Fabrication of Polyurethane-Based Foams with Incorporated “Waste” Glycerol from Tranesterification Synthesis and “Waste” Agricultural Residues (Chopped Rice Hull Fibers)

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Abstract
We are interested in fabricating green materials that could potentially be used in building construction applications. Ideally, the inputs to these materials would not lead to further deforestation, and rely minimally on nonrenewable fossil fuels. To make a sustainable product, we aim to incorporate “wastes” from current industrial and agricultural processes. The green building material will be a “sandwich” composite where foam will serve as the compressible, light-weight core, and a hemp/bioresin board will be the rigid, dense outer sheath. The foam we have made is based on polyurethane chemistry where we have used modified castor oil as the polyol. We have utilized “waste” glycerol that is a byproduct of transesterification chemical reactions (such as biodiesel synthesis) into the foam. We also incorporated waste agricultural residues, i.e., rice hulls into the foam as a filler. FT-IR spectroscopy and scanning electron microscopy revealed that the incorporation of these two “waste” components did not disrupt the polyurethane chemistry. Furthermore, we measured the compression strength (using ASTM D3575-08) of these foams as a function of the percent of “waste” added and found there can be an increase in strength. We also have successfully used a vacuum infusion method to make rigid boards from woven hemp fabrics and “SuperSap”™ bioresin. Hemp was used because it is plant-based and it has one of the highest mechanical strengths among plant fibers. Sandwich composite boards are now being assembled, and we are measuring their bending strength. We envision that these boards can perhaps be utilized as substitutes for non-load bearing panels in the construction of green buildings.

1. Introduction
Polyurethane (PU) foams are widely used in industrial applications because they can be made with tailored physical and chemical properties. The bulk of the ingredients for PU foams are polyols and isocyanates that are derived from petroleum feedstocks. As the world moves towards energy and environmental sustainability, there is a push of research and development to synthesize these foams from plant based polyols, so called biopolyols.[1] The goals are to derive biopolyols from renewable biomass resources with energy efficient and cost-effective methods. As reported in the literature, efforts include the conversion of plant starches,[2] and lignocellulosic biomass such as wood,[3] wheat straw [4] and corn stalks [5] to biopolyols. The disadvantages of these methods are that they require substantial amounts of additional petroleum-based material, energy, and extensive chemical processing routes. In some of these chemical synthesis procedures, the solid biomaterial is converted to a liquid with a liquefaction
agent that can be polyethylene glycol, for example. These processes require approximately 100 g of solvent per 20 g of lignocellulosic biomass to obtain appropriate biopolyols. Furthermore, this chemical reaction requires a catalyst, typically sulfuric acid, and the reactions are carried out at elevated temperatures (~200 °C), at ambient pressure or under vacuum, for an extended amount of time (1-2 hours). PU foams made from these plant based biopolyols exhibit comparable properties to PU foams made from petroleum based polyols.[3],[4],[6] Although these methods take advantage of the renewable biomass, they require additional solvents and chemicals, as well as energy inputs to fabricate the biopolyols.

Our intention is to make PU foams employing glycerol that is a byproduct from transesterification chemical reactions such as in the synthesis of biodiesel from plant based oils. For the biodiesel synthesis, plant oil is reacted with an alcohol in the presence of a catalyst to produce primarily biodiesel, and about 10% is converted to the by-product glycerol. This glycerol byproduct tends to contain unreacted methanol, fatty acids, soaps and the catalyst. According to Johnson et al., the production of biodiesel was about 300 million gallons in 2007, which translates to 30 million gallons of biodiesel waste glycerol.[7] Many commercial applications of glycerol such as cosmetics, soaps and food, however, require that it be purified, and this further raises the cost of the glycerol. In short, there is a glut of glycerol on the market, and researchers are trying to find economically viable methods of utilizing the biodiesel waste glycerol. Recently, Hu et al. have reported on the use of biodiesel waste glycerol as the liquefaction agent of soybean straw for the production of biopolyols for the purpose of producing PU foams.[8] They found that the biodiesel waste glycerol is as effective as petroleum derived pure glycerol to liquefy the soybean straw that is an abundant agricultural crop waste product.

In addition to utilizing waste glycerol from transesterification reactions, the added novelty of our PU foams is that we incorporate waste agricultural residues. Banik et al. infused commercially available cellulosic paper fibers into PU foams made from soy biopolyol and investigated their effects on the foam density and chemical structure.[9] There are many reports on PU foams reinforced with inorganic particles of various compositions and shapes.[10] Recently, Li et al. published an article where they demonstrated that the addition of up to 1 % cellulose nanowhiskers had a significant effect on the tensile and compression strengths of PU foams.[11]

In this work, we have synthesized PU foams that are composed of polyols derived from castor oil. We have also incorporated “waste” rice hulls and calcined rice hulls into the structure of these hybrid foams. Our goal was to make hybrid foams with a substantial portion of plant-based compounds that have mechanical properties that are comparable to the traditional PU foams. We also report results on the fabrication of “sandwich” composites where the PU is the soft inner core and hemp boards are the rigid outer sheaths. The procedures that we have developed are not as energy intensive as the liquefaction methods described earlier, and the chemistry is much simpler. In this paper, we first describe the procedure employed to fabricate the hybrid PU foams. Then we present results on the chemical composition, microstructure and compressive strength.
2. Experimental

2.1 Materials

We performed polyurethane chemistry with the polyol derived from castor oil, a plant-based oil that is therefore sustainable and renewable. This was done in the presence of a KOH catalyst to synthesize a natural plant-based biopolyol with the byproduct glycerol.

![Synthetic route to obtain castor oil-based polyols.](image)

The crude castor oil and catalyst used were both purchased from Fisher Scientific. In addition to the polyol, the polyurethane foam requires an isocyanate, catalyst, foaming agent and surfactant. The isocyanate we used was diphenylmethane 4,4'-diisocynate (MDI), the catalyst was dibutyltin dilaurate (DBTL), the foaming agent was water and the surfactant was silicone oil. These chemicals were purchased from Fisher Scientific.

We also fabricated “sandwhich” composites where the foam was the soft core material and two parallel hemp boards were the rigid sheaths. The woven hemp fabric was 12.5-ounce and was purchased from Pickering International. The bio-resin was “SuperSap” purchased from Entropy Resins, Inc. Although the exact composition of the SuperSap resin is proprietary, the manufacturer claims that at least 50% of the content is from tree sap. The resin vacuum infusion process supplies were purchased from AirTech. The rice-hulls were purchased from Midwest Supplies.

2.2 Procedures

Polyurethane is the product of an isocyanate and an alcohol. In this experiment the following chemicals were combined in a 50 ml beaker: 20.0 g of the castor oil polyol, catalyst DBTL, surfactant and double distilled water. The reactants were mixed using a magnetic stirring rod and stir plate for 4 minutes. 11.5 g of MDI were heated until all the MDI was in liquid form. Afterwards both the MDI and the polyol mixture were poured into a plastic cup and manually stirred for one minute. Once the two were evenly stirred together, the stirring rod was removed to allow the mixture to foam for approximately 1 minute. Alterations to the biofoam were done by adding cooked rice hulls: cleaned rice hulls were calcined in a furnace at 750 °C until the organic fibers were completely burned off leaving behind only amorphous silica rice hull ash.
We also used uncooked rice hull fibers: pretreated with a diluted hydrochloric acid solution to wash off contaminates and other unwanted residue such as the wax left on the outer shells. Either cooked or uncooked rice hulls were added to the cup at the moment where the two reactants were mixed together. Three variations were done: one set with 3 wt%, 5 wt%, 7 wt% and 10 wt% of cooked rice hulls, one set with 3 wt%, 5 wt% uncooked rice hulls, and one test was done of a blend of both cooked and uncooked rice hulls.

To prepare a laminate, we first cut the hemp fabric to the desired size. We cut such that the two-ply fabric orientations were one at 45°/45° and the other at 0°/90°. The fabric swaths were stacked on a rigid metal surface. The fabric was bagged and tubing was put in place for resin vacuum infusion. After proper bagging, the resin was prepared for infusion. The Super-Sap bio-resin used was a 3:1 weight ratio of epoxy to hardener. Once prepared we uniformly flowed the epoxy into the fabric by pulling a vacuum. The resin infused sample was left overnight under vacuum to cure. After nine hours, the sample was completely hardened and the hemp/Bio-Resin board was ready to be cut to the desired dimensions.

2.3 Instrumentation
The chemical analysis was performed on a Nicolet 380 Fourier transform infrared (FTIR) spectrophotometer. The mechanical property measurements were performed with a Tinus-Olsen Super L Universal Testing Machine. The compression strength measurements were done following the procedures as prescribed in ASTM D3575-08.[13] The foam samples had a cylindrical shape. The foam samples were compressed at rate of 12.5 mm/min. The measurements were terminated when the sample was densified to a level of 70%.

3. Results
3.1 Foam Microstructure
A Leica scanning electron microscope (SEM) was used to image the microstructure of the various foam samples. Presented in Figure 2 are images for the original foam, and foam with 5% cooked and uncooked rice hulls. All foam samples have an open cell morphology. The original foam has somewhat uniform pore sizes with approximate average diameter of 0.25 mm. The sample with 5% cooked rice hulls, however, exhibits more variability in pore diameter where the pores seem to be disrupted. Finally, the 5% uncooked sample has poorly formed pores with the presence of large air pockets. Based on these images, we surmise that for the original foam the surfactant was effective at stabilizing the foam and that the polyurethane chemical reaction proceeded with the proper kinetics. However, the addition of the cooked and uncooked rice hulls to the foam may require further optimization of surfactant and catalyst to improve the microstructure.
3.2 Chemical Analysis

The FTIR spectra of the original foam, and the foam samples with 5% cooked and uncooked rice hulls are shown in Figure 3. The formation of urethane linkage was confirmed by FTIR spectroscopy: the first band 3349 cm\(^{-1}\) is assigned to the stretching vibration –N-H and the broad band between 1703-1699 cm\(^{-1}\) is attributed to the carbonyl group of urethane linkage. Also, the band at 1519 cm\(^{-1}\) is characteristic of the –C-N- of urethane group and the peak at 1020 cm\(^{-1}\) is characteristic of the vibration of C-O linkage. Almost all of these peaks were the same for the original foam and 5% cooked and uncooked rice hulls indicating that the primary chemical structure of the foams was not altered by the presence of the rice hulls.

![Figure 3: FTIR spectra of original foam (top), foam with 5% cooked rice hulls (center), and foam with 5% uncooked rice hulls (bottom).](image-url)
3.3 Compressive Strength
The methods described in ASTM D3575-08 were used to perform the mechanical strength measurements. In Figure 4 we present the compression stress versus strain of various foam samples. As noted in the Procedure section above, all of these samples were made with slightly different ratios of surfactant and catalyst to preserve the foam structure and to tailor a desired firmness. Therefore, we cannot directly use this plot to determine the effect of cooked and uncooked rice hulls or the effect of the percentages upon the compressive strength. It is a complex interplay of surfactant, catalyst and rice hull additive that determine the final structure of the foam. With this caveat in mind, we can compare the strengths between the samples with cooked rice hulls: the plots show that increasing the percentage of the cooked rice hulls greatly increases the compressive strength and stiffness. There is a linear elastic regime and the elastic modulus increases with increased cooked rice percentage. A possible reason for this increase might be that the cooked rice hulls are composed primarily of amorphous silica in micrometer sized particles. The silica probably chemically reacts with the isocyanates and becomes incorporated within the polyurethane foam. These results are similar to the published work of Li et. al, where they found that increasing the amounts of cellulose nanowhiskers led to an increase in the strength.[11] The data also indicates that the addition of uncooked rice hulls results in the decrease of compression strength and stiffness. We speculate that this may be due to the disruption of the open-cell foam structure by the relatively large rice hull fibers. For this preliminary data, the “noise” in the data is due to the instrumentation and somewhat low stiffness of the foam samples. At larger strains (not shown in Figure 4), we can see the foam exhibit three regimes in stress-strain curve: initial linear elastic regime, short collapse plateau regime, and finally densification regime where the stress rises steeply as reported Li et. al.[11]
Figure 4: Compressive strength measurement. Stress-strain curves for various foam samples with cooked and uncooked rice hulls.

3.4 Foam/Hemp/Bioresin Composites
We are in the process of fabricating sandwich composite boards with the foam and hemp/bioresin laminates. In Figure 5, we show sample that has the foam as the soft, light-weight inner core, and two outer stiff hemp/bioresin laminates. Currently, we are making rectangular samples for three-point bending measurements.

Figure 5: Photograph of foam/hemp sandwich composite.
4. Conclusions
A preliminary, exploratory study was performed to determine if we could make bio-based foams and sandwich composites with foam and hemp/bioresin laminates. We explored the effects of adding agricultural waste residues to the foam upon the microstructure and compressive strength. We incorporated cooked and uncooked rice hulls into the foams that were made with castor oil based polyols. These initial experiments indicate that the rice hulls could indeed be fixed within the foam with some detectable change in the structure and strength. Although our compression strength data is somewhat inconclusive, we did observe that increasing the amounts of cooked rice hulls increases the compression strength. Finally, we fabricated sandwich composites with foam and hemp boards that were infused with a bio-resin. Our vision was to make such boards for building construction applications with sustainable, plant-based materials that also utilize agricultural wastes.

References