Investigation of Nanofibrillated Cellulose for Hydrophobic Packaging Material: Examining Alternatives to Solvent Exchange and Lyophilization

Gareth Christian Birkett, [a] Steven Sicoli,[b] Laszlo Horvath,[a] Johan Foster,[c]
Young-Teck Kim,[d] Scott Renneckar,[e] and Barry Goodell [f,]*

A bio-based polyurethane and a thermosetting acrylic were tested in conjunction with nano-fibrillated cellulose and conventional kraft fiber to evaluate their use as a bio-derived, biodegradable packaging foam. Foams were evaluated for their density, water uptake, and compressive creep behavior. Bio-based urethane had a mean density of 68 kg/m^3, mean water uptake of 4% in 24 h, and exceeded the 10% limit on compressive strain when tested at 71 °C and 22 °C, but remained below the limit when tested at -54 °C. The thermosetting acrylic had a mean density of 128 kg/m^3, mean water uptake of 337% in 24 h, and showed less than 10% compressive creep at all three temperature conditions. The bio-derived urethane was able to incorporate 4% cellulose by mass, and the thermosetting acrylic was able to incorporate 48% cellulose by mass. In a 12-week test of biodegradation under fungal attack by *Gloeophyllum trabeum* and *Rhodonia placenta*, the urethane foam had < 3% mass loss and the acrylic foam had < 1% mass loss. The acrylic foams showed potential for durable packaging, particularly if they could be combined with a surface sealant that could be ruptured at the end of service life to promote degradation of the foam.

Keywords: Nanofibrillated cellulose; Nanocellulose; Biodegradable; Packaging; Foam; Polyurethane

Contact information: a: Department of Sustainable Biomaterials, Brooks Forest Products Center (0503), Blacksburg, VA 24060, USA; b: United States Army Armament Research, Development and Engineering Center, P. O. Box 1000, Acme, OH 44308 USA; c: Macromolecules Innovation Institute, Department of Materials Science and Engineering, 445 Old Turner Street, Blacksburg, Virginia 24061, USA;
d: Department of Sustainable Biomaterials, 310 W Campus Drive, #230C, Blacksburg, VA 2406, USA;
e: Forest Sciences Centre 4034, 2424 Main Mall, Vancouver, British Columbia, V6T 1Z4, Canada;
f: Department of Microbiology, Morrill Science Center IV 639 North Pleasant Street, University of Massachusetts Amherst, MA 01003-9298 USA;
** Corresponding author: bgoodell@umass.edu*

INTRODUCTION

Global production of polymer foams reached over 20 million tons in 2014, making them a significant component of polymer consumption (NewsRx 2016). The majority of foam manufacture is generally through either of two routes: Reaction of monomer resins or the expansion of a thermoplastic polymer. The former route is typical for polyurethane (PU) foams, while the latter is typical of polystyrene (PS) and polyethylene (PE) foams. Their raw materials are generally derived from natural gas and petroleum, although some processes exist that allow for the production of polymer foams from bio-derived feedstocks (Bos *et al*. 2012; Wang *et al*. 2015). Unfortunately, these plant-based feedstocks tend to be produced from agricultural products like vegetable oil or glucose, which puts them in competition with food production (Bos *et al*. 2012).

Nanocellulose is a relatively new product with a growing supply in the marketplace (Rebouillat and Pla 2013). It is a derivative of cellulose fiber, with a nanofibril diameter of less than 100 nm and an aspect ratio (length to diameter) greater than ten (Li *et al.* 2015). Nanocellulose is most often derived from wood waste or agricultural residues, and has no major occupational or environmental health or safety issues associated with its manufacture (O'Connor *et al.* 2014). Many previous studies have shown the ability of nanocellulose to form aerogels, which are low-density foams derived from a gel-state material (Jin *et al.* 2004). Additionally, many recent studies have investigated the possibility of improving polyurethane foam properties through the addition of nanocellulose (Auad *et al.* 2007; Wik *et al.* 2011; Faruk *et al.* 2013; Amin *et al.* 2016; Lee *et al.* 2016; Ivdre *et al.* 2016; Zhou *et al.* 2016).

If these foams could be made in an economical and energy efficient manner, they could be used as a more sustainable substitute for conventional polymers. This would serve to reduce petroleum consumption and carbon dioxide production while avoiding increased competition with food markets. Ideally, a cellulose foam could be produced with a very small proportion of non-cellulosic adjunct to retain cellulose's inherent biodegradation properties and be compatible with existing technologies for cellulose product recycling. Sharing these properties with unprocessed cellulose could potentially smooth a market transition from conventional polymer foams by reducing the need for new investments in recycling or disposal technologies.

Unfortunately, current capabilities remain insufficient for providing an economical process for this role. Solvent exchange and lyophilization (freeze drying) are the two major methods used to create an aerogel from nanocellulose (Tejado *et al.* 2014). Both begin with a hydrogel of nanocellulose and remove the water hydrating the cellulose while leaving the expanded network of fibers that was present in the hydrated state. Lyophilization and solvent exchange procedures are relatively easy to perform in a laboratory setting, requiring only freeze drying or a large amount of solvent, respectively. Unfortunately, they are energy intensive and require a 24-hour or greater process time and thus they would not be economically feasible in scaled up production. The use of these techniques is currently necessary, however, because of an inconvenient property of atmospheric drying: the large capillary forces exerted during water's evaporation exceed the strength of cellulose fiber interactions. This disrupts the wet network of nanofibers in its expanded state, creating instead a xerogel, a high-density mat of fibers (Ali and Gibson 2013; Tejado *et al.* 2014, Ganesan *et al.* 2016). The development of a manufacturing method that can generate a low-density product without lyophilization or solvent exchange would provide a way to reduce manufacturing costs and open new markets for nanocellulose's commercial use.

Our key interest was in exploring the potential of cellulose-based foams for use as a replacement for the petroleum derived high-density polyethylene (HDPE) used in some current packaging foams. This objective was chosen because of the need to decrease the environmental impacts of foam manufacture and because bio-based foam packaging materials can potentially be disposed of using simply biological processes such as composting. In particular, foam used in equipment transport and storage for military field operations was chosen as the intended product role. For experimental cellulose foams to be considered as a viable replacement for the conventional HDPE material, they needed to show density, hydrophobicity and mechanical creep properties that were comparable to conventional foams, but also must have relatively rapid biodegradation properties at the end of service life. Three resin materials were selected for evaluation: a thermosetting acrylic and two polyurethane formulations. The goal of this research was to evaluate methods of manufacture using these three adjunct polymers to find relatively low-cost and low environmental impact routes for the creation of a cellulose-based foam with satisfactory mechanical and hydrophobic properties without using lyophilization or solvent exchange.

EXPERIMENTAL

Materials

Cellulose

Two cellulose sources were used in the experiments. The first was nanofibrillated cellulose (ultra-refined bleached softwood kraft pulp NFC) used as purchased from the Process Development Center of the University of Maine (Orono, Maine USA), consisting of roughly 3% cellulose content by mass. The other was a conventional kraft softwood pulp, manufactured by WestRock, Covington, VA. It was acquired in a never-dried state with 37% cellulose content by mass.

The nanocellulose was used with both the polyurethane and acrylic resin systems. It was chosen due its proven potential in forming foams, and its generally superior mechanical performance compared to conventional plant fiber. Conventional cellulose pulp was used only with the acrylic resin system, for reasons discussed below.

Polyurethane

"Botanithane" polyurethane (EZFlow Foam Packaging Systems, San Diego, California, USA) was used with NFC. Botanithane is a bio-based urethane (BBU) resin system made with a soy-derived polyol component and a synthetically derived isocyanate component. A petroleum-derived two-part polyurethane resin, purchased from Fisher Scientific (Waltham, MA, USA), was also used with NFC to investigate the possibility of producing a foam material from more conventional, non-bio-based resins. However, preliminary results indicated that the NFC would separate from the resin as it cured, and this comparative study was therefore abandoned, and the foams used instead were only as a control condition for biodegradation testing.

Thermoset acrylic

"Acrodur" (BASF Corp., Ludwigshafen, Germany), a relatively new thermosetting acrylic, was also investigated. Its primary commercial use is as a zero-formaldehyde adhesive for natural fiber composites in the automotive sector. Both the NFC and kraft pulp fiber were tested with the acrylic.

Methods

BBU experiments

Early experiments found that a more homogenous mixture could be obtained by dispersing the non-dried nanocellulose in the polyol component before the addition of the isocyanate component. Mechanical blending was used to mix the resins as quickly as possible upon addition of the nanocellulose to promote homogeneity in the product. Mixing was performed with an overhead stirrer at < 300 rpm, using a three bladed propeller style stirring head. The mixing time was estimated to vary between 30 s and 120 s, until the samples were homogenized. The reactions were performed in disposable plastic containers to permit cross-sectioning for observation of the homogeneity of the foams' internal structure, with an increase in the number and sizes of internal voids considered to be an indication of lower homogeneity. Additionally, the presence of visible cellulose particulates or internal discoloration was observed as an indication of lower homogeneity.

The first of three experiments with BBU explored the use of additional isocyanate with the NFC gel to ensure that the foam was fully cured after the reaction. The BBU foams that were stiff with non-adhesive surfaces were considered cured. This addition of excess isocyanate was hypothesized to be beneficial in allowing the foam to accommodate the additional hydroxyl groups introduced with the water component of the NFC gel. It was expected that both the cellulose fibers and their absorbed water would compete with the polyurethane's polyol to react with the isocyanate.

The second set of experiments used the NFC gel with a higher cellulose weight percentage (6.5% *vs* the original 3%) obtained *via* centrifugal filtering. This was done to reduce problems that were believed to stem from an excess of water introduced with the NFC.

The third and final set of experiments attempted to determine the upper bounds for cellulose content that the polyurethane could accommodate while still forming a light, flexible foam.

From these three sets of experiments, a formulation was selected to maximize cellulose content without compromising the foam's apparent mechanical properties.

Acrylic experiments

Nanocellulose-acrylic composites were mixed by hand, while those composites that included conventional pulp were mixed with a consumer-grade food blender. The samples were formed in molds or, in the case of more viscous mixtures, as free-standing blocks. The mixtures of pulp, nanocellulose, and acrylic resin formed a viscous slurry, which could be poured into molds to create specimens. The specimens were then baked at 215 °C until they had cured to a solid state, and they were allowed to cool to room temperature overnight before any subsequent testing.

Early testing with nanocellulose mixtures showed severe issues with the acrylic-nanocellulose blend, with the samples shrinking to a fraction of their original size while in the oven. This shrinkage was observed when the temperature was increased, prior to the acrylic's recommended curing temperature, and was likely due to the blend forming a xerogel simply due to drying in the heated environment. Because of this, conventional kraft pulp was introduced to increase the volume and stiffness of the mixture prior to curing to help overcome the weak force bonding as water was removed from the fiber. At the same time, the addition of the kraft pulp helped to reduce the density of the cured material.

Analysis of the Foams

Foams were qualitatively assessed for friability in handling. If a foam formulation created excessive loose powder during sample examination, it was eliminated from further evaluation. Foam hydrophobicity was measured indirectly through the mass ratio of water absorbed after 24 h submersion in reverse osmosis filtered water. The formula is shown in Eq. 1,

$$Mass\ ratio = \frac{(wet\ mass) - (dry\ mass)}{(dry\ mass)} \tag{1}$$

where the ‘dry mass’ is the measured mass (g) before the submersion and the ‘wet mass’ is the mass afterwards (g).

Creep testing was performed using a modified version of ASTM D3575 (2014) part BB at -54 °C, 22 °C, and 71 °C. The deviations from ASTM D3575 (2014) were the use of a vertically secured ruler instead of a dial manometer. Samples were cut into rectangular prisms and loaded with a pure compressive load of 20.6 MPa. This value corresponded to the guideline from A-A-59136 for Type III polymers as defined in the US Federal Commercial Item Description (CID) A-A-59136 (1997). Deformation measurements were taken at increasing intervals from time (t) = 0 (immediately upon loading) to $t > 168$ h. If the foam exceeded more than three times the nominal limit for constant compression creep (defined as a 10% strain in A-A-591236), the test was ended.

Biodegradation tests were performed in accordance with the American Wood-Preservers’ Association (AWPA) standard E10-01 for fungal biodegradation (AWPA 2016). All samples approximated cubes with an edge length of approximately 25 mm. Glass chambers (570 mL gross volume) with soil media were inoculated with both *Gloeophyllum trabeum* and *Rhodonia placenta* for the foam samples. Control wood specimens (southern yellow pine sapwood blocks) that were run in duplicate were also assayed using the same E10 test for controls; however, these blocks were incubated in decay chambers with the two fungi used separately. After an inoculation period of 2 weeks, foam samples or the wood controls were placed into the containers and allowed to degrade for 12 weeks. After removal from the decay chambers, samples were dried at ambient conditions for 24 h under a fume hood before their ‘degraded’ mass was measured. Drying was performed to reduce the introduction of inaccuracy due to water uptake by the samples during the biodegradation test.

RESULTS AND DISCUSSION

Foam properties

The BBU showed a moderate degree of compatibility with cellulose, and several parameters were varied (Table 1) to optimize the foams produced.

Table 1. BBU Trials with Ratios of Resin, NFC, and Results Summary When Using Varied Processing Parameters

Sample	Component Volume Ratio (Isocyanate:Polyol:NFC)	wt.% NFC Added	Comments
Sample Set:			
A	1:1:0	0.0%	Control
B	1:1:1	1.5%	Very heterogeneous foam; procedure amended to include polyol-cellulose premixing
C	1:1:0.5	0.7%	Reduced volume compared to control
D	1.5:1:0.5	0.6%	Loose, open structure
E	2:1:0.5	0.5%	Over-energetic reaction, large volumes of brittle foam created
F	1:1:1	1.5%	Homogenous foam
G	2:1:1	1.0%	Loose, open structure
H	1.5:1:1	1.2%	Loose, open structure, but less so than 2:1:1 formulation
Second Set: NFC with higher cellulose mass content			
I	1:1:1	1.5%	Replication to check for incidental differences in process
J	1:1:1 with concentrated NFC	2.9%	Very brittle
K	1.6:1:1.6	3.6%	Loose, open structure
L	1.4:1:1	2.4%	Better foam structure, still too friable
Third Set: Attempts to incorporate larger amounts of cellulose			
M	1:1:1.6	4.6%	Resilient, non-friable, apparently Homogenous
N	1:1:3	8.3%	Failed to foam, resulted in dense solid
O	1:1:4	10.7%	Failed to foam, resulted in dense solid

The results from the first set of experiments did not support the hypothesis that additional isocyanate would improve the ability of the polyurethane to tolerate the wet nanocellulose. The foams made with an excess of isocyanate showed very large and highly variable foam cell size and many were too brittle to be bisected without large portions breaking apart. Some had an undesirable ‘open’ structure with large voids that extended from the surface into the interior of the material. The second set of experiments had similarly low performances, despite the use of the nanocellulose gel with a higher cellulose to water ratio.

The acrylic foams were much less sensitive to the ratio of reactants, with all samples containing a proportion of conventional pulp yielding a qualitatively similar appearance. Table 2 details the categories of the trials performed with acrylic, but does not include every trial that produced unsuccessful foams.

Table 2. Acrylic Trials

Form of Cellulose	Mass Cellulose (%)
First Set:	
Dry paper	Unrecorded
Wet paper	Unrecorded
6.5 wt.% NFC gel	Unrecorded
14.1 wt.% NFC gel	28%
Second Set: Additional of pulp	
Conventional pulp	37%
Conventional pulp with NFC	44%
Third Set: Contrasting dried pulp	
Conventional pulp	35%
Dried conventional pulp	20%
Fourth Set: Repeatability	
Conventional pulp	52%
Conventional pulp	53%
Conventional pulp	50%
Formulation for testing	
Conventional pulp with NFC	48%

The first set of experiments was designed to determine the compatibility of the resin with wet *versus* dry cellulose, using pulp fiber as a surrogate for the bast fibers employed in the commercial use of the acrylic resin. Because the test materials appeared to have similar properties after curing, the testing moved to the incorporation of nanocellulose into resin. Initial work with two samples showed that the nanocellulose samples collapsed during the heating process, which resulted in less than 20% of the uncured volume. The next set of experiments tested kraft pulp as a ‘bulking’ agent with the nanocellulose to prevent the gel’s collapse while drying. A follow-up experiment tested air-dried kraft pulp to determine whether the material could cure more quickly or more thoroughly without the water present in the wet pulp. Drying caused the cellulose content to drop to an unacceptable amount in the final product due to the additional resin needed to make the material fluid enough to mix and cohere, and so this path was not pursued further. The fourth set of samples used identical formulations to investigate whether process differences caused appreciable variation in the cured foam, although the nature of the mixing process introduced some variation in the final resin:cellulose ratio. This formulation was the final one for all samples produced for creep and biodegradation testing.

The acrylic-based materials all produced a hard, slightly yellow shell of dense material surrounding a much softer interior (Fig. 1). Additionally, the interior material showed much more swelling due to water exposure than the exterior layer. This appeared to indicate that the exterior reached a higher degree of cure compared to the interior.

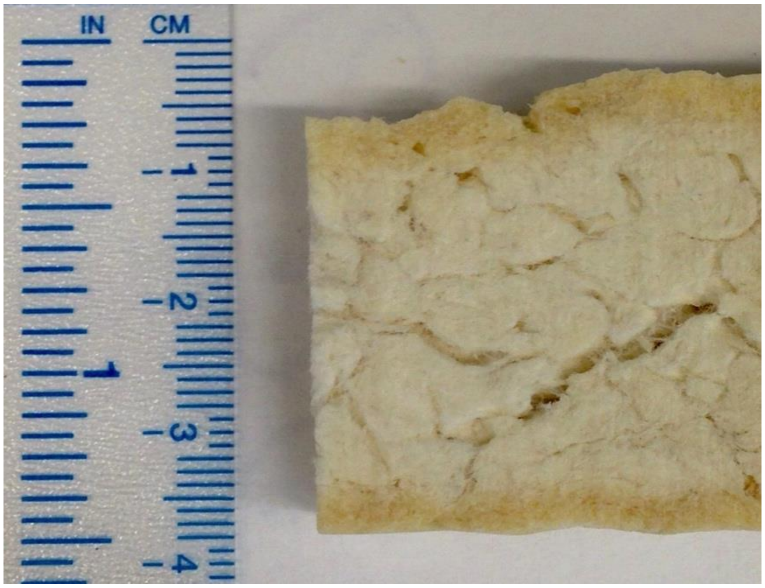

Fig. 1. Close-up optical photograph of sawn acrylic composite, with the exterior layers visible top and bottom

Table 3 shows the mean water uptake values for the acrylic and BBU foams. The acrylic samples performed poorly in the 24-h hydrophobicity test; they absorbed a mean value of over 300% of their original mass in water. However, this property could be beneficial for biodegradability if the foam could be satisfactorily protected from moisture during its service life. Alternately, a foam with these properties could be useful in products where an absorbent foam material is desired. The BBU foams absorbed less than 5% of their original mass in water. However, this measurement may have overestimated the hydrophobicity of BBU, as some water was observed to be physically trapped in the pores of the foam during the weighing of the samples, and it was not actually bound to the sample material.

Table 3. Water Uptake Ratio after 24 h Submersion

Foam Type	Water Mass Uptake Ratio
Acrylic	3.37
BBU	0.04

The density of the foams was very different between the two polymer systems tested, with the BBU being almost half the density of the acrylic system. Table 4 compares the experimental foams with conventional HDPE foams. Both of the foam densities fell within the target range of values for existing packaging foams.

Table 4. Mean Densities of the Tested Foams, and Comparable HDPE Foams Used for Durable Packaging

	Acrylic	BBU	HDPE
Density (kg/m^3)	128	68	64 to 144

Creep testing was performed on both the BBU and acrylic foams. The acrylic data are not listed because zero measurable creep was recorded at all times under all three testing conditions. A sample creep test (Fig. 2.) of a BBU sample containing 4% by mass of cellulose showed that it was highly affected by temperature change, with unacceptable creep that occurred at a temperature of 71 °C. This BBU foam contained the highest amount of nanocellulose that could be incorporated without compromising other foam properties.

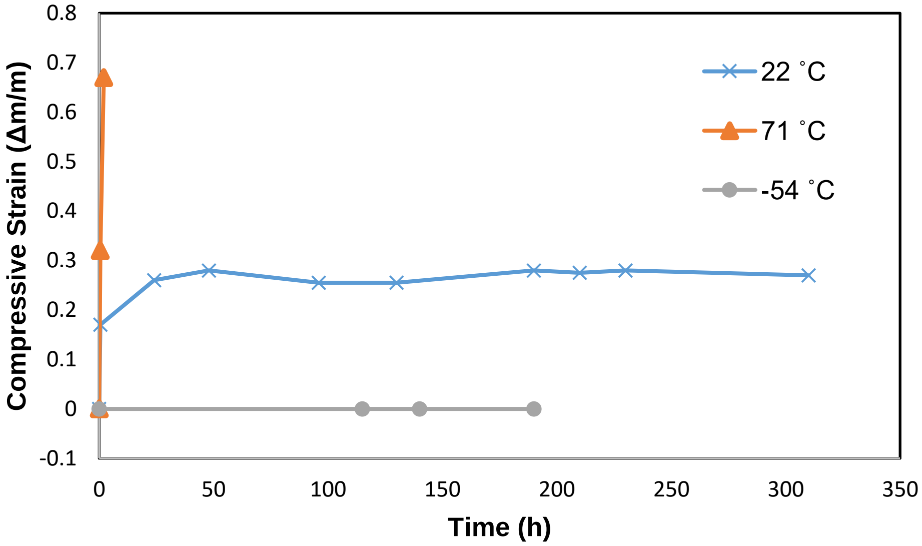

Fig. 2. Creep performance of BBU modified with nanocellulose

Biodegradation testing

Table 5 lists the percentage mass lost by each type of polymer foam when the samples were exposed during the AWPA decay tests. The BBU foam degraded substantially more than the conventional control. The addition of NFC did not appear to make a considerable difference in degradation.

Table 5. Comparison of Mass Loss between Different PU Formulations When Exposed in an AWPA E10 Decay Test

Foam System	Mass Loss
Conventional PU	0.4% ± 0.21 %
BBU	2.5% ± 0.68%
BBU with added NFC	2.7% ± 0.15%
Acrylic	0.1% ± 0.10%

No tested foam degraded at a rate comparable to current ‘biodegradable’ materials like PLA or starch, though further testing is needed to determine if the BBU will continue to slowly biodegrade. For comparison, southern yellow pine tested in similar conditions showed mass losses of 32.5% for *G. trabeum*, and 15.3% for *R. placenta*.

Visually, the fungal hyphae showed no adhesion to the surface of the acrylic foam material or the conventional polyurethane. Some hyphae did attach to the surface of the BBU, which suggested that it might have been more susceptible to biodegradation under appropriate conditions.

Five dimensions of performance (Table 6) were used to compare the properties of each foam. These were chosen to gage the foam performance as a replacement for conventional foam packaging products, used in munitions packaging as described by CID A-A-59136, as well as the desired environmental advantage of biodegradability.

Table 6. Comparison of Key Performance Dimensions between Foams

	Acrylic + Cellulose	BBU + NFC
Hydrophobicity	Unsatisfactory	Satisfactory
Bio-derived Mass	48%	63%
Cellulose Mass	48%	4%
Creep Behavior	Satisfactory	Unsatisfactory
Biodegradation	Unsatisfactory	Unsatisfactory

Current hydrophobicity standards are required for foams by the CID A-A standards. However, these may need to be modified for biodegradable foams because one of the key properties would be water adsorption at some point in the life cycle to permit recycling and degradation. Neither foam had a clear overall advantage in performance when comparing the complete suite of properties. The BBU foam showed good hydrophobicity despite its cellulose content, but it failed to meet creep performance requirements at ambient and elevated temperatures. The acrylic foams had a cellulose mass content of almost 50% with excellent creep performance, but they did not possess the needed hydrophobicity in accordance with the current standard. However, if the foam could be produced with a hydrophobic surface barrier, to prevent moisture intrusion during service life, the acrylic foam would meet or exceed the target mechanical properties. All of the other properties were in the targeted range. The author's testing did not extend to saturation of the samples prior to biodegradation testing, but this may be desirable in future tests of similar samples.

One possible scenario for production of a biodegradable foam would be to produce a moisture-sorbing acrylic-nanocellulose foam that also incorporated an impermeable surface barrier. This surface barrier could potentially be ruptured at the end of service life as a "trigger" to aid in biodegradation. The acrylic-nanocellulose foam would then be saturated with water to enhance biodegradation. However, under current test conditions, although both foams had a large biologically derived portion, neither showed rapid mass loss under fungal attack. Further testing is needed to determine if the acrylic-nanocellulose foams would degrade more rapidly if first saturated with water or a nutrient solution.

The methods investigated did not provide a viable way to create an ultralow-density foam from cellulose outside of the conventional routes of lyophilization and solvent exchange. However, for the replacement of HDPE high-density foams, which was the target of this work, both foams would potentially be adequate with further development.

It was possible that a higher cellulose percentage in the BBU foam could have accelerated its rate of biodegradation. It was also quite likely that allowing water to saturate the acrylic foam would have promoted biodegradation. For the two wood decay fungi, which originally were isolated from forest soil cultures, fiber saturation of the substrate was essential to initiate degradation. If the foam blocks failed to attain a sufficient level of moisture in the testing, the rate of degradation would have been retarded. However, in the relatively dry state tested, it appeared that the acrylic foam was resistant to decomposition. If a foam can be maintained in a sufficiently dry condition, it would have improved resistance to fungal attack and would therefore also have utility as a material in durable goods.

Developing a biodegradable foam is challenging because the foam must survive service life conditions without undergoing loss of mass or performance degradation. But at the end of its service life, the foam must then be triggered to degrade and lose both mass and mechanical properties rapidly. The use of a biodegradable adjunct polymer together with the cellulose fiber matrix may enhance biodegradation, but it could also do so at the expense of the product service life. The combination of a relatively durable polymer mixed with biodegradable cellulose may offer the best strategy for development of a foam that will deteriorate only when desired. The results suggest that a strategy to achieve this desired sequence of events is to use an impermeable barrier over a foam that adsorbs moisture. Incorporating biodegradable materials, such as cellulose and nanocellulose that swell, for example, may aid in rupturing the polymeric network and increasing the potential for biodegradability. Once reduced to microscopic-sized polymeric particles with greater surface area, even “non-biodegradable” polymers are subject to deconstruction by a combination of biological agents, ultra-violet rays, and other environmental agents (Leja and Lewandowicz 2010; Hajji and Rhachi 2013). Additional routes to achieving biodegradable foams may involve integrating other polymers, such as modified HDPE or polysiloxanes (which are simultaneously biodegradable, hydrophobic, and environmentally benign), into the foam composite.

CONCLUSIONS

1. The objective to produce bio-based foams of a density competitive with conventional HDPE foams was met. However, it was not possible to produce an ultralow-density foam from cellulose without using lyophilization or solvent exchange.
2. Thermoset acrylic-based cellulose foams have poor hydrophobicity, good creep behavior, and were resistant to fungal degradation under the conditions tested. However, those conditions as required by standard did not allow for the moisture uptake of the samples prior to exposure to fungal degradation. For testing of cellulosic foams, the standards may therefore need to be modified to generate data more representative of those that may occur in the field with a “trigger” event used to initiate degradation at the end of useful service life.
3. Bio-based polyurethanes made with polyols can incorporate only a limited percentage of wet cellulose into their structure, and this may limit their use in bio-based foam products.
4. Bio-based polyurethanes show excessive creep at moderate or elevated temperatures. They also are hydrophobic, and this contributed to their resistance to fungal degradation. The Acrylic/NFC-cellulose fiber composition showed the greatest promise for the development of a bio-based, biodegradable foam that also met density requirements for HDPE foams.

ACKNOWLEDGMENTS

The authors are grateful for the support of the U.S. Army Armament Research, Development, and Engineering Center (ARDEC) through their grant FA4600-06-D0003: SUB1122437-003. This work was also supported by the USDA-National Institute for Food and Agriculture – Hatch Multistate Project 1012143,

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Article submitted: January 11, 2017; Peer review completed: March 12, 2017; Revised version accepted; April 25, 2017; Published: April 28, 2017.
DOI: 10.15376/biores.12.2.4314-4326