 degrees Celsius. End-group analysis of the polycarbonate provided no evidence of residual phenols, and the polycarbonate fraction was readily extracted from the polycyanurate network, suggesting that no chemical grafting occurred. These new polymer systems represent promising potential alternatives to similar systems derived from Bisphenol A.
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POLICYANURATES AND POLYCARBONATES BASED ON EUGENOL: ALTERNATIVES TO THERMOSETTING AND THERMOPLASTIC POLYMES BASED ON BISPHENOL A

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Outline

• Eugenol Polycyanurates:
  – Low Moisture Uptake

• Eugenol Polycarbonates
  – Flexible Backbone

• Eugenol Polycyanurate Toughened with Eugenol Polycarbonate
  – High Compatibility

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Cyanate Esters for Next-Generation Aerospace Systems

- **Glass Transition Temperature**
  - 200 – 400 °C (dry)
  - 150 – 300 °C (wet)

- **Onset of Weight Loss**
  - > 400 °C with High Char Yield

- **Resin Viscosity**
  - Suitable for Filament Winding / RTM

- **Compatiblility**
  - With Thermoplastic Tougheners and Nanoscale Reinforcements

- **High T<sub>g</sub>**

- **Resistance to Harsh Environments**

- **Ease of Processing**

- **Good Flame, Smoke, & Toxicity Characteristics**

- **Low Water Uptake with Near Zero Coefficient of Hygroscopic Expansion**

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Cyanate Esters Around the Solar System

Our Solar System

- On Earth, cyanate ester / epoxy blends have been qualified for use in the toroidal field magnet casings for the ITER thermonuclear fusion reactor.

- Unique cyanate ester composites have been designed by NASA for use as instrument holding structures aboard the James Webb Space Telescope.

- The science decks on the Mars Phoenix lander are made from M55J/cyanate ester composites.

- The solar panel supports on the MESSENGER space probe use cyanate ester composite tie layers.

Images: courtesy NASA (public release)
Why Bio-Based Cyanate Esters

- Materials qualification efforts are costly; developing bio-based materials that deliver both improved performance and decreased dependence on petroleum enables a higher and more robust return on investment.
- Cyanate esters are generally easy to process; they do not require stoichiometric balance and form co-networks readily, hence they tolerate variation in monomer chemistry relatively well.
- The superior flame, smoke, and toxicity characteristics of cyanate esters, the excellent adhesion and durability characteristics of the networks, and the very high selectivity of the reaction (which makes de-polymerization easier), all confer benefits from a sustainability perspective.
- Bio-based feedstocks for cyanate esters are interesting because of the combinations of physical properties provided by structure of the molecules themselves, not just because of the cost or environmental impacts.
- Bio-based materials offer potential alternatives to the use of Bisphenol A.
Toughening Polycyanurates

- Rubber particles can be used (as with epoxies) but with a thermal performance penalty.
- Thermoplastics may be added and will form a separate micro-phase during cure; the thermoplastic domains act like rubber particles, but with improved thermal stability. The phase separation process must be carefully controlled.
- Nanoparticles such as silica can be added, but these may introduce difficulties in composite processing.
- Compatible thermoplastics that do not undergo phase separation offer thermal stability and easy processing, but may not improve toughness as much as other methods.

Recent work from the Kessler group illustrating the effect of loading level on morphology of polycyanurate toughened with poly(ether sulfone).

Synthesis of Eugenol CE

- The terminal vinyl group on eugenol serves as a handle for Ru-catalyzed coupling. The coupled product may be reduced to eliminate the double bond for increased molecular flexibility. The resulting polyphenol is then readily converted to the di(cyanate ester) using cyanogen halide treatment, and thermally cyclotrimerized.
**DSC and FT-IR of Eugenol CE**

- Melting point is in line with expectations for a larger, symmetric cyanate ester monomer. Heat of reaction and exotherm temperature indicate reasonable purity for synthesis at the 1-gram scale.
- FT-IR confirms cure proceeds normally, with near complete conversion to cyanurate at modest temperatures.

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\Delta H_{\text{cure}} = 101 \text{ kJ/eq.}
\]

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T_m = 104 \degree \text{C}
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TGA of Eugenol CE

• The methoxy groups as well as the large aliphatic bridge reduce char yield compared to many cyanate esters, but a high onset of decomposition is still maintained.
• Other key properties of the cured eugenol CE include a $T_G$ near 190 °C and a moisture uptake of 1.8% after 96 hours of immersion in water at 85 °C.
Thermal Degradation of Eugenol CE Yields Eugenol!

- FT-IR of eugenol (blue) is closely related to FT-IR collected by TGA/IR of eugenol CE decomposition at 400 °C.
- As a product of decomposition, eugenol is an environmentally-friendly alternative to Bisphenol A.
Synthesis of Thermoplastic and Thermoset Polymers from Eugenol

[Chemical reaction diagram showing the synthesis process from Eugenol to polycarbonate and polycyanurate thermoset]
Eugenol Polycarbonate Properties

- DSC indicates $T_G$ values between 50 and 70 °C.
- $M_n$ for batch 1, 4300 g/mol (PDI 2.25); $M_n$ for batch 2, 8400 g/mol (PDI 1.88)
- No evidence yet seen of phenol end groups by $^1$H NMR or FT-IR.
SALLS of Eugenol PC / CE Blend

- Heating ramp experiment from solid monomer to cured resin.
- 20 wt% polycarbonate in CE monomer shows depression of melting point, but no phase separation during subsequent cure.
DSC confirms that cure has taken place over temperatures where no light scattering pattern emerges. Cured samples are transparent and homogeneous with a TG of around 125 °C.
Summary

- The naturally occurring substance eugenol was successfully converted to both a thermosetting monomer (cyanate ester) and a thermoplastic polycarbonate.
- The decomposition of the cured cyanate ester yielded a significant quantity of eugenol, demonstrating both an interesting possibility for regeneration of monomer at the end of service as well as an alternative to generation of Bisphenol A.
- The physical properties of both the cured cyanate ester network as well as the polycarbonate were in line with expectations based on the chemical structure.
- The high level of chemical similarity between the cyanate ester and the polycarbonate appears to have led to very high compatibility, making possible the formation of a toughened thermosetting resin by homogeneous incorporation of thermoplastic.
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