Structural Bio-Composites from Engineered Corn Straw Fibers and Novel Soy-based Resins

Project Number: GR01-037

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Statement of Challenge

This project was intended to add value to the corn and soybean crops, the most important crops in Michigan. The main objective was to use corn straw and soybean oil in a synergistic manner to create a new generation of biobased structural materials of significant commercial value in order to provide economic benefits to Michigan's farmers.

Objectives

The purpose of this project is to develop eco-friendly-biobased structural materials from both corn straw and soybean oil. These products will contain a soybean based component, precisely a polyol made from soybeans (soy polyol), an aromatic isocyanate (made from petroleum) and corn straw fiber (harvested in Michigan). The objectives of this project were:

* Modification of corn straw through the ammonia explosion process

* Identification and characterization of a soy polyol suitable for use in materials

* Preparation of a biobased polyurethane by reaction of soy polyol with isocyanate

* Preparation of bio-composites from corn straw fiber and the biobased soyoil polyurethane matrix.

* Preparation of bio-composites from other natural fibers (hemp and jute) and the biobased soyoil polyurethane matrix.

Results and Accomplishments

Our research has demonstrated the feasibility of producing biobased materials from soybean oil and corn that can be used for structural applications. Indeed, we successfully prepared polyurethanes that contain polyol made from soybean oil and used corn fibers to improve the mechanical properties of these materials. Our main findings are:

- It is technologically possible to make polyols from plant oils such as soybean oil. Our conclusions are based on a study of two kinds of polyol. The first one is a commercial polyol produced by ATOFINA and is prepared by acid hydrolysis of epoxidized soybean oil. The second has been made via a proprietary process in our laboratory and is a combination of vegetable oil and multi-functional hydroxy compound. The hydroxyl content of the polyol and thus the properties of the subsequent polyurethanes can also be controlled by this process.

• The cost of commercial soy polyols produced by ATOFINA is about 60-65 cents/lb while the one synthesized in our laboratory will be less expensive, i.e. about 50-60 cents/lb.

• Moreover, the technology developed in our lab is not limited to soyoil. Various types of natural oils (i.e. corn, cottonseed, peanut and even animal oils) (Chart 1) can be utilized with this process.

• Our research proved that polyurethanes with thermo-mechanical properties comparable to petroleum-based products could be easily produced. By carefully designing the polyol characteristics (mainly the hydroxyl content) through the amount of multi-functional hydroxy compound (proprietary) used, we can prepare either a rigid material (Fig. 1A) or a flexible one (Fig. 1B).

• Corn straw proved to be useful as source of fibers that can be use to reinforce the polyurethane matrix and thus increase properties such as stiffness and glass transition temperature. Properties of these fibers can be improved by surface treatment such as ammonia explosion. Indeed, by this process the effective fiber diameter is increased and the interior portion of the fiber is more accessible resulting in higher stiffness in the composite. Moreover, the thermal stability improved by more than 50 C as compared to the untreated corn fiber.

• Bio-composites materials have been prepared using corn straw fibers (with fiber content up to about 35 wt %) and soy polyol (Fig. 2). Mechanical performances of such bio-composites are superior to the neat resin, i.e. polyurethane matrix.

• Biobased polyurethane composites reinforced with either hemp or jute have been produced and characterized. In both case thermo-mechanical properties were improved after fiber loading (as high as 30 wt % fibers).

• *Publications, presentations & patents:*

- ✓ Polyurethanes are prepared from soy polyol made by ATOFINA and aromatic isocyanate (polymeric diphenylmethane diisocyanate: pMDI). We have presented some of our results in conference held in Detroit, MI (GPEC 2003 conference, February, 26-28) as well as in San Diego, CA (ICCM 14, July 14-18, 2003).
- ✓ Four (4) publications have been submitted dealing with materials we made in our laboratory. One has already been accepted (Journal of Polymers and the Environment).
- ✓ One presentation is scheduled for November 2003 (AIChE annual meeting at San Francisco, CA).
- ✓ The patent entitled *"Polyol Fatty acid Polyesters process and Polyurethanes thereform"* has been submitted to MSU and a US patent has been filed (April 2003).

Impacts

1. Based on our research, the feasibility of producing biobased structural materials from corn straw and soybean oil has been demonstrated, thus benefiting to Michigan's farmers.

2. Soybean-based polyols should be economically competitive (chart 2). Soy polyols either developed by ATOFINA or prepared by our process, should be competitive with petroleum-based polyols thus leading to biobased polyurethanes of comparable price (2 to 2.5 $/lb). The addition of natural fiber reinforcement will improve mechanical properties and lower the cost of the final biobased composite products since the price of natural fibers is generally low (up to 30 cts/lb).

Funding Partnerships

ATOFINA Chemicals, Inc. Blooming Prairie, MN has expressed interest in our work.

***Chart 1. Examples of Polyols prepared from Plant Oils*.**

Entry	Plant oil used	Yield (%)	Hydroxyl content of the polyol (mg KOH/g)	Amount prepared (g)
1	Soybean	95	151	227
2	Soybean	96	209	223
3	Corn	> 90	278	27
4	Peanut	> 90	327	26
5	Cottonseed	> 90	265	130

Chart 2. Comparison of prices of raw materials for polyurethane preparation.

Material	Price (cts/lb)
Isocyanate	70 – 80
Petro Polyols	50 – 70
Soy Polyol (ATOFINA)	60 – 70
Soy Polyol (MSU: CMSC)	< 60

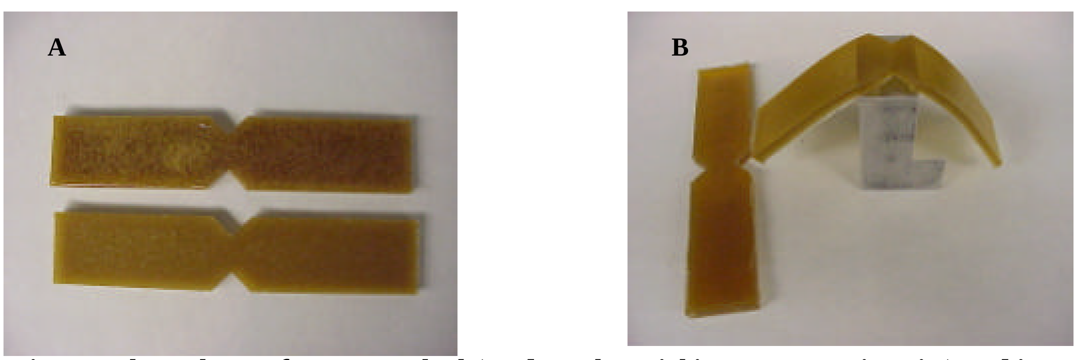

Fig. 1. Polyurethanes from soy polyol (made at the Michigan State University) and isocyanate: (A) diphenylmethane diisocyanate (pMDI); (B) hexamethylene diisocyanate.

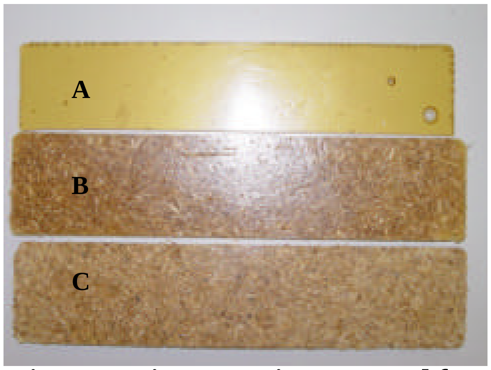

Figure 2. Bio-composites prepared from soy polyol (ATOFINA) / pMDI and corn straw fibers: (A) Matrix; (B) Matrix + 13 wt % corn, (B) Matrix + 32 wt % corn straw fibers.