

Development of Soy/Corn Oil Plastic Composites

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a. Executive Summary

After 2 years of research on this project, the cationic, free radical and ring opening metathesis copolymerizations of various vegetable oils, various commercially available comonomers, and a variety of inexpensive fillers have been carried out in order to prepare a variety of vegetable oil-based resin and composite materials. The vegetable oil resins have been prepared by mixing commercially available soybean oil (SOY), low saturation soybean oil (LSS), tung oil (TUN), linseed oil (LIN) or conjugated derivatives of these oils (conjugated soybean oil = CSOY, conjugated low saturation soybean oil = CLS, conjugated corn oil = CCOR) with the industrially important alkene comonomers styrene (ST), divinylbenzene (DVB), dicyclopentadiene (DCP), and methacrylonitrile (MAN), in the presence of boron trifluoride diethyl etherate (BFE) for the cationic polymerizations, cumene hydroperoxide (CHP) for the free radical polymerizations and Grubbs ruthenium catalysts for ring-opening metathesis polymerizations. Glass fibers, kenaf fibers, wood flour, carbon black, and the ethanol by-products distillers dried grains and solubles (DDGs) or spent germ have been used as fillers to strengthen the composites, and the ratio of resin to filler has been varied widely under different molding conditions. The resulting composites show a significant increase in thermal stability and mechanical properties and the very high potential for industrial applications. In fact, we are presently talking with a major window company about the commercialization of the soy glass fiber composites for window frames and have received matching money from them to do so. We are also in serious discussions with a venture partner firm about setting up our own company to commercialize this technology.

b. Research Activities and Progress

During 2 years of research, we have successfully prepared a wide variety of bioplastic and biocomposite materials, using several different oils, comonomers and fillers. Optimization of the compositions, fabrication conditions, and structure-property relationships of the composites have been carefully investigated. The bioplastics and biocomposite materials include vegetable oil-based resin/glass fiber composites, vegetable oil-based resin/organoclay nanocomposites, and vegetable oil-based resin/DDGs biocomposites. In fact, we are now talking with Illinois and Iowa companies about scaling up and commercializing the various products made from the vegetable oil/glass fiber composites. The highlights of the research follow.

A series of novel biocomposites exhibiting high performance have been successfully prepared using glass fibers as a reinforcement for the COR, CCOR, SOY and LSS-based resins cationically copolymerized with ST and DVB. The effect of the matrix composition and glass fiber loading on the morphology, thermal stability and mechanical properties of the resulting composites have been investigated by scanning electron microscopy, dynamic mechanical analysis, thermogravimetric analysis and tensile testing. Increasing the glass fiber loading and/or the crosslinker concentration of the matrix results in composites with an increase in thermal stability, modulus, and ultimate tensile strength. For example, increases from 150 to 2730 MPa and 7.9 to 76 MPa are observed in the Young's modulus and ultimate tensile strength of the composites from the LSS-based resin in going from 0 to 50 wt % glass fiber reinforcement. These vegetable oil-based composites have good structure damping properties and potential applications where reduction of both unwanted noise and vibration is important. It is worth noting that the cure times for the linseed, corn and soybean oil-based composites reinforced with glass fibers have been dramatically shorted from our previous 24-48 h to just 10-20 min now, without any loss in the thermal and mechanical properties. Furthermore, the BF_3 catalyst content has been decreased from 5 wt % to 2-3 wt % without any increase in the gel time for these reactive systems. The gel time is now only 2-5 min at 110 °C. These improvements make our systems much more suitable for a commercial molding processes. (Y. Lu, R. C. Larock, *Journal of Applied Polymer Science* **2006**, *102*, 3345-3353. Y. Lu, R. C. Larock, *Macromolecular Materials and Engineering* **2007**, *292*, 1085-1094).

A major international molding company has agreed to let us use their molds to examine the commercial possibilities of our glass fiber composites. Right now, we are also talking with a major window company about commercialization of the soy glass fiber composites for window frames and have received matching money from them to do so. We are also seriously discussing with a venture

capital firm the establishment of our own company to pursue the commercial possibilities offered by this and our other technologies involving biocomposites, coatings and adhesives.

A reactive organomodified montmorillonite (VMMT) clay has been prepared by cationic exchange between the sodium ions of montmorillonite (MMT) clay and (4-vinylbenzyl)-triethylammonium chloride in aqueous solution and then used as a reinforcing phase for various vegetable oil-based resins cationic polymerized from COR, CCOR, CSOY) and CLS with ST and DVB. The structures of the resulting nanocomposites have been determined using wide angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM). The results from WAXD and TEM indicate that heterogeneous structures consisting of intercalation and partial exfoliation or an intercalation structure exist in the nanocomposites, depending on the amount of the VMMT in the polymer matrix. A significant improvement is observed in the thermal stability, the dynamic bending storage modulus, the compressive modulus, the compressive strength, the compressive strain at failure, and the vapor barrier performance for the CSOY- and CLS-based nanocomposites with 1-2 wt % VMMT loading, where some individual exfoliated silicate platelets occur. For example, the CLS-based nanocomposite with 1-2 wt % VMMT exhibits increases of 100-128%, 86-92% and 5-7% in compressive modulus, compressive strength and compressive strain at failure, respectively. CLS with higher unsaturation and reactivity affords nanocomposites with higher thermal stability and higher mechanical properties than CSOY. (Y. Lu, R. C. Larock, *Biomacromolecules* **2006**, 7, 2692-2700; Y. Lu, R. C. Larock, *Macromolecular Materials and Engineering* **2007**, 292, 863-872)

Biocomposites have also been prepared by the cationic copolymerization of linseed oil (LIN), ST, and DVB using bio-fillers, such as kenaf fibers or wood flour, as the reinforcing phase. The resulting biocomposites exhibit a significant increase in the Young's and flexural moduli (Table I). However, the tensile strength and flexural strength decrease slightly when compared to the polymers without fillers. The use of a coupling agent or modification of the filler surface is currently being investigated in order to obtain biocomposites with improved performance.

Table I. Mechanical properties of the linseed oil-based biocomposites.

Composites			Flexural properties / MPa	
Resin	Filler	Content /wt%	Modulus	Strength
LIN50-ST22-DVB20-NFO4-BFE4	Kenaf fiber	0	648.6	21.8
		21	1216.7	16.3
		25	1542.8	18.6
		30	1765.5	19.7
		36	1886.3	19.7
		50	2176.5	23.1
LIN50-ST22-DVB20-NFO4-BFE4	Wood flour	20	686.2	18.4
		30	785.3	19.5
		37	838.4	20.1
		40	882.5	18.1
		50	1050.7	14.5

Other novel composites have also been made from a bio-based resin and spent germ (a by-product of wet-mill ethanol production). The spent germ is either (1) mixed with the resin and cured to give a composite, or (2) the oil is first extracted, yielding only the cellulose and hemicellulose mixture (ESG), which is then mixed with the resin and cured. The resin employed consists of tung oil (TUN), methacrylonitrile (MAN) and DVB. The resulting composites, containing approximately 50 wt % fillers, are hard, brittle, and black in color. Tensile testing yields modulus and toughness values which range from 910 to 1380 MPa, and 0.04 to 0.06 MPa, respectively. Flexural testing has given flexural modulus values between 960 and 1180 MPa. From the initial results, it seems that the extracted spent germ has higher mechanical properties than the non-extracted spent germ, due to removal of the oil, which plays the role of a plasticizer in the composites. We have recently received funding to extend this work on biocomposites to agricultural co-products, such as distillers dried grains and solubles, soy hulls, and corn stover.

Some bio-based rubber-like materials have been made via free radical polymerization. These new materials are composed of tung oil, Ebecryl 860 (an acrylated epoxidized soybean oil), and carbon black (1-15 wt %). As the carbon black loading increases, the material exhibits elasticity and softness. We are currently studying the viability of increasing the carbon black loading to 40 or 50 wt %. Some other properties are still being investigated as well. Funding has recently been received for the fabrication of commercial rubbers using this technology.

In addition to these composites, novel biobased rubbers and hard resins have also been developed by the cationic, free radical and ring-opening metathesis polymerization of vegetable oils

with commercially available vinyl monomers. The morphology, structure and properties of the resulting materials have been carefully investigated. The results suggest that these biobased thermosets may prove useful alternatives to current petroleum-based plastics and find widespread utility. (D. D. Andjelkovic, R. C. Larock, *Biomacromolecules* **2006**, *7*, 927-936; P. H. Henna, D. D. Andjelkovic, P. P. Kundu, R. C. Larock, *Journal of Applied Polymer Science* **2007**, *104*, 979-985; M. Valverde, D. Andjelkovic, P. P. Kundu, R. C. Larock, *Journal of Applied Polymer Science* **2008**, *107*, 423-430; P. H. Henna, R. C. Larock, *Macromolecular Materials and Engineering* **2007**, *292*, 1201-1209.)

c. Equipment

No equipment was purchased that cost \$5,000 or more.

d. Publications, patent, abstracts and presentations

1. Y. Lu, R. C. Larock, Novel biobased nanocomposites from soybean oil and functionalized organoclay. *Biomacromolecules* **2006**, *7*, 2692-2700.
2. Y. Lu, R. C. Larock, Corn oil-based composites reinforced with continuous glass fibers: fabrication and properties. *Journal of Applied Polymer Science* **2006**, *102*, 3345-3353.
3. Y. Lu, R. C. Larock, Bio-based nanocomposites from corn oil and functionalized organoclay by cationic polymerization. *Macromolecular Materials and Engineering* **2007**, *292*, 863-872.
4. Y. Lu, R. C. Larock, Fabrication, morphology and properties of soybean oil-based composites reinforced with continuous glass fibers. *Macromolecular Materials and Engineering* **2007**, *292*, 1085-1094.
5. R. C. Larock, F. Li, Y. Lu, Bio-based thermoset plastic composite materials and methods of making same. U.S. patent, Appl. No. 60/839918, 2006, pending.
6. D. D. Andjelkovic, R. C. Larock, Novel rubbers from cationic copolymerization of soybean oils and dicyclopentadiene. 1. Synthesis and characterization. *Biomacromolecules* **2006**, *7*, 927-936.
7. P. H. Henna, D. D. Andjelkovic, P. P. Kundu, R. C. Larock, Biobased thermosets from the free-radical copolymerization of conjugated linseed oil. *Journal of Applied Polymer Science* **2007**, *104*, 979-985.
8. M. Valverde, D. Andjelkovic, P. P. Kundu, R. C. Larock, Conjugated low-saturation soybean oil thermosets: Free-radical copolymerization with dicyclopentadiene and divinylbenzene, *Journal of Applied Polymer Science* **2008**, *107*, 423-430.

9. P. H. Henna, R. C. Larock, Rubbery thermosets by ring-opening metathesis polymerization of a functionalized castor oil and cyclooctene, *Macromolecular Materials and Engineering* **2007**, 292, 1201-1209.
10. P. H. Henna, R. C. Larock, Rubbery thermosets prepared by ring opening metathesis copolymerization of a functionalized castor oil and cyclooctene. *PMSE Preprints* **2007**, 96, 954-955.
11. M. Valverde, R. C. Larock, Free radical synthesis of rubbers made entirely from highly unsaturated vegetable oils and derivatives. *PMSE Preprints* **2007**, 97, 76-77.
12. P. H. Henna, R. C. Larock Rubbery thermosets prepared by ring opening metathesis polymerization of a functionalized castor oil and cyclooctene. *Abstracts of Papers*, 233rd ACS National Meeting, Chicago, IL, United States, March 25-29, 2007.
13. M. Valverde, R. C. Larock, Free radical synthesis of rubbers made entirely from highly unsaturated vegetable oils and derivatives. *Abstracts of Papers*, 234th ACS National Meeting, Boston, MA, United States, August 19-23, 2007.

Professor Larock has presented talks on various aspects of this project to the conference entitled "Renewable Resources and Biorefineries", Ghent, Belgium (09/20/2005); the conference entitled "Oleochemistry: When Fats and Oils Become Useful to Industry", Thetford-Mines, Quebec, Canada (10/04/2005); the University of North Texas, Denton, Texas (10/20/2005); Concordia College, Fargo, North Dakota (12/01/2005); Minnesota State University at Moorhead, Moorhead, Minnesota (12/02/2005); Iowa State University, Ames, Iowa (01/13/06); Cytec, Stamford, Connecticut (04/13/06); the Iowa Advanced Manufacturing Research and Collaboration Cluster, Newton, Iowa (04/17/06); American Oil Chemist's Society 97th annual meeting and exposition, St. Louis, Missouri (05/02/06); Goodyear Tire and Rubber Company, Akron, Ohio (05/04/06); Ashland Specialty Chemical Company, Dublin, Ohio (05/05/06); Grain Processing Corp., Muscatine, Iowa (08/02/06); Avery Dennison, Pasadena, California (08/04/06); Biobased Industry Outlook Conference at Iowa State University (08/29/06); First University of Nevada at Reno Chemistry Graduate Student Association Distinguished Lecture Award, Reno, Nevada, (02/16/2007); Ag-West Bio and National Research Council Plant Biotechnology Institute Third Plant Bio-Industrial Oils Workshop, Saskatoon, Saskatchewan, Canada (02/27/2007); University of California, Davis, California, First Larock Undergraduate Research Conference (05/09/2007); Okayama University, Okayama, Japan, JSPS Lecture Award, (05/30/2007).