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(54) **BIOBASED COMPOSITIONS FROM
DISTILLERS' DRIED GRAINS WITH
SOLUBLES AND METHODS OF MAKING
THOSE**

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(57) **ABSTRACT**

A composition and process of making the composition having a dried particulate by-product of starch fermentation of a grain to produce ethanol such as DDGS, and a polymerized polyurethane binder derived from a polyurethane prepolymer that is a reaction product of at least one polyol and at least one isocyanate. The by-product is present in the composition in an amount between about 20 and 90% by weight of the composition.

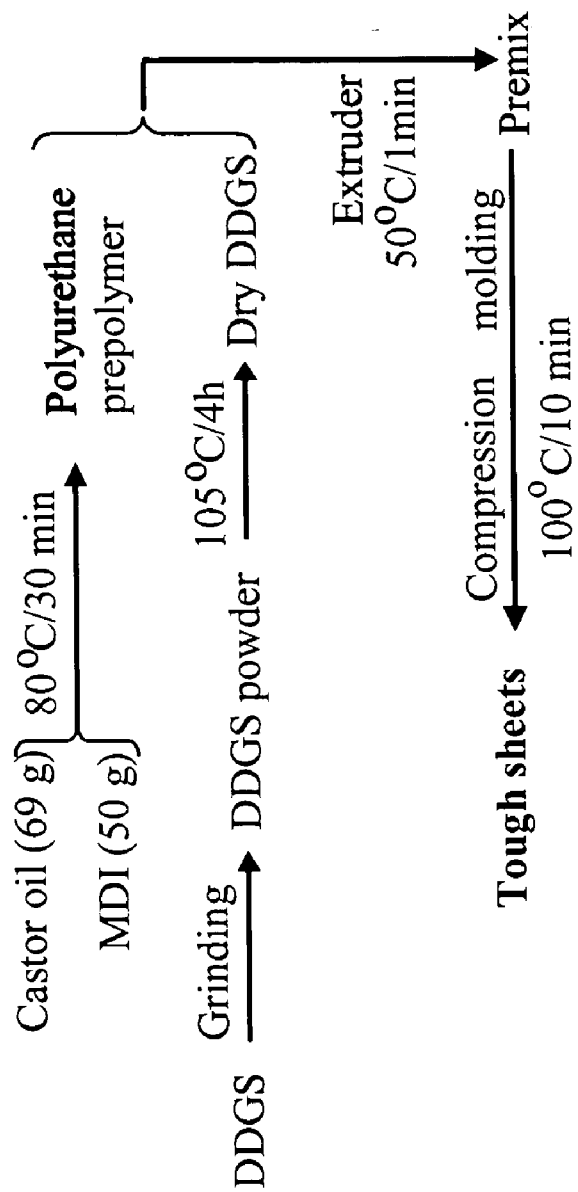


Figure 1

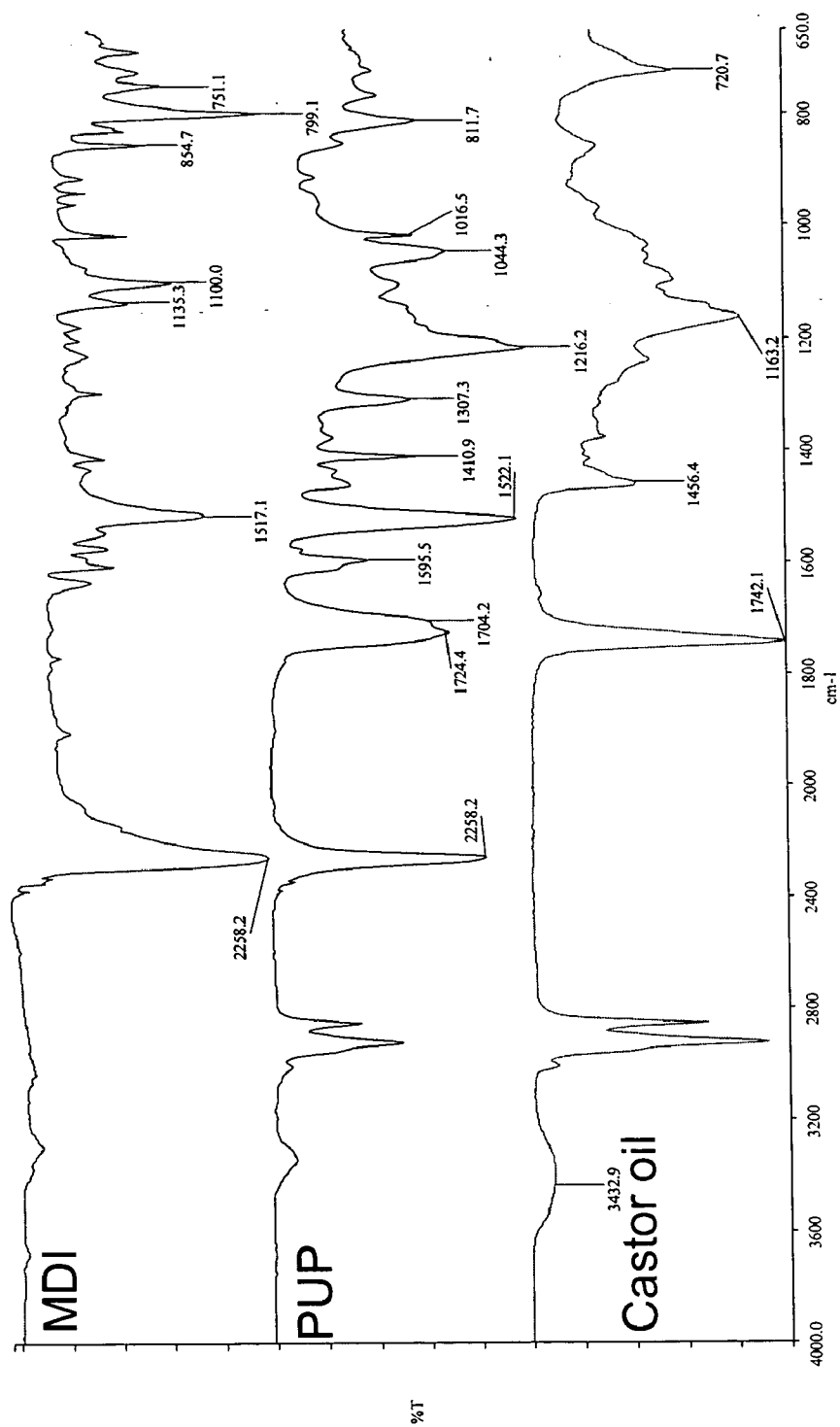


Figure 2

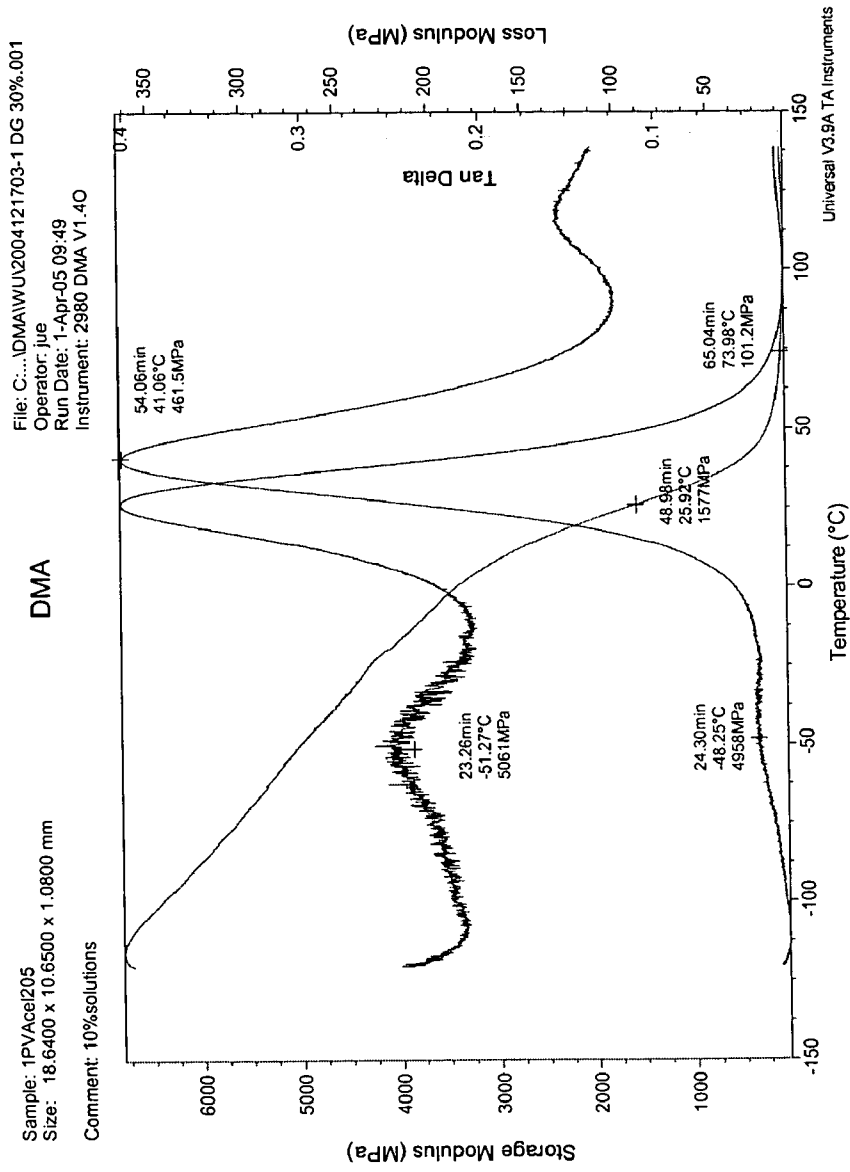


Figure 3

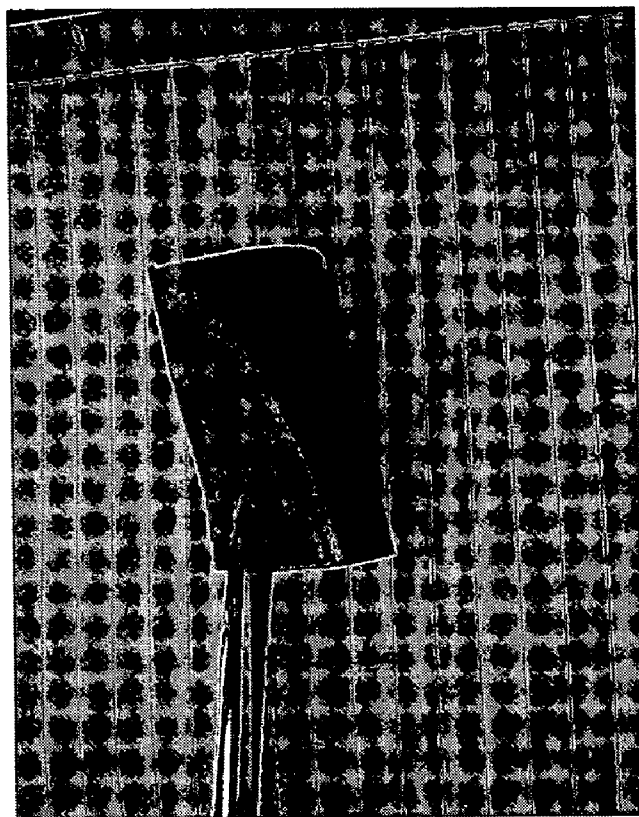


Figure 4A

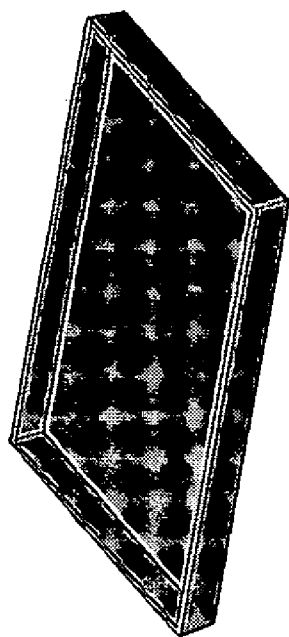


Figure 4C

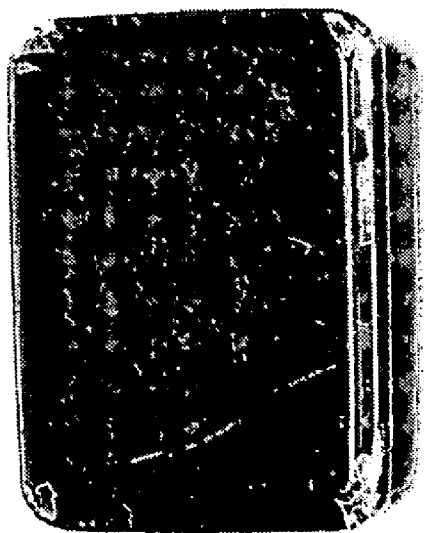


Figure 4B

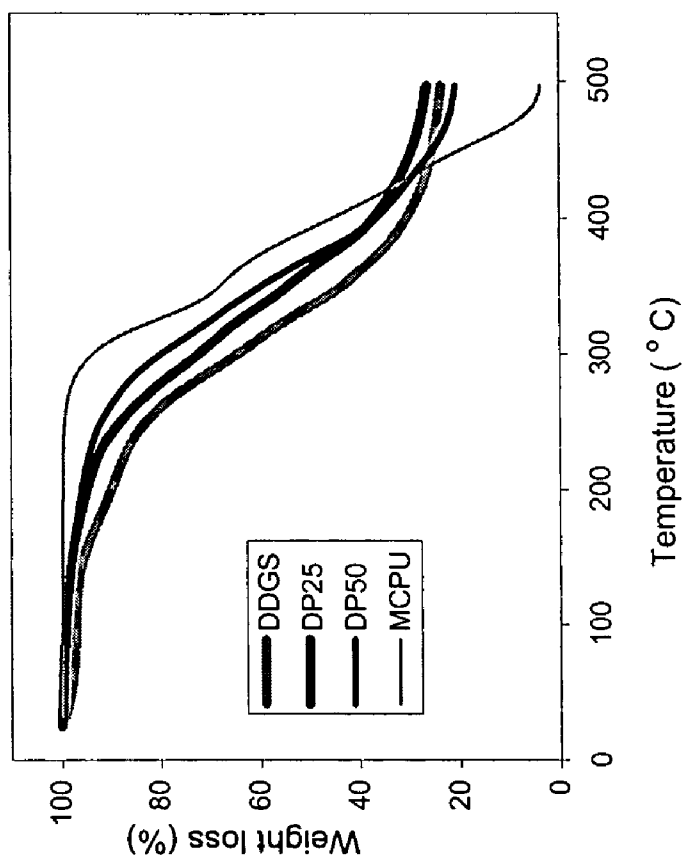


Figure 5

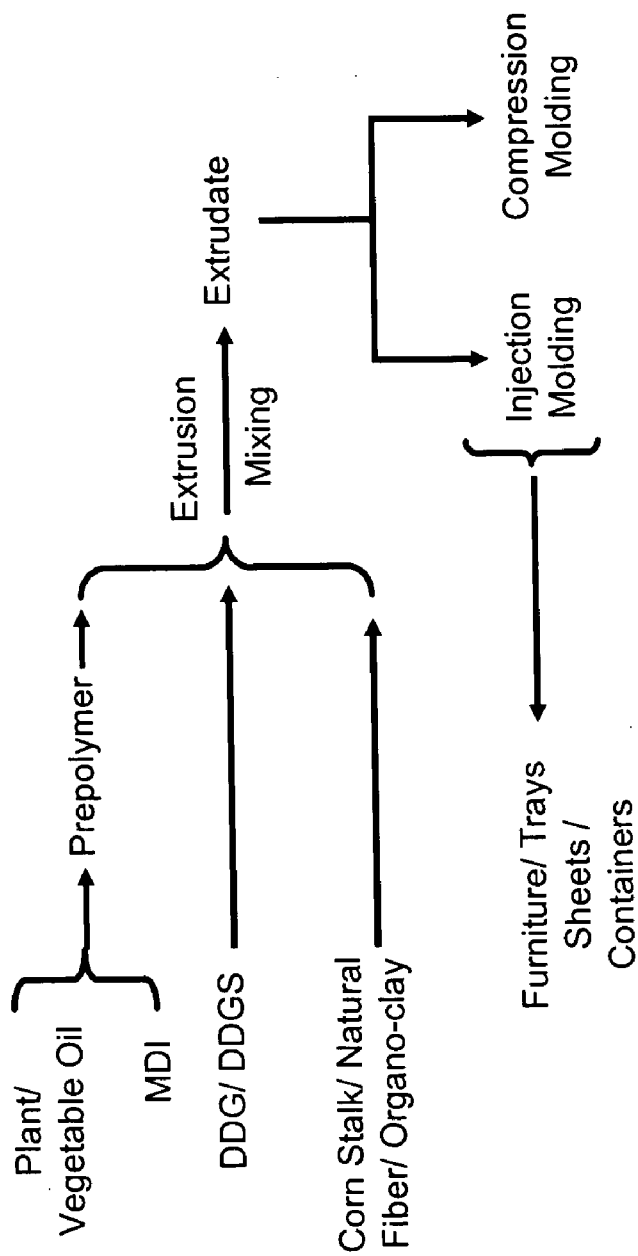


Figure 6

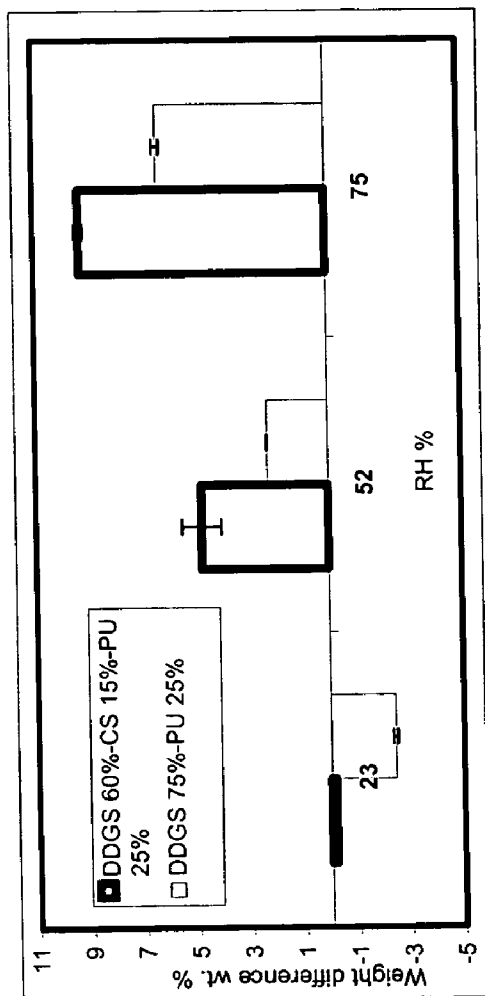


Figure 7

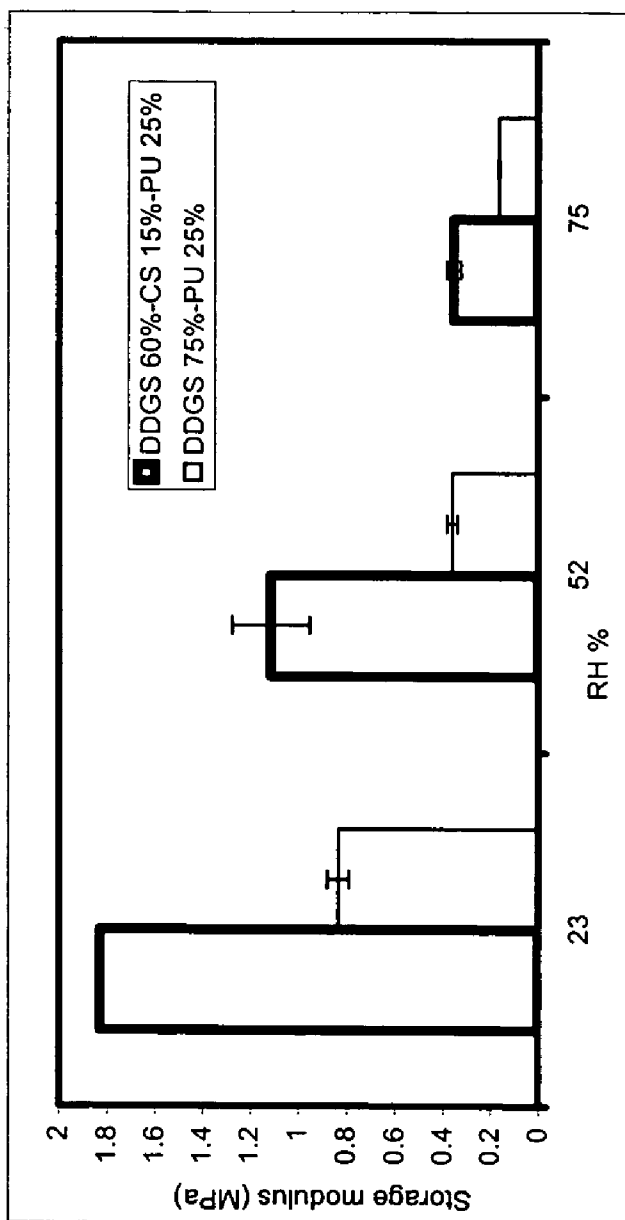


Figure 8

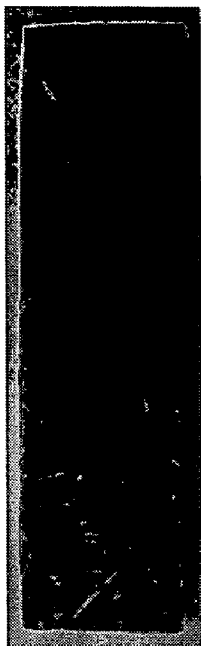


Figure 9B

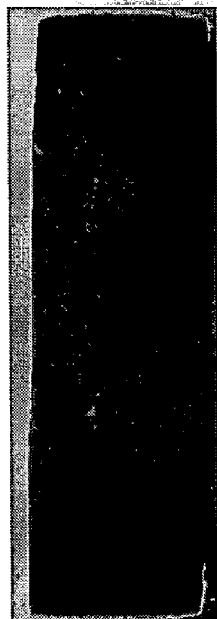


Figure 9A

BIOBASED COMPOSITIONS FROM DISTILLERS' DRIED GRAINS WITH SOLUBLES AND METHODS OF MAKING THOSE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application No. 60/750,099, filed Dec. 14, 2005 incorporated herein by reference in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] Not Applicable

BACKGROUND OF THE INVENTION

[0003] (1) Field of the Invention

[0004] The present invention relates to the utilization of distillers' dried grains as well as distillers' dried grains with solubles in finding value-added biobased materials.

[0005] (2) Description of the Related Art

[0006] In ethanol industries, corn is usually processed to prepare ethanol. Distillers' dried grains with solubles (DDGS) are coproducts from dry milling ethanol industries, containing about 27% protein. Corn gluten meal (CGM) is a byproduct from wet milling ethanol industries, containing around 60% of protein. Currently, the two types of coproducts/byproducts are mainly consumed as livestock feeds. Recently, several attempts have been made in developing CGM-based material (Wu, Q. X.; Sakabe, H.; Isobe, S. *Ind. Eng. Chem. Res.* 42, 6765, 2003; Di Gioia, L.; Guilbert, S. *J. Agric. Food Chem.* 47, 1254, 1999). The research on DDGS-based biodegradable material is rarely reported. Compared with CGM, DDGS is difficult to be processed in an extruder due to low protein content. As per our knowledge DDGS is cheaper (~\$0.05/lb) than CGM (~\$0.3/lb), which attracts attention on DDGS-based new materials. Schilling et al. (Schilling, C. H.; Tomasik, P.; Karpovich, D. S.; Hart, B.; Shepardson, S.; Garcha, J.; Boettcher, P. T.; *J. Polym. Environ.* 12 (4): 257-264, 2004) have prepared DDGS/soy protein based material. The maximum strength of such material was found to be 1.67 MPa. Such strength is quite low and thus unsuitable for many applications. In addition, the process cost seems quite high because of the use of several chemicals in modifying DDGS.

[0007] Polyurethane (PU) has been used to modify paper (Lee S. H.; Teramoto Y.; Shiraishi N. *J. Appl. Polym. Sci.* 83 (7): 1482-1489, 2002) and starch (Cao, X. D.; Zhang, L. N.; Huang, J.; Yang, G.; Wang, Y. X. *J. Appl. Polym. Sci.* 90 (12), 3325-3332, 2003) in making tough material. The toughness of pure corn protein increased sharply by incorporation of 10-30 wt % of PU prepolymer (Wu, Q. X.; Yoshino, T.; Sakabe, H.; Zhang, H. K.; Isobe, S. *Polymer* 44, 3909-3919, 2003) indicating an important role of PU in making tougher material from brittle protein matrix. However in this study, the processing was conducted in chemical solution, which increased the processing cost and was limited in practice. The research using PU prepolymer to prepare tough DDGS-PU composite is rarely reported.

[0008] Polyester-based polyurethane can also be hydrolyzed into small molecules in usage, and thus is considered

as environmental-friendly material. But polyester polyol is expensive (\$1.4/lb) (Information from Bayer Polymers LLC, in February, 2004 (e-mail communication)). The weight percentage of PU should be controlled to a low level (<50%) to prepare low cost material. In this work, low quantity of polyester-based PU prepolymer was synthesized and mixed with DDGS in the micro-extruder and the resulting extruded material was molded to prepare low cost, tough and water resistant composite.

SUMMARY OF THE INVENTION

[0009] The present invention provides a composition which comprises: a dried particulate by-product of starch fermentation of a grain to produce ethanol; and a polymerized polyurethane binder derived from a polyurethane prepolymer comprising a reaction product of at least one polyol and at least one isocyanate, the by-product being present in an amount between about 20 and 90% by weight of the composition. In further embodiments, the polyol is a plant oil-based polyol. In further embodiments, the plant oil-based polyol is selected from the group consisting of castor oil, soybean oil, rapeseed oil and mixtures thereof. In further embodiments, the isocyanate is a diisocyanate selected from the group consisting of 4,4'-methylenedi-p-phenyl diisocyanate (MDI), naphthalene 1,5-diisocyanate (NDI), toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), IPDI, H₁₂-MDI, tetramethylene diisocyanate, and mixtures thereof. In further embodiments, the by-product is derived from corn. In still further embodiments, the by-product is distiller's dried grains with solubles (DDGS). In further embodiments, the polyurethane prepolymer was formed in the presence of an organometallic or amine catalyst. In still further embodiments, the organometallic catalyst is selected from the group consisting of tin (II) 2-ethylhexanoate, tinbutyltin dilaurate, and stannous octoate. In further embodiments, the composition was extruded. In still further embodiments, the composition was rapidly extruded and then molded under pressure at elevated temperatures. In further embodiments, the composition further comprises natural fibers and organo-clay. In further embodiments, the natural fibers are corn fibers.

[0010] The present invention provides a process for producing the composition as set forth in Claims 1, 2 or 4, which comprises extruding a mixture of the prepolymer and the by-product at a temperature between about 25° C. and 80° C. In further embodiments, the composition is molded under pressure at elevated temperatures between 80° C. and 150° C.

[0011] The present invention provides a process for producing a composition comprising: providing a polyurethane prepolymer comprising a reaction product of at least one polyol and at least one isocyanate; extruding a mixture of the polyurethane prepolymer and a dried particulate by-product of starch fermentation of a grain to provide an extrudate; and molding the extrudate of step (b) to form the composition, wherein the by-product is present in an amount between about 20 and 90% by weight of the composition. In further embodiments, the extrudate of step (b) is compression molded in step (d).

[0012] The present invention provides a composition produced by the process of Claim 15. In further embodiments, the composition is formed as a product selected from the group consisting of a piece of furniture, a tray, a sheet, and a container.

[0013] The present invention provides a process for producing a composition comprising: providing a polyurethane prepolymer comprising a reaction product of at least one polyol and at least one isocyanate; providing natural fibers; extruding a mixture of the polyurethane prepolymer, the natural fibers, and a dried particulate by-product of starch fermentation of a grain to provide an extrudate; and molding the extrudate of step (b) to form the composition, wherein the by-product is present in an amount between about 20 and 90% by weight of the composition. In further embodiments, the extrudate of step (b) is compression molded in step (d). In further embodiments, the extrudate of step (b) is injection molded in step (d).

[0014] The present invention provides a composition produced by the process of Claim 18. In further embodiments, the composition is formed as a product selected from the group consisting of a piece of furniture, a tray, a sheet, and a container.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] FIG. 1 is a scheme illustrating the preparation of tough distillers' dried grains with solubles (DDGS)/polyurethane based composite. (MDI: 4,4'-methylenedi-p-phenyl diisocyanate).

[0016] FIG. 2 illustrates the FTIR spectra of castor oil, MDI, and PU prepolymer.

[0017] FIG. 3 is a graph illustrating the DMA results for DP30.

[0018] FIG. 4A is an image of the DDGS-PU composite containing 44% of PU. FIG. 4B illustrates an image and FIG. 4C illustrates a schematic diagram of DDGS-PU container containing 30 wt % of polyurethane. Weight=107.8 g, Base length=210 mm, Base width=148 mm, Thickness of the wall=3.63 mm.

[0019] FIG. 5 illustrates a TGA diagram of DDGS, MCPU and DDGS/PU composites.

[0020] FIG. 6 is a scheme illustrating the preparation of tough and water resistant DDGS/DDG-based Materials (MDI—4,4'-methylenediphenyl diisocyanate).

[0021] FIG. 7 illustrates the effects of RH % on the weight difference of the composites.

[0022] FIG. 8 illustrates the effects of RH % on the storage modulus at 25° C. for the composites

[0023] FIG. 9A and FIG. 9B illustrate images of (FIG. 9A): DDGS 75%-PU 25% and (FIG. 9B): DDGS 60%-CS 15%-PU 25% after buried in soil for one month.

DETAILED DESCRIPTION OF THE INVENTION

[0024] All patents, patent applications, government publications, government regulations, and literature references cited in this specification are hereby incorporated herein by reference in their entirety. In case of conflict, the present description, including definitions, will control.

[0025] Preparation of biobased material from the byproduct/co-product of the dry milling corn ethanol industry e.g. distillers' dried grains with solubles (DDGS) and biobased polyurethane. The resulting biobased material can contain as

high as approximately seventy-five percent (75%) of inexpensive DDGS thus making the product commercially attractive.

[0026] The present invention provides a composition which comprises: (a) a dried particulate by-product of starch fermentation of a grain to produce ethanol; and (b) a polymerized polyurethane binder derived from a polyurethane prepolymer comprising a reaction product of at least one polyol and at least one isocyanate, the by-product being present in an amount between about 20 and 90% by weight of the composition.

[0027] As used herein, the term "by-product of starch fermentation" as used herein can refer to, but is not limited to, byproducts/coproducts of the corn ethanol industry. Examples include distiller's dried grains with solubles (DDGS) and distillers' dried grains (DDG). Other grains from which the by-product is derived can include, but are not limited to sorghum (milo), wheat, or barley.

[0028] As used herein, the term "polyol" as used herein refers to any monomeric or polymeric molecule with more than one hydroxyl functional groups. In some embodiments, the polyol is biodegradable. In some preferred embodiments, the term "polyol" refers to plant derived oils such as castor oil, soybean oil, and rapeseed oil, however the term is not limited thereto.

[0029] As used herein, the term "isocyanate" as used herein refers to any isocyanate including, but not limited to aromatic, cycloaliphatic (alicyclic), and aliphatic isocyanates. The term includes diisocyanates such as 4,4'-methylenedi-p-phenyl diisocyanate (MDI), naphthalene 1,5-diisocyanate (NDI), toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), methylene bis(p-cyclohexyl isocyanate) (H₁₂ MDI), and tetramethylene diisocyanate.

[0030] This is the first report on preparation of DDGS-based tough material with DDGS content of around 75%. The preliminary cost analysis taking in to account the materials costs is quite encouraging. The current price of castor oil is \$675/ton (\$0.31/lb) (http://www.ipex.gov.mz/precos_en.php3?en=1, access date: 2006-Dec.-04). The price of MDI is \$1.1/lb (<http://www.plasticsnews.com/subscriber/resin/price4.html>, access date: 2006-Dec.-04). PU price is $69/(50+69) \times 0.31 + 50/(50+69) \times 1.1 = \$0.64/\text{lb}$.

[0031] The materials' costs of the biobased DDGS-PU product containing approximately 75% DDGS and approximately 25% polyurethane (PU); designated here as DP25, was found out to be approximately \$0.20/lb. The cost calculation is shown as follows: Material cost of DP25=PU cost \times 25%+DDGS cost \times 75%=\$0.64/lb \times 25%+0.05 \times 75%=\$0.20/lb. Processing cost is not included in this calculation.

[0032] The content of biobased material (DDGS and natural polyol) in the composite was found out to approximately 90%. Such calculation is represented as follows: Content of biobased material in DP25=DDGS percentages+castor oil percentages=75%+castor oil percentage in PU \times PU percentages in DP25=75%+69/(69+50) \times 25%=75%+15%=90%.

[0033] Experimental.

[0034] Materials: Castor Oil, 4,4'-methylenedi-p-phenyl diisocyanate (MDI), and Tin (II) 2-ethylhexanoate (95%), were purchased from Sigma-Aldrich Fine Chemicals, St.

Louis, Mo. Distillers' dried grains with solubles (DDGS) of Michigan Ethanol, Caro, Mich. was used in this work.

[0035] Synthesis of PU prepolymer: The ratio of isocyanate/hydroxyl group (NCO/OH) was 2.0. Castor oil (69.0 g) and MDI (50.0 g) were added into a 250 mL four-necked flask fitted with a thermometer, a stirrer, an inlet and an outlet of dry nitrogen, and stirred at 80° C. The stirring speed was 300 rpm. Then 30 min later, the temperature decreased to 30° C. and 110 μ L of Tin (II) 2-ethylhexanoate catalyst was introduced into the flask under dry nitrogen with a syringe. The reaction was carried out at 30° C. for fifty minutes. The polyurethane prepolymer (PUP) was sealed in a glass bottle. The bottle was placed into a silica gel desiccator and stored at -20° C. in a refrigerator. U.S. Pat. No. 6,359,023 to Kluth et al., incorporated herein by reference in its entirety, describes polyurethane prepolymer containing NCO groups made from isocyanates and polyols derived from natural oils.

[0036] Preparation of DDGS-PU composites: DDGS was milled into powder (297 μ m) in a mill machine (Cyclone Sample Mill, UDY Corporation, Colo., USA). The powder was dried at 105° C. for four hours and stored in a desiccator for the following experiment. DDGS and polyurethane prepolymer (PUP) were mixed in a beaker by use of a glass rod and then fed into a micro-extruder (15 cm³ in volume capacity, DSM Research, Netherlands). Extrusion temperature was 50° C., speed was 50 rpm. The extruded material (5.0 g) was compression-molded in a compression-molding machine (Carver Laboratory Press, Model M, Fred S. Carver Inc, Menomonee, Wis.) at 100° C. Rectangular mold dimension was 1.0 \times 60 \times 70 mm³, molding force was 10 ton and time was ten minutes. The mold was cooled to below 40° C. by a water-cooling system at a rate of 10° C./min. The molded sheet was cut into strips with dimension of: 1.0 \times 10 \times 70 mm³. The strip-like samples were stored in a desiccator. The sheets containing various PU contents (25%, 30%, 40% and 50%) were prepared, and coded as DP25, DP30, DP40 and DP50 respectively. DP25 represents sheet from DDGS/PU composite containing 25% of PU. As a control, PUP (polyurethane prepolymer) was exposed to ambient conditions to be cured by moisture. One month later, the cured PUP was compression-molded at 150° C., for 30 min to prepare thin sheets. This material was designated as "MCPU" to represent "MDI/castor oil based polyurethane". The procedure for preparing tough DDGS/PU sheet is represented in FIG. 1.

[0037] Characterization.

[0038] Fourier transform infrared spectroscopy (FTIR): A FTIR spectrometer (Spectrum One, PerkinElmer, Massachusetts, USA) using an attenuated total reflectance (ATR) cell at room temperature is used here for characterization studies. All the spectra were recorded at a resolution of 2 cm⁻¹ with accumulation of 5 scans. Three duplications were conducted.

[0039] Tensile Test: The tensile strength, percent (%) elongation and tensile modulus of the samples were tested using an Instron tensile tester (Instron 5565, Instron Co., Massachusetts, USA) according to ISO6239-1986 (E) with cross head speed of 50 mm min⁻¹. Toughness is defined by the area under stress-strain curve and its unit is MPa (Zhang, J; Mungara, P; Jane, *J. Polymer*, 2001, 42, 2569).

[0040] Water Uptake Measurement: Sheets with a dimension of 1 mm \times 10 mm \times 100 mm, were dried in a desiccator

for one month, then weighed (W_d) and then immersed in water. Two days later the wet samples were taken out and dried by use of paper towel and reweighed (W_w). The water uptake was calculated using the following equation:

$$\text{Water uptake (\%)} = [(W_w - W_d) / W_d] \times 100 \quad (1)$$

[0041] Soxhlet Extraction: Sheets were dried at 100° C. for seventeen hours and weighed (W_d). The dried samples were extracted in a Soxhlet extractor using toluene for twenty-four hours, then dried in air for eight hours, then in an oven at 70° C. for fifteen hours, and at 110° C. for four hours and then weighed (W_e). The weight loss was calculated using the following equation:

$$\text{Weight loss (\%)} = [(W_d - W_e) / W_d] \times 100 \quad (2)$$

[0042] The equation for calculating the reaction ratio of PUP is shown as follows:

$$\text{Reaction ratio} = [W_L / W_I] \times 100 \quad (3)$$

[0043] where W_L is the weight of the PUP linked to DDGS and W_I is the weight of the PUP incorporated into DDGS. Four duplications were carried out.

[0044] Dynamic Mechanical Analysis (DMA): The thermo-mechanical properties were evaluated with a dynamic mechanical analyzer (DMA Q800, TA Instruments, Delaware, USA) in single cantilever mode. The DMA testings were investigated from -120° C. to 140° C. at a heating rate of 3° C./min. A variable-amplitude, sinusoidal tensile stress (frequency=1 Hz) was applied to the samples to produce a sinusoidal strain of ± 30 μ m amplitude. Two duplications were done.

[0045] Thermo Gravimetric Analysis (TGA): Testing was conducted using a thermal gravimetric analyzer (TGA 2950, TA Instruments, Delaware, USA). Approximately 10 mg of the sample cut from the sheet were equilibrated at ambient conditions, and then subjected to heating from 30° C. to 500° C. at 10° C./min in a nitrogen atmosphere.

TABLE 1

Evaluation of the reaction ratio of PUP in DDGS/PU composites			
Samples	DDGS percentage % ^a	Weight loss %	PUP reaction ratio ^b
1-DDGS	100	16.5 \pm 0.1	—
2-DP25	75	10.0 \pm 0.2	92.7
3-DP30	70	9.1 \pm 0.2	95.1
4-DP40	60	7.2 \pm 0.1	98.4
5-DP50	50	6.1 \pm 0.0	98.7
Average	—	—	96.2 \pm 2.8

^a calculated from the addition amount of PUP.

^b calculated on the base of that corn oil content was hypothesized to be 10.9 wt. %.

[0046] Results and Discussion.

[0047] FTIR spectra of castor oil, MDI, and PU prepolymer (PUP) are shown in FIG. 2. Two new peaks in the spectrum of PUP at 1724 and 1704 cm⁻¹ were assigned to the stretching of C=O in urethane group, and a new peak at 1522 cm⁻¹ was assigned to the combination of in-plane bending of N—H and stretching of C—N in urethane group. It can be concluded that urethane groups have been formed, indicating a successful synthesis.

[0048] Soxhlet Extraction.

[0049] The weight loss of extracted samples is shown in Table 1. Toluene-soluble components in the DDGS were 16.5% as shown in Table 1. The toluene-soluble components are mainly comprised of corn oil and non-corn oil fraction. Because corn oil would not react with diisocyanate groups due to the chemical structure of corn oil, the corn oil was extracted from the DDGS/PU composites and was the main weight lost from the samples. The non-corn oil fraction contained a part of alcohols, acids and amides according to the composition analysis (Biswas, S.; Staff, C. *J. Cereal Sci.* 2001, 33, 223) and would react with PUP in the composites. The existence of the non-oil fractionation made it difficult to calculate the actual corn oil content in the DDGS on the basis of weight loss during extraction. According to the studies reported in the literatures (Belyea, R. L.; Rausch, K. D.; Tumbleson, M. E. *Bioresource Technol.* 2004, 94, 293; Shukla, R.; Cheryan, M. *Ind. Crops Prod.* 2001, 13, 171), the corn oil content in DDGS generally ranged from 10.9 to 13 wt. %. If 13 wt. % was selected as the corn oil content, the calculated average reaction ratio would be 100.3%, further indicating the actual corn oil content in the DDGS was lower than 13 wt. %. The PUP reaction ratio was calculated on the basis of corn oil content as 10.9 wt. % in this study. As shown in Table 1, the average reaction ratio of PUP reached as high as 96.2%, suggesting reaction ratio was very high.

[0050] Mechanical properties of the distillers' dried grains with solubles-polyurethane (DDGS-PU) composite are shown in Table 2.

TABLE 2

Mechanical properties of DDGS-PU composites						
Sample (DDGS-PU composites)	PU content (%)	DDGS content (%)	σ_b ^a (MPa)	ϵ_b ^b (%)	E ^c (MPa)	Toughness (MPa)
DP25	25	75	11.6 ± 0.0	5.2 ± 0.2	249 ± 7	44 ± 3
DP30	30	70	13.3 ± 0.7	6.2 ± 0.2	273 ± 23	65 ± 21
DP40	40	60	15.7 ± 1.1	8.6 ± 0.8	391 ± 40	103 ± 17
DP50	50	50	16.0 ± 1.0	13.8 ± 1.4	312 ± 38	148 ± 24

^a σ_b strength at break,

^b ϵ_b elongation at break,

^c E is Young's modulus at 0.5–2%.

[0051] The toughness, strength at break and elongation at break of the DDGS-PU composites were increased with the content of PU under the present experimental conditions. As a control, DDGS without adding of PU cannot be processed into sheets. This indicates polyurethane can efficiently improve the mechanical properties of the composite.

[0052] The mechanical properties of wet (immersed in water) DDGS/PU composites were also shown in Table 3. With an increase of PU content from 25 to 50 wt. %, the water uptake was reduced and ranged from 27.5 to 5.3 wt. %, suggesting the PU component improved the water resistance of the DDGS/PU composites. After immersion in water for 24 h, all composites still were flexible, although the strength of all composites decreased compared to that of dried samples. As shown in Table 3, the strengths in the wet state of the composites also were improved with the increas-

ing PU content, further suggesting that polyurethane improved the water resistance of DDGS-based materials.

TABLE 3

Properties of wet DDGS/PU composites			
Samples	Water uptake (%)	σ_b (MPa)	ϵ_b (%)
DP25	27.5 ± 0.7	2.5 ± 0.2	34 ± 3
DP30	27.2 ± 1.8	3.0 ± 0.2	47 ± 3
DP40	8.1 ± 0.5	7.0 ± 0.2	27 ± 2
DP50	5.3 ± 0.3	8.9 ± 0.4	31 ± 3

[0053] The visco-elastic property of the DP30 composite as evaluated through DMA is shown in FIG. 3 and the related results for other DDGS-PU composites are shown in Table 4.

TABLE 4

DMA results of DDGS/PU composites	
Samples	T(tan δ) (° C.)
DP25	35.3 ± 0.4
DP30	35.7 ± 0.6
DP40	41.2 ± 1.0
DP50	44.4 ± 0.2
Extracted DP25	45.8 ± 0.5
MCPU	43.9 ± 0.2

[0054] The T_g of DP30 was 41° C. Its storage modulus was 1.7 GPa at 25° C. and 150 MPa at 60° C. Hence, the

composite was tough and strong at room temperature. An image of DDGS/PU composites containing 44% of PU is shown in FIG. 4A. An image and schematic representation of a container made from DP30 are shown in FIG. 4B and FIG. 4C, respectively.

[0055] Weight loss versus temperature curves of MCPU, DP25, DP50 and DDGS are shown in FIG. 5. There are two stages in the decomposition of MCPU (FIG. 5, MCPU), one is from 270° C. to 350° C., and the other is from 350° C. to 500° C. At 500° C., the MCPU had the quickest degradation of the all samples, implying that the polyurethane has less thermal resistance at this temperature. Owing to the improvement of thermal stability for the cross-linked DDGS/PU composites, the residues content of both DP25 and of DP50 at 500° C. were higher than that of the pure PU sample. Because the PU components in the DDGS/PU composites had lower thermal resistance at 500° C., the

composites containing high amount of PU component were easily decomposed and the residual content decreased. This is the reason why the residue content of DP50 at 500° C. was lower than that of DP25. In FIG. 5 (DDGS curve), moisture evaporation led to the weight loss of DDGS from 25° C. to 140° C. and corn oil evaporation resulted in the weight loss of DDGS from 140° C. to 240° C.

[0056] Further embodiments of processes for preparing compositions that can be prepared as products, such as but not limited to furniture, trays, sheets and containers are represented in FIG. 6. Castor oil or soy oil or other vegetable/plant oils-based polyols can be used. The polyols are mixed with MDI to prepare active prepolymer. The process is cost effective because the reaction can be done in melt/liquid state. The prepolymer, DDGS and fiber/organo-clay/fiber and organo-clay can be mixed in an extruder. The extruded material on further injection or compression molding can result various shaped articles such as furniture, tray, pot, container, sheet etc. These articles are likely to be tough and water-resistant.

[0057] Preparation of the corn fiber-enforced DDGS-PU composites and the ageing properties of the DDGS-PU composites.

[0058] Preparation of the DDGS-CS-PU composites.

[0059] Method: Corn stovers (CS) were obtained from Farm # 3660, Meridian Road, Mich. The corn stovers include stalks, leaves, no ears and no roots. The CS were palletized in a granulator (B.T.P. Granulator, Granulator Div. Berlin, Conn.) and passed through a screen (2.7 mm mesh diameter) for preparing CS powder. DDGS powder (60%) and corn stovers (CS, 15%) powder were dried at 90° C. for four hours. The dried powder and polyurethane prepolymer (PUP, 25%) were extruded in the DSM mini extruder. The extrudates were compression-molded at 100° C. for 10 min. The sample was named as: DDGS 60%-CS 15%-PU 25%. The samples were cut into rectangular sample for tensile testing.

[0060] Results: Mechanical properties of the DDGS-PU composites are shown in Table 5.

TABLE 5

Mechanical properties the composites			
Samples	Strength at break (MPa)	Elongation at break (%)	E' (25° C.), (GPa)
DDGS 60%-CS 15%-PU 25%	18.3 ± 1.6	2.5 ± 0.5	2.2 ± 0.2
DDGS 75%-PU 25%	11.6 ± 0.0	5.2 ± 0.2	1.2 ± 0.2

[0061] DDGS (60%)-CS (15%)-PU (25%) showed higher strength (18.3 MPa) than that of DDGS (75%)-PU (25%) (11.6 MPa). The storage modulus of the former sample (2.2 GPa) was also much higher than that of the later sample (1.2 GPa).

[0062] Conclusions: The stiffness and strength of the DDGS -based materials were improved after incorporation of 15% of corn fiber.

[0063] Properties of the Composites After Ageing Treatment (Relative Humidity Treatment)

[0064] Method: Samples sheets (DDGS 60%-CS 15%-PU 25% and DDGS 75%-PU 25%) were equilibrated at a given RH % for 1 month. The weight difference before and after the treatment was calculated. The storage modulus at 25° C. [E' (25° C.)] was tested.

[0065] Results: Effects of RH % on the weight difference for the composites (DDGS 60%-CS 15%-PU 25%, DDGS 75%-PU 25%) are shown in FIG. 7. At 23% RH, both two samples lost moisture due to low relative humidity condition. At 52% and 75% RH, the two composite samples showed a weight increasing trend due to absorption of moisture from outside. With an increase of RH values, the two samples will absorb more moisture. DDGS contains about 13 wt. % of corn oil, which can increase the hydrophobic properties of the DDGS. DDGS can be considered more hydrophobic than corn fiber because of the presence of corn oil in DDGS. At a given RH value as shown in FIG. 7, DDGS 75%-PU 25% would absorb less moisture content than DDGS 60%-CS 15%-PU 25%.

[0066] Effects of RH % on the storage modulus at 25° C. for the composites are shown in FIG. 8. The E' (25° C.) decreased with an increase of RH value. This indicates that the materials are sensitive to moisture. At a given RH value, the DDGS 60%-CS 15%-PU 25% showed much higher E' (25° C.) than that of DDGS 75%-PU 25%, indicating that corn fiber significantly improved the stiffness of the composite. Conclusion: The composites are sensitive to moisture. Corn fiber significantly improved the stiffness of the composite

[0067] Effects of microwave oven treatment on the properties of the composites.

[0068] Method: composites samples were first weighed (W1) and put into a microwave oven (Emerson, MW8625, 600W, Emerson Radio Corp. Parsippany, N.Y., USA) at the "reheat" function. After a given time, samples were taken out and weighed again (W2). Weight loss (%) was calculated using the following equation:

$$\text{Weight loss (\%)} = (W1 - W2) / W1 \times 100$$

[0069] A digital camera was used to take the image of the surface of the samples.

[0070] Results: Properties of the DDGS 75%-PU 25% samples after microwave oven treatment are shown in Table 6.

TABLE 6

Properties of the DDGS 75%-PU 25% samples after microwave oven treatment			
Time (min)	Weight loss %	Surface	Smell
0	0.0	Smooth	A little
5	2.5	Burned	Strong
10	5.1	Burned/black	Very strong

[0071] After the microwave oven treatment for 5 or 10 min, DDGS 75%-PU 25% showed burned surfaces and weight loss because the sample contained moisture. The smell of the sample also became strong after the microwave

oven treatment. Conclusions: The DDGS -PU materials cannot resist microwave oven treatment because DDGS contains moisture and is easy to be degraded at high temperature.

[0072] Ageing treatment in soil.

[0073] Methods: DDGS 75%-PU 25% and DDGS 60%-CS 15%-PU 25% composites were put in to soil for ageing. One month later, the samples were taken out and inspected by vision.

[0074] Results: The water up-take of the composites aged in soils that were taken out after one month is shown in Table 7 and the images are shown in FIG. 9A and FIG. 9B. FIG. 9A illustrates DDGS 75%-PU 25% and FIG. 9B illustrates DDGS 60%-CS 15%-PU 25%.

TABLE 7

Properties of the DDGS-PU composites aged in soil for one month	
Samples	Water uptake (%)
DDGS 60%-CS 15%-PU 25%	57.2 ± 0.5
DDGS 75%-PU 25%	24.2 ± 0.3

[0075] Properties of the DDGS-PU Composite Aged at Out-Door Conditions.

[0076] DDGS 75%-PU 25% and DDGS 60%-CS 15%-PU 25% composites were put and tied on a wood board. The system was placed on the ground and exposed to out door environments (2 rain days and 3 snow days). Water uptake and the surface properties of the composites were studied.

[0077] Results: The properties of the two composites are shown in Table 8. After exposed to out door conditions for 2 rain days and 2 snow days, the two samples absorbed water, indicating the materials were water sensitive. The storage modulus of the DDGS 60%-CS 15%-PU 25% was also decreased from the original value (2.2 GPa, in Table 5) to 1.4 GPa as shown in Table 8. Similarly the storage modulus of the DDGS 75%-PU 25% was also decreased from the original value (1.2 GPa, in Table 5) to 0.7 GPa as shown in Table 8.

TABLE 8

Properties of the DDGS-PU composites exposed in out-door conditions			
Samples	Water uptake (%)	E' (25° C.), (GPa)	Surface properties
DDGS 60%-CS 15%-PU 25%	21.5 ± 1.8	1.4 ± 0.2	Smooth
DDGS 75%-PU 25%	17.3 ± 0.8	0.7 ± 0.3	Smooth

[0078] Conclusions: The composites will absorb water after aged at out-door conditions, resulting in a decrease in the stiffness of the composites.

[0079] While the present invention is described herein with reference to illustrated embodiments, it should be understood that the invention is not limited hereto. Those having ordinary skill in the art and access to the teachings herein will recognize additional modifications and embodiments within the scope thereof. Therefore, the present invention is limited only by the Claims attached herein.

We claim:

1. A composition which comprises:

(a) a dried particulate by-product of starch fermentation of a grain to produce ethanol; and

(b) a polymerized polyurethane binder derived from a polyurethane prepolymer comprising a reaction product of at least one polyol and at least one isocyanate, the by-product being present in an amount between about 20 and 90% by weight of the composition.

2. The composition of claim 1, wherein the polyol is a plant oil-based polyol.

3. The composition of claim 2, wherein the plant oil-based polyol is selected from the group consisting of castor oil, soybean oil, rapeseed oil and mixtures thereof.

4. The composition of claim 1, wherein the isocyanate is a diisocyanate selected from the group consisting of 4, 4'-methylenedi-p-phenyl diisocyanate (MDI), naphthalene 1,5-diisocyanate (NDI), toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), IPDI, H₁₂-MDI, tetramethylene diisocyanate, and mixtures thereof.

5. The composition of claim 1, wherein the by-product is derived from corn.

6. The composition of claim 5, wherein the by-product is distiller's dried grains with solubles (DDGS).

7. The composition of claim 1, wherein the polyurethane prepolymer was formed in the presence of an organometallic or amine catalyst.

8. The composition of claim 1, wherein the organometallic catalyst is selected from the group consisting of tin (II) 2-ethylhexanoate, tinbutyltin dilaurate, and stannous octoate.

9. The composition of claims 1, 2 or 5, wherein the composition was extruded.

10. The composition of claims 1, 2 or 5, wherein the composition was rapidly extruded and then molded under pressure at elevated temperatures.

11. The composition of claims 1, 2 or 5, further comprising natural fibers and organo-clay.

12. The composition of claim 11, wherein the natural fibers are corn fibers.

13. A process for producing the composition as set forth in claims 1, 2 or 5, which comprises extruding a mixture of the prepolymer and the by-product at a temperature between about 25° C. and 80° C.

14. The process of claim 13 wherein in addition the composition is molded under pressure at elevated temperatures between 80° C. and 150° C.

15. A process for producing a composition comprising:

(a) providing a polyurethane prepolymer comprising a reaction product of at least one polyol and at least one isocyanate;

(b) extruding a mixture of the polyurethane prepolymer and a dried particulate by-product of starch fermentation of a grain to provide an extrudate; and

(c) molding the extrudate of step (b) to form the composition, wherein the by-product is present in an amount between about 20 and 90% by weight of the composition.

16. The process of claim 15, wherein the extrudate of step (b) is compression molded in step (d).

17. A composition produced by the process of claim 15.

18. The composition of claim 17, wherein the composition is formed as a product selected from the group consisting of a piece of furniture, a tray, a sheet, and a container.

19. A process for producing a composition comprising:

(a) providing a polyurethane prepolymer comprising a reaction product of at least one polyol and at least one isocyanate;

(b) providing natural fibers;

(c) extruding a mixture of the polyurethane prepolymer, the natural fibers, and a dried particulate by-product of starch fermentation of a grain to provide an extrudate; and

(d) molding the extrudate of step (b) to form the composition, wherein the by-product is present in an amount between about 20 and 90% by weight of the composition.

20. The process of claim 19, wherein the extrudate of step (b) is compression molded in step (d).

21. The process of claim 19, wherein the extrudate of step (b) is injection molded in step (d).

22. A composition produced by the process of claim 19.

23. The composition of claim 22, wherein the composition is formed as a product selected from the group consisting of a piece of furniture, a tray, a sheet, and a container.

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