Analytical and Experimental Studies of Properties of Ethanol Coproduct-Filled Plastics

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Abstract

As the renewable fuels industry continues to grow, the quantity of resulting byproducts has expanded in tandem. Currently, these materials are primarily used for animal feed, but at some point will saturate the animal feeds market. Thus, it is necessary to investigate alternative methods and applications by which these coproducts can be utilized. One potential application for these process residues involves plastics manufacturing. Due, in part, to the increasing cost of resins and conventional fillers, alternate fillers have been increasingly sought. Many of these include biological materials such as grasses, bamboo, starch, chicken feathers, soy protein, and cellulose. Not only do these have the additional benefit of improving mechanical properties, but they have the added benefit of biodegradability. Biological fillers have been shown to improve various plastic properties but, in some cases, can actually slightly degrade resulting mechanical properties, such as tensile strength, and ductility. There exists the potential to use fuel ethanol processing coproducts as plastic fillers. To date, however, this has not yet been investigated. This paper reports on preliminary results of a study aimed at determining mechanical and physical properties of plastics filled with these coproducts. Several blends were compression molded and resulting mechanical properties were determined. This information was then used in a theoretical Finite Element Analysis (FEA) model to predict processing behavior and ultimate performance of the coproduct/plastic composite materials. Predicted mechanical properties were then compared with experimental results to refine the model.

Introduction

Modern manufacturing involves complex interactions between many factors, including product design, raw materials, manufacturing processes, as well as product distribution and sales [1-3]. In recent years, much interest has developed in incorporating non-

traditional, biological materials into traditional manufacturing operations to produce high-quality, cost-competitive, biodegradable finished products. Progress in industrial biomaterials has intensified as raw material costs have increased and as environmental consciousness has gained greater visibility. There are now many viable bio-based products that are produced in industry [4-5]. Practices range from processing biomaterials into completely finished products to utilizing them as additives or reinforcements in plastics [6]. The product category that currently encompass the greatest potential is plastic composites.

Inclusion of biomaterials has often been shown to improve the physical and mechanical properties of conventional plastics, or least to provide equivalent strength compared to conventional fillers. Much research has been conducted in recent years, and composites encompass a broad array of materials [7-15]. Examples discussed in literature involve use of materials produced in large quantities as a result of agroprocessing, as well as specific biomass crops grown for dedicated use in biomaterials: bagasse [16, 17], flax fibers [15,18,19], palm fibers [20,21], sisal fibers [22,23], jute fibers [24,25], soy products [26,27], and corn ethanol processing residues [10,28].

Process residues from corn ethanol manufacturing are a very promising source of potential biofillers. For every 1 kg of corn that is processed into ethanol, approximately 1/3 kg of nonfermentable residues (primary fiber, protein, and oil) remain. These residues are known as "distillers dried grains with solubles", or DDGS. The number of corn ethanol plants, and their processing capacities, has been markedly increasing in recent years. For example, in 2005, 97 manufacturing plants in the U.S. had an aggregate production capacity of nearly 15.8 billion liters per year (4.2 billion gal/yr), which represents a growth of 156% over the previous five years. More information on the growth of this industry can be found in [29-31]. This industry is projected to expand for the foreseeable future. As the industry grows, however, so too does the quantity of DDGS. Thus, DDGS may have potential for use as a biodegradable filler in plastic composites.

The goals of utilizing a biomaterial, such as DDGS, often include offering utilization alternatives for processing byproducts, decreasing manufacturing costs, and improving final product biodegradability. But, the applicability of a specific biomaterial must first be determined before it can be used in an actual manufacturing process. In addition, its compatibility with specific polymers and resins must be determined before it can be used economically in these processes. Therefore, the objective of this study was to determine mechanical and physical properties of plastics filled with ethanol manufacturing coproducts, using both experimental and theoretical modeling approaches.

Materials and Methods

Experimental

Test specimens were made from phenolic resin and DDGS by compression molding. The experimental setup for the molding process is shown in Figure 1; Figure 2 provides details of the mold itself.

Figure 1. Experimental compression molding test equipment

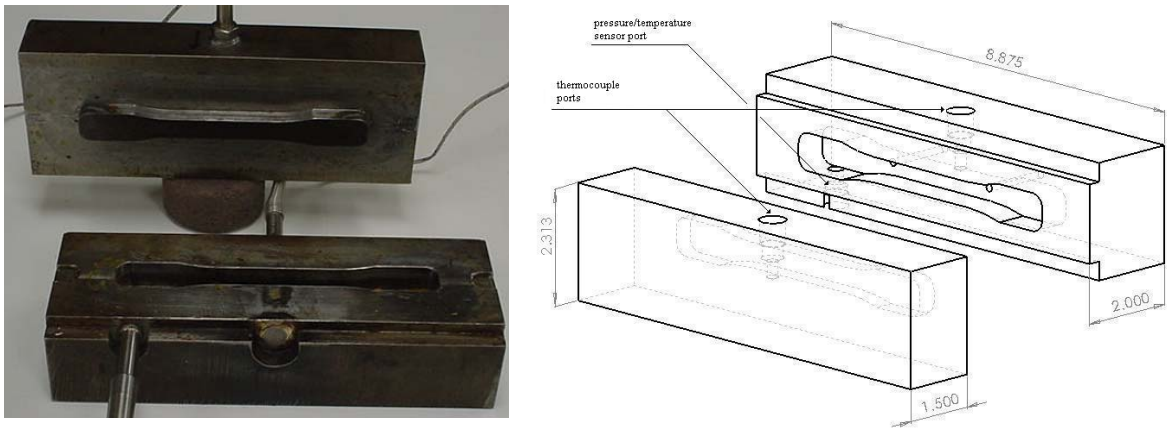

Figure 2. Details of the experimental mold (all dimensions in inches)

The phenolic resin (Type 14043, Plastics Engineering Company, Sheboygan, WI) was in powder form and consisted of 91.5% phenolic with 8.5% curing agent (hexamethylenetetramine). The powder was weighed and mixed with appropriate quantities of DDGS in a small (3 ounce) plastic container; it was then stirred for 90 seconds. Each test specimen required approximately 0.5 oz of the blend for molding. Prior to molding, both mold halves were thoroughly cleaned to remove any debris from previous runs, and release wax was coated onto both halves to prevent the specimen from sticking after molding. The specimens were molded at a pressure of 3.7 tons/in^2 with temperatures between 330 and 335 ^{o}F for 30 minutes. Pressure and temperature data were recorded every five minutes during processing. Because of the moisture content in the DDGS, with perhaps the presence of other volatile chemicals, it was necessary to begin the molding process with the mold and platens at room temperature (i.e., cold molding). After molding was complete, the specimens were removed and conditioned in a constant humidity/temperature chamber for at least 48 hours at 70 to 77 ^{o}F and 45 to 55 % relative humidity prior to tensile testing, as required by ASTM D638-03, "Standard Test Method for Tensile properties of Plastics" [32].
After equilibration, width and thickness in the narrowed (i.e., break) region were measured using a vernier calipers, and cross-sectional area was determined for each specimen. For each tensile test, approximately 100 data points (consisting of tensile force and corresponding elongation) were collected until the specimen failed.

Model Development

To study the elastic and viscoelastic behavior of the plastics and predict some of the resulting important mechanical properties, a finite-element analysis (FEA) was carried out. Although most of these properties can be obtained through experimentation, the elastic-plastic transition behavior in plastics is not easily studied under experimental conditions only, hence a need for theoretical modeling. In addition to validating experimental findings, the theoretical prediction of these properties can shorten the cycle time for determining optimum filler quantities that will maximize the resulting composite properties.

A finite element model of the experimentally molded specimens was created using ANSYS™ software. Preliminary results from tensile tests indicated that the composite material was very brittle but exhibited linear deformation in its elastic state. Thus the model was developed using a SOLID 95 element, using an elastic material, with linear stress-strain characteristics. Because we are considering a thermosetting plastic with granular additives, behavior is fairly uncertain. SOLID 95 elements permit irregular shapes, and its 20 nodes allow for any spatial orientation. The meshed model is shown in Figure 3. Models of pure resin (0% DDGS), 25% DDGS, and 50% DDGS were tested with simulated loads of up to 50 lb_f.

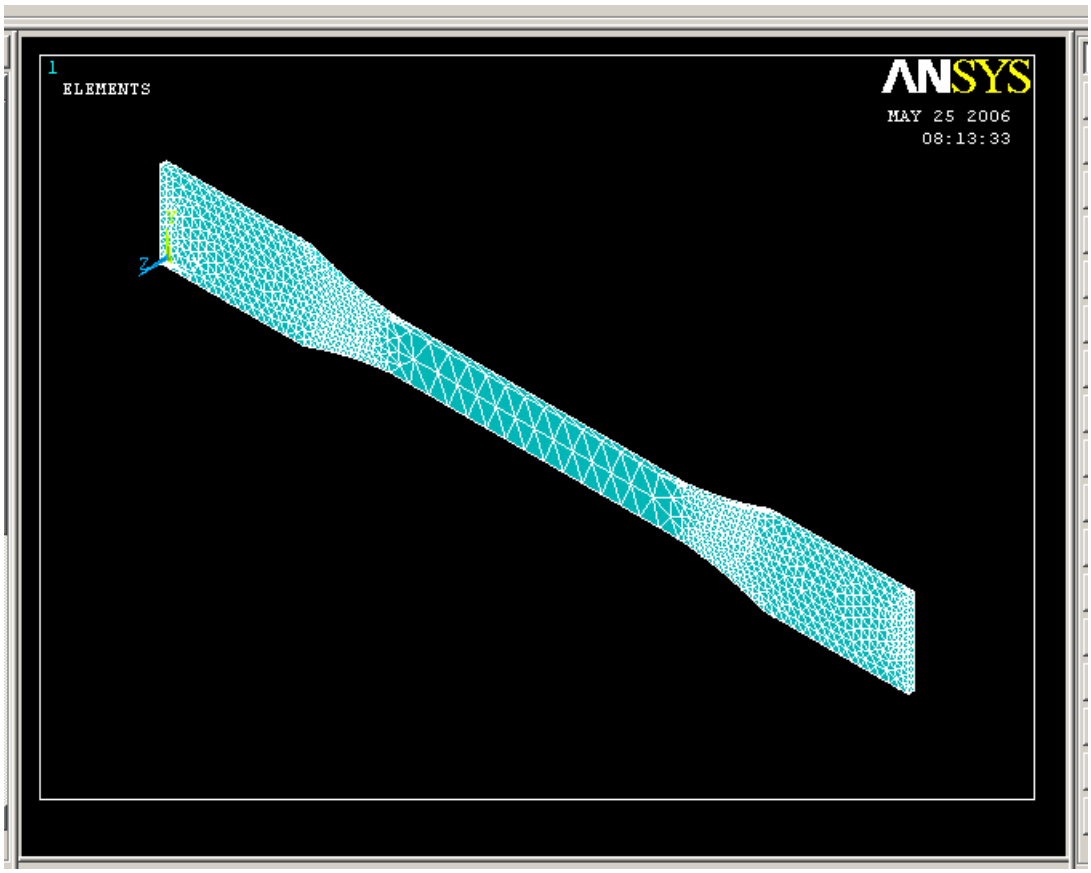

Figure 3. FEA model of the tensile test specimen

Results and discussion

Experimental

Results of the tensile tests for pure resin (0% DDGS), 25% DDGS, and 50% DDGS are shown in Figures 4 through 6, respectively. Based on these data, the Young's Modulus for each blend was determined; this information is summarized in table 1. As the inclusion of DDGS increased, both the stress at failure and the Young's Modulus progressively decreased. At 25% addition, the maximum achievable stress reduced by 39.6% compared to that of the pure resin, while at 50% addition, the maximum stress was reduced by 44.2%. The addition of 50% DDGS to the resin resulted in a decrease in stiffness (as quantified by Young's Modulus) by 26.6% compared to pure resin. Addition of 25% DDGS, on the other hand, reduced stiffness by only 3.1%. At 25% inclusion, elongation at failure was reduced by 39.2%, while at 50% inclusion, the elongation was reduced by only 24.8%.

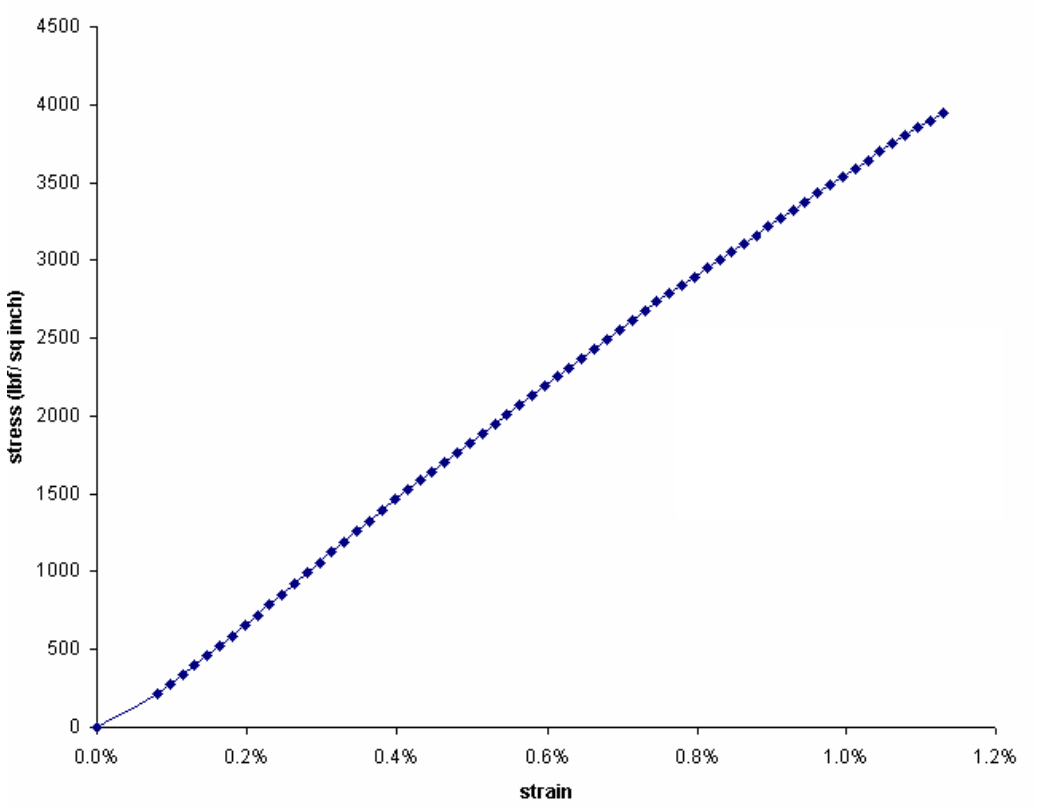

Figure 4. Experimental stress-strain curve for 0% DDGS (pure resin) test specimen

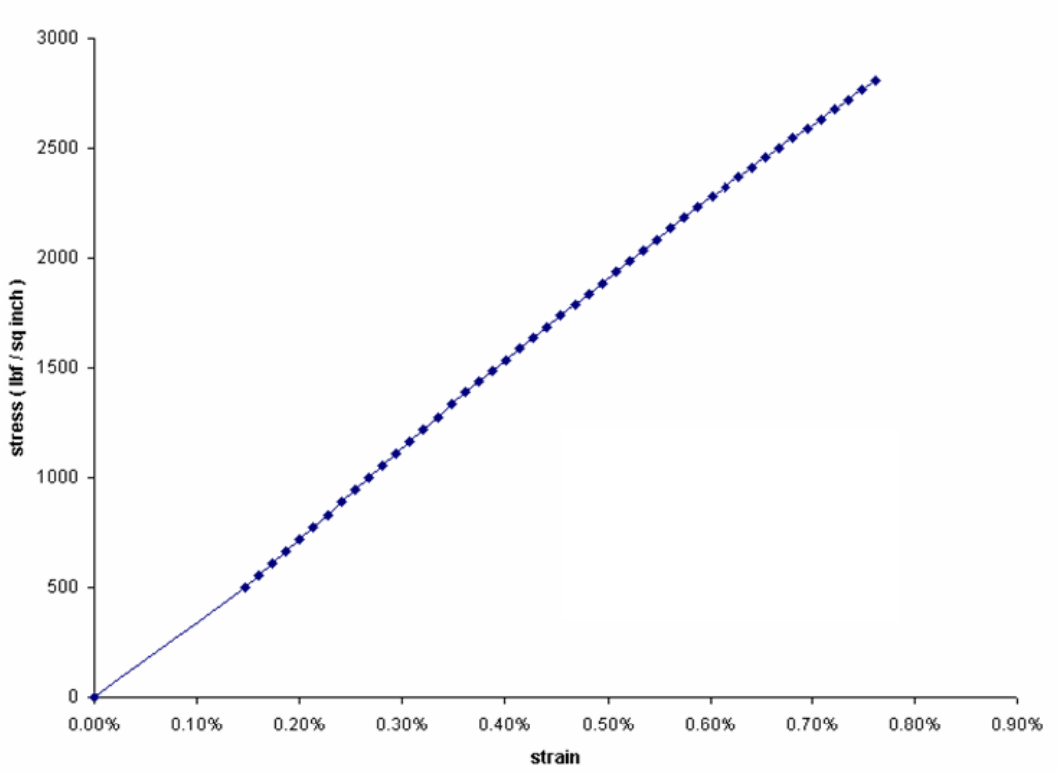

Figure 5. Experimental stress-strain curve for 25% DDGS test specimen

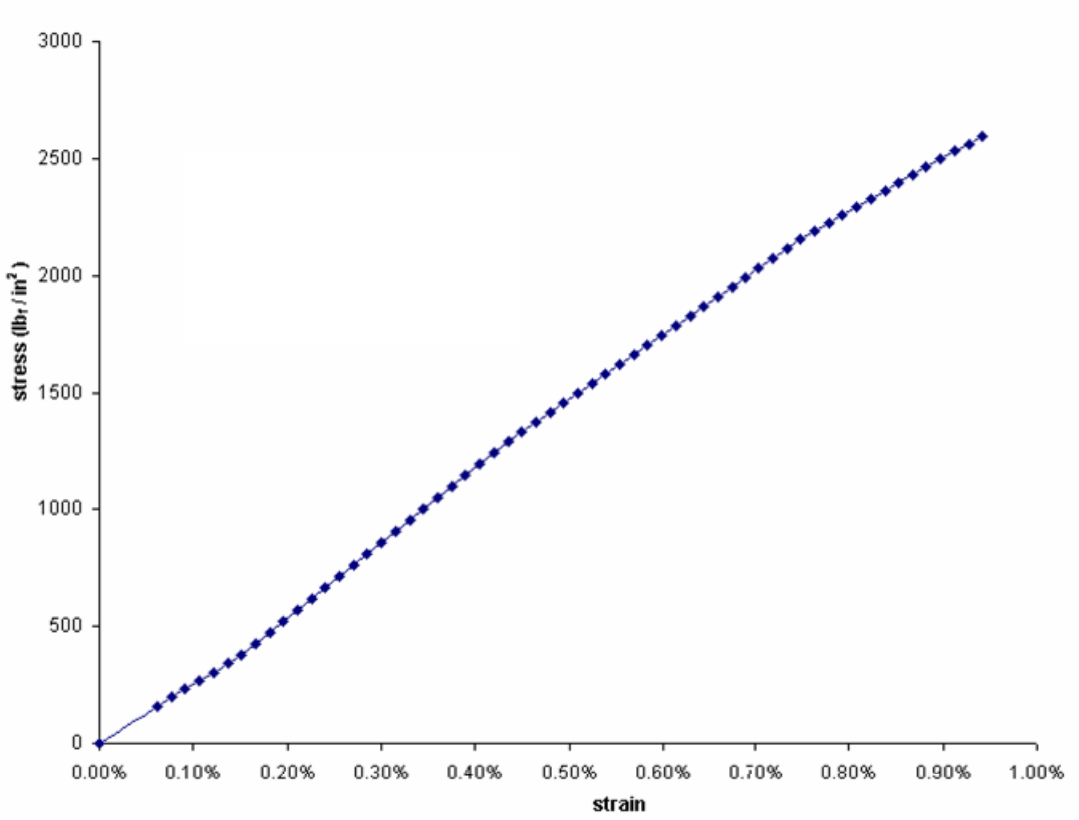

Figure 6. Experimental stress-strain curve for 50% DDGS test specimen

Material	Stress at failure (psi)	Young's Modulus (psi)	Elongation at failure (%)
Pure resin	4654	388490	1.25
25% DDGS	2809	376344	0.76
50% DDGS	2598	285305	0.94

Table 1. Results of experimental tensile tests

Simulation

The simulated stress distribution for pure resin, shown in Figure 7, indicates large values as high as 13,000 psi can occur. These are due to stress concentration factors at the curvature and at some of the constrained corner nodes. The maximum stress and strain are averages of the values of the center elements used in the FEA. The plots of the nodal solutions showing simulated strain distributions for pure resin, 25% DDGS, and 50% DDGS, are shown below in Figures 8, 9, and 10, respectively. As these results indicate, strain experienced by the specimens increased as the inclusion of DDGS increased. Based on these graphical outputs, Table 2 summarizes the numerical results of the predicted strain data for these specimens. Comparing simulated with actual results, it appears that the model was fairly accurate. Predicted strain results differed from actual values from 3.8 to 4.7%., which is quite good when examining model effectiveness. Future modifications to the model may reduce these differences.

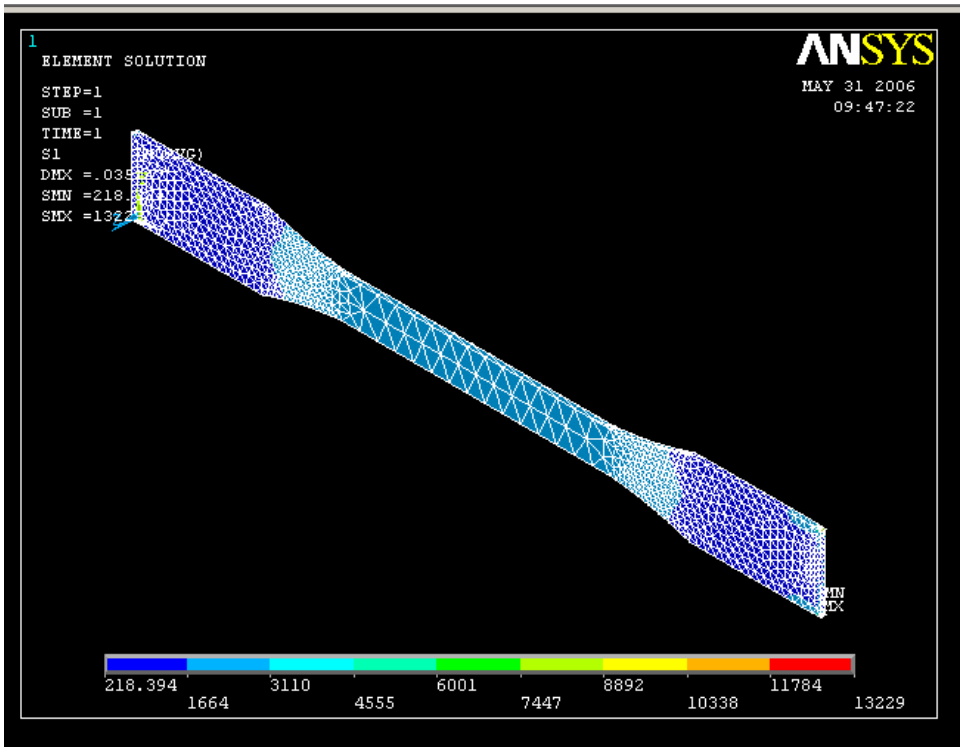

Figure 7. Plot of the tensile stress distribution for pure resin (0% DDGS)

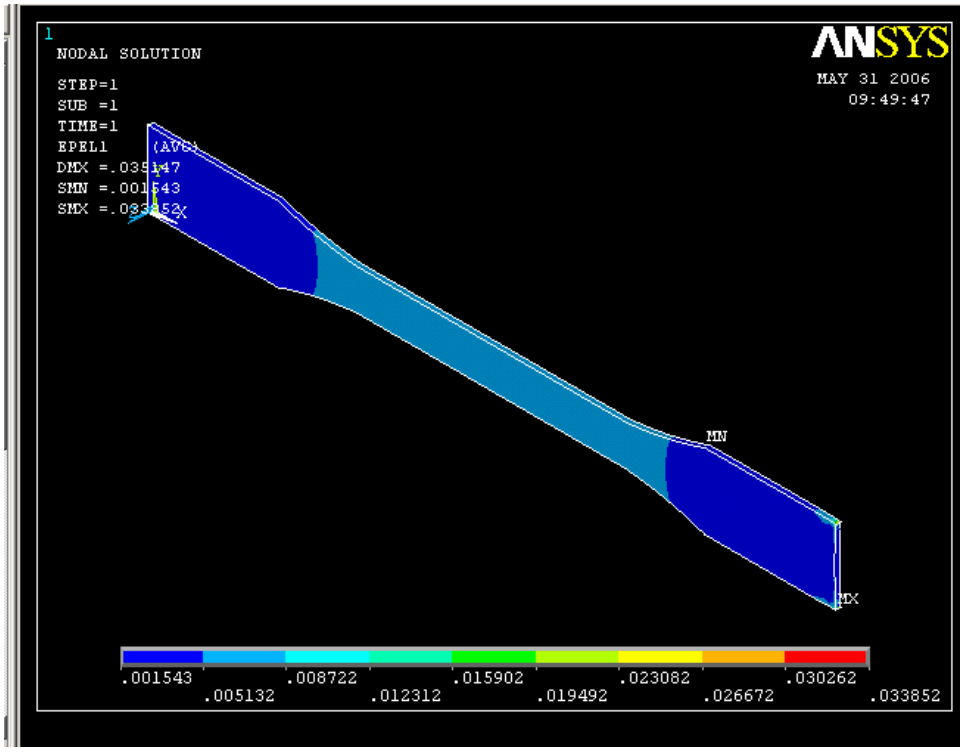

Figure 8. Plot of simulated strain distribution for 0% DDGS (pure resin)

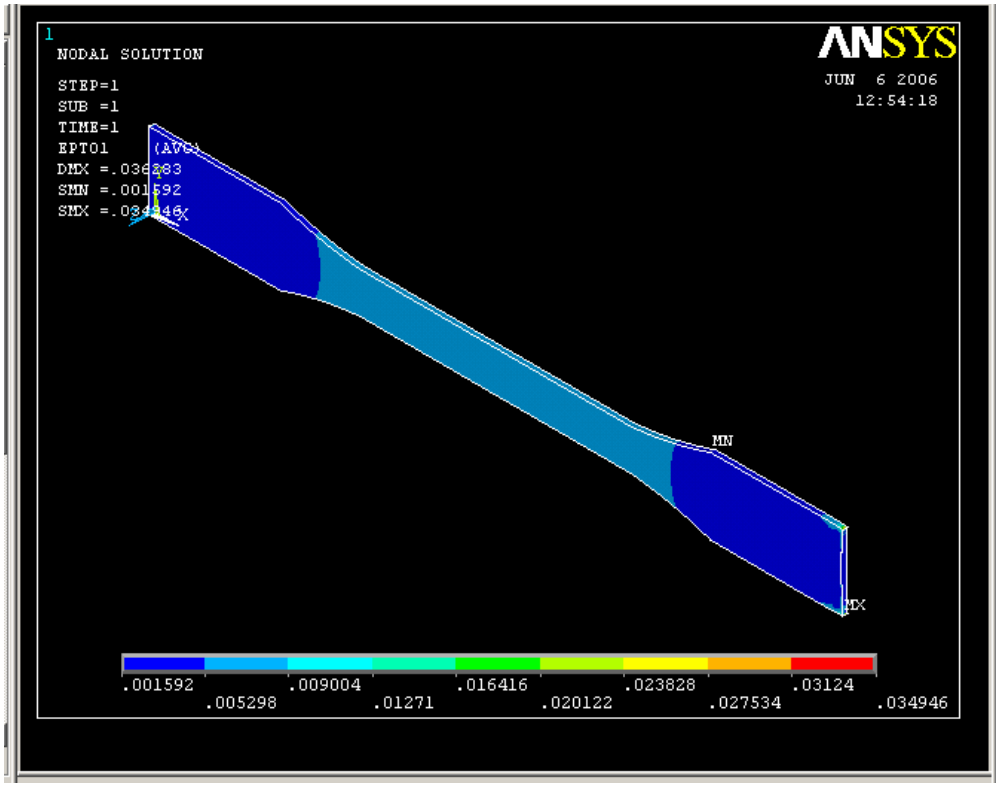

Figure 9. Plot of simulated strain distribution for 25% DDGS

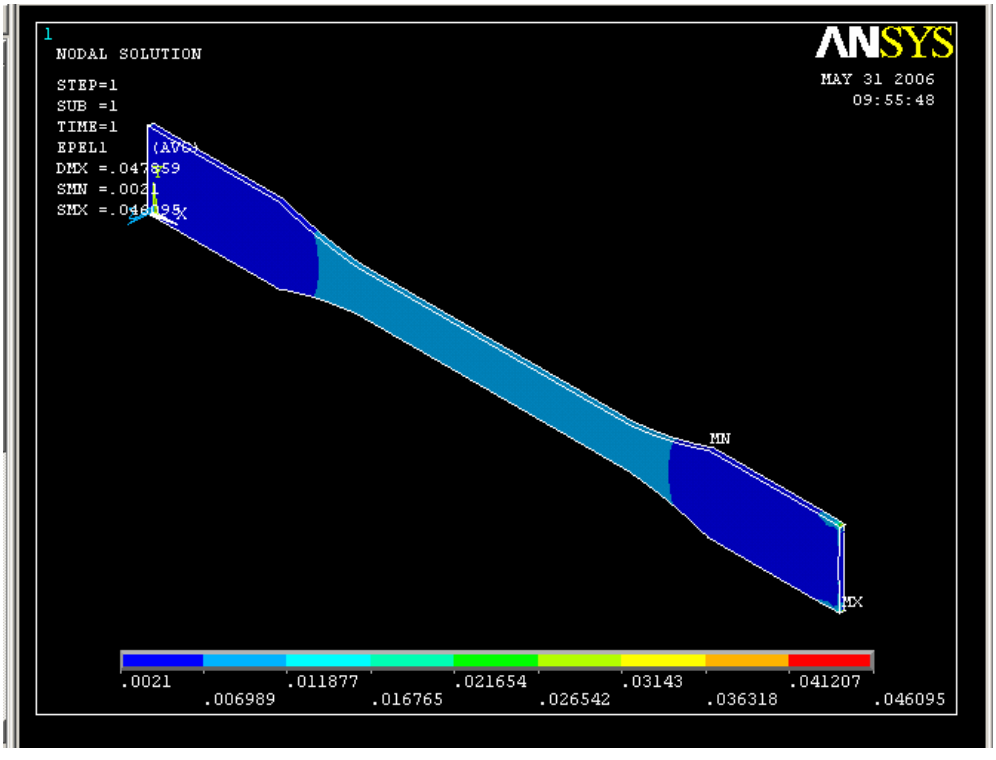

Figure 10. Plot of simulated strain distribution for 50% DDGS

Material	Stress (psi)	Strain (%)		Difference (%)
		FEA	Experimental	
Pure resin	2609	0.671	0.70	4.14
25% DDGS	2609	0.724	0.76	4.74
50% DDGS	2609	0.914	0.95	3.79

Table 2. Results of the finite element modeling at simulated loads of 50 lb_f

Conclusions

From the experimental results, it appears that addition of DDGS to phenolic resin will reduce the ultimate tensile strength of the composite materials. Ductility, on the other hand, was not as drastically reduced as much as the strength. Addition at 25% significantly dropped the ductility of the material compared to 50% DDGS. Theoretical results show a similar pattern. Given that the material was modeled as a linear elastic material, the results should be treated with caution. Although more studies are required to study the properties of these composite materials, these initial results show that DDGS may be a promising filler for plastic materials.

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Biographies

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