

Year End Progress Report:

Biorenewable Composites Reinforced with Under-used Co-products from Ethanol Production

Michael R. Kessler
Materials Science and Engineering, Iowa State University
2220 Hoover Hall
Ames, IA 50011-2300
Phone: 515-294-3101
Fax: 515-294-5444
mkessler@iastate.edu

Richard C. Larock
Department of Chemistry, Iowa State University
1605 Gilman Hall
Ames, IA 50011-2300
Phone: 515-294-4660
Fax: 515-294-0105
larock@iastate.edu

Year one of a two year project
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Introduction

In year one of this two year project, we have made significant progress in investigating the processing and properties of a new class of biocomposites created by reinforcing thermosetting vegetable-oil-based polymers with ethanol and bio-diesel co-products (spent germ and soy hulls), and to relating the properties of these biocomposites to the by-product loading and distribution, the crosslink density and the chemistry of the biopolymer matrix material.

The scientific objectives of the project are to (1) develop a manufacturing process to produce quality composite specimens with varying reinforcement levels and matrix chemistries based on ring-opening metathesis polymerization (ROMP), (2) determine how the incorporation of spent germ and soy hull fillers influence the mechanical properties of the biopolymers, and (3) investigate how the structure of the polymer matrix (crosslink density, co-monomer concentration, polymerization routes) influences the thermal and mechanical properties of the composites. In the following sections of the report, we review our progress towards three topics aimed at meeting these scientific objectives: development of ROMP-based resins, development and characterization of composites using spent germ (from ethanol production), and development of composites using soy hulls (from biodiesel production).

Development of ROMP-Based Resins

New polymeric thermosetting resins prepared by the ROMP of a commercially available vegetable oil derivative (Dilulin) and dicyclopentadiene (DCPD) have been prepared and characterized. A thorough characterization of the modified vegetable oil itself has been carried out to elucidate its structure. Grubbs second generation catalyst has been used to effect the ROMP of the strained unsaturated norbornene-like rings in the commercial oil. Dynamic mechanical analysis of the thermosetting resins reveals that glass transition temperatures from 36 °C to -29 °C can be obtained when the proper ratio of oil and DCPD is employed. Extraction analysis indicates that all samples have at least a 20% soluble fraction and that the soluble fraction is composed of oligomers, unreacted triglyceride oil or both. The effect of the soluble fraction as a plasticizer has also been explored.

In addition, the Dilulin has been blended with a bicyclic norbornene-based crosslinking agent (CL) (at loadings ranging from 0 to 50 wt %) to undergo ROMP with the Grubbs' catalyst forming a biorenewable polymer network. Cured polymer samples with various crosslinker loadings are shown in Figure 1. These show a trend towards increased cloudiness (and more microphase separation in the copolymers) with higher crosslinker content. This is an indication of a reaction induced phase separation, caused by the difference in ROMP reactivity and structure between the CL component and the Dilulin. The thermal and mechanical properties of the cured systems have been investigated by dynamic mechanical analysis (DMA), and their thermal decomposition behaviors have been evaluated by thermogravimetric analysis (TGA). Broad tan delta peaks suggest inhomogeneous phase morphologies, which result in complex crosslinking behaviors and glass transition temperatures which increase with CL loading (Figure 2). The thermal stability of the polymers increases with increasing crosslinker content.

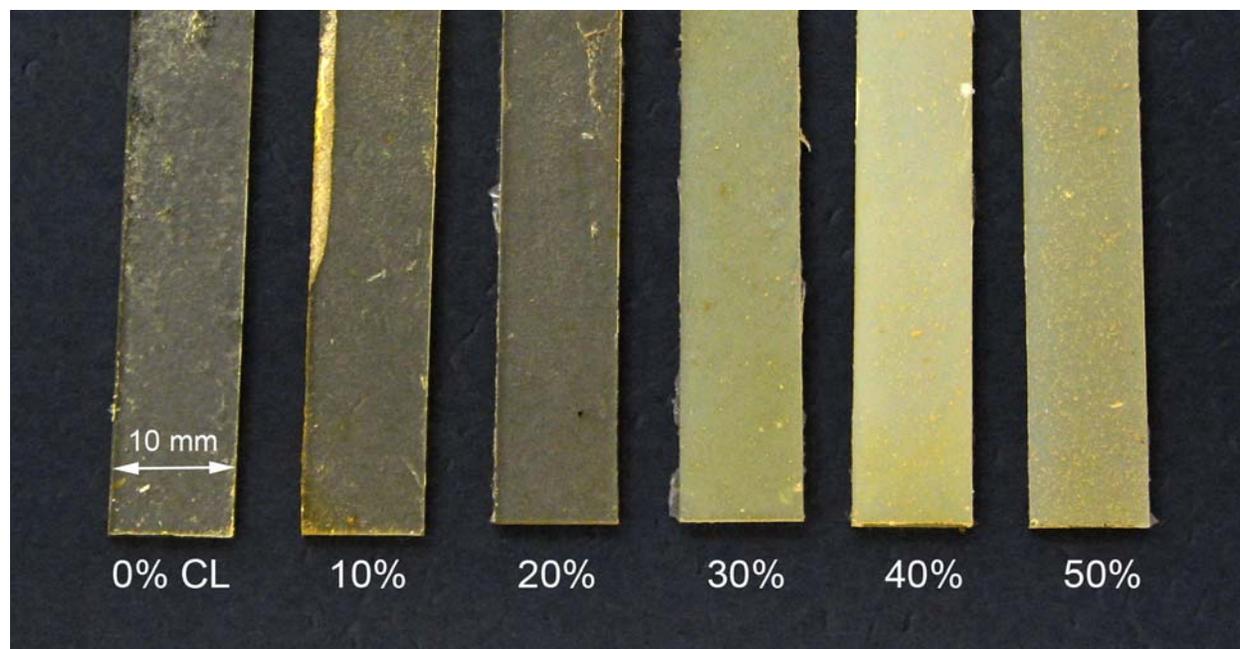


Figure 1. Thin strip samples of Dilulin™/CL copolymer at various crosslinker loadings.

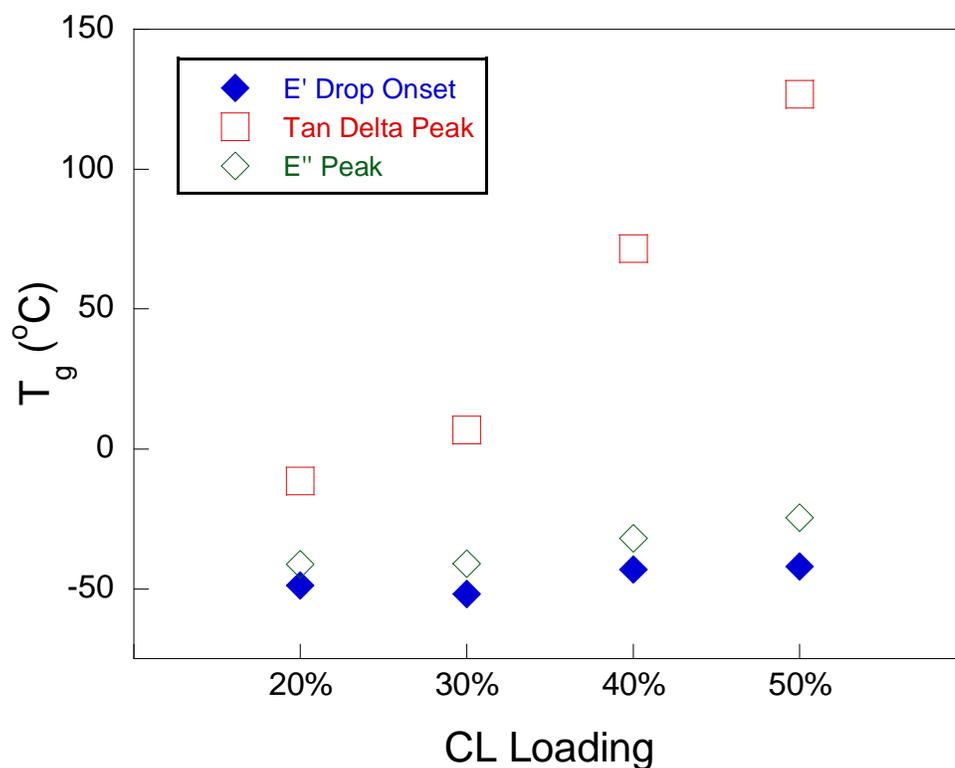


Figure 2. Thermomechanical behavior from DMA experiments of Dilulin™/CL copolymers showing the major transition temperature as measured by E' onset, tan δ peak, and E'' peak

Glass fiber-based biocomposites have also been prepared by the ROMP of commercially available Dilulin vegetable oil and dicyclopentadiene (DCPD). The composites and the corresponding resins have been characterized thermophysically and mechanically. While the resins are yellow and transparent (and vary

from being hard and strong to soft and flexible), the composites are translucent. The effect of DCPD and glass fiber concentrations has been analyzed. The glass transition temperatures for both the resins and the composites range from 18 °C to 82 °C, with higher glass transition temperatures for resins and composites with higher DCPD content. Glass fibers significantly improve the tensile modulus of the resin from 28.7 MPa to 168 MPa and the Young's modulus from 525.4 MPa to 1576 MPa. The toughness also increased with increasing glass fiber content due to its ability to inhibit crack propagation and fracture. These bio-based composites utilize only a limited amount of expensive petroleum-based monomers, while employing a renewable resource. The gel time of these ROMP resins are in the range of 5-10 min at 65 °C.

In addition to the bio-resins and composites mentioned above, several different ROMP-based catalytic systems have also been used to cure dicyclopentadiene, and the resulting curing behavior has been analyzed by DSC. It has been shown that, compared to the 2nd generation Grubbs' catalyst **1** [(IMesH₂)(PCy₃)(Cl)₂Ru(=CHPh)], catalyst **3** [(H₂IMes)(PMe₃)(Cl)₂Ru(=CHPh)] was much more latent and is potentially useful to increase the pot-life of polymers made by ruthenium-based ROMP. These systems are either slow or completely inactive at ambient temperatures, yet at higher temperatures the superior curing activity of other ROMP catalysts is retained. The resulting thermosets show glass transition temperatures from 10-25 °C higher than when cured with other ROMP catalysts. These latent ROMP catalysts are very important for the successful liquid resin processing of composites.

Some other thermophysical properties of the resins and biocomposites from cationic and ROMP polymerization are still being investigated.

Composites Using Spent Germ From Ethanol Production

“Green composites” have been prepared from a free radical initiated, tung oil-based resin using spent germ (SG), the coproduct of wet mill ethanol production, as a natural filler. The matrix used in this study is highly crosslinked, causing the resulting composites to contain a low percent of soluble materials. This soluble portion is primarily composed of the corn oil present in the SG. The composites produced are quite thermally stable with temperatures of maximum degradation in the area of 430 °C. The composites produced have glass transition temperatures and storage moduli ranging from 12-37 °C and 465-1434 MPa, respectively. The Young's moduli and tensile strengths range from 196-867 MPa and 5.5-15.1 MPa, respectively. In general, the thermal and mechanical properties of the composites are improved by decreasing the size of the filler. This is most likely the result of an enhanced interfacial adhesion and filler-matrix interaction. As more SG is added to the composite, the properties tend to decrease, due to the filler-filler agglomerations and an increase of voids expected when the amount of filler is increased, while holding the pressure constant. Divinylbenzene (DVB) is used as an effective crosslinker and, as expected, the thermal and mechanical properties of the composites increase as the concentration of DVB in the matrix increases. For the most part, as the pressure during the cure is increased, the properties increase. When decreasing the pressure, while holding the amount of filler constant, incomplete wetting of the filler by the matrix is expected, resulting in poorer properties. By removing the corn oil from the SG prior to composite preparation, an improvement in thermal and mechanical properties is obtained.

Composites Using Soy Hulls From Biodiesel Production

Resin containing 50 wt % conjugated soybean oil (CSO) was combined with soy hulls to investigate these novel biocomposites. Soy hulls are an attractive biorenewable reinforcement because they are readily available and low cost, especially in the state of Iowa. Initial tests in small vials resulted in promising materials containing 50 and 60 wt % soy hulls, the remainder of the mass being the resin (CSO combined

with divinylbenzene/dicyclopentadiene/*n*-butylmethacrylate) that has been cured through a free radical reaction.

A study of the properties of the soy hull composites was designed to assess the influence of several parameters (soy hull particle size, wt % of soy hulls, resin composition and pressure during cure) on the final mechanical behavior of the new materials. We have also focused on the replacement of more reactive resin components (divinylbenzene and *n*-butylmethacrylate) by cheaper dicyclopentadiene, reducing production costs and increasing the crosslink density.

A screening of several free radical initiators indicated *t*-butyl peroxide as the best option for the system studied. Indeed, a higher degree of resin incorporation was obtained when this peroxide was used. The degree of resin incorporation was determined by Soxhlet extraction with methylene chloride and the extracts were compared by ¹H NMR spectroscopy.

The optimum cure sequence was determined by dynamic scanning calorimetry (DSC), which indicated that the composites had to be compression molded at 130 °C for 5 hours and post-cured at ambient pressure for 2 hours at 150 °C. The cure/post-cure temperature should never exceed 180 °C to prevent degradation of the soy hull components (hemicellulose) as determined by thermogravimetric analysis (TGA).

A study of the influence of pressure during cure showed that pressures higher than 276 psi resulted in brittle composites, with Young's and storage moduli equal to 551 MPa and 356 MPa, respectively. For pressures varying from 92 psi to 276 psi, an overall increase in the mechanical properties was observed and the optimum pressure during cure was found to be 276 psi.

The particle size and wt % of the filler affected the properties of the composites. For smaller particle sizes better dispersion of the soy hulls in the resin was obtained and consequently higher values of Young's modulus, tensile strength and storage modulus were obtained. Higher loadings of soy hulls (higher wt %) had the opposite effect on the mechanical properties of the composites. Agglomeration of filler particles and voids yielded weak points that resulted in lower values of tensile strength and Young's and storage moduli.

The effect of resin composition is more complex and can be better understood after analysis of the results in Table 1 below. The difference in reactivity between divinylbenzene (DVB) and dicyclopentadiene (DCPD) results in worse properties for composites where DCPD is substituted for DVB in the resin composition. On the other hand, whenever *n*-butyl methacrylate (BMA) is substituted by DCPD, the higher crosslink density obtained compensates for the lower reactivity of the DCPD and comparable properties are seen.

Table 1. Biocomposite Properties.

Entry	Sample ^a	Young's Modulus (MPa)	Tensile Strength (MPa)	E' at 25 °C (MPa)
1	DVB15-BMA35	672 ± 31	2.6 ± 0.2	536
2	DVB10-DCPD5-BMA35	480 ± 58	1.8 ± 0.1	492
3	DVB5-DCPD10-BMA35	473 ± 62	1.5 ± 0.2	340
4	DVB15-DCPD10-BMA25	645 ± 74	2.3 ± 0.2	686
5	DVB10-DCPD10-BMA30	441 ± 51	1.4 ± 0.2	291

^a All samples contained 50 wt % of soy hulls, particle size < 425 µm diameter and the cure was conducted at 276 psi.

Future studies regarding surface treatments of the soy hulls for better interaction with the resin are intended in the near future in order to improve the properties of these biocomposites for more specific applications.

Publications, Patents, Abstracts, and Presentations

1. P. Badrinarayanan, Y. Lu, R. C. Larock, M. R. Kessler, Cure Characterization of Soybean Oil-Styrene-Divinylbenzene Thermosetting Copolymers, submitted to *Journal of Applied Polymer Science*.
2. T. C. Mauldin, M. R. Kessler, Latent Catalytic Systems for Ring-Opening Metathesis-Based Thermosets, *Proceedings of the North American Thermal Analysis Society Annual Conference*, 2008.
3. T. C. Mauldin, K. Haman, X. Sheng, P. Henna, R. C. Larock, M. R. Kessler, Ring-Opening Metathesis Polymerization of a Modified Linseed Oil with Varying Levels of Crosslinking. *Journal of Polymer Science Part A*. In Press.
4. P. H. Henna, T. C. Mauldin, M. R. Kessler, R. C. Larock, Novel Thermosets Obtained by ROMP of a Functionalized Vegetable Oil and DCPD, to be submitted.
5. P. H. Henna, M. R. Kessler, R. C. Larock, Fabrication and Properties of Vegetable Oil-Based Glass Fiber Composites by Ring Opening Metathesis Polymerization, *Journal of Applied Polymer Science*, 2008, to be submitted.
6. M. R. Kessler, R. C. Larock, D. Grewell, Structural Composites From Agricultural Oils and Proteins, *International Conference on Natural Polymers, Bio-Polymers, Bio-Materials, their Composites, Blends, IPNs, and Gels: Macro to Nano Scales (ICNP – 2007)*, November 19-21, 2007, Kottayam; Kerala, India. Invited.
7. D. P. Pfister, J. R. Baker, P. H. Henna, Y. Lu, R. C. Larock, Preparation and Properties of Tung Oil-based Composites Using Spent Germ as a Natural Filler, *Journal of Applied Polymer Science* 2008, 108, 3618-3625.
8. D. P. Pfister, J. R. Baker, P. H. Henna, Y. Lu, R. C. Larock, Preparation and Properties of Tung Oil-based Composites Using Spent Germ as a Natural Filler, abstracts of Papers, *235th ACS National Meeting*, New Orleans, LA, United States, April 6-10, 2008.
9. D. P. Pfister, J. R. Baker, P. H. Henna, Y. Lu, R. C. Larock, Preparation and Properties of Tung Oil-based Composites Using Spent Germ as a Natural Filler, *PMSE Preprints* 2008, 98, 794-795.
10. Poster at the 2008 Cotton Uphaus Award (Chemistry Department, Iowa State University, Ames, IA).
11. Poster at the 2008 VEISHEA (Iowa State University, Ames, IA).
12. Poster at the 2008 Midwest Biopolymers and Biocomposites Workshop (Iowa State University, Ames, IA).

13. Poster at the 2008 Biorenewable Resources for Biofuels and Biobased Products Conference (Plant Sciences Institute, Iowa State University, Ames, IA).
14. Presentation at the 2008 RRTTC meeting, April 7, 2008 (University of Northern Iowa, Cedar Falls, IA).

In addition to those listed above, Professors Kessler and Larock have presented talks on various aspects of this project to the conference entitled “SERMACS 2007 – Advanced Materials in Transportation Symposium”, Greenville, South Carolina, (10/25/2007); The Università della Calabria, Calabria, Italy (11/20/2007); University of Rome, Rome, Italy (11/23/2007); Rice University, Houston, Texas (03/5/2008); Consortium for Plant Biotechnology, Inc. Symposium, Washington D.C. (2/12/2008).

Expenses for Matching Funds

Iowa State University contributed a total cost share of \$17,285. This was in the form of half a month salary for Dr. Kessler (\$7,899) and Dr. Larock (\$9,386) during the academic year.