Journal of Polymers and the Environment, Vol. 12, No. 4, October 2004 (© 2004)

Preliminary Studies on Converting Agricultural Waste into Biodegradable Plastics, Part I: Corn Distillers' Dry Grain

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Distillers' dry grain (DDG) was derivatized either by carboxymethylation, glutaration, maleiation, phthallation, or succination in order to produce anionic materials suitable for complexation with soy protein isolate. Infrared spectroscopy confirmed that derivatization of DDG by all reagents was successful. Blending of derivatized anionic products with soy protein resulted in instant precipitation of gels. The gels were centrifuged, molded, and dried into solid pellets with tensile strengths as high as 1.67 MPa, suggesting that these materials could be promising as biodegradable structural materials. Infrared spectroscopy suggested the possibility of complexes forming between soy protein isolate and each of the derivatized DDG samples.

KEY WORDS: Anionic polysaccharides; polysaccharide–protein complexes; biodegradable plastics; distiller's grain.

INTRODUCTION

Derived from petroleum feedstocks, two hundred billion pounds of plastics were manufactured globally in the year 2002, 40% of which came from the US [1]. US consumption of these plastics grew from 44 billion tons in the year 1986 to 85 billion tons in the year 2001, representing an increase of approximately 49%. Most of these plastics are used for disposable packaging, which represents the fastest growing component of the municipal solid waste stream in the US: 4 billion pounds discarded in the year 1970, 60 billion pounds in the year 2002 (about half a pound per person each day). Petroleum-derived plastics biodegrade slowly and persist for many years after landfilling. Satisfactory landfill sites are becoming scarce, and alternative disposal methods are limited. Several authors provide excellent reviews of this subject [1–4].

In order to address these problems, a growing number of manufacturers are currently producing biodegradable polymers, which are derived from organic plant matter and can be safely disposed by the enzymatic action of microorganisms such as bacteria, fungi, and algae [3]. Target markets include consumer items having a short-use lifetime (e.g., packaging, hygeine products). Worldwide production of biodegradable plastics grew five-fold between the years 1996 and 2001. There is ample room for market growth, as global production of biodegradable plastics in the year 2001 was approximately 8% of that of petroleum-derived plastics in the same year [3].

At the present time, market growth for these new materials is slowed by high costs inherent in the

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1566-2543/04/1000-0257/0

sophisticated chemical processes (e.g., distillation, microbial fermentation) that are used to produce most of today's commercially-available biodegradable polymers. Technological breakthroughs are needed to make altogether new types of biodegradable plastics from less expensive chemical processes. Ideally, these new processes would rely on cheap and abundant biomass feedstocks that are considered by-products or waste products from industrial sources. For example, the US currently generates 500 billion pounds of lignocellulosic wastes annually, including 200 billion pounds of corn stover, 120 billion pounds of paper mill waste, and 75 billion pounds of urban tree residue [1].

In order to address this problem, several researchers have conducted laboratory experiments to produce biodegradable solids from inexpensive polysaccharide feed stocks including wood cellulose, hemi cellulose from straw, grass, leaves, fruits and vegetables, and starch from cereals and tubers [5–19]. Other researchers have demonstrated the feasibility of making biodegradable plastics either from soy protein or from complexes of proteins with polysaccharides [20–27].

Protein complexation with polysaccharides requires the latter to be anionic [28, 29]. There are several papers published on complexes of protein with anionic polysaccharides including potato starch [30–32], pectins [33–35], carageenans [36, 37], xanthan gum [38, 39] and carboxymethylcellulose [40–42]. It has been proven that interactions between proteins and those anionic polysaccharides involved mainly electrostatic interactions but also random covalent bonding between proteins and polysaccharides. In another two papers, milk casein was complexed with either potato starch [43] or cornstarch (Najgenauer et al., submitted) ionized by phosphation. The same type of electrostatic and covalent interactions was proven in those papers, and biodegradability of resulting complexes was also demonstrated.

The following series of four papers reports a set of procedures to synthesize anionic polysaccharide — protein compounds from a variety of polysaccharide by-products (corn ethanol distiller's grain, corn cob, sawdust, and sugar beet pulp) anionized by different methods including carboxymethylation, oxidation, or acylations [44–46]. Our intent is to produce biodegradable solids from simple, aqueous, economical, and environmentally-safe methods that rely on abundant, low cost biomass feedstocks usually considered by-products or waste products from industrial sources. Having the look and feel of hard plastic or wood, these solids appear to have promise as strong, lightweight, biodegradable structural materials. Potential applications include furniture, architectural panels, temporary landscaping structures, and fugitive patterns to replace wood and polystyrene foam in composite molding applications.

The first paper in this series focuses on distillers' dry grain (DDG), which is a voluminous by-product of corn ethanol production: approximately one kg of DDG residue is generated per kg of ethanol produced. Significant growth in the worldwide production of DDG is anticipated as a result of rapid growth in the mass production of corn-derived ethanol for transportation fuel. Because of its composition [47–50], DDG is mainly marketed as animal feed [51]. It can also be incorporated into human snack food [52–54] and spaghetti [55]. One publication reports a non-nutritional application of DDG as an extender and thickener in urea–formaldehyde plywood adhesives [56].

Our approach entails loosening of the compact structure of DDG by soaking in an aqueous sodium hydroxide solution followed by acylation with either maleic-, succinic-, phthallic-, or glutaric-anhydride. Alternatively, carboxymethylation with sodium chloroacetate was performed. The proportions of reagents in this study were arbitrarily selected based on previous studies showing that highly anionic polysaccharides provide weak and brittle solids, whereas polysaccharides with randomly distributed anionic centers (a low degree of derivatization) provide strong, elastic compounds [29].

EXPERIMENTAL

Materials

DDG, containing 88.38% dry matter with 30% crude protein, 12% crude fiber, 11.5% crude fat and 5.38% ash, was provided by the manufacturer (Dakota Commodities Incorporated Scotland, South Dakota, USA). As-received DDG powder was pulverized in a kitchen blender prior to experimentation.

The following reagant grade chemicals were purchased from the manufacturer: glutaric, maleic, phthalic, and succinic anhydrides as well as sodium chloroacetate (Aldrich, Milwaukee, Wisconsin, USA). Soy protein isolate (066-974, PRO-FAM 974) was kindly provided by the manufacturer (Protein Specialties Division, Archer Daniels Midland Company, Decatur, Illinois, USA) and contained 6% moisture, 90% protein, 5% total fat, and 5% ash according to the manufacturer.

Procedures

Acylation

DDG powder (5 g) was suspended in either 0.1 or 1.0 M aq. NaOH solution (50 mL) and agitated for 24 h at room temperature in a closed flask. Subsequently, deionized water (125 mL) and 0.1 mole of one of the following acyl anhydrides was admixed to each suspension at room temperature: glutaric-, maleic-, phthallic-, and succinic-anhydride. The reaction mixture was subsequently agitated for 24 h in a sealed flask at room temperature, followed by room-temperature centrifugation (30 min at 6000 rpm). Supernatants were decanted and the resulting centrifuge cakes were dried in air at 50°C.

Carboxymethylation

DDG powder (5 g) was suspended in deionized water (175 mL) at room temperature, and solid NaOH (4.5 g) was subsequently added. The reaction mixture was agitated for 6 h at room temperature in a closed flask, followed by the addition of sodium chloroacetate (0.1 mole). The reaction mixture was subsequently agitated for 12 h in a sealed flask at room temperature, followed by room-temperature centrifugation (30 min at 6000 rpm). Supernatants were decanted and the centrifuge cakes were dried in air at 50°C.

Reactions of Derivatized DDG with Soy Protein Isolate

Aqueous Solution Approach

Soy protein isolate (5 g) was dissolved in deionized water (100 mL), and derivatized DDG (5 g) was admixed at room temperature. The reaction mixture was agitated for 24 h in a closed container at room temperature, followed by room-temperature centrifugation (30 min at 6000 rpm). Centrifugation was chosen as a simple, rapid, method of consolidating slurries in the laboratory. Supernatants were decanted and the resulting centrifuge cakes were transferred with a spatula into a pellet mold placed on a flat ceramic surface at room temperature. The mold consisted of a flat acrylic sheet (8 mm thickness) perforated with an array of individual holes (12.5 mm diameter). The filled mold was subsequently dried in air at room temperature for 24 h. Moist pellets were then transferred to an oven and dried in air at 50°C. Ten pellets were prepared from each reaction product for subsequent mechanical property measurements.

Control sample pellets were also made by the above centrifugation, molding, and drying procedures. The following control formulations were used to prepare individual centrifuge cakes: (1) DDG powder (5 g) suspended in deionized water (50 mL) and agitated for 24 h at room temperature; (2) DDG powder (5 g) suspended in 1.0 M aq. NaOH solution (50 mL) and agitated for 24 h at room temperature; (3) formulation (2) above subsequently derivatized by each of the acylation and carboxymethylation procedures described above; (4) soy protein isolate (5 g) dissolved in deionized water (100 mL) and agitated for 24 h; (5) sample (1) above subsequently mixed with sample (4) above for 24 h at room temperature; and (6) sample (2) above subsequently mixed with sample (4) above for 24 h at room temperature.

Compression Approach

A separate set of pellets was prepared by mechanical compression using three types of powder: (*i*) pulverized DDG powder, (*ii*) pulverized DDG that was treated with 0.1 M aq. NaOH solution for 24 h and then air dried, and (*iii*) pulverized DDG that was derivatized by either carboxymethylation or acylations. Samples (*i*), (*ii*), and (*iii*) (3 g) were blended with soy protein isolate (3 g) and water (1 g) at room temperature and sealed in a polyethylene container for 24 h. Uniaxial compression was subsequently performed at room temperature in a cylindrical die (9.53 mm diameter) made of precision-machined stainless steel. A weighed amount of each blend was individually compressed at 1.2 GPa for 5 min using a hydraulic press (Model C Laboratory Press, Fred Carver Inc. Menomonee Falls, Wisconsin, USA).

IR Spectra

Infrared spectra were measured using a Bruker Equinox 55 (Bruker, Madison, Wisconsin, USA) FTIR spectrometer fitted with a Pike Technologies ATR attachment. Spectra were recorded with 32 scans at 4 cm^{-1} resolution at room temperature.

Differential Scanning Calorimetry

Samples were evaluated with a DSC 550E (Instrument Specialists Inc. Spring Grove, Illinois, USA) from room temperature to 250°C at a heating rate of 20°C per minute. These measurements were obtained on solid samples contained in open pans in a stream of nitrogen.

Scanning Electron Microscopy

Imaging was performed using a JSM-5400 scanning electron microscope (Jeol USA Inc., Peabody, Massachusetts, USA). Samples were gold sputtered for 5 min to reduce charging.

Mechanical Properties Tests

Tensile strengths of individual pellets were measured by the diametric compression method [57]. Individual pellets were compressed between flat compression platens in a computer-instrumented mechanical testing machine at room temperature (model 1125, Instron Corp., Canton, Massachusetts, USA). At least 10 separate specimens of each specimen composition were subjected to mechanical testing. During each test, the displacement rate of the compression platens was 5 mm / min. Load versus displacement data were computer recorded for each compression test. The fracture strength, σ_f, of each specimen was determined by the following formula [57]:

$$\sigma_f = 2P/(\pi Dt) \quad (1)$$

In this expression, P is the load at fracture, D is the pellet diameter, and t is the pellet thickness.

RESULTS AND DISCUSSION

The addition of all types of derivatized DDG to solutions of soy protein isolate immediately resulted in the precipitation of a solid reaction product having a gel-like consistency. In contrast, no reaction product precipitated after blending non-derivatized DDG with protein solution [control samples (5) and (6)].

Qualitative evaluation of the derivatization of DDG was based on IR analysis. Figure 1 represents the IR spectrum of pulverized DDG before derivatization. The spectrum, particularly in the regions of 1000–1200, 1200–1500, and 1500–1700 cm^{-1}, strongly resembled spectra of polysaccharides [30, 31, 34, 35, 41, 58]. These bands might be ascribed to C—O stretching, OH bending, and C=O stretching modes, respectively [59]. Protein present in DDG might be manifested by bands incorporated in the region of 1500–1700 cm^{-1} in Fig. 1. This is suggested from comparison of the spectrum of pulverized DDG with the spectrum of soy protein isolate in Fig. 1.

As shown in Fig. 1, soaking DDG in the aqueous solution of NaOH produced changes in the IR spectrum, particularly in the regions of 1500–1700 cm^{-1} and also at 3400 cm^{-1}. Changes are also visible in the group of intensive bands in the C—O stretching region of 1000–1200 cm^{-1} with subtle changes also in the 1200–1500 cm^{-1} region. These changes suggest that soaking in NaOH influenced the hydroxyl groups in the polysaccharide portion of DDG.

Figure 2 illustrates changes in the IR spectrum of DDG after reaction with glutaric anhydride. Particularly the C=O stretching vibrations between 1500 and 1600 cm^{-1} increased in intensity relative to the rest of

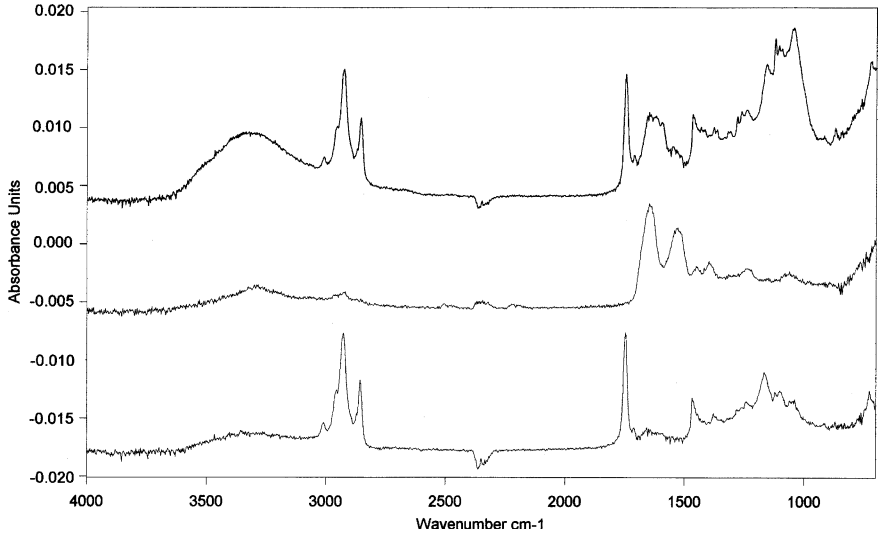

Fig. 1. Infrared spectra of original DDG (top), original soy protein isolate (center), and DDG soaked in aqueous solution of NaOH (bottom).

the spectrum, and the C—O stretching region changed slightly. This is possibly due to the addition of specific C=O vibrations from the addition of glutaric anhydride. Similar changes were observed in IR spectra of DDG resulting from other acylating agents (not shown). Upon mixing glutarated DDG with soy protein, further changes in the IR spectrum occurred (Fig. 2). In particular, the protein C=O bands appeared in the region of 1500–1700 cm^{-1}. Furthermore, the band at 1750 cm^{-1} disappeared; this band can be attributed to an acid or ester C=O stretch and its disappearance may indicate reaction of those groups to other forms. Subtle changes in the group of vibrations corresponding to the C—O stretch (1000–1200 cm^{-1}) and O—H bend (1200–1500 cm^{-1}) of the hydroxyl groups may also suggest interaction of these groups with protein. These results support the hypothesis that glutarated DDG powder complexes with soy protein. Similar changes were observed in IR spectra of DDG resulting from all other acylations (not shown).

Carboxymethylation of DDG produced changes in the entire IR spectrum (Fig. 3). Subsequent reaction of carboxymethylated DDG with soy protein isolate evoked further changes in the IR spectrum. The most significant changes again were the appearance of protein bands and the vanishing free acid or ester C=O band. These results support the hypothesis that carboxymethylated DDG powder complexes with soy protein.

Differential scanning calorimetry did not reveal significant information on the character of interactions of soy protein isolate with carboxymethylated or acylated DDG. For all samples, calorimetric diagrams presented only one main feature: a broad and shallow endothermic peak from which determination of precise parameters was difficult. For pulverized and non-derivatized DDG, the onset and peak temperatures were estimated as 91.9 and 133.4°C, respectively, and the corresponding enthalpy change was 86.68 J/g. As a rule, calorimetric measurements of all complexes of derivatized DDG with soy protein isolate showed a decrease in both the onset and peak temperatures by 10–30°C. In addition, enthalpy changes were weaker by approximately one order of magnitude.

In all specimens, centrifugation yielded supernatants that were transparent to the naked eye. In all cases, centrifuge cakes had a viscous, paste-like consistency and were easily smeared into pellet molds with a hand-held laboratory spatula. Pellets dried from all control formulations (1–6) disintegrated into powder. In contrast, hard solids were made from drying all pastes that were previously isolated from aqueous suspensions of protein mixed with derivatized DDG, regardless of the method of derivatization. This suggests the possibility of protein complexing with anionized polysaccharide.

Measurements of drying shrinkage and tensile strength are summarized in Table I. Shrinkage of carboxymethylated samples was exceedingly high, resulting in the formation of irregularly shaped, fragmented pellets that were too distorted in shape

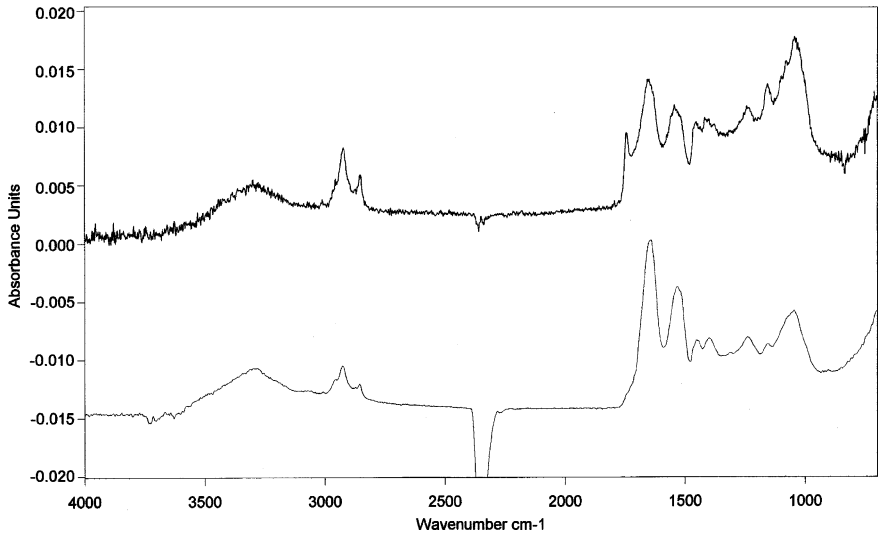

Fig. 2. Infrared spectra of DDG derivatized with glutaric anhydride (top) and the complex of glutarated DDG with soy protein isolate (bottom). The peak near 2350 cm^{-1} is due to the asymmetrical stretching vibration of CO_2, which is present as a result of the ATR attachment being exposed to the laboratory atmosphere.

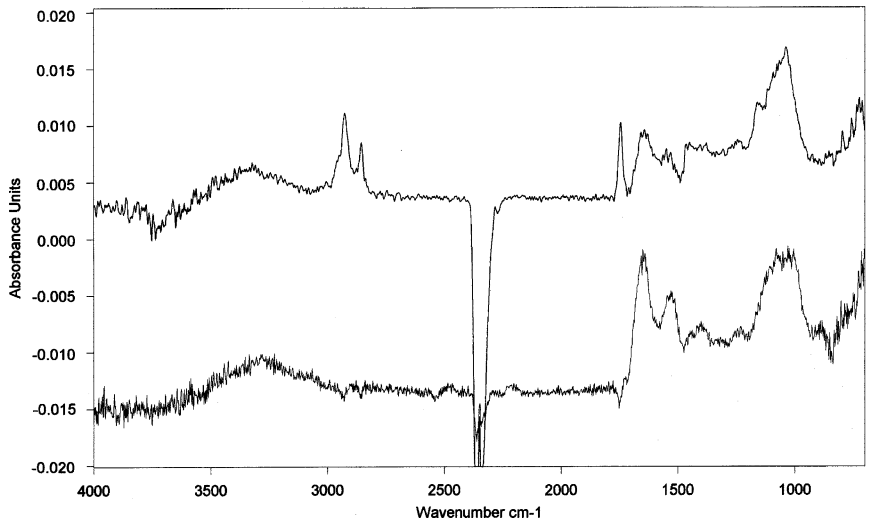

Fig. 3. Infrared spectra of carboxymethylated DDG (top) and the complex of carboxymethylated DDG with soy protein isolate (bottom). The peak near 2350 cm^{-1} is due to the asymmetrical stretching vibration of CO_2, which is present as a result of the ATR attachment being exposed to the laboratory atmosphere.

for viable measurements of shrinkage or tensile strength. Pellets that were made of protein with DDG maleiated in 1.0 M NaOH solution exhibited the highest shrinkage (29% along the diameter) and the highest tensile strength (1.67 MPa). In contrast, maleiation in 0.1 M NaOH solution led to pellets with minimum shrinkage (18% along the diameter) and minimum strength (0.22 MPa). Calculation of reagent proportions showed that in the first case there was a deficiency of NaOH in solution to provide complete acylation. Glutaration, phthallation, and succination led to pellets that were slightly weaker than pellets resulting from maleiation in 1.0 M NaOH.

Although samples maleiated at 1.0 M NaOH exhibited the highest strength of 1.67 MPa, this strength is low compared with traditional, petroleum-derived engineering plastics. For example, polytetrafluorethylene and high-density polyethylene have strengths that range between 20 and 35 MPa; butadiene-acrylonitrile and butadiene-styrene elastomers have strengths that range between 7 and 20 MPa [60]. By comparison, biodegradable soy protein plastics have been reported with strengths between 23.6 and 42 MPa [23].

Upon drying, all pellets exhibited microscopic pores of approximately 300–700 microns in size, based on optical microscopy observations. It is proven from fracture mechanics theory that microstructural pores function as stress concentrators that reduce the tensile strength of a broad range of engineering materials, including metals and plastics [61,62]. Fracture mechanics theory also proves that reducing the pore size can significantly increase

Table I. Drying Shrinkages and Tensile Strengths of Reaction Products of Soy Protein Isolate with Derivatized DDG

	Pellet dimensions after drying shrinkage[a,b]		
Derivatized DDG in complexes	Diameter (mm)	Thickness (mm)	Mean Tensile Strength[b] (Mpa)
Carboxymethylated[c]	–	–	–
Maleiated[d]	10.3 ± 0.1	6.1 ± 0.2	0.22 ± 0.0.1
Maleiated[e]	8.9 ± 0.3	4.2 ± 0.3	1.67 ± 0.7
Glutarated	9.2 ± 0.3	5.6 ± 0.3	1.39 ± 0.4
Phthallated	9.2 ± 0.2	4.4 ± 0.2	1.21 ± 0.4
Succinated	9.1 ± 0.2	4.6 ± 0.2	1.27 ± 0.4

[a]Original size of cylindrical pellets was 12.5 mm dia × 8 mm thick. [b]Standard deviation appears to the right of the ± symbol. [c]No pellets suitable for measurements could be formed because of significant shrinkage. [d]Pellets made of DDG soaked in 0.1 M aqueous NaOH solution prior to derivatization. [e]Pellets made of DDG soaked in 1 M aqeous NaOH solution prior to derivatization.

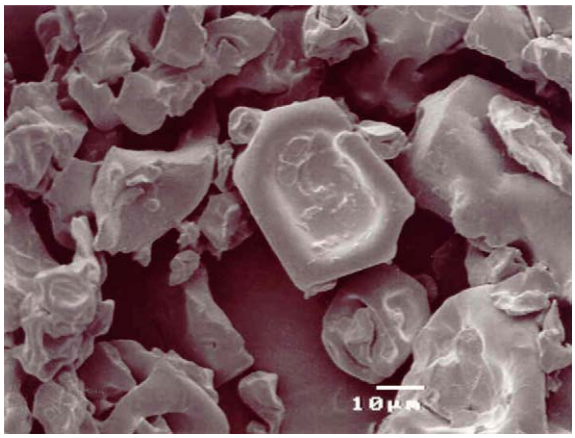

Fig. 4. Scanning electron micrograph of maleiated DDG after compression with soy protein isolate.

tensile strength. It is possible that high pressure filtration, instead of centrifugation, could consolidate gels into higher density pastes prior to drying. In turn, the formation of smaller pores during subsequent drying would be likely, thereby increasing tensile strength. There is precedent for this behavior in industrial processes involving the dewatering and subsequent drying of liquid suspensions of inorganic colloidal solids [63–65]. Additional research is needed to validate this hypothesis for the DDG-protein reaction products in this study.

Formation of complexes of derivatized DDG with soy protein isolate was also attempted by uniaxial compression at 1.2 GPa. All pellets prepared by such compression were very weak and readily disintegrated into powder. Figure 4 reveals an SEM image of grains of maleiated DDG mixed with soy protein isolate and compressed. One may observe that compression did not bond particles of the maleiated DDG – soy protein blend together. We originally hypothesized that the small amount of water added to the blend prior to compression might facilitate dissolution of soy protein isolate during subsequent compression. In this manner, we hypothesized that this solution might form adhesive pendants chemically bound to the surfaces of maleiated DDG. Figure 4 showed no evidence of such pendants.

CONCLUSIONS

Derivatization of DDG by reaction with cyclic carboxylic acid anhydrides in alkaline media proceeded successfully, based on infrared spectroscopy analysis. Blending of derivatized anionic products with soy protein resulted in instant precipitation of gels. Pellets made of these materials had low tensile strengths comparable to butadiene-styrene elastomers. The formation of complexes between soy protein isolate and each of the derivatized DDG samples was suggested by infrared spectroscopy.

ACKNOWLEDGEMENTS

The authors wish to thank the Corn Marketing Program of Michigan, the Saginaw Bay Watershed Initiative Network, and Saginaw Valley State University for supporting this research.

REFERENCES

1. E. S. Stevens (2002) *Green Plastics: An Introduction to the New Science of Biodegradable plastics,* Princeton University Press, Princeton, NJ.
2. G. Scott (1995) *Degradable Polymers*, Chapman & Hall, New York, p. 44.
3. R. A. Gross and B. Kalra (2002). *Science* **297**, 803–807.
4. Y. Poirier, D. E. Dennis, K. Klomparins, and C. Somerville (1992) *Science*, **256**, 520–622.
5. C. Okkerse and H.van Bekkum (1996) in *Starch 96* (H. van Doren and N. van Swaaj Eds.), Zestec bv/Carbohydrate Research Foundation, Chap.1.
6. H. Ruck (1996). *żywn. Technol. Jakość,* **2** (7 Suppl.) 138–157.
7. P. Tomasik, M. Pałasiński, and S. Wiejak (1989) *Adv. Carbohydr. Chem. Biochem.* **47,** 203–278.
8. P. Tomasik, S. Wiejak, and M. Pałasinski (1989) *Adv. Carbohydr. Chem. Biochem.* **47,** 279–344.
9. P. Tomasik and C.H. Schilling (1998) *Adv. Carbohydr. Chem. Biochem.* **53,** 263–343.
10. P. Tomasik and C. H. Schilling (1998) *Adv. Carbohydr. Chem. Biochem.* **53,** 345–426.
11. P. Tomasik and C. H. Schilling (2004) *Adv. Carbohydr. Chem. Biochem.* **59**.
12. P. Tomasik and M. F. Zaranyika (1995) *Adv. Carbohydr. Chem. Biochem.* **51,** 243–318.
13. A. C. Albertson and B. Ranby (1979) *J. Appl. Polym. Sci.* **35,** 413–430.
14. J. G. Batelaan and P. M. Van der Horst (2000) U.S. Patent 6, 103, 885.
15. J. A. Youngquist, A. M. Krzysik, B. W. English, H. N. Spelter, and P. Chow (1996) *Proc. Symp. The use of recycled, wood, and paper in building applications, Madison, WI., 1996*. 123–134.
16. R. M. Rowell, A. R. Sanadi, D. T. Caufield, and R. E. Jacobson (1997) *Lignocellulosic Plastic Composites* (A .L. Leao, F. X. Carvalho, and E. Frollini, Eds.), Universidad de Sao Paulo, Sao Paulo, pp. 23–51.
17. P. J. Andersen and S. K. Hodson (2001) US Patent 6, 231, 970.
18. J. A. Youngquist, B. E. English, Z. R. C. Schramer, Poo Chow, and R. S. Shooh (1998) *US Department of Agriculture, General Technical Report FPL-GTR-80*.
19. J. L.Wilett and W. M. Doane (2001) US Patent 6, 362, 256.
20. L. A. Johnson, D. J. Myers, and D. J. Burden (1992) *Inform* **3** (3), 282–290.
21. A. Satkofsky (2002) *J. Comp. Org. Recycl.* **43**(3), 61–68.
22. J. Jane and S. T. Tim (1995) *Progresss in Plant Polymeric Carbohydrate Research* (F. Meuser, D. J. Munnes, and W. Seibel, Eds.), Behr's Verlag, Hamburg, pp.165–168.
23. C. H. Schilling, T. Babcock, S. Wang, and J. Jane (1995) *J. Mater. Res.* **10,** 2197–2202.

24. J. Zhang, P. Mungara, and J. Jane (2000) *Polymer*, **42,** 2569–2578.
25. I. Pateau, C. A. Chen, and J. Jane (1994) *Ind. Eng. Chem. Res.* **33,** 1821–27.
26. J. Jane and S. Zhang (1995) U.S. Patent 5, 710, 190.
27. J. Jane and K. Spence (1995) U.S. Patent 5, 397, 834.
28. S. K. Samant, R. S. Singhal, P. R. Kulkarni, and D. V. Rege (1993) *Int. J. Food Sci. Technol.* **28**, 547–562.
29. C. Schmitt, C. Sanchez, S. Desobry-Banon, and J. Hardy (1998) *Crit. Rev. Food Sci. Nutr.* **38**, 689–733.
30. H. Zaleska, P. Tomasik, and S. G. Ring (2001) *Carbohydr. Polym.* **45,** 89–94.
31. H. Zaleska, S. G. Ring, and P. Tomasik (2001) *Int. J. Food Sci. Technol.* **36,** 509–515.
32. T. Grega, D. Najgebauer, M. Sady, and P. Tomasik, M. Faryna (2003) *J. Polym. Environ.* **11,** 75–83.
33. A. Dejewska, J. Mazurkiewicz, P. Tomasik, and H. Zaleska (1995) *Starch/Staerke,* **47,** 219–223.
34. H. Zaleska, J. Mazurkiewicz, P. Tomasik, and M. Baczkowicz (1999) *Nahrung,* **43,** 278–283.
35. H. Zaleska, S. G. Ring, and P. Tomasik (2000) *Food Hydrocoll.* **14,** 371–382.
36. C. Y. Lii, H. H. Chan, S. Lu, and P. Tomasik (2003) *J. Polym. Environ.* **11,** 115–121.
37. C. Y. Lii, H. H. Chan, S. Lu, and P. Tomasik (2003) *Int. J. Food Sci. Technol.* **38,** 787–793.
38. C. Y. Lii, S. C. Liaw, V. M.-F.Lai, and P. Tomasik (2002) *Eur. Polym. J.* **38,** 1377–1381.
39. C. Y. Lii, S. C. Liaw, and P. Tomasik (2003) *Pol. J. Food Nutr. Sci.* **12/3,** 25–29.
40. C. Y. Lii, P. Tomasik, H. Zaleska, and S. C. Liaw (2002) *Carbohydr. Polym.* **50,** 19–26.
41. H. Zaleska, P. Tomasik, and S. C. Lii (2002) *J. Food Eng.* **14,** 215–224.
42. H. Zaleska, P. Tomasik, and C. Y. Lii (2002) *Carbohydr. Polym.* **53,** 249–257.
43. T. Grega, D. Najgebauer, M. Sady, and P. Tomasik (2003) *J. Polym. Environ.* **12,** 17–25.
44. C. H. Schilling, P. Tomasik, D. S. Karpovich, B. Hart, J. Garcha, and P. T. Boettcher (2004) *J. Polym. Environ.* **13** [1], in press.
45. J. Polym. Env., in press.
46. J. Polym. Env., in press.
47. Y. W. Wu, K. R. Sexson, and A. A. Lagoda (1985) *Cereal Chem.* **62,** 470–473.
48. Y. W. Wu, K. R. Sexson, and J. S. Woll (1981) *Cereal Chem.* **58,** 343–347.
49. Y. W. Wu and A. C. Stringfellow (1982) *J. Food Sci.* **47,** 1155–1157, 1180.
50. Y. W. Wu and A. C. Stringfellow (1986) *Cereal Chem.* **63,** 60–61.
51. C. T. Tibelius (1996) *Agriculture and Agri-Food Canada, Research Branch, Final Report,* **01531-5-7157,** Chap. 1.
52. B. W. Hauck (1980) *Cereal Foods World,* **25,** 594–599.
53. C. H. Kim, J. A. Maga, and J. P. Martin, *J. Food Process Preserv.* **13,** 219–231.
54. B. A. Rasco and W. J. McBurney (1989) U.S. Patent 4, 828, 846.
55. Y. W. Wu, V. L. Youngs, K. Warner, and G. N. Bookwalter (1987) *Cereal Chem.* **64,** 434–436.
56. R. J. Alexander (1987) *Corn: Chemistry and Technology,* (S. A. Watson and P. E. Ramstadt, Eds.), American Association of Cereal Chemists, New York, pp. 351–76.
57. D. Bortzmeyer (1992) *J. Mater. Sci.* **27,** 3305–3308.
58. M. P. Filippov (1992) *Food Hydrocoll.* **6,** 115–118.
59. R. M. Silverstein, G. C. Basler, and T. C. Morrill (1991) *Spectrometric Identification of Organic Compounds,* 5th ed. Wiley, New York.
60. W. D. Callister (2000) *Materials Science and Engineering, An Introduction.* 5th ed. Wiley, New York, pp. 800–801.
61. R. W. Hertzberg (1996) *Deformation and Fracture Mechanics of Engineering Materials.* 4th ed.Wiley, New York, pp. 315–321.
62. L. J. Gibson and M. F. Ashby (1988) *Cellular Solids, Structure and Properties* –2nd ed. Cambridge University Press, Cambridge, UK, pp. 219–222.
63. J. S. Reed (1991) in S. J. Schneider (eds.), *Engineered Materials Handbook, Vol. 4, Ceramics and Glasses,* ASM International, Metals Park, Ohio, pp. 130–134.
64. G. Y. Onoda (1976) *J. Am. Ceram. Soc.* **58,** 236–239.
65. C. H. Schilling, V. J. Garcia, R. M. Smith, and R. A. Roberts (1998) *J. Am. Ceram. Soc.* **81,** 2629–2639.