MRS Communications (2018), *8*, 257–265
© Materials Research Society, 2018
doi:10.1557/mrc.2018.37

MRS Communications

Research Letter

Developing fire-retardant and water-repellent bio-structural panels using nanocellulose

Nadir Yildirim, Bursa Technical University, 16310 Bursa, Turkey
Address all correspondence to Nadir Yildirim at **nadir.yildirim@btu.edu.tr**

(Received 23 January 2018; accepted 28 February 2018)

Abstract

The fire-retardant and water-repellent bio-structural panels (BISPs) were successfully developed using cellulose nanofibrils, corn starch, boric acid, and *n*-dodecenyl succinic anhydride with adhesive-free character. Its performance properties were evaluated and compared with other well-known products on the market. The BISP's density (0.1 g/cm^3) and permeance value [41.81 g/day/m^2 with 5.76% coefficient of variation (CV)] were found higher than compared competitor products. The BISPs' contact angle was found 132.13° (1.59% CV) for BISP. The BISP was the only fire-retardant product, and the only one developed almost no smoke 2.20%.

Introduction

Energy conservation has been getting an increased amount of attention all over the world as a crucially important strategy for reducing overall energy costs. Energy conservation or energy efficiency is also one of the most effective ways to combat climate change and result in cleaner air. One way to save energy is to develop building envelopes that reduce the heat loss; however, most insulating materials are composed of potentially harmful chemicals and are not biodegradable or compostable. The use of bio-based structural panels made from renewable and natural polymers decreases the usage of petroleum-based products, offers a cleaner environment, and may be a "zero landfill" material. For these reasons, interest and demand in sustainable, eco-friendly, and biodegradable polymers and products derived from organic sources is gaining a more critical role in material science.[1]

This research focused on developing fire-retardant and water-repellent bio-structural panel (BISP) to provide energy efficiency in an eco-friendly way compared with petroleum-based products on the market. Cellulose nanofibrils (CNFs) and corn-starch (CS) were used to design the BISP. Nanocelluloses; cellulose nanofibrils, cellulose nanocrystals, cellulose nanowhiskers, cellulose microfibrils, and bacterial celluloses are a relatively new field in nanotechnology and material science; however, they are getting significant attention[2–5] due to their lightweight structure that offers high thermal and mechanical performance.[1,6–8] These materials are also great candidates for reinforcements to strengthen otherwise weak materials.[9] CS is another environmentally friendly polymer commonly used in various industries, including food, packaging, and pharmaceutical[10]. Although both materials are abundant and environmentally friendly polymers, they both have drawback properties, specifically flammability and hydrophilicity[11] that limits their use in many potential industrial applications.[12]

The cellulosic and CS-based materials[13] are flammable due to atoms (C, H, and O) found in their chemical structure that help start combustion. Also, having highly available hydroxyl groups makes them easy to catch fire.[14–16] To overcome this challenge and develop fire-retardant BISP; a boric acid [BA—[B(OH)$_3$]—99.94% pure] treatment was applied, which is one of the most frequently used fire retardants for starch-based and cellulosic materials,[17,18]. The addition of BA reduces the flame spread of cellulosic material[19] by increasing char formation and releasing the water in the composite structure. Addition of the BA also provides better mechanical performance by crosslinking.[13] The available free hydroxyl groups (OH^-) in CNFs and CS make final products superhydrophilic.[20] The easy interaction with water produces chemical and physical degradation and ends up with a decrease in overall mechanical and thermal performances[21,22] through cell collapses. The *n*-dodecenyl succinic anhydride (*n*-DDSA), commonly used in pulp and paper industry[23] was used to create a hydrophobic character.

In this research, a fire-retardant and water-repellent BISP to be used in wall systems as an alternative to petroleum-based products was developed, characterized, evaluated, and compared with the current products on the market (commercially available thermal insulation panels). The competitor products [Owen's Corning Pink Foam (PF), Dow Super Tuff-R (BF), Lowe's Green Foam (GF)] were purchased from local stores, and their performance properties were investigated and compared by applying the same tests to the BISP developed under this research.

https://doi.org/10.1557/mrc.2018.37 Published online by Cambridge University Press

Developed BISP uses nanotechnology and bio-based ingredients. It has meaningfully unique features and clearly highlights the significant advantages over the competitors. It is an eco-friendly alternative to petroleum-based rigid insulation panels on the market and potentially has a very low carbon footprint. It is expected to have comparable insulation property to products currently on the market,[24] is lightweight, is easy to cut and resize, and is very easy to assemble with nails or screws.

Materials and methods

Wood-based CNFs purchased from The University of Maine and industrial CS (Ethylex 2025—Tate&Lyle) were used as raw materials in this study. The *n*-DDSA (Vertellus Inc., USA) was used to provide water-repellent character to the final product. BA [$(B(OH)_3$—99.94% pure] (Rose Mill Co., USA) was used to obtain fire retardancy.

The cooked CS solution (cooking conditions: 20% solid content—1 h at 190°F) was mixed with CNF–water suspension (1% solid content by weight). The DDSA (5% by weight) was added to the suspension and mixed for 20 min at 2000 rpm at 7.8 pH. The pH was adjusted 4.59 using hydrochloric acid (HCl—2% solid content by weight) prior to adding BA (10% by weight) to the suspension. Once all the ingredients were poured into suspension the final mixture was mixed for additional 20 min at 2000 rpm and poured into freeze-drying trays.

The BISPs was manufactured using the freeze-drying technique to remove the liquid without collapsing the cellular structure (Fig. 1). This cutting-edge technique has many different and critical parameters; specifically, temperature, pressure, and time, that directly affects the performance properties of the final product. For instance, the porosity increases with a decrease in initial freezing temperature and the pore diameter is greater for freezing at −80 °C compared with −30 °C.[25]

Through the development and manufacturing process of the BISPs, a variety of freeze-drying recipes were developed to determine the optimum freeze-drying parameters. As a result, the recipe was determined using thermocouples and screening the instant temperature changes in different locations of the trays to see when the drying was successfully completed. The successful freeze-drying recipe used in this study is given in Table I.

BISPs with rigid character were successfully produced using the recipe given in Table I. Afterward, the physical and thermal properties of BISPs were investigated. In addition to the developed product, performance properties were investigated for the following competitor products, Owen's Corning PF, Dow Super Tuff-R (BF), and Lowe's GF by applying the same tests at same conditions. The following subsections present the measurements and tests performed under this research.

pH Measurement

pH is a critical factor for successful suspension preparation and successful treatment. To achieve successful treatment, each time that a suspension was made a small sample (100 mL) was taken out and its pH was determined using a Symphony B10P pH analyzer. The pH meter was calibrated before each use. Both the temperature and the pH of the suspension were measured and reported.

Density properties

Density measurements were taken according to ASTM C303-10 (2016). The mass of the samples [six (6) repetition] were measured with a scale. Then, the measured mass was divided by the measured volume to acquire the value for density.

Moisture content

Six (6) 50.8 mm × 50.8 mm × 12.7 mm samples were cut from each product for moisture content testing according to ASTM D4442-16. The moisture in each sample was driven off using an oven. The initial and final mass located in the equation provided in the standard and the moisture content of the samples was calculated.

Water vapor transmission

Water vapor transmission tests were conducted according to ASTM E96-16. Water was put into beakers and then covered by the insulation samples and sealed around the top of the beaker. The temperature of the chamber was increased from

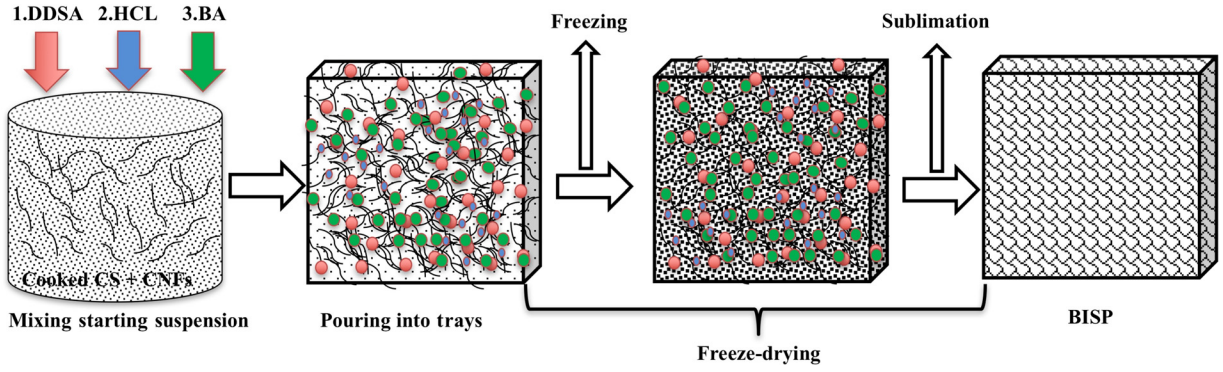


Figure 1. Production demonstration of BISP.

https://doi.org/10.1557/mrc.2018.37 Published online by Cambridge University Press

Table I. Successful freeze-drying recipe.

Freeze-drying step name	Step #	T1 (°C)	T2 (°C)	Pressure	Time (h)	R/H [a]
Thermal treatment	1	30	30	760 Torr	1	H
	2	30	5	760 Torr	1	R
	3	5	1	760 Torr	0.5	H
	4	1	−50	760 Torr	1	R
	5	−50	−50	760 Torr	4	H
Freeze-condenser-vacuum	1	−50	−50	500 Torr	4	H
Drying cycle	1	−50	−50	150 MTorr	4	H
	2	−50	0	150 MTorr	8	R
	3	0	0	150 MTorr	8	H
	4	0	30	150 MTorr	8	R
	5	30	30	150 MTorr	20	H
	6	30	30	150 MTorr	20	H
	7	30	30	150 MTorr	20	H
	8	30	30	150 MTorr	20	H
	9	30	30	150 MTorr	20	H
Final drying	1	30	30	150 MTorr	0.5	H

[a]R, Ramp and H, Hold.

23 to 28°C. The samples were removed and weight at various points throughout the test to determine the weight loss, and then the permeance was determined. The tests were applied at 23 ± 1 °C and 50% RH.

Contact angle properties

Contact angle measurements were performed according to ASTM C272-16. A drop of distilled water was placed on three (3) 76.2 mm × 76.2 mm × 12.7 mm samples of each product and the contact angle was measured using an OCA 20 video-based contact angle measuring system.

Burning (flammability) properties

The rate of burning tests was conducted at the University of Maine Advanced Structures and Composites Center according to ASTM D635-14. A sample with dimensions 125 mm × 13 mm × 13 mm was held in a horizontal position and burned from the end. The time for the sample to burn 75 mL was recorded.

Smoke development properties

The density of smoke tests was performed according to ASTM D2843-16. Three (3) 25.4 mm × 25.4 mm × 1.27 mm samples were burned, and the density of smoke was determined by how well the light was transmitted through the smoke.

Thermal resistivity (R-values)

A total of six (6) BISP specimens were cut down to 300 mm × 300 mm × 25.4 mm for thermal conductivity tests. The steady-state thermal transmission was measured (at 25 °C mean temperature) using a heat flow meter (NETZSCH Lambda 2000 heat flow meter) according to ASTM C518-10. The *R*-values of the commercially available insulation panels were obtained from online sources (Technical Reports).

Trueness and squareness

Trueness and squareness measurements were taken according to ASTM C550-15. The BISPs were measured to see how to square all of the edges and faces were. Total of four (4) 250.4 mm × 250.4 mm × 1.27 mm samples were measured.

Statistical analysis

Under this effort, the density, moisture content, water vapor transmission, contact angle, burning, smoke development behaviors, and thermal resistivity values were analyzed and compared by conducting a one-way means/ANOVA to check if there was a significant overall difference [significance level (α) = 0.01] among the evaluated products (BISP, PF, BF, and GF). Significant differences between groups were evaluated by use of a Tukey–Kramer Honestly Significant Differences (HSD) test, with $\alpha = 0.05$.

https://doi.org/10.1557/mrc.2018.37 Published online by Cambridge University Press

Results

The overall results of the study are discussed in the following sections

pH Measurement

Literature studies showed that the*n*-DDSA response values showed a rise from pH 7 to 8.6[26] and then fell as the pH went above 8.6. In this research, the pH value was 7.8 for the starting slurry. Therefore, the *n*-DDSA was added to CNF + CS suspension before the BA addition (at pH 7.8). Then, the pH value was adjusted to 4.59 with 5.35% coefficient of variation (CV), and the temperature was set to be 23.65 °C with 0.55% CV (Table II). These pH value adjustments were performed according to previous studies and technical reports (pH 3.70 for 4.7% solution 20 °C and pH 6.10 for 0.1% solution 20 °C) (http://www.rosemill.com/v/html/msds/boractech.pdf).

In previous studies, it was shown that BA provides successful results for flame retardancy under pH 6.0 and shows highly acidic character at pH 4.[27] Other research on pH dependence of the stability of esters of BA performed in the 1980s provided parallel results to this study.[28]

Wicklein et al. studied the complexation of BA and nanocellulose interactions and showed that the BA treatment creates flame-retardant CNF composites and enhances the thermal stabilities of the final product.[29] As a result, the optimum pH and temperature for the starting material suspension were determined for developing a fire-retardant and water-repellent BISP as discussed in the following sections.

Density properties

The density of the BISP was found statistically higher than the commercially available products PF, GF, and BF (Table III). In addition, the material's density can be decreased or increased by revising the solid content of the starting suspension. To produce a super light wall system component, the density can be decreased; however; this density reduction also results in lower mechanical performance. For a wall system component with higher mechanical performances and rigidity, the density can be increased by revising the starting material's solids content. Also, the raw and the treatment materials that construct solid structure of the BISP can be revised using higher or lower density raw and the treatment materials to adjust the final product's density.

Table II. The final suspension pH value and temperature.

BISP	pH	Temperature (°C)
1	4.27	23.66
2	4.74	23.66
3	4.44	23.44
Mean	4.48	23.59
STD	0.24	0.13
CV (%)	5.35	0.55

Table III. Density and moisture content (%) results.

Sample	Density (g/cm^3)	Moisture content (%)
BISP	0.10 (8.16) A	13.40 (1.17) A
PF	0.03 (0.35) C	0 B
GF	0.04 (0.03) BC	0 B
BF	0.04 (3.79) B	0 B

Parentheses indicate the coefficient of variation (CV, %). A, B, and C letters indicate the significant differences between the products.

Moisture content

Moisture content was measured in order to provide information about the developed products' condition prior to testing under this study. This information is critical for potential future studies to provide a more accurate comparison with commercial products. The moisture content of BISP varied from 9% to 16% (Table III), and the mean value was determined to be 13.40% with 1.17% CV.

Parentheses indicate the CV (%). A, B, and C letters indicate the significant differences between the products.

The moisture content is a critical factor for any type of hygroscopic materials. Increases in moisture content can affect the thermal properties by creating potential cell collapses or can decrease the mechanical performances by collapsing the beams, columns, or walls that bonds the cells together. It was shown in earlier studies that higher moisture contents decrease the mechanical performances of wood-based materials.[30] The CNFs are made from long polymer chains connected with hydrogen bonds parallel to each other. These hydrogen bonds are easily affected by increasing moisture content and this damage negatively affects the overall mechanical performance of the final product. It was determined that the effect of the hydrogen bond damages due to a 9% change in moisture content could result in a 12% reduction in mechanical properties.[31]

Water vapor transmission

As shown in Table IV, BF has almost no water vapor transmission. This result was expected because the top and bottom of

Table IV. Permeance results.

Sample	Permeance (g/m^2-s-Pa)	Permeance (g/day/m^2)
BISP	3.63×10^{-6} (5.76) A	41.81
PF	4.06×10^{-8} (5.18) B	0.47
GF	4.19×10^{-8} (2.37) B	0.48
BF	5.17×10^{-9} (6.38) B	0.06

Parentheses indicate the coefficient of variation (CV, %). A and B letters indicate the significant differences between the products.

https://doi.org/10.1557/mrc.2018.37 Published online by Cambridge University Press

Table V. Contact angle (°) results.

Sample	Density (g/cm^3)	Contact angle (°)
BISP	0.10 (8.16) A	132.13 (1.59) A
PF	0.03 (0.35) C	88.83 (3.83) BC
GF	0.04 (0.03) BC	101.40 (9.66) B
BF	0.04 (3.79) B	81.30 (7.01) C

Parentheses indicate the coefficient of variation (CV, %). A, B, and C letters indicate the significant differences between the products.

the product are coated with a material that significantly lowers the water vapor transmission rate[20] by creating an additional barrier against transmission.

The BISPs were developed using bio-based polymers, which include many hydrogen bonds in their structure. These hydrogen bonds make the BISP a breathable product. This is a positive property because it has less potential for mildew/mold growth (https://www.fema.gov/pdf/rebuild/recover/fema_mold_brochure_english.pdf). However, if the product does not have enough breathable surface and edge to remove the moisture, it can lower the *R*-value because it may cause cell collapses in the BISP's microstructure and nanostructure. This failure in porous structure and the structural imperfections would produce lower thermal resistivity.

Test results for uncoated BISP showed similar or even better water vapor barrier properties (41.81 g/m^2/day) compared with previous studies. The coated (coating weight 40 g/m^2) CNF-based composites' water vapor barrier property was reported 34.6—164.9 g/m^2/day.[20] BISP also showed very similar water vapor barrier property compared with CNF–nanoclay composites (15.4–70.3 g/m^2/day).[32] Differences in water vapor transmission rates can be explained by the various composite components and their different ratios. Also, because the cellular structure has an effect on the water vapor transmission rate, the tortuosity and water vapor pathway is the critical structural property for water vapor transmission.[33,34] The *n*-DDSA molecules potentially act as physical barriers against water vapor transmission and provide similar or lower water vapor transmission rates for the BISP compared with previous studies.

Contact angle properties

As was shown in previous studies, CNFs and CS have a superhydrophilic character because of having highly available free hydroxyl groups[12,35] that easily adsorb water and loosen the material's cellular structure.

The BISP developed under this study showed a very high water-repellent (hydrophobic) character with a mean contact angle of 132.13° (Table V) (Fig. 2.) that can also be called super hydrophobic.[36]

Furthermore, BISP was not only water repellent at the edges and surfaces of the sample, but also inside the panel. Because the BISP was treated for water repellency throughout its three-dimensional (3D) structure, water would not be absorbed on uncoated, cut edges when the product is resized for installation.

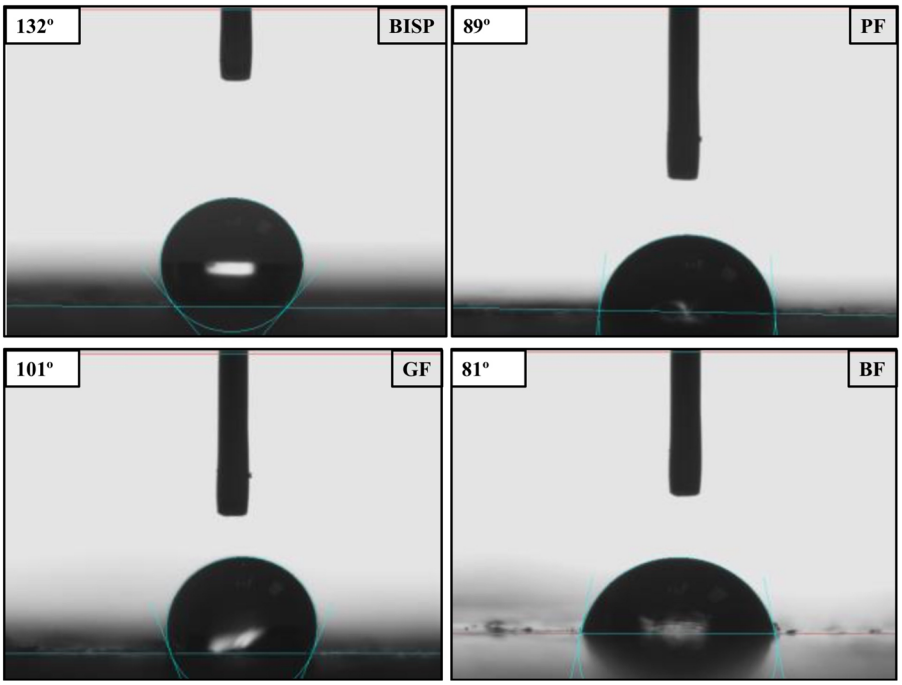


Figure 2. Contact angle measurements.

https://doi.org/10.1557/mrc.2018.37 Published online by Cambridge University Press

Table VI. Burning rate (V, mm/s) results.

Sample	Density (g/cm^3)	Burning rate (V, mm/s)
BISP	0.100 (8.16) A	(0) B
PF	0.03 (0.35) C	(0) B
GF	0.04 (0.03) BC	105.87 (5.91) A
BF	0.04 (3.79) B	80.28 (17.26) A

Parentheses indicate the coefficient of variation (CV, %). A, B, and C letters indicate the significant differences between the products.

Table VII. Maximum smoke density (%) results.

Sample	Density (g/cm^3)	Maximum smoke density (%)
BISP	0.100 (8.16) A	2.20 (13.38) B
PF	0.03 (0.35) C	32.10 (19.40) A
GF	0.04 (0.03) BC	43.20 (14.69) A
BF	0.04 (3.79) B	36.68 (17.45) A

Parentheses indicate the coefficient of variation (CV, %). A, B, and C letters indicate the significant differences between the products.

Burning (flammability) properties

The BA bridged through a hydrogen bond network and successfully increased BISP's flame retardancy. The BISP was found to be statistically better than the other commercially available products evaluated under this study. The BISP found to be a 100% fire-retardant product with zero (0) burning rate after the treatments (Table VI).

It was interesting to note that Owen's Corning PF melted within seconds of applying the flame; however, the flame did not progress forward. This is why it was reported to have a "0" burning rate even though the material is not fire retardant and clearly melts in seconds and creates hazardous black color smoke. The developed BISP was the only prototype with 100% fire-retardant character (Fig. 3).

Researchers who previously studied the flame retardancy of CNF–BA–Sepiolite hybrid composites showed that the BA treatment works successfully against flame retardancy. Also, provides 70% increase in organic residue compared with pure CNF.[29]

Smoke development properties

Blackish and hazardous smoke was developed from the commercially available, petroleum-based products tested. As shown in Table VII, BISP created almost zero smoke (2.20% maximum smoke density) while the other market products created 15–20 times more smoke than the BISP. Smoke from the petroleum-based products has been shown to potentially result in death through poisoning in case of fire in buildings.[37]

The developed smoke produces light adsorption, which decreases the quality (clearness) of the view in the building.

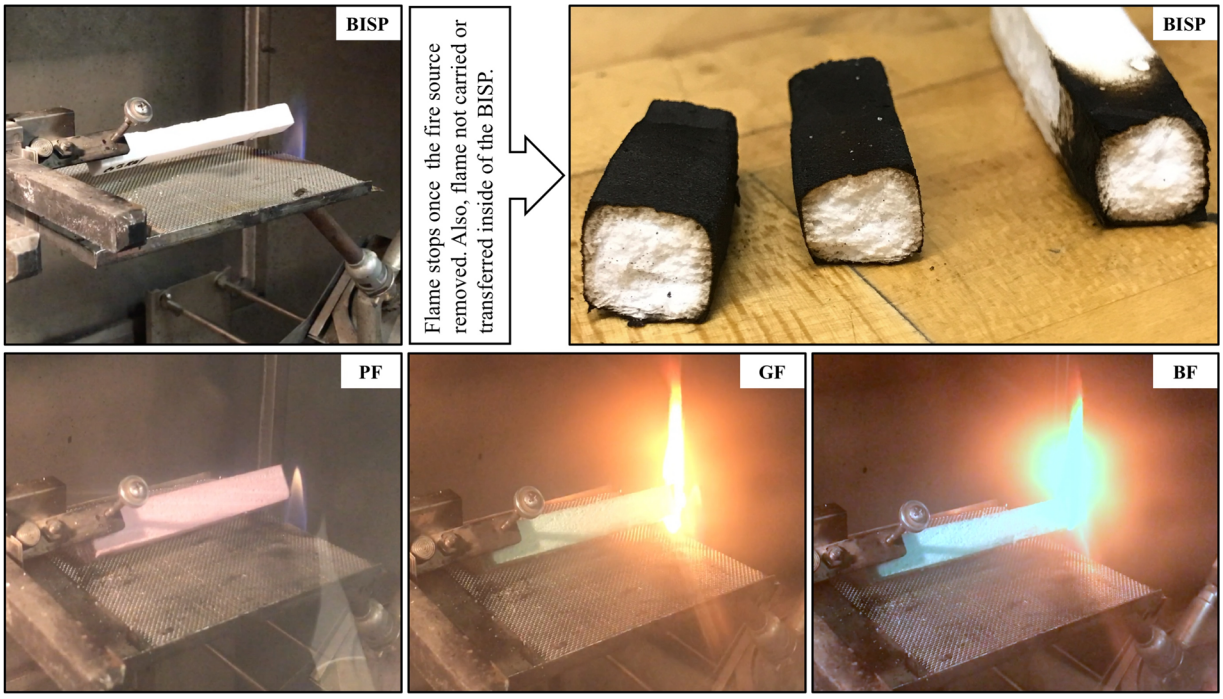


Figure 3. Burning properties of BISP and petroleum-based products (PF, GF, and BF).

https://doi.org/10.1557/mrc.2018.37 Published online by Cambridge University Press

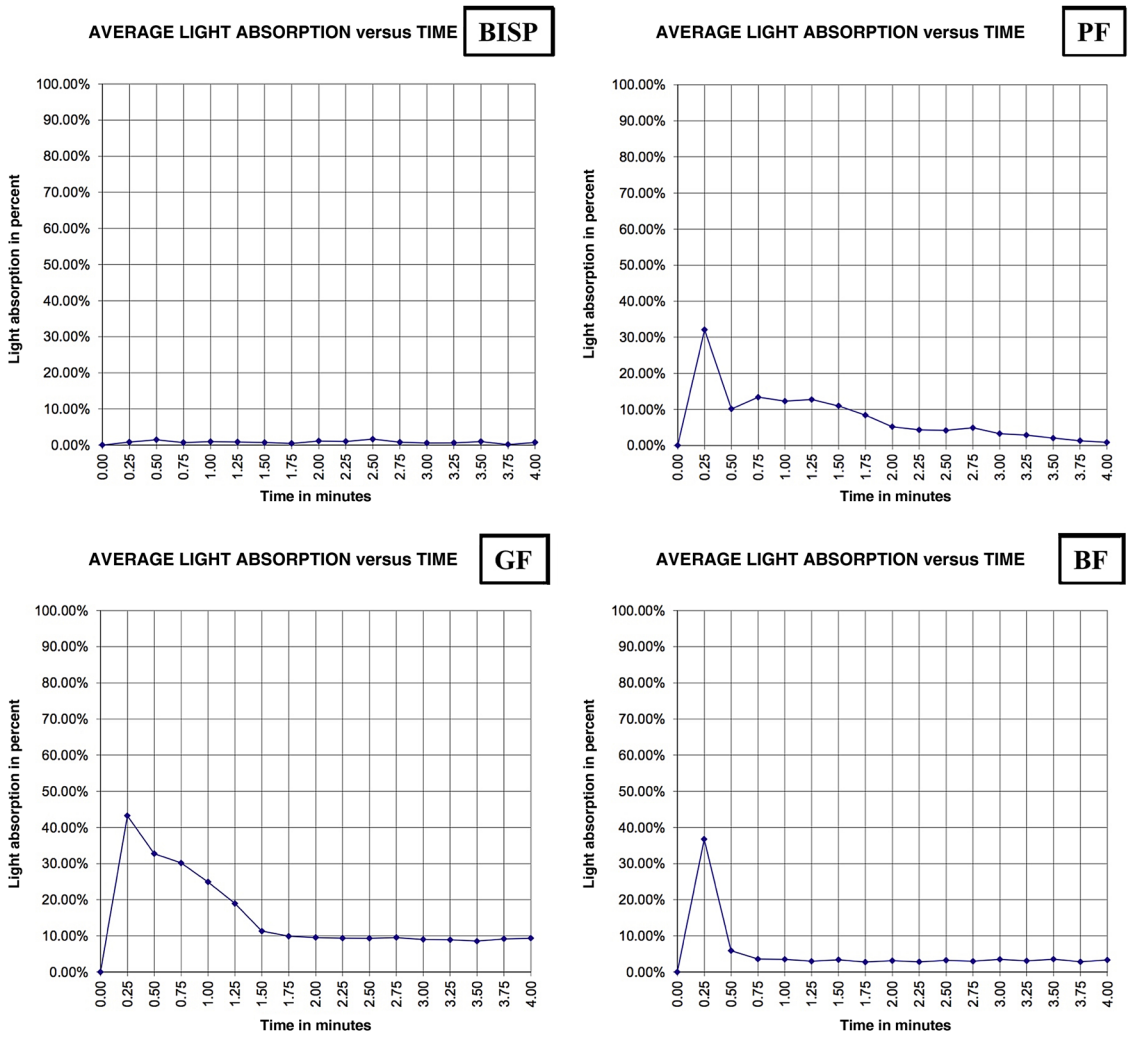


Figure 4. Light absorption (smoke development) by time.

Table VIII. Thermal resistivity (*R*-values) results.

Sample	Density (g/cm^3)	*R*-values
BISP	0.100 (8.16) A	3.17 (1.39) C
PF	0.03 (0.35) C	5.00 B[a]
GF	0.04 (0.03) BC	5.00 B[b]
BF	0.04 (3.79) B	6.50 A[c]

Parentheses indicate the coefficient of variation (CV, %). The CV values were not reported for the PF, GF, and BF because the values were obtained from online sources. A, B, and C letters indicate the significant differences between the products.

[a]http://www.owenscorning.com/networkshare/eis/23513-h-foamular-150-xps-insulation-product-data-sheet.pdf

[b]http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_09a8/0901b803809a8de7.pdf?filepath=styrofoam/pdfs/noreg/179-07932.pdf&fromPage=GetDoc

[c]https://www.lowes.com/pd/Kingspan-Insulation-Common-2-in-x-4-ft-x-8-ft-Actual-2-in-x-4-ft-x-8-ft-R10-Unfaced-Polystyrene-Foam-Board-Insulation/999972968

As shown in Fig. 4, BISP creates no smokes over time. The petroleum-based products melt in under 2 min and create a significant amount of blackish smoke.

*Thermal resistivity (*R*-values)*

The BISP was designed to be used as a structural panel in wall systems; therefore; the thermal resistivity value of the BISP is a critical property. The *R*-value of the BISP was determined under this study using heat flow meter and compared with the *R*-value of the commercial products obtained from the product data sheets available from online sources (Table VIII).

BF, which has surface coatings, showed the highest *R*-values compared with others. The BISPs' *R*-value was found to be lower than that of the other products (PF, GF, and BF); however; BISP was not designed to be used as an insulation foam board The BISP was designed to be used as structural panel and also would provide an insulation property to decrease the overall energy consumption in building system. Consequently, BISP

https://doi.org/10.1557/mrc.2018.37 Published online by Cambridge University Press

Table IX. Trueness and squareness of the BISP.

BISP	Deviation from edge and end trueness (mm)	Deviation from edge trueness across the width (mm)	Deviation from edge trueness across the length (mm)	Deviation from end squareness (mm)	Deviation from corner squareness (mm)	Deviation from flatness along the length of the board (mm)	Deviation form flatness across the width of the board (mm)
1	0	0	0	0	0	0.75	0.75
2	0	0	0.75	0	0.75	0.76	0.75
3	0	0	0	0	0.75	0.75	0
4	0	0	0	0	0.75	0.75	0
Mean	0	0	0.19	0	0.56	0.75	0.36

is not only a BISP with unique features but also increases the overall insulation value of wall systems.

Trueness and squareness

Products that will be used as wall panels need to have a perfect shape at their edges and corners and across the surface. The BISP was evaluated according to ASTM C550-15 standards for this purpose and the shape imperfections were found to be negligible (Table IX).

In this current study, the fire-retardant and water-repellent bio-based structural panel (BISP) made from organic polymers and environmentally friendly treatment materials were introduced. The performance properties and the value propositions against competitors were evaluated and discussed. The BISP showed very promising results based on its use a fire-retardant and water-repellent BISP in the building and construction industry. The BISP developed under this research will not only offer a unique product but also will decrease the use of petroleum-based products, is safer for use, and will decrease the landfill.

Broader impact

The ability to provide a BISP that not only provides unique features but also reduces petroleum usage and has a lower carbon footprint is ideally suited for the eco-conscious market. The innovative production technology (freeze-drying) is currently used in different industries but has not been applied to the construction and insulation industries. The freeze-drying technology is made viable for producing panel products for use in a variety of industries including but not limited to; building and construction.

The developed BISP supports a cleaner environment through using bio-based materials that will not be required to be placed in a landfill when they are ready for disposal.

Conclusions

This research focused on developing a BISP with fire-retardant and water-repellent properties using cutting-edge freeze-drying technology. The BISP developed has 3D hydrophobic (water-repellent) and 3D fire-retardant characteristics; therefore, it can be resized into small pieces and can be thinned as needed without losing its resistance against water and fire.

The physical properties of the BISP were found to be very promising for a product to be used as a BISP in wall systems. The BA and the *n*-DDSA were found compatible to treat the BISPs against fire and water. The BISP offered good insulation property that will help to enhance the overall energy efficiency of wall systems.

Consequently, a novel fire and water-retardant BISP was introduced as a potential product to be used in the building and construction industry. Future studies will include investigating additional performance properties, economic feasibility, scale-up studies, and the environmental effects of the BISP.

Acknowledgments

The authors thank Revolution Research Inc. for supplying nanocellulose in this study and thank Will West for contributing to the manufacturing process. This work was partly supported by the National Science Foundation (NSF) under the Small Business Technology Transfer (STTR) Phase I Program (Eco-friendly Thermal Insulation Composite Foam Boards—Award #1521326).

Conflicts of interest

The author declares no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

References

1. K. Oksman, A.P. Mathew, and M. Sain: Novel biocomposites: processing, properties and potential applications. *Plast. Rubber Compos.* **38**, 396–405 (2009).
2. M.A. Hubbe, O.J. Rojas, L.A. Lucia, and M. Sain: Cellulosic nanocomposites: a review. *BioResources* **3**, 929 (2008).
3. T.H. Wegner and P.E. Jones: Advancing cellulose-based nanotechnology. *Cellulose* **13**, 115–118 (2006).
4. K. Oksman and M. Sain: Cellulose nanocomposites: processing, characterization, and properties. *ACS Symp. Ser.* **938**, 2–8 (2006).
5. M.A.S.A. Samir, F. Alloin, and A. Dufresne: Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. *Biomacromolecules* **6**, 612–626 (2005).

https://doi.org/10.1557/mrc.2018.37 Published online by Cambridge University Press

6. N. Yildirim and S. Shaler: A study on thermal and nanomechanical performance of cellulose nanomaterials (CNs). *Materials* **10**, 718–730 (2017).
7. A. Dufresne: Nanocellulose: a new ageless bionanomaterial. *Mater. Today* **16**, 220–227 (2013).
8. Y. Aitomäki and K. Oksman: Reinforcing efficiency of nanocellulose in polymers. *React. Funct. Polym.* **85**, 151–156 (2014).
9. K.Y. Lee, Y. Aitomäki, L.A. Berglund, K. Oksman, and A. Bismarck: On the use of nanocellulose as reinforcement in polymer matrix composites. *Compos. Sci. Technol.* **105**, 15–27 (2014).
10. B.E. Dale and J. Chem: 'Greening' the chemical industry: research and development priorities for biobased industrial products. *Technol. Biotechnol.* **78**, 1093–1103 (2003).
11. N. Lavoine, I. Desloges, A. Dufresne, and J. Bras: Microfibrillated cellulose – its barrier properties and applications in cellulosic materials: A review. *Carbohydr. Polym.* **90**, 735 (2012).
12. I.S. Bayer, D. Fragouli, A. Attanasio, B. Sorce, G. Bertoni, R. Brescia, R. D. Corato, T. Pellegrino, M. Kalyva, S. Sabella, P.P. Pompa, R. Cingolani, and A. Athanassiou: Water-repellent cellulose fiber networks with multifunctional properties. *ACS Appl. Mater. Interfaces* **3**, 4024–4031 (2011).
13. Y. Yin, J. Li, Y. Liu, and Z. Li: Starch crosslinked with poly (vinyl alcohol) by boric acid. *Appl. Polym. Sci.* **96**, 1394–1397 (2005).
14. S. Gaan and G.J. Sun: Effect of phosphorus and nitrogen on flame retardant cellulose: A study of phosphorus compounds. *J. Anal. Appl. Pyrolysis* **78**, 371–377 (2007).
15. P. Rupper, S. Gaan, V. Salimova, and M. Heuberger: Characterization of chars obtained from cellulose treated with phosphoramidate flame retardants. *J. Anal. Appl. Pyrolysis* **87**, 93–98 (2010).
16. V. Salimova, N. Dimitry, and S. Gaan: Effect of chemical environment of organophosphorus compounds on thermal decomposition of cellulose. *PMSE Prepr.* **98**, 250–251 (2008).
17. A.R. Horrocks: Fire retardant challenges for textiles and fibres: new chemistry versus innovatory solutions. *Polym. Degrad. Stab.* **96**, 377–392 (2011).
18. J. Alongi and G. Malucelli: Cotton flame retardancy: state of the art and future perspectives. *RSC Adv.* **5**, 24239–24263 (2015).
19. Z.A. Nagieb, M.A. Nassar, and M.G. El: Effect of addition of boric acid and borax on fire-retardant and mechanical properties of urea formaldehyde saw dust composites. *Int. J. Carbohydr. Chem.* **2011**, 1–6 (2011).
20. Z. Song, H. Xiao, and Y. Zhao: Hydrophobic-modified nano-cellulose fiber/PLA biodegradable composites for lowering water vapor transmission rate (WVTR) of paper. *Carbohydr. Polym.* **111**, 442–448 (2014).
21. D. Topgaard and O. Soderman: Diffusion of water absorbed in cellulose fibers studied with H-NMR. *Langmuir* **17**, 2694–2702 (2001).
22. K. Hofstetter, B. Hinterstoisser, and L. Salmen: Moisture uptake in native cellulose – the roles of different hydrogen bonds: a dynamic FT-IR study using deuterium exchange. *Cellulose* **13**, 131–145 (2006).
23. A. Salminen: Hydrophobic micrfibrous cellulose and method of producing the same. Patent WO 2012089929A1 (2012).
24. N. Yildirim, S.M. Shaler, D.J. Gardner, R. Rice, and D.W. Bousfield: Cellulose nanofibrils (CNFs) reinforced starch insulating foams. *Cellulose* **21**, 4337–4347 (2014).
25. M. Balaxi, I. Nikolakakis, and S. Malamataris: Preparation of porous microcrystalline cellulose pellets by freeze-drying: effect of wetting liquid and initial freezing conditions. *J. Pharm. Sci.* **99** 2104–2113 (2010).
26. Z. Liu, Y. Li, F. Cui, L. Ping, J. Song, Y. Ravee, L. Jin, Y. Xue, J. Xu, G. Li, Y. Wang, and Y. Zheng: Production of octenyl succinic anhydride-modified waxy corn starch and its characterization. *J. Agric. Food Chem.* **56**, 11499–11506 (2008).
27. K.C. Chen and Y.F. Lin: Immobilization of microorgansizms with phosphorylated polyvinyl alcohol (PVA) gel. *Enzyme Microb. Technol.* **16**, 79–83 (1994).
28. M.V. Duin, J.A. Peter, A.P.G. Kieboom, and H. Van Bekkum: Studies on borate esters I. *Tetrahedron* **40**, 2901–2911 (1994).
29. B. Wicklein, A. Kocjan, G. Salazar-Alvarez, F. Carosio, G. Camino, M. Antonietti, and L. Bergström: Thermally insulating and fire-retardant lightweight anisotropic foams based on nanocellulose and graphene oxide. *Nat. Nanotechnol.* **10**, 277–283 (2014).
30. N. Sombatsompop and K. Chaochanchaikul: Effect of moisture content on mechanical properties, thermal and structural stability and extrudate texture of poly (vinyl chloride)/wood saw dust composites. *Polym. Int.* **53**, 1210–1218 (2004).
31. F. Yin, C. Tang, X. Li, and X. Wang: Effect of moisture on mechanical properties and thermal stability of meta-aramid fiber used in insulating paper. *Polymers* **9**, 537–551 (2017).
32. C. Aulin, G. Salazar-Alvarez, and T. Lindstrom: High strength, flexible and transparent nanofibrillated cellulose-nanoclay biohybrid films with tunable oxygen and water vapor permeability. *Nanoscale* **4**, 6622–6628 (2012).
33. S.S. Ray and M. Okamoto: Polymer/layered silicate nanocomposites: a review from preparation to processing. *Prog. Polym. Sci.* **28**, 1539–1641 (2003).
34. K.Y. Yano, A. Usuki, A. Okada, T. Kurauchi, and O. Kamigaito: Synthesis and properties of polyimide-clay hybrid. *J. Polym. Sci.* **31**, 2493–2498 (1993).
35. N.T. Cervin, C. Aulin, P.T. Larsson, and L. Wagberg: Ultra porous nanocellulose aerogels as separation medium for mixtures of oil/water liquids. *Cellulose* **19**, 401–410 (2012).
36. H. Jin, M. Kettunen, A. Laiho, H. Pynnonen, J. Paltakari, A. Marmur, O. Ikkala, and R.H.A. Ras: Superhydrophobic and superoleophobic nanocellulose aerogel membranes as bioinspired cargo carriers on water and oil. *Langmuir* **27**, 1930–1934 (2011).
37. A.A. Stec and T.R. Hull. Assessment of the fire toxicity of building insulation materials. *Energy Build.* . **43**, 498–506 (2011).

https://doi.org/10.1557/mrc.2018.37 Published online by Cambridge University Press