Final Technical Report - Nov. 1, 2001 – Dec. 31, 2003

Title: **Affordable Resins and Adhesives From Optimized Soybean Varieties** (ARA Program)

Covering Period: Nov 1, 2001 – Dec. 31, 2003.

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Recipient: University of Delaware (UD)

Award Number: DE-FC07-01ID14217

Subcontractors: Kansas State University (KSU), Cara Plastics, Inc., Sandia National Lab (SNL).

Other Partners: Ashland Chemicals, Georgia Pacific, North Central Kansas Processor, Agriboard, USDA National Soybean Germplasm Center, Cara Plastics, Tyson Food, Diab, Interstate Resources, USB, and Dock Resins.

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Project Objectives:

The Mission of the ARA Program was to develop the Corporate Infrastructure to mass-produce new bio-based materials from Soybeans. The resins were integrated with the bio-fuels program. In support of this Mission, the Goals were as follows:

1) to research, develop, and commercialize low cost adhesives and resins from soy oil and protein, the co-products of the soy bio-diesel process.
2) to study structure-functionality of soy oil and proteins at molecular and genomic levels;

The Goals of the ARA Project were pursued with six Research and Development Targets, which include the following:

1) Research, develop, scale-up, and commercialize low-cost soy oil-based adhesives and resins using by-products from bio-diesel (UD);
2) Research, develop, scale-up, and commercialize low-cost soy flour/protein-based adhesives (KSU);
3) Identify chemical composition and structure-function of soybean oil/protein and soybean varieties that are favorable for adhesive properties (UD and KSU);
4) Improve adhesion performance of soy oil/flour/proteins interactions by chemical modification (UD, KSU);

5) Explore and develop new applications of soy oil-based adhesives and resins (UD); and
6) Conduct commercial feasibility testing of soy oil/flour/protein adhesives and resins (UD, KSU, CARA).

Background:

The mission of the ARA research program was to promote the widespread use of sustainable composites, resins, and adhesives from renewable resources to meet future national and environmental needs. The objective of this research was to use a systematic approach to develop the fundamental science in support of the corporate strategic partnerships that will impact a $50B market by providing an affordable replacement for petroleum-based materials with bio-based environmentally friendly and high-performance sustainable materials. The new resins, adhesives and bio-based materials developed by this DoE contract are commensurate with the Principles of Green Chemistry and Green Engineering and will have considerable environmental influence with impacts on both bio-based products and the bio-energy program.

***UD Achievements*:**

1. **Resin Development**: For plant-oil based resins, the relation between the fatty acid distribution function (FAD), level of chemical functionalization and properties such as elastic modulus and tensile strength, were determined using vector percolation theory. This allows us to optimize the design of oils and select FADs that are best suited to cost and property requirements. The resin SOMG/MA was developed for potential high-volume low-cost applications such as hurricane resistant housing. The advantage of this resin is that it is integrated into the bio-fuels program by being a net user of glycerol, a by-product of the bio-diesel process. Improvements were made in the SOMG/MA resin by chemically modifying it to improve its compatibility with the commoner and its stability. Microscopic analyses were done on the SOPER/MA and SOMG/MA as blends with styrene to determine the cause of the poor compatibility. It was determined that micelles are formed and that a compatibilizer surfactant is needed to break up these micelles for commercial use of these resins. An initial search was done to identify potential candidates. The new resins were characterized and examined for scale-up.

2. **Pressure Sensitive Adhesives**: The first bio-based adhesive patent was issues on Nov 11, 2003 as US Patent No. 6,646,033, entitled "Pressure Sensitive Adhesives from Plant oils, inventors R. P. Wool and S. P. Bunker from the University of Delaware. Dow Chemical has expressed interest in developing this high volume bio-based material and negotiations are in progress. Two acrylated resins based on soybean oil have been scaled up. The acrylated epoxidized soybean oil (AESO) has been formulated for our use by a supplier and sampled to our partners. The acrylated oleic acid methyl ester (AOME) has been scaled up for use in pressure sensitive adhesives (PSA). Discussions were held with Dow, Eastman, Georgia Pacific, and Johns Manville about commercialization of our proprietary adhesive formulation. A meeting with the U.S. Post Office was conducted to review the process for placing a new bio-based PSA into their product lines, such as the adhesive on postage stamps. The "Buy Bio" program offers

an opportunity to penetrate this market. Estee Lauder has also expressed interest in using bio-based adhesives in their cosmetic packaging and containers. The high-oleic fatty acids used in this bio-based psa can be extracted from bio-diesel using fatty acid separations technology developed by the ARA program.

3: **Fiber Reinforced Construction Materials**: The Hurricane Resistant Roof design was featured in Newsweek, Oct 27, 2003 issue. A patent has been filed on this new design, which was also featured in the Architectural Record, Nov 2003 issue. This application is potentially the highest volume of bio-based materials that can be used, far exceeding the entire plastics and adhesives industry. We have evaluated more than 20 different formulations of fibers and resins for housing applications. The best engineering unit-beam properties were obtained with cellulose fibers derived from recycled newspapers and cardboard, interlaced with chicken feather mats, and infused with resin using Vacuum Assisted Resin Transfer Molding (VARTM). Further work has now demonstrated that a cellulose-corrugated composite gives even better process and product results. Our partner, Interstate Resources, has been able to provide us commercial corrugated paper for composite applications. A longer beam has been produced and analyzed from this material, demonstrating that the properties are acceptable for roofing applications. Discussions are occurring with Hardcore Composites and TPI to produce a roof of 400 square feet. This roof would be a demonstration of our capability to move forward with this technology and also enable us to begin coating and weathering trials. If successful, these high volume structures derived largely from materials waste streams and low cost resins would save approximately a quad of energy in the USA and have high impact on bio-fuels by-products.

Related Developments in Bio-Based Materials at UD:

Patents: Patents are pending in the following areas:

a) Pressure Sensitive Adhesives from Plant Oils, US Patent No. 6,646,033. November 11 issue date. Inventors, S. P. Bunker and R. P. Wool
b) Sheet Molding Compound from Plant Oils, US Patent Application Serial Number, 10/166,849: Inventors, R.P. Wool, Jue Lu and S.N. Khot
c) Low Dielectric Constant Materials from Plant Oils and Chicken Feathers, US Patent Serial Number, 60/396,319: Inventors, R. P. Wool and C.K. Hong
d) Rigid Thermosetting Liquid Molding Resins from Plant Oils, US Patent Application UD02-21: Inventors, Erde Can and R. P. Wool.
e) A Monolithic Hurricane Resistant Roof made from Low Density Composites, UD04-17, filed October 17, 2003: Inventors, R. P. Wool, M. A Dweib, H.S. Shenton III and R. Chapas.

Media Interviews: Results of this research were discussed in interviews with CNN Headline News, CNN Financial News, NPR, Tech News, Voices of Innovation, Newsweek and numerous newspaper, magazines and web sites.

KSU Technical Achievements

Scale-up low cost soy protein adhesive: Low cost soy protein adhesives have been

developed for particleboard applications. We have identified a major feedstock process company and teamed up with our resin industry partner to accomplish the commercial feasibility testing. Pilot scale testing was done and the results were encouraging. KSU received funding from industry to continue working on commercial feasibility testing and related issues.

High performance soy protein adhesives: The objective was to develop protein-based adhesives with performance comparable to phenol formaldehyde resin for wood and non-wood application. Research progress has been made. New adhesives have been developed with high adhesion strength and water resistance, comparable to phenol formaldehyde resin in dry, wet, pressure-vacuum aging, and boiling aging tests. One patent has been filed, and another patent is in preparation. Industry partners in their labs evaluated the patented adhesive, and the results were encouraging. KSU received research funds from industry to continue working on this adhesive development.

Latex Like Adhesives: KSU recently discovered that soy protein could be used for latex based adhesive that are currently used in packaging, labeling, office glue, envelope glue, etc. The soy latex adhesive has similar adhesive performance as the synthetic latex based adhesives, and is environmental friendly in processing and application. One patent has been filed. This adhesive was found to have great potential for the foundry industry. A foundry industrial partner evaluated the adhesive, and the initial test results were encouraging.

Protein structure and adhesive performance: Many results were obtained. We have a better understanding of why soy protein has adhesive properties and identified protein fractions that are favorable for adhesive performance. This information is very useful to improve soy protein based adhesives and other applications. We have also designed and synthesized oligopeptides and one of the oligopeptide showed strong adhesive strength, indicating that it may be the key structure for protein adhesive use. This would be a great initiation of new research on "biomaterials by design" and will result in many new materials. One disclosure has been filed. We are currently seeking funding to continue this exciting research.

Soybean genotypes identification (second cycle): 400 Soybean genotypes were planted in May 2002 and winter nursery 2002. These beans are being evaluated for protein adhesives to confirm results obtained in year one. Beans were harvested in Oct 2003. The results obtained so far are a very useful reference for future research.

Budget

The negotiated funds for this DoE contract have been spent, the cost share commitment was met, and a final invoice will be submitted