

Starch foams containing biomass from the second generation cellulosic ethanol production

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ABSTRACT: Second generation bioethanol is produced from lignocellulose which comes from agricultural waste instead of agricultural feedstock. This study utilized the residuals from the extraction of C5 and C6 sugars in the second generation bioethanol while 20 and 40 wt % of the biomass was blended with starch into a starch/biomass foam. After adding the biomass into starch foam, the morphology of the starch foam changed significantly, showing rough surfaces, higher cell densities, as well as smaller cell areas than the starch only foam. Adding the biomass into the starch overall resulted in the reduction of the compressive strength, the stiffness, and the density of the starch foam. The water sensitivity of the starch foam/biomass was reduced by 60%, indicating a significant improvement of the hydrophilic nature of the starch foam. The foam/biomass demonstrated a lower thermal stability than neat starch foam due to the decomposition of the biomass. The study concluded that the biomass from the second generation cellulosic ethanol process possess similar physical, mechanical, and thermal properties as the other starch foam composite, and yet, no additive is required. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41940.

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INTRODUCTION

Cellulosic ethanol is a type of bio fuel that is produced from lignocellulose, a structural material that comes mostly from the mass of plants. Lignocellulose is composed mainly of cellulose, hemicellulose and lignin. While the first generation bioethanol utilizes agricultural feedstock, such as sugar cane, sugar beet, and corn, the cellulosic ethanol production, as the second generation, produces bioethanol from lignocellulose generated from agricultural wastes, such as wheat straw, sugar cane bagasse, corn stover, and wood chips. The Environmental Protection Agency (EPA)¹ in the USA has set the minimum volume of the cellulosic biofuel in 2013 to be 14 mill gal. The cellulosic ethanol process primarily converts six-carbon (C6) sugars from cellulose and five-carbon (C5) sugars from the hemicellulose part in the biomass. The cellulosic ethanol process still produces a significant amount of the solid waste that mainly goes to landfill.

Sustainable polymer foam composites such as starch foam have existed in the market for some time due to the nature of their biodegradation. Starch biodegrades in water in a relatively short time compared to plastic polymer foam, and is therefore widely seen as a sustainable polymer material. However, the advantage of the water sensitivity of the starch foam is also a major concern in many applications. In dry conditions, the starch foam

becomes brittle; and in wet conditions, the foam becomes soft. The mechanical properties also change when the moisture contents in the starch foam change.² Blending starch with natural fibers or biomass is an alternative solution to improve the mechanical strength and water sensitivity. Both natural fibers based on plant materials and plant biomass are composed of a variety of chemical substances such as cellulose, hemicellulose, and lignin that may enhance the mechanical properties and reinforce the starch polymer matrix. Since natural fiber is hydrophilic in nature, chemical treatment and additives are required in order to incorporate the fiber into starch foam.³ Researchers found that the starch foam/fiber without treatment or additives had little effect on the water absorption capacity.⁴ Some examples are starch foam/cotton linter and starch foam/hemp.⁵ In some cases, the fiber made the foam/fiber composite more hydrophilic than the starch foam by itself.⁶

Adding additives into starch foam/fiber can effectively change the water sensitivity. For example, blending chitosan into cassava starch and fiber together, resulted in a decreased water absorption index⁷ where the combination of chitosan prevents the starch foam's reaction to water molecules. Combining starch foam/fiber with polyvinyl alcohol (PVA) and poly(lactic acid) (PLA) was also found to significantly reduce the water absorption of the foam/starch composite, such as in the cases of core fiber/PVA,⁶

Table I. Processing Table

| Starch/biomass foam | Starch : biomass | Critic acid (wt %) | Sodium bicarbonate (wt %) | Glycerol (wt %) | Water (wt %) |
|---------------------|------------------|--------------------|---------------------------|-----------------|--------------|
| Matrix-1-1 | 100 : 0 | 1 | 1 | 25 | 10 |
| Matrix-2-2 | 100 : 0 | 2 | 2 | 25 | 10 |
| SB-80/20-1 | 80 : 20 | 1 | 1 | 25 | 10 |
| SB-80/20-2 | 80 : 20 | 2 | 2 | 25 | 10 |
| SB-60/40-1 | 60 : 40 | 1 | 1 | 25 | 10 |
| SB-60/40-2 | 60 : 40 | 2 | 2 | 25 | 10 |

sugarcane bagasse fiber/starch foam/PVA,^{3,8} empty fruit bunch/starch/PLA,⁹ and starch/PLA/fiber.¹⁰ Polat *et al.*¹¹ added beeswax into the starch foam/fiber that increased the water resistance. Schmidt and Laurindo¹² impregnated the starch acetate foam/fiber in chloroform solutions at various concentrations, and the sensitivity to water of the foam composite was decreased. Mello and Mali¹³ blended the malt bagasse, a byproduct of the brewery industry into starch foam and found that the composite decreased the initial moisture absorption rate of the trays when lignocellulosic material was below 15 wt %.

The biomass from the second generation cellulosic ethanol is an abundant and thermally treated material via the enzymatic hydrolysis process. During the lignocellulose ethanol production, the thermal treatment ruptures the lignin walls surrounding the cellulose and hemicellulose fibers to make the fibers available for fermentation to ethanol. After converting six-carbon (C6) sugars from cellulose and five-carbon (C5) sugars from the hemicellulose parts in the biomass, the residuals left over contain mainly lignin based material. This process changes the in-take lignocellulose properties permanently and resulted in improved functionality of the residuals such as the reduction of the hydrophilicity.¹⁴ The heat treatment for the fiber is not widely discussed in the literature, but it is used in wood treatment such as pine flour in order to make the lignin more hydrophobic.¹⁵ The “retification” process is very close to the thermal treatment in lignocellulose ethanol production.

The purpose of this study is to investigate the feasibility of utilizing the solid waste from the second generation cellulosic ethanol as filler contents in a starch foam. The evaluation is aimed to examine whether a composite foam containing cellulosic bioethanol processed biomass and starch exhibit better water resistivity and if the resulting properties of the starch/biomass foam are similar or better than the properties of starch/natural fiber in the presence of the additives.

EXPERIMENTAL

Materials

Making the starch based foam blend with fiber involves the selection of starch, fiber, foam agent, and plastizer. The biomass material LENS FBMTM used in this study was acquired from Cedar Creek Products and Technologies. It is a lignin enriched nonsulfonated fractionated biomass extracted through yeast fermentation. The biomass is composed of 34.1% lignin, 22.3%

cellulose, and 0.1% hemicellulose. Remaining contents include protein, ash, and lignin–carbon compounds.

The corn starch was supplied by MP Biomedicals, comprised of 75% amylopectin and 25% amylose, with a pH level of 4.9, and approximately 11–15% moisture content. Water, used to act as a swelling agent was taken from the tap. Citric acid and sodium bicarbonate, as blowing agents, were added into the starch mix to improve the cell growth and expansion characteristics. The critic acid monohydrate (EMD Chemicals) powder used had a molar mass (MW) of 210.14 g/mol. Sodium bicarbonate (VWR), with a melting point of 60°C and MW of 84.01 g/mol, was used in combination with the critic acid. Stearic acid 50 powder (Mallinckrodt Baker), with a specific gravity of 0.94 kg/L and melting point of 69°C, was incorporated as a starch granule swelling agent and external lubricant. Glycerol was added as a plastizer into the starch foam extrusion to make the foam flexible (Table I).

Sample Preparation

Overall, all of the materials were mixed gravimetrically to yield 1 kg batches. First, starch was put into a convection oven for approximately 24 h at 90°C to remove previously absorbed moisture. Mixing all of the materials into a homogenous blend takes place in a vertical mixer with a six quart mixing bowl where starch is poured into the mixing bowl first, followed by glycerol, continuously, for 10 min of mixing. Sodium bicarbonate and critic acid were weighed in one dish and stearic acid in another. After the 10 min mixing phase, the sodium bicarbonate, citric acid, stearic acid, and tap water were dispensed into the mixing bowl, with the mixer still in rotation. The materials were mixed for another 5 min. A primary shear process was performed by feeding the mixture through an electric meat grinder (LEM #779) as a secondary mixing process before the starch blends were fed into the single screw extruder. During the primary shearing process the biomass were conglomerated into the starch before being fed through the meat grinder. The foam processing was derived from a previous method by authors in Reims University.^{16,17}

Extrusion Foam

The aforementioned starch/biomass were then extruded through a single screw extruder (Yellow Jacket, Wayne Machine and Die Company). Starting from the feed throat, the temperature profile was as follows: 104, 124, 138, 138, 135, 132, and 132°C. The screw had a barrel diameter of 25.4 mm with an $L/D = 30$. Upon exiting the die, the foam extrusion passed through an aluminum tube simultaneously with compressed air for a

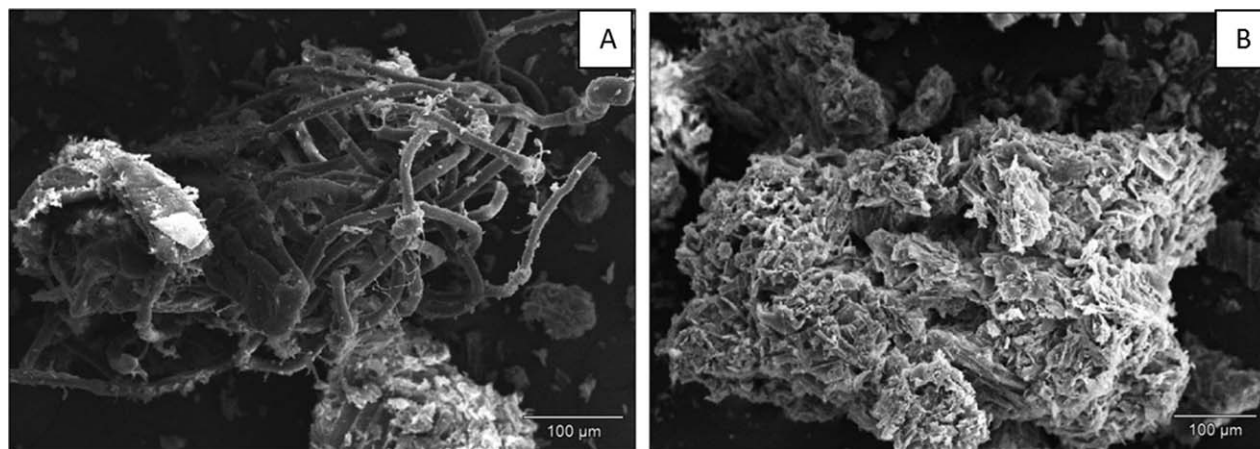


Figure 1. The micrographs ($\times 190$) of the biomass from the second generation cellulosic ethanol production.

quenching effect. The back pressure observed was 6.895 MPa at 50 screw/min.

Foam Characterization and Analysis

Samples were stored in open plastic bags and conditioned in an environment chamber at 23°C and 53% RH for at least 1 week in order for moisture content in the starch foam composite to be equilibrated before carrying on the testing and evaluation specified below.

Density. The density was determined using the apparatus density determination kit (Ohaus Corporation). Because starch foam absorbs water, the gravimetric method cannot be directly applied to measure the density. This study combines the water absorption and gravimetric method, and subtracts the weight of the absorbed water from the sample immersed in the water. The foam density was measured by weighing a sample foam, both in the air and water, for computing its volume using eq (1). Ten specimens were measured for each starch/biomass formulation.

$$\rho = \frac{A + B_0}{A + B_0 - B}(\rho_0 - \rho_L) + \rho_L \quad (1)$$

where ρ is the density of the sample (g/cm^3), A represents weight of the sample in the air (g), B is the weight of the sample immersed in the water for 1 min (g), B_0 is the weight of sample absorbed in water after 1 min of soaking (g), ρ_0 is the density of the water (g/cm^3), and ρ_L is the air density ($0.0012 \text{ g}/\text{cm}^3$).

Water Absorption and Water Uptake Rate. The immersion gravimetric method was used for measuring water absorption. Specimens of foams were cut into the size of 3 cm. The samples were weighed and immersed in a water bath for a specified interval of 5 min starting from 1 to 30 min. The amount of absorbed water was calculated as the weight difference between before and after the immersion. The reported values are the means of ten samples for each formulation.

Thermal Properties. The thermal properties of the starch foam/biomass were obtained through thermal gravimetric analysis (TGA) model TGA 500 manufactured by TA Instruments. TGA determines the mass loss (%) in the composite due to decom-

position or loss of volatiles (such as moisture) through measuring the change in the mass of the sample when it is heated in a furnace.

Scanning Electron Microscopy and Microscope. In order to investigate the dispersion of the biomass in the starch matrix, the cross sectional profile of the samples were examined by microscope and scanning electron microscopy (SEM) in two different magnifications: 35 \times and 80 \times . At 35 \times magnification, the overall distribution of the cell structure in the foam composite was assessed. Then SEM pictures were obtained at 80 \times magnification to show the dispersion of the biomass in the matrix and whether there is an adhesion between the biomass and the matrix present in the composite. A piece of foam sample along the cross section was cut into the approximate dimensions of 0.30 \times 0.30 \times 0.30 cm. These samples were then sputter coated with AuPd to make them conductive. The cross sectional profile of the samples was then examined by SEM.

Compression Test. It is difficult to conduct a compression test for a single extruded foam sample. For this reason, multiple sections of the extruded foam were cut perpendicular to the machine direction at a length of 3.80 mm. Five samples with the most identical length and diameter were selected. The five samples were sandwiched between two aluminum discs with five holes and oriented such that stress was applied in the machine direction. The diameter of each section was measured and a mean diameter was calculated and used to compute the cross sectional area of each sample, the sum of all five areas was then entered into the program (Instron model 5567 with Bluehill 2 interface). The method was set to five compression cycles at a rate of 12 mm/min and a compression stress at 50% stain.

RESULTS AND DISCUSSION

Morphology of the Biomass

A scanning electron microscope (SEM) micrograph of the biomass is illustrated in Figure 1. Two types of morphological structures were found and distinguished clearly from each other in the observed biomass. They appear to be the cellulose (A) and lignin components (B). The length of the cellulose fibers are long, about hundreds of microns long, and the diameter of the cellulose is about 15 μm . The lignin are all relatively shorter,

Table II. Density and Radial Expansion of the Starch/Biomass Foam

| Starch/ biomass foam | Cross sectional area (mm ²) | Density (g/cm ³) | Radial expansion |
|----------------------------|--|---------------------------------|---------------------|
| Matrix-1-1 | 53.6 ± 1.27 | 1.05 ± 0.03 | 2.54 ± 0.08 |
| Matrix-2-2 | 42.6 ± 1.84 | 1.04 ± 0.03 | 2.15 ± 0.03 |
| SB-80/20-1 | 48.5 ± 0.69 | 0.99 ± 0.01 | 2.07 ± 0.05 |
| SB-80/20-2 | 38.9 ± 1.04 | 1.01 ± 0.01 | 1.70 ± 0.06 |
| SB-60/40-1 | 49.4 ± 1.48 | 0.99 ± 0.02 | 2.01 ± 0.04 |
| SB-60/40-2 | 41.1 ± 1.82 | 0.93 ± 0.01 | 1.62 ± 0.08 |

most of them being around 20 μm long. This SEM result confirmed the supplier's specification that not all of the cellulose was converted to sugar, with 22.3 wt % of the cellulose still remaining in the biomass.

Density and Radial Expansion

From Table II, it was observed that the addition of fibers contributed to a lower composite density. The density of the starch foam without foaming is 1.46 ± 0.1. Both matrix samples have a higher radial expansion than the samples containing biomass.

The density of starch/natural fiber foam conducted by other studies range between 0.175 and 0.136 g/cm³ for starch-natural fiber foam,⁴ 0.23–0.31 g/cm³ for starch-lignin foam¹⁸ and 0.20–0.32 g/cm³ for starch/sugarcane bagasse/PVA which are less than the foam/fiber density observed in this study. The radial expansion of this study is close to starch-natural fiber foam.⁵ The overall relative lower radial expansion and higher density of the foam/starch samples in this study is due to the use of the single screw extruder. The foam density obtained from a single extrusion is usually twice the foam density produced from commercial facilities, with the same formulation.¹⁹ In addition, the sodium bicarbonate content and the extruder temperature as well as the back pressure of the single extruder are also the factors that affect the foam density and expansion ratio.¹⁶

Water Absorption and Water Uptake Rate

The nature of the starch and biomass determined the water absorption capacity of the starch/biomass composite (Figure 2). The water absorption capacity of the samples went down significantly after adding the biomass into the starch foam, especially with the 40 wt % biomass. Noticeably, matrix-1 has a significantly higher water absorption weight and take up ratio than other samples during the 15–20 min soaking time. This is probably due to the presence of the large cell areas in the matrix, allowing more water to be contained in the cells (refer Table III). Matrix-1 was taken out for comparison due to the aforementioned reason. Compared to the starch foam sample, the water absorption capacity of the 40 wt % biomass sample was reduced by 49–63% after soaking for 15–30 min. The water absorption rate of the starch-biomass composite decreased by 60.0% after soaking for 10–15 min. Water absorption rate represents a composite's sensitivity to water and the results demonstrated that the reduction of the hydrophilicity of the biomass via cellulosic ethanol production influenced the sensitivity to

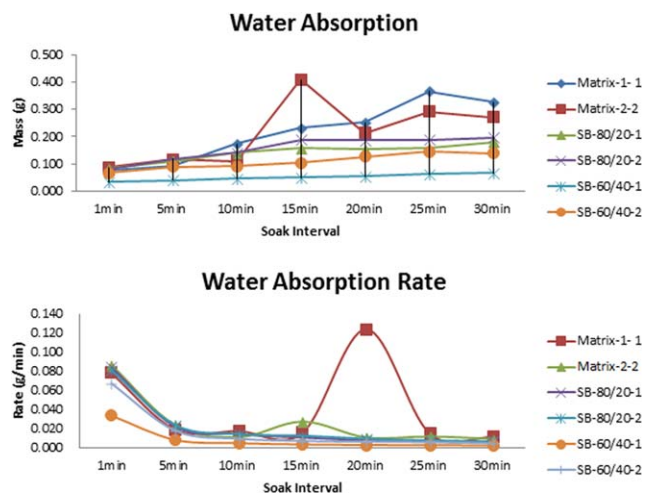


Figure 2. Water absorption capacity and take up ratio. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

water. The results of this study are similar to prior research on cassava starch/natural fiber⁷ and starch foam/lignin,¹⁸ in that the water absorption index decreased with increasing of the fiber content, as well as corn fiber/starch/PVA⁶ foam where the water absorption was reduced by 21 and 49%.

Thermal Properties

Figure 3 shows that the neat starch started decomposition around 300°C. The neat biomass started to have weight loss at around 200°C, indicating the start of a decomposition of the lignin, and had a sharp drop between 300 and 400°C, indicating the weight loss of cellulose components in the biomass. Then, a moderate drop of the weight loss of the neat biomass occurred between 400 and 900°C, reflecting the lignin components. Overall, 75 wt % of the biomass was vaporized. The residuals are most likely lignin-carbon^{15,20} that was formed during repolymerization reaction during the hydrolysis steps. The TGA curve is in agreement with Yang *et al.*'s finding on the pyrolysis characteristics of the lignin,²¹ such that lignin decomposition takes place slowly at a very low mass loss rate, and the significant residuals are left after 900°C.²¹

Compared to the neat biomass and starch, the TGA curve of the LDPE/biomass based composite showed a graduate stage decomposition range where the first drop corresponded to the biomass decomposition with an onset temperature of 200°C, and the second decomposition region took place with an onset temperature of 300°C that mirrored the beginning of the decomposition of the starch matrix and the remaining lignin components. The nonvaporized remains of the starch/biomass in the TGA curves correlated the fractions of the biomass added and its lignin-carbon component.

Derivative thermo-gravimetric analysis (DTG) curves show the decomposition rate (Figure 4). The peaks at 300 and 350°C in DTG corresponds to the decomposition of the neat starch and the weight loss of the biomass, respectively. The single DTG peak of blended starch foam/biomass occurred in the region around 300–310°C, representing mostly the starch

Table III. The Measured Cell Numbers and Mechanical Properties of the Starch/Biomass Foam

| Starch/biomass foam | Number of cells in cross section | Area sum of cells (%) in cross section | Compressive strength (MPa) | Young's modulus (MPa) |
|---------------------|----------------------------------|--|----------------------------|-----------------------|
| Matrix-1-1 | 4.30 ± 1.50 | 27.0 ± 1.90 | 7.46 ± 1.77 | 26.3 ± 4.49 |
| Matrix-2-2 | 6.50 ± 1.30 | 11.8 ± 0.30 | 9.17 ± 1.94 | 22.3 ± 2.93 |
| SB-80/20-1 | 3.50 ± 1.00 | 7.5 ± 0.40 | 9.67 ± 0.70 | 29.7 ± 2.68 |
| SB-80/20-2 | 11.5 ± 1.90 | 24.0 ± 0.80 | 6.10 ± 1.04 | 19.8 ± 2.96 |
| SB-60/40-1 | 12.0 ± 3.60 | 19.3 ± 0.50 | 5.33 ± 1.49 | 20.0 ± 3.77 |
| SB-60/40-2 | 13.0 ± 4.70 | 25.2 ± 0.40 | 6.37 ± 1.92 | 19.4 ± 4.57 |

decomposition temperature. This is due to the reason that only a fraction of the biomass are present in the starch foam/biomass (20–40 wt %), and of them, the 25% nonvaporized lignin–carbon are not decomposable.

Morphology of the Foam

The Morphology. Figure 5 illustrates the morphology of the exemplary cross section profiles of the foam. Table III shows that the control sample with 1 wt % foaming agent has the most cell areas among the measured samples. When the 20 wt % biomass was added, the cell areas of the 1 wt % foaming agent sample was reduced, and the cell areas of the 2 wt % foaming agent sample was increased. When further increasing the biomass loading to 40 wt %, the number of the cells increased in all samples. In the presence of the 2 wt % foaming agent, 40 wt % biomass of the starch resulted in an increase in both cell number and cell area compared to the matrix samples. In general, adding biomass increased the cell numbers and cell areas with the exception of SB-80/20-1. On one hand, the biomass increased the viscosity of the starch so that the cell growing ability is lowered. On the other hand, the biomass played a role as a nucleating agent that helped increase the number of cells. The biomass were not completely wetted during the polymer melting due to the high viscosity and contact angle restraint. Therefore, the gas cavities at the interface between the starch matrix and biomass could be created, which lead to form the micro cells.

Figure 6 shows that the starch only foam had a relatively smooth surface, and the wall thickness is thick, with all closed

cells. The surface of the biomass added foams are rough and some of the samples have cracks. The starch foam appears to have dispersed well with the biomass. Noticeably, most of the original long cellulose fibers seen in Figure 1 of the raw biomass, have disappeared. The disappearance of the fibers is probably due to the cellulose melting at 136.24°C,²² and the starch forming linkages with the cellulose during the extrusion process under the extrusion temperature of about 138°C. Because the sample only consists of 0.1% hemicellulose, the residuals observed are most likely the lignin. This finding is matched with the research of Guan and Hanna,²³ from which it was found that lignin and hemicellulose tend to maintain the matrix in starch–fiber foams manufactured at temperatures above the melting point of cellulose. However, the results are in disagreement with Stevens's conclusion¹⁸ that starch/lignin foam's morphology does not change after replacing 20% of starch with lignin. It is probably due to the difference between kraft pine virgin lignin and biomass lignin. Compared to the starch foam with the same forming agent and plasticizer,¹⁶ the cell densities (cell numbers/cross section area) of the twin extruder produced foam were between 15.0 and 50.8 cells/cm². The cell densities of this study were much smaller, ranging from 7.97 to 15.2 cells/cm², and after adding the biomass, the cell density of the foam/biomass increased to 31.6 cells/cm² (refer to Tables II and III).

Compression Strength

In general, the starch/biomass foam showed a reduction in compressive strength when the biomass was added, except in

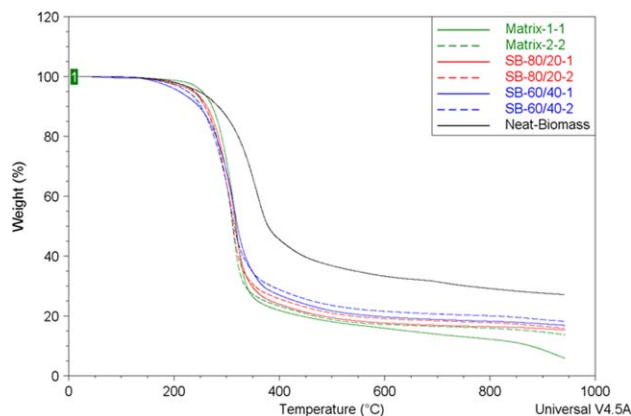


Figure 3. TGA curves of the Starch/biomass foam. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

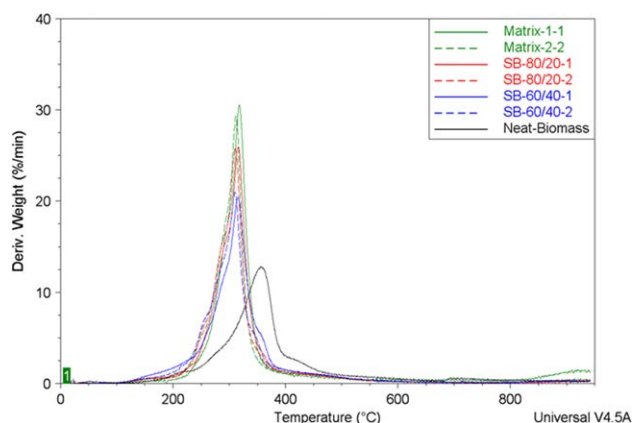


Figure 4. Derivative thermo-gravimetric curves of the starch/biomass foam. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 5. Microscope image ($\times 35$) of the exemplary cross section profiles of the foam. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the case of the sample foam SB-80/20-1. Comparing the compressive strength in Table III, the foams with most cells and cell areas exhibited a lower compressive strength, and the foams with the least cells, i.e. SB-80/20-1, had the highest compressive strength. This led us to believe that the compression strength of the starch/biomass foam is largely contributed by the starch foam, not the biomass. From the Young's modulus in Table III, overall, the stiffness of the biomass added starch foam was slightly reduced when compared to the starch foam sample.

While most studies on starch/fiber foams measure the mechanical strength by tensile testing, and have concluded that adding fiber does enhance the tensile strength for most fibers, few studies have used compression strength as the measurement of the mechanical strength, and their results were not the same as the tensile strength of the starch foam/fiber. The compressive strength of the starch/PVA/natural fiber³ showed no better

results than the foam without the fiber. In Teixeira's study,¹⁰ the starch foam/fiber has less compressive strength (0.46 Mpa) than starch only foam (1.18 Mpa), however, the starch/PLA/fiber exhibited better compressive strength (2.54 Mpa). The starch/lignin foam¹⁸ exhibited a lower flexural stress in three-point flexural tests compared to the starch only foam, ranging from 2.20 to 2.71 Mpa. The results showed a similar change pattern as this study, with most of the foam samples having a lower flexural strength than the foam samples without lignin, except for one combination with lower concentrations of foam agent and biomass.

CONCLUSION

The residuals from the second generation bioethanol hold great promise as a potentially widely used biodegradable filler thanks to its unique functionality through the enzymatic hydrolysis

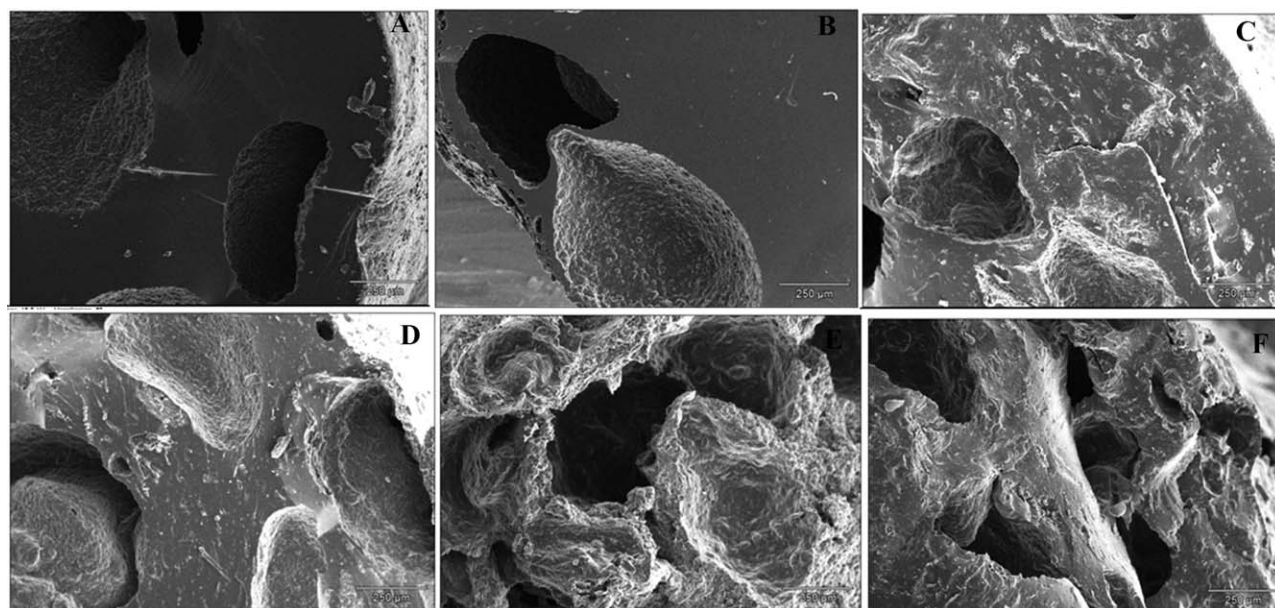


Figure 6. SEM micrographs ($\times 80$) for Matrix-1-1 (A), Matrix-1-2 (B), SB-80/20-1 (C), SB-80/20-2 (D), SB-60/40-1 (E), and SB-60/40-2 (F).

process. The lignin enriched biomass after the extraction of the C5 and C6 sugars can change the hydrophilic nature of the starch foam. Both water absorption capacity and sensitivity to the water of the starch/biomass foam reduced in great extent in the presence of this biomass. When compared to the starch only foam, the developed starch/biomass foam demonstrated similar properties of starch foam/natural fiber, especially starch/lignin foam. These properties include a denser and smaller morphological cell structure in the foam, a lower foam density, as well as the reduced compressive strength and stiffness. The thermal properties of the starch/biomass mainly reflected the starch's thermal degradation behavior. This study concluded that the biomass from the second generation cellulosic ethanol production could potentially suppress the original natural fiber and provide a cost effective and sustainable reinforcement for the starch foam. The future starch/biomass foam is suggested to be produced using twin extruder and commercial foaming facilities for achieving a lower foam density and higher expansion ratio.

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