

Synthesis and Characterization of Highly Flexible Thermoplastic Films from Cyanoethylated Corn Distillers Dried Grains with Solubles

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ABSTRACT: Corn distillers dried grains with solubles (DDGS) can be made into highly flexible thermoplastic films without the need for plasticizers. DDGS is an abundantly available coproduct of ethanol production that is inexpensive (\$80–130/ton) compared to most of the polymers used for thermoplastic applications. In this research, oil-and-zein-free DDGS was cyanoethylated using acrylonitrile, and cyanoethylation conditions were optimized to obtain high percent weight gain of up to 42%. Cyanoethylated DDGS was characterized using ¹H NMR, FTIR, DSC, and TGA. Cyanoethylated DDGS was compression molded into thermoplastic films, and the tensile properties of the films were studied. It was found that DDGS films with elongation as high as 38% and strength of 14 MPa could be obtained without the use of any plasticizers. Alternatively, films with strength as high as 651 MPa but with relatively low elongation (2.5%) were obtained by varying the extent of cyanoethylation. This research showed that cyanoethylation could be a viable approach to develop biothermoplastics from biopolymers for applications such as packing films, extrudates, and resins for composites.

KEYWORDS: DDGS, cyanoethylation, thermoplastics, flexible, films

INTRODUCTION

Efforts to develop biodegradable thermoplastics from biopolymers such as starch, cellulose, and plant proteins have met with limited success mainly due to the poor properties and high cost of the products developed.^{1,2} Biothermoplastics developed from natural polymers have low elongations and are considerably brittle, which restricts the use of biothermoplastics for applications such as films for food packing and adhesives that require good elongation. Attempts have been made to improve the flexibility of the biothermoplastics developed from natural polymers.^{3–6} The use of plasticizers, blending with synthetic polymers, and chemical modifications are some of the common approaches used to improve the mechanical properties including flexibility of biothermoplastics.^{3–6} Although incorporating plasticizers makes the biothermoplastics flexible, plasticizers considerably decrease the mechanical properties, especially under high humidity or aqueous conditions.^{6,7} For instance, silk films without glycerol had tensile strength of 58 MPa and elongation of 2.1%, but the strength decreased to 9.4 MPa and the elongation increased to 15% with 20% glycerol.⁶ The wet strength of the silk films with 20% glycerol was only 2.7 MPa, but the elongation was 177%.⁶ Similarly, blending with synthetic polymers raises concerns on the compatibility, may not provide good properties, and could also make the products less biodegradable. Therefore, it is necessary to develop methods that can provide biothermoplastics with good mechanical properties at low cost without affecting the inherent advantages of the biopolymers. For example, attempts have been made to develop binary and ternary blends of synthetic biopolymers and starch to utilize the inherent advantages of each polymer.⁸

Chemical methods are commonly used to modify biopolymers such as cellulose and starch to develop various thermoplastic

products. Acetylation is a common approach to develop biothermoplastics because acetylation is simple and inexpensive and provides good properties to the product.³ In addition to acetylation, other chemical modifications such as etherification have also been used to make biopolymers thermoplastic and suitable for developing various products.

Cyanoethylation using acrylonitrile is one of the most common methods of etherification due to the relatively low cost, simplicity, and ability of acrylonitrile to provide the desired properties to products.⁹ Cellulose in bamboo was modified using poly(acrylonitrile) to obtain cyanoethylated cellulose with a degree of substitution of 2.2.⁹ Similarly, sugar cane bagasse was cyanoethylated to develop thermoplastic films. It was reported that cyanoethylated bagasse could be pressed into films above 140 °C.¹⁰ The effect of reaction conditions on the degree of substitution and reaction efficiency of starch modified with acrylonitrile was studied by Hebeish.¹¹ A highest degree of substitution of 1.2 and reaction efficiency of 40% were obtained by optimizing the reaction conditions.¹¹ In addition to cellulose and starch, casein proteins were also modified by grafting acrylonitrile, and the grafted product was used to develop films.¹² Acrylonitrile has also been grafted to chitosan to develop films and fibers.¹³ The above reports suggest that carbohydrates and proteins can be modified using acrylonitrile and that the modified polymers can be used to develop biothermoplastics.

The recent increase in the production of biofuels has led to the availability of carbohydrate- and protein-containing coproducts

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in large quantities at low cost. Corn distillers dried grains with solubles (DDGS) contains high amounts of proteins (25–30%) and carbohydrates (35–50%).¹⁴ The proteins and carbohydrates in DDGS can be chemically modified and used to develop biotermoplastic products. Chemically modified (carboxymethylation, glutaration, maleiation, phthallation, and succination) DDGS was blended with soy protein isolates and used to develop thermoplastics.¹⁵ In another report, DDGS was mixed with phenolic resin and wood glue for prototyping applications.¹⁶ Similarly, DDGS was mixed with polypropylene to develop plastic fiber composites.¹⁷

However, chemical modification of DDGS is challenging because DDGS is a mixture of carbohydrates and proteins. The conditions reported in the literature to modify carbohydrates in DDGS may damage proteins, whereas the protein modification conditions may not provide the desired level of modification to the carbohydrates. For instance, cyanoethylation of cellulose is performed under alkaline conditions at temperatures of 40–60 °C, which could hydrolyze the proteins in DDGS.⁹ Therefore, it is necessary to develop cyanoethylation conditions for DDGS that cause minimal damage to the proteins and carbohydrates and at the same time provide the desired level of thermoplasticity to be able to develop thermoplastic products from DDGS with good properties. In this research, conditions of cyanoethylation of DDGS were optimized and the modified DDGS was used to develop thermoplastic films. The effect of cyanoethylation conditions on the properties of the films was also studied.

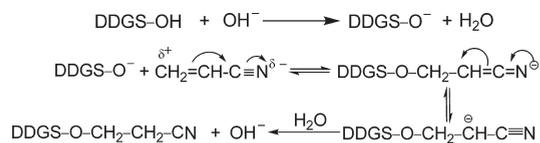
MATERIALS AND METHODS

Materials. DDGS was supplied by Abengoa BioEnergy Corp. located in York, NE. Chemicals such as acrylonitrile and sodium hydroxide required for chemical modification were purchased from VWR International, Bristol, CT. All chemicals were used as received without any further treatment or purification.

Methods. *Preparation of Oil-and-Zein-Free DDGS.* The DDGS was powdered in a laboratory-scale Wiley mill to pass through a 20 mesh dispenser to facilitate better reaction with the chemicals. The oil and zein in the powdered DDGS were extracted because oil and zein are expensive and could be used for other high-value applications. Oil and zein were extracted from DDGS using a novel procedure developed in our previous research.¹⁴ Briefly, DDGS was treated with anhydrous ethanol in a Soxhlet extractor to remove oil until the DDGS was colorless. The DDGS obtained after removal of the oil was treated again with 70% ethanol (4:1 ethanol to DDGS ratio) and 0.125% sodium sulfite on weight of DDGS at pH 2 at 70 °C for 30 min to remove zein. The extracted zein was collected and the oil-and-zein-free DDGS washed using 70% ethanol to remove any residual zein and later with hot water to remove any soluble substances. The oil-and-zein-free DDGS had an approximate composition of 31.6% hemicellulose, 26.4% cellulose, 22.5% protein, 8.6% starch, and ash and lignin accounting for the remaining constituents, based on the composition of unmodified DDGS and the oil and zein obtained after extraction. The amount of cellulose and hemicellulose in the oil-and-zein-free DDGS was determined in terms of the acid detergent (ADF) and neutral detergent fiber (NDF) according to AOAC method 973.18. Lignin in the samples was determined as Klason lignin according to ASTM standard D1106-96, and ash was determined according to ASTM standard E1175-01.¹⁸

Cyanoethylation of Oil-and-Zein-Free DDGS. Cyanoethylation of the oil-and-zein-free DDGS was performed using acrylonitrile and sodium hydroxide as both the swelling agent and catalyst. The reaction between carbohydrates and proteins (DDGS–OH) in oil-and-zein-free DDGS and acrylonitrile in the presence of sodium hydroxide is believed

Scheme 1. Possible Reaction between Acrylonitrile and the Hydroxyl Groups in Oil-and-Zein-Free DDGS under Alkaline Conditions^a



^a DDGS–OH represents the hydroxyl groups in the carbohydrates and proteins in DDGS.

to be a typical nucleophilic addition reaction. The possible mechanism of the reactions between acrylonitrile and the hydroxyl groups in the carbohydrates and proteins in DDGS is given in Scheme 1. Scheme 1 represents the reaction between the hydroxyl groups in the carbohydrate (cellulose, hemicellulose, starch) and proteins and acrylonitrile. The reaction between the acrylonitrile and the hydroxyl groups in DDGS results in the formation of the cyanoethylated DDGS.

To perform the cyanoethylation, an aqueous solution of sodium hydroxide (with a concentration of 1, 5, 10, 15, or 20% (w/w)) was added into dried oil-and-zein-free DDGS in a 1:1 weight ratio with continuous stirring at room temperature for 30 min. Later, a specified amount of acrylonitrile ranging from 1:1 to 10:1 acrylonitrile to DDGS weight ratio was added. The cyanoethylation was completed by heating the mixture containing DDGS, acrylonitrile, and sodium hydroxide for a specified time ranging from 30 to 180 min at the specified temperature ranging from 10 to 50 °C. At the end of the reaction, the products formed were added into 50% ethanol to precipitate the products by neutralizing with hydrochloric acid (20% v/v). The precipitate obtained was first washed with ethanol and then thoroughly washed with distilled water, followed by absolute ethanol, and finally dried in an oven at 50 °C for 12 h.

The amount of acrylonitrile consumed during the reaction was determined by titrating the double bonds in acrylonitrile using potassium bromate. Acrylonitrile containing 30% aqueous sodium hydroxide was heated at 70 °C for 1 h. After heating, the amount of double bonds was determined and compared to the number of bonds before treatment. It was found that <2% of acrylonitrile was consumed during the reaction.

Percent Weight Gain. Percent weight gain values, which describe the percent increase in the weight of cyanoethylated DDGS compared to the weight of unmodified DDGS, were obtained to quantitatively determine the efficiency of cyanoethylating the DDGS. The modified DDGS was thoroughly washed to remove chemicals and soluble impurities and then later dried in an oven at 50 °C until constant weight was obtained. The percent weight gain values were calculated according to the formula

$$\% \text{ weight gain} = ((W_{\text{mod}} - W_{\text{unmod}}) / W_{\text{unmod}}) \times 100$$

where W_{unmod} was the initial oven-dried weight of the oil-and-zein free DDGS before chemical modification and W_{mod} was the oven-dried weight of the modified samples.

Fourier Transform Infrared (FTIR). FTIR spectra of the unmodified oil-and-zein-free DDGS and cyanoethylated DDGS were collected on an attenuated total reflectance ATR spectrophotometer (Nicolet 380; ThermoFisher, Waltham, MA). DDGS samples were placed on a germanium plate, and 64 scans were collected for each sample at a resolution of 32 cm^{-1} .

Nuclear Magnetic Resonance. ¹H NMR spectroscopy was used to analyze the cyanoethylated DDGS. The cyanoethylated DDGS samples were dissolved in DMSO-*d*₆, and the concentration of DDGS was adjusted to 20–30 mg/mL for ¹H NMR measurements. ¹H NMR spectra were recorded at 40 °C using a Bruker Advance DRX-600 spectrometer operating at 600 MHz with standard Bruker programs (Bruker, Billerica, MA). Chemical shifts were reported using DMSO-*d*₆ (δ_{H} 2.50) as an internal reference. ¹H NMR spectra were recorded at

313 K using a Bruker Advance DRX-600 (Bruker, Billerica, MA) spectrometer operating at a proton frequency of 600.18 MHz ($B_0 = 14.5$ T). Typically, 64 scans were collected into 64K data points over a spectral width of 12376 Hz with a relaxation delay of 5 s, an acquisition time of 2.6 s, and 90° flip angle. All free induction decays (FID) were multiplied by an exponential function with a 1 Hz line broadening factor prior to Fourier transformation (FT). The spectra were phase corrected interactively using TOPSPIN. Baseline correction was carried out manually using each time the appropriate factors. Chemical shifts were reported using DMSO- d_6 (δ_H 2.50) as an internal reference.

Thermal Analysis. Thermogravimetric analysis (TGA) was performed on the unmodified and cyanoethylated DDGS with an instrument (Perkin-Elmer STA 6000, Norwalk, CT) calibrated with nickel. Samples (18–26 mg) were placed under nitrogen atmosphere and heated from 50 to 650 °C at a heating rate of 20 °C min^{-1} . A Mettler Toledo (model DSC822^e) DSC was also used to study the thermal behavior of the acetylated products. Samples (about 10 mg) were placed in the DSC and heated at a rate of 20 °C min^{-1} and were held at 50 °C for 10 min to remove moisture in the samples. The samples were then heated to 160 °C at a rate of 20 °C min^{-1} .

Developing Thermoplastics. The unmodified oil-and-zein-free DDGS and DDGS obtained after cyanoethylation were compression molded in a Carver (Wabash, IN) press to evaluate their thermoplasticity and potential for various applications. Samples were heated at 150 °C for 2 min under a pressure of 275 MPa. The press was cooled by cold running water, and the films formed were collected.

Properties of Thermoplastic DDGS Films. The DDGS films were conditioned for at least 24 h at 21 °C and 65% relative humidity. The films were tested for their tensile properties according to ASTM standard 882 on an MTS (Q test 10) tensile tester using a gauge length of 2 in. and a crosshead speed of 10 mm/min. At least five samples were tested for each condition, and the average \pm one standard deviation is reported.

Statistics. All of the experiments were repeated three times unless specified. The data reported are the mean \pm one standard deviation. Fisher's least significant difference (LSD) was used to test the effect of various conditions on the properties of products using SAS (SAS Institute Inc., Cary, NC). Statistical significance was considered at $p < 0.05$.

RESULTS AND DISCUSSION

Effect of Reaction Time on Percent Weight Gain. The effect of increasing reaction time on percent weight gain is illustrated in Figure 1. As seen from the figure, increasing time from 30 to 120 min continuously increased the percent weight gain. There was no significant increase in percent weight gain when the reaction time was increased above 120 min, indicating that the reaction had reached equilibrium. The highest percent weight gain obtained was approximately 35% when the reaction was carried out for 120 min with a reaction temperature of 40 °C. At short reaction times, the acrylonitrile was unable to penetrate and cyanoethylate the DDGS efficiently. However, long reaction times are not preferable for industrial production. Therefore, a reaction time of 120 min was chosen to optimize other cyanoethylation conditions.

Effect of Reaction Temperature on Percent Weight Gain. Figure 2 shows the effect of increasing reaction temperature on the percent weight gain of cyanoethylated DDGS. The percent weight gain of DDGS after reaction at 10 °C for 120 min was only 5.7%, much lower than the percent weight gain obtained at higher temperatures. The percent weight gain increased substantially to 25% when the reaction temperature was increased from 10 to 20 °C. Further increase in reaction temperature

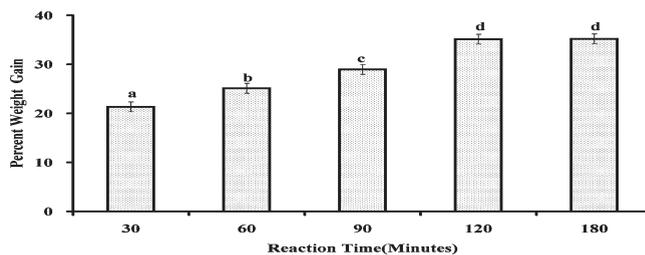


Figure 1. Effect of reaction time on percent weight gain of product obtained after cyanoethylation. The cyanoethylation was carried out at a temperature of 40 °C, an acrylonitrile DDGS ratio of 5:1, and a sodium hydroxide concentration of 10%. Data points with the same letters indicate that they were not statistically different from each other.

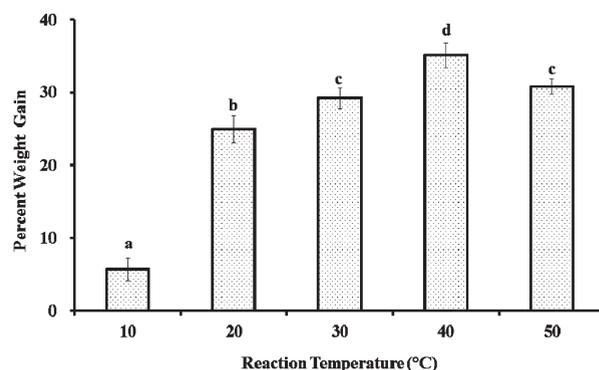


Figure 2. Effect of reaction temperature on percent weight gain of cyanoethylated DDGS. The cyanoethylation was carried out for 120 min with an acrylonitrile to DDGS ratio of 5:1 and a sodium hydroxide concentration of 10%. Data points with the same letters indicate that they were not statistically different from each other.

steadily increased the percent weight gain. The highest percent weight gain obtained was 35% at a temperature of 40 °C. Temperatures above 40 °C decreased the percent weight gain as seen from Figure 2. At low temperatures (10–30 °C), the reaction time of 120 min was insufficient to provide high percent weight gain as seen from Figure 2. However, higher percent weight gains could be obtained even at lower temperatures if the reaction was carried out for sufficient time (<120 min). The reaction between acrylonitrile and DDGS was exothermic and, therefore, the percent weight gain decreased at high temperatures.

Effect of Concentration of Sodium Hydroxide on Percent Weight Gain. Low ratios (1 and 5%) of sodium hydroxide provided low percent weight gain, but increasing the alkali concentration to 10% substantially increased percent weight gain to about 35% as seen from Figure 3. Further increasing the alkali concentration to 15% increased the percent weight gain to 42%. However, the percent weight gain decreased to 36% when the concentration of alkali was 20%. Alkali acted as a catalyst and increased the rate of reaction. At low concentrations, there was not enough alkali to accelerate the reaction, and we therefore observed low percent weight gain. An alkali concentration between 10 and 15% seemed to be the most optimum to obtain high percent weight gain. Cyanoethylation is a competitive reaction that occurs between acrylonitrile and the functional groups in DDGS and also between acrylonitrile and the hydroxyl groups in water. Initially, the reaction with DDGS was more favorable and we therefore observed an increased percent weight gain with increase in concentration of sodium hydroxide. After a

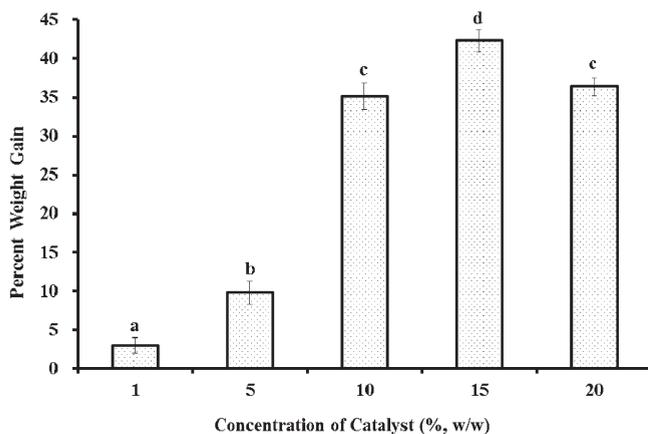


Figure 3. Effect of concentration of sodium hydroxide on percent weight gain of DDGS obtained after cyanoethylation. The cyanoethylation was carried out at 40 °C for 120 min with an acrylonitrile to oil-and-zein-free DDGS ratio of 5:1. Data points with the same letters indicate that they were not statistically different from each other.

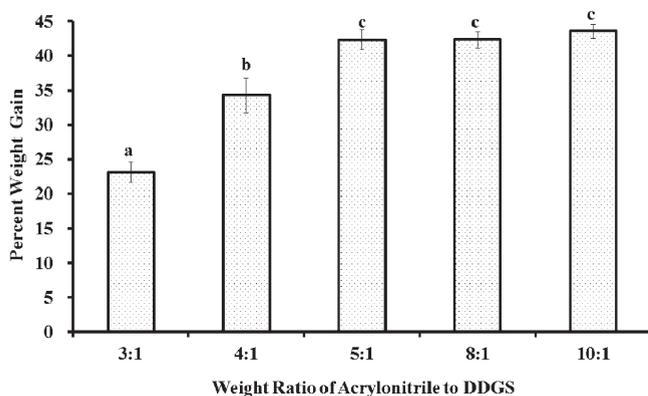


Figure 4. Effect of weight ratio of acrylonitrile to DDGS on the percent weight gain. The cyanoethylation was carried out at 40 °C for 120 min with a sodium hydroxide concentration of 15%. Data points with the same letters indicate that they were not statistically different from each other.

certain level of cyanoethylation of DDGS, the acrylonitrile reacts predominantly with the hydroxyl groups in water, resulting in lower availability of acrylonitrile for cyanoethylation of DDGS. Therefore, the percent weight gain decreased at high concentrations of sodium hydroxide.

Effect of Acrylonitrile to DDGS Ratio on Percent Weight Gain. The effect of increasing the weight ratio of acrylonitrile to DDGS on the percent weight gain of cyanoethylated DDGS is depicted in Figure 4. Increasing the ratio of acrylonitrile above 3:1 increased the weight gain up to a ratio of 5:1. The percent weight gain obtained increased substantially to 34% and then to 42% when the ratio of acrylonitrile to DDGS was increased to 4:1 and 5:1, respectively. However, the percent weight gain did not show any considerable increase above an acrylonitrile ratio of 5:1. At low amounts of acrylonitrile (3:1), the amount of acrylonitrile available was not sufficient to adequately cyanoethylate DDGS. Therefore, the percent weight gain obtained was low. At an acrylonitrile concentration of 5:1, most of the available hydroxyl groups had reacted, and we therefore did not see any increase in percent weight gain when the ratio of acrylonitrile was increased above 5:1.

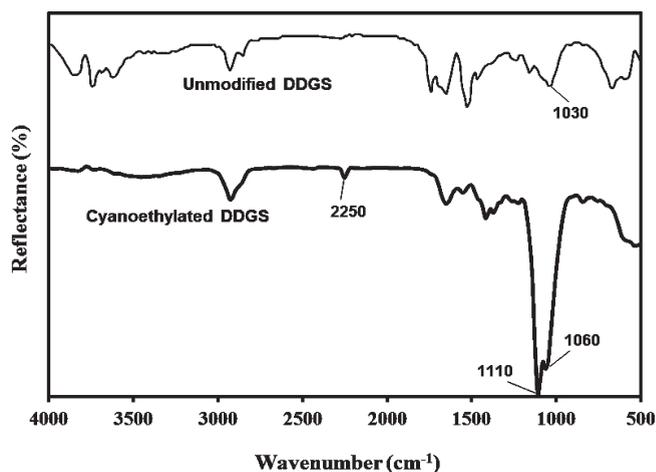


Figure 5. Infrared spectrum of unmodified DDGS and cyanoethylated DDGS with 42% weight gain.

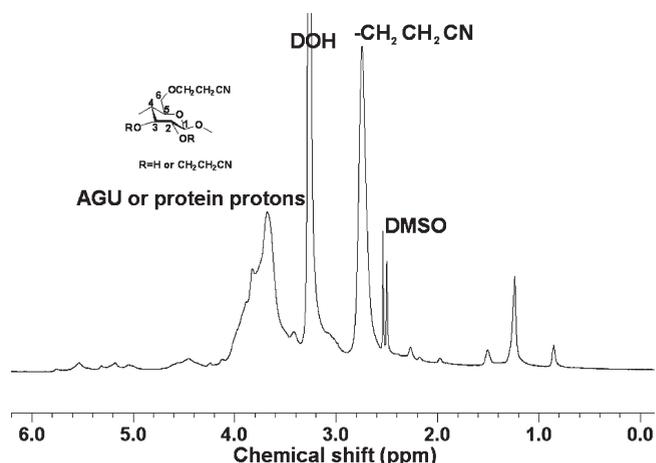


Figure 6. ^1H NMR spectrum of the cyanoethylated DDGS.

Confirming Cyanoethylation of DDGS. FTIR spectra of the cyanoethylated and unmodified DDGS are shown in Figure 5. The cyanoethylated DDGS had much stronger absorption peaks compared to the unmodified DDGS in the region of 1000–1100 cm^{-1} . The unmodified DDGS had a small peak at 1030 cm^{-1} , whereas the modified DDGS showed two peaks at 1060 and 1110 cm^{-1} that are due to the COC stretching in the cyanoethylated DDGS. Another absorption peak attributed to the stretching of nitrile groups was seen at about 2250 cm^{-1} for the modified DDGS but was not apparent in the unmodified DDGS. Broad peaks seen around 3500 cm^{-1} for the cyanoethylated and unmodified DDGS are due to the unreacted hydroxyl groups in DDGS and the hydroxyl groups in water absorbed by DDGS. The ^1H NMR spectrum of the cyanoethylated DDGS is shown in Figure 6. In the spectra, signals due to cyanoethylated methylene protons δ 2.6–2.9 appeared separately, indicating the cyanoethylation of DDGS.^{19,20} The presence of the two additional peaks in the FTIR spectrum (1110 and 2250 cm^{-1}) and the appearance of the peaks due to the methylene protons in the ^1H NMR spectrum indicated cyanoethylation of DDGS.

Thermal Analysis. TGA curves in Figure 7 showed that cyanoethylation provided better thermal stability to DDGS up to a temperature of 290 °C compared to unmodified DDGS. However, the weight loss of cyanoethylated DDGS increased

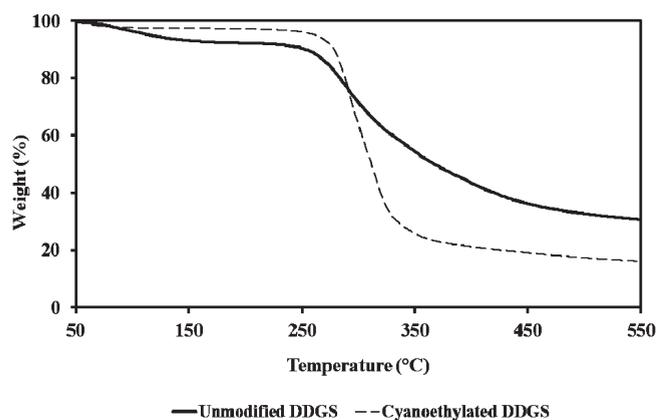


Figure 7. Comparison of the thermogravimetric curves for unmodified DDGS and cyanoethylated oil-and-zein-free DDGS with 42% weight gain.

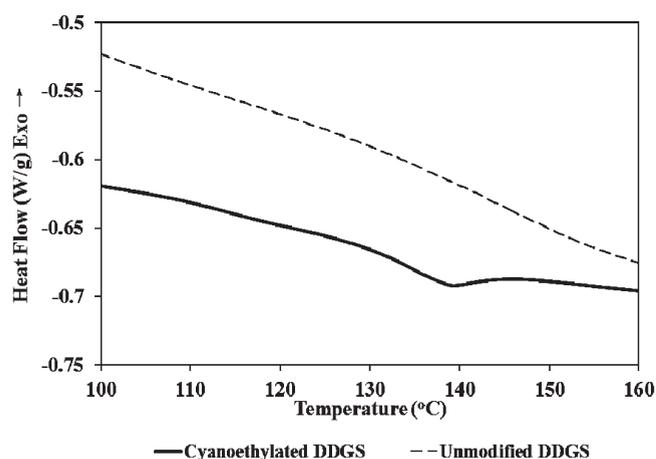


Figure 8. DSC thermogram of unmodified and cyanoethylated DDGS with a weight gain of 42%.

sharply above 290 °C. Modified DDGS had a weight loss of 86% at 550 °C compared to 70% for unmodified DDGS. Cyanoethylated DDGS was more stable under heat, and it therefore had lower weight loss up to 290 °C. However, the cyanoethylated DDGS showed higher final weight loss than the unmodified DDGS because the cyanoethylated DDGS contained lesser amounts of ash and minerals that remained after the samples had been burned at 550 °C. DSC analysis showed that the cyanoethylated DDGS had a small melting peak at about 140 °C, whereas the unmodified DDGS did not show any peak as seen from Figure 8.

Biothermoplastics from DDGS. Figure 9 shows a digital image of DDGS before and after cyanoethylation. The unmodified compression molded DDGS (A) did not melt and was loosely compacted after compression molding, whereas the cyanoethylated DDGS formed thin transparent films (B), indicating good thermoplasticity. Table 1 shows the properties of thermoplastic DDGS films prepared with various levels of cyanoethylation. As seen from the table, the properties of the DDGS films varied considerably with increasing ratio of acrylonitrile to DDGS used. At low ratios of acrylonitrile to DDGS, the films had high strength, as high as 651 MPa, and modulus as high as 3.5 GPa, but relatively low elongation (1.9–2.5%). This was mainly due to the nonthermoplastic part of DDGS that acted as reinforcement and provided high strength and modulus. Also, the DDGS had relatively poor flexibility due to the



Figure 9. Digital image of DDGS without modification (A) and transparent thermoplastic film (B) developed from the cyanoethylated DDGS.

Table 1. Properties of Cyanoethylated DDGS Films Prepared at Various Concentrations of Acrylonitrile^a

ratio of acrylonitrile to DDGS	peak stress, MPa	breaking elongation, %	modulus, MPa
2:1	462 ± 81	1.9 ± 0.6	3327 ± 382
3:1	651 ± 95	2.5 ± 0.6	3536 ± 292
4:1	20 ± 3	40 ± 3	125 ± 26
5:1	16 ± 3	44 ± 56	62 ± 16

^aThe films were compression molded at 150 °C for 2 min.

low degree of cyanoethylation, making the films brittle and with low elongation. Increasing the ratio of acrylonitrile to DDGS to 4:1 substantially decreased the strength and modulus but increased the elongation by >15 times. Further increase in the ratio of acrylonitrile to 5:1 decreased the strength and modulus even more, whereas the elongation increased to 44%.

Etherification using acrylonitrile added bulky side groups (C≡N) onto DDGS. The ether linkage with three carbons made DDGS films flexible by allowing the polymers to slide easily under strain. At low ratios of acrylonitrile, there was insufficient acrylonitrile, and therefore the films had low elongation. Increasing the ratio of acrylonitrile to DDGS to 4:1 and above provided good cyanoethylation, and therefore the films had high elongation. However, the high flexibility decreased the tensile strength because adjacent molecules were able to slide easily and could not share the load. The variation in the properties of the films with changing ratio of acrylonitrile indicated that the properties of the films could be controlled by varying the conditions of cyanoethylation and compression molding. An acrylonitrile to DDGS ratio of 4:1 was found to provide the most optimum strength and elongation to the films.

Although the DDGS films with high acrylonitrile had relatively low strength, the strength of the DDGS films was higher than that of films previously developed from other biopolymers. Table 2 provides a comparison of the properties of DDGS films with similar films developed from various biopolymers. As seen from the table, DDGS films had much higher strength than any other film, whereas the wheat gluten and acetylated soy protein films had much higher breaking elongation than the DDGS films. However, high amounts of glycerol were used in the wheat gluten films. Starch acetate films had low elongation even after using 20% glycerol because carbohydrates are relatively inflexible compared to proteins. It should be noted that the DDGS films had an elongation of 39.5% with a strength of 19.7 MPa, higher than any of the films in Table 1, when cyanoethylated with an acrylonitrile to DDGS ratio of 4:1. The elongation of the DDGS could be further increased by modifying the cyanoethylation conditions or by using plasticizers. Comparison of the properties

Table 2. Comparison of the Properties of the DDGS Films Developed in This Research to Some Common Biothermoplastic Films Reported in the Literature

type of film	peak stress, MPa	breaking elongation, %	ref
silk fibroin + 20% glycerol	9.4 ± 1.6	15 ± 11	6
wheat gluten + 0.62 mol glycerol/mol of amino acid acetylated soy protein	4.2 ± 0.8	179 ± 46	7
starch acetate + 20% glycerol	1.8–2.5	73–113	21
cianoethylated DDGS	10.2 ± 1.3	2.4	22
	20 ± 3	40 ± 3	this paper

of the films indicated that cyanoethylated DDGS could be a better alternative to obtain flexible films with good strength than the films developed from common biopolymers.

This research demonstrated that cyanoethylated DDGS can be made into thermoplastic films with high flexibility and strength without the need for plasticizers. Optimum conditions for cyanoethylation of DDGS were temperature of 40 °C, time of 120 min, acrylonitrile to DDGS ratio of 5:1, and 15% alkali based on the weight of DDGS. Both ¹H NMR and FTIR confirmed cyanoethylation of DDGS. The cyanoethylated DDGS could be compression molded into films at 150 °C, close to the melting point seen from DSC curves. DDGS films developed had tensile strength ranging from 15.9 to 651 MPa and elongation ranging from 1.9 to 44% depending on the extent of cyanoethylation. The DDGS films had much higher strength even at high elongation compared to films developed from various biopolymers. Etherification with acrylonitrile added bulky side groups onto DDGS and made the DDGS more flexible, providing good elongation to the films. Because no plasticizers were necessary, the cyanoethylated films can be expected to retain their properties at high humidity and temperatures. Cyanoethylation can overcome the low tensile strength and brittleness problems associated with thermoplastics developed from biopolymers and could be a viable approach to the development of useful thermoplastic products from various biopolymers.

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REFERENCES

- Cho, Y. S.; Rhee, C. Sorption characteristics of soyprotein films and their relation to mechanical properties. *Lebensm.-Wiss. -Technol.* **2002**, *35*, 151–157.
- Sun, S.; Mitchell, R. J.; MacNaughtan, W.; Foster, J. T.; Harabagiu, V.; Song, Y.; Zheng, Q. Comparison of the mechanical of cellulose and starch films. *Biomacromolecules* **2010**, *11*, 126–132.
- Ifuku, S.; Morooka, S.; Morimoto, M.; Saimoto, H. Acetylation of chitin nanofibers and their transparent nanocomposite films. *Biomacromolecules* **2010**, *11*, 1326–1330.
- Russo, R.; Malinconico, M.; Santagata, G. Effect of cross-linking with calcium ions on the physical properties of alginate films. *Biomacromolecules* **2007**, *8*, 3193–3197.

(5) Godbole, S.; Gote, S.; Latkar, M.; Chakrabarti, T. Preparation and characterization of biodegradable poly-3-hydroxybutyrate–starch blend films. *Bioresour. Technol.* **2003**, *86* (1), 33–37.

(6) Mangavel, C.; Rossignol, N.; Perronnet, A.; Barbot, J.; Popineau, Y.; Gueguen, J. Properties and microstructure of thermo-pressed wheat gluten films: a comparison with cast films. *Biomacromolecules* **2004**, *5*, 1596–1601.

(7) Lu, S.; Wang, X.; Lu, Q.; Zhang, X.; Kluge, A. J.; Uppal, N.; Omenetto, F.; Kaplan, L. D. Insoluble and flexible silk films containing glycerol. *Biomacromolecules* **2010**, *11*, 143–150.

(8) Sarazin, P.; Li, G.; Orts, J. W.; Favis, D. B. Binary and ternary blends of polylactide, polycaprolactone and thermoplastic starch. *Polymer* **2008**, *49* (2), 599–609.

(9) Khullar, R.; Varshney, V. K.; Naithani, S.; Soni, P. L. Study of the influence of reaction conditions for production of cyanoethylcellulose from cellulosic material from bamboo. *J. Nat. Fibers* **2008**, *5* (2), 138–147.

(10) Hassan, L. M.; El-Wakil, A. N.; Sefain, Z. M. Thermoplasticization of bagasse by cyanoethylation. *J. Appl. Polym. Sci.* **2001**, *79*, 1965–1978.

(11) Hebeish, A.; Khalil, M. I. Characterization of the reaction products for starch and acrylonitrile. *Starch/starke* **1988**, *40*, 104–107.

(12) Somanathan, N.; Sanjeevi, R. Effect of temperature on the mechanical properties of casein-g-poly(acrylonitrile) films. *Eur. Polym. J.* **1994**, *30* (12), 1425–1430.

(13) Lv, P.; Bin, Y.; Li, Y.; Chen, R.; Wang, X.; Zhao, B. Studies on graft copolymerization of chitosan with acrylonitrile by the redox system. *Polymer* **2009**, *50* (24), 5675–5680.

(14) Xu, W.; Reddy, N.; Yang, Y. An acidic method of zein extraction from DDGS. *J. Agric. Food Chem.* **2007**, *55* (15), 6279–6284.

(15) Schilling, C. H.; Tomasik, P.; Karpovich, D. S.; Hart, B.; Shepardson, S.; Garcha, J.; Boettcher, P. T. Preliminary studies on converting agricultural waste into biodegradable plastics, part I: corn distillers' dry grain. *J. Polym. Environ.* **2004**, *12*, 257–264.

(16) Cheesbrough, V.; Rosentrater, K.; Visser, J. Properties of distillers grains composites: a preliminary investigation. *J. Polym. Environ.* **2008**, *16*, 40–50.

(17) James, L. J.; Gurram, S.; Stokke, D. D.; Heath, H. G.; Muthukumarappan, K. Mechanical properties of biorenewable fiber/plastic composites. *J. Appl. Polym. Sci.* **2004**, *93*, 2484–2489.

(18) Xu, W.; Reddy, N.; Yang, Y. Extraction, characterization and potential applications of cellulose in corn kernels and distillers dried grains with solubles. *Carbohydr. Polym.* **2009**, *76* (4), 521–552.

(19) Xie, H.; King, A.; Kilpelainen, I.; Granstrom, M.; Argyropoulos, D. S. Thorough chemical modification of wood-based lignocellulosic materials in ionic liquids. *Biomacromolecules* **2007**, *8* (12), 3740–3748.

(20) Nakayama, E.; Azuma, J. I. Substituent distribution of cyanoethyl cellulose. *Cellulose* **1998**, *5* (3), 175–185.

(21) Bonacucina, G.; Di, M. P.; Piombetti, M.; Colombo, A.; Roversi, F.; Palmieri, G. F. Effect of plasticizers on properties of pregelatinised starch acetate (Amprac 01) free films. *Int. J. Pharm.* **2006**, *313*, 72–77.

(22) Foulk, A. J.; Bunn, M. J. Properties of compression-molded, acetylated soy protein films. *Ind. Crops Prod.* **2001**, *14*, 11–22.