Coating

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Improving fire retardancy of cellulosic thermal insulating materials by coating with bio-based fire retardants

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Abstract: Sustainable thermal insulating materials produced from cellulosic fibers provide a viable alternative to plastic insulation foams. Industrially available, abundant, and inexpensive mechanical pulp fiber and recycled textile fiber provide potential raw materials to produce thermal insulating materials. To improve the fire retardancy of low-density thermal insulating materials produced from recycled cotton denim and mechanical pulp fibers, bio-based fire retardants, such as sulfonated kraft lignin, kraft lignin, and nanoclays, were coated onto sustainable insulating material surfaces to enhance their fire retardancy. Microfibrillated cellulose was used as a bio-based binder in the coating formula to disperse and bond the fire-retardant particles to the underlying thermal insulating materials. The flammability of the coated thermal insulating materials was tested using a single-flame source test and cone calorimetry. The results showed that sulfonated kraft lignin-coated cellulosic thermal insulating materials had a better fire retardancy compared with that for kraft lignin with a coating weight of 0.8 kg/m². Nanoclay-coated samples had the best fire retardancy and did not ignite under a heat flux of 25 kW/m², as shown by cone calorimetry and single-flame source tests, respectively. These cost-efficient and bio-based fire retardants have broad applications for improving fire retardancy of sustainable thermal insulating materials.

Keywords: bio-based; cellulose; coating; fire retardant; thermal insulating material.

Introduction

Buildings are the largest consumers of energy all over the world, e. g., 40 % of global energy is used for heating and cooling in buildings (El-Darwish and Gomaa 2017). To improve the energy efficiency of buildings, thermal insulating materials are used to reduce energy consumption.

Bio-based materials produced from renewable resources have recently been developed based on bioeconomy and low-carbon economy concepts. Renewable raw materials, such as pulp fiber and recycled textile fiber, have been used to produce value-added products, such as environmentally friendly thermal insulating materials (Zheng et al. 2017a, Zheng et al. 2017b, Lacoste et al. 2018). These materials are promising alternatives to traditional oil-based thermal insulating products. However, fire safety concerns of low-density thermal insulating materials have yet to be addressed. Generally, the fire retardancy of thermal insulating materials is improved using fire retardants. Conventional halogen-based fire retardants have potential health risks and produce toxic gases when inflamed (Yurdaskal and Celik 2018). As such, alternative bio-based fire retardants have been proposed to address health and environmental concerns. A few bio-based fire retardants, such as lignin and nanoclay, have been shown to have the potential to decrease flammability.

Lignin is an abundant by-product that can be obtained from pulp and paper industries. The aromatic chemical structure in lignin promotes the formation of a high char yield after decomposition (approximately 40 % at 900 °C) (Ferry et al. 2015). The char layer can protect the underlying substrate from further decomposition and improve fire retardancy. Therefore, lignin has potential as a fire retardant. While lignin has seldom been studied as a fire retardant in cellulosic thermal insulating materials, several studies have explored applications of lignin as fire retardants in plastic. For example, lignin has been shown to create protective char layers in polypropylene (PP), polyethylene terephthalate (PET), polyhydroxybutyrate (PHB), and acrylonitrile butadiene styrene (ABS) to enhance the fire retardancy of these plastics (Canetti et al.

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2006, Canetti and Bertini 2007, Mousavioun et al. 2010, Song et al. 2011, Bertini et al. 2012). Nanoclays, such as montmorillonite and vermiculite, have been used as fire-retardant coatings or fillers in polymers. The ordered distribution of nanosized clay particles can improve the gas barrier property, fire retardancy and mechanical performance (Shan et al. 2015, Chatterjee et al. 2017, Hu et al. 2017).

Fire retardant coatings have become promising treatment options for improving the fire retardancy of materials due to their effective, efficient, and economic advantages. Recent research on the applications of fire retardant coatings has shown that these coatings protect underlying substrate materials from fire damage and enhance their mechanical properties. At present, oil-based binders, such as acrylic resin and epoxy resin, are the most commonly used additives in coating formulation for creating thin films on substrate surfaces. Novel coating materials have been under development as sustainable alternatives in pulp fiber-based packaging material to replace these oil-based coatings. One such material, microfibrillated cellulose (MFC), can improve the strength and stiffness of paper materials. As a coating additive in paper coating formulations, MFC can be used as a co-binder or thickener and thus, serve as a renewable and sustainable alternative to synthetic latex and binders in most coating formulations (Richmond 2014).

In the present study, MFC was used as a binder in coating formulations for different types of fire retardants, namely, sulfonated kraft lignin, kraft lignin, nanoclay, commercial expandable graphite and synergetic fire retardants. These fire retardants dispersed in MFC were coated on the surfaces of cellulosic thermal insulating materials produced from recycled cotton denim fiber and mechanical pulp fiber. The objective of this work was to evaluate and compare the effects of these fire retardant-MFC combinations on fire retardancy and on the thermal and mechanical properties of cellulosic thermal insulating materials.

Materials and methods

Materials

Recycled textile fibers with an average length of 1.5 cm were obtained from the milling of worn-out denim (88.7 % cotton, 9.8 % polyurethane, and 1.5 % spandex). Chemithermomechanical pulp fiber produced from high-temperature processes (HTCTMP) was provided by SCA (Östrand, Sweden). The size distribution of pulp was as follows: 49 % of 3–7.5 mm, 14 % of 2–3 mm, 14 % of 1–2 mm,

9 % of 0.5–1 mm, and 14 % of 0.2–0.5 mm. Sodium dodecyl sulfate (≥ 99.0 %), sulfonated kraft lignin (average Mw $\sim 10,000$, 4 % sulfur, pH 10.5, soluble in water, particle size 125–180 μm), and kraft lignin (5 % moisture, pH 6.5, solubility in NaOH is 0.05 %, insoluble in water) were purchased from Sigma-Aldrich (Stockholm, Sweden). The two types of kraft lignin were produced by a hot alkaline (sulfate) process, and the sulfonated kraft lignin was modified by sulfonation. Nanoclay montmorillonite (Cloisite Na⁺, the average thickness of individual platelets is 1 nm, with 10–1000 nm dimensions, and a density of 2.86 g/cm³) was provided by BYK Additives (Germany). Microfibrillated cellulose (MFC; 2 %) was provided by a local company. Commercial fire retardant-expandable graphite was provided by GrafTech (USA), and a commercial synergetic fire retardant (50 % ammonium sulfate, 10 % ammonium polyphosphate, and 40 % aluminum hydroxide) were obtained from a local company.

Methods

Preparation of thermal insulating materials

Cellulosic thermal insulating materials were produced using a foam-forming technique (Zheng et al. 2017a, Zheng et al. 2017b). Briefly, 23 g of HTCTMP and 23 g of recycled textile fibers were mixed with 1.3 g of sodium dodecyl sulfate surfactant in 1 L of water. The mixtures were mechanically stirred (3000 rpm, 15 min) in an L&W Pulp Disintegrator (ABB, Zürich, Switzerland) to produce foams, which were then dried (90 °C, 8 h) in a TS8000 oven (TERMAKS, Bergen, Norway).

Coating on thermal insulating materials

The MFC suspension concentration was diluted to 1 % and homogenized using a T25 Ultra Turrax mixer (IKA, Staufen im Breisgau, Germany) at 10,000 rpm for 10 min. The coating formulas are shown in Table 1. The coating weight on each surface was 0.8 kg/m² and was quantified using an XA 204 balance (Mettler-Toledo, Greifensee, Switzerland). The coating process is depicted in Figure 1. The coated samples were dried at 80 °C for 3 h. The reference material was prepared without any coating.

Density and coating weight gain percent

The density of the insulating materials was calculated by dividing the weight determined using an XA 204 balance

Figure 1: Coating process.

Table 1: Coating composition.

Sample	Coating composition
Reference	No coating
MFC	100 % of MFC
Sulfonated kraft lignin + MFC	10 % of sulfonated kraft lignin and 90 % of MFC
Kraft lignin + MFC	10 % of kraft lignin and 90 % of MFC
Nanoclay + MFC	10 % of nanoclay and 90 % of MFC
Synergetic fire retardant + MFC	10 % of synergetic fire retardant and 90 % of MFC
Expandable graphite + MFC	10 % of expandable graphite and 90 % of MFC

(Mettler-Toledo, Greifensee, Switzerland) by the volume. The samples were conditioned at 23 °C and 50 % relative humidity for 24 h prior to weighing. The coating weight gain percent was calculated by the equation below; W_0 and W_1 are the weights of materials before and after coating.

$$\text{Weight gain (\%)} = \frac{W_1 - W_0}{W_0} \times 100 \quad (1)$$

Scanning electron microscopy (SEM)

The surface morphologies of the uncoated reference and coated insulating materials were observed in a scanning electron microscope (Hitachi S-4800 FE-SEM, JEOL Ltd., Japan) after gold/palladium sputtering. The thickness of the fire-retardant coating was measured using SEM software.

Thermogravimetric analysis (TGA)

The required coatings films were prepared by casting the fire retardants-MFC on Petri dishes and subsequently drying them for 3 hours at 80 °C. The thermal stabilities of the uncoated reference and the coating films without fiber were evaluated in nitrogen, from 25 to 800 °C at a heating rate of 10 °C/min using a TGA/SDTA 851e (Mettler Toledo, Greifensee, Zürich, Switzerland). The samples (approximately 5 mg) were placed in alumina pans in a nitrogen

atmosphere (gas flow, 50 mL/min). $T_{\text{onset } 10\%}$ (temperature at 10 % of weight loss), T_{max} (temperature at a maximum rate of weight loss), and the residue at 800 °C were measured.

Ignition ability

Single-flame source tests were carried out to evaluate the ignition ability of cellulosic thermal insulating materials. A single flame was applied to the surface or edge of the conditioned (23 °C, 50 % RH) samples (250 mm long by 90 mm wide). Surface exposure was conducted when the flame was applied on the centerline of the sample surface, 40 mm above the bottom edge of the test sample. Edge exposure was carried out when the flame was applied to the center of the width of the bottom edge of the test sample, following standard EN ISO 11925-2 (CEN ISO 2010). The position reached by the flame after a 15-s flame application time and 20-s duration time was recorded. If the flame tip did not reach a 150-mm limit, then the material was classified as class E according to standard EN 13501-1 (CEN 2007).

Cone calorimetry

The combustion of cellulosic thermal insulating materials (a length $\times$ width $\times$ thickness of 100 $\times$ 100 $\times$ 20 mm³) was measured by cone calorimetry (Fire Testing Technology, FTT, West Sussex, UK). The samples (100 mm $\times$ 100 mm $\times$ 20 mm) were subjected to a 25 kW/m² of radiant heat flux following the procedure described in standard ISO 5660-1 (ISO 2015). The time to ignition (TTI, s), peak heat release rate (Peak-HRR, kW/m²), and total heat release (THR, MJ/m²) were determined. Two repetitions of each sample were performed.

Compressive strength

Compressive strengths of cellulosic thermal insulating materials were measured using an Instron 5944 (Instron, High Wycombe, UK) instrument with a compression rate of 10 % of the original sample thickness per min. The final strain

Table 2: Density and weight gain percentage of the uncoated reference and coated thermal insulating materials.

Sample	Density before coating (kg/m ³)	Density after coating (kg/m ³)	Weight gain percent (%)
Reference	34±2	—	—
MFC	33±0	33±0	0
Sulfonated kraft lignin + MFC	35±1	42±1	20±0
Kraft lignin + MFC	33±2	39±3	19±0
Nanoclay + MFC	35±1	40±1	17±0
Synergetic fire retardant + MFC	32±0	39±0	20±2
Expandable graphite + MFC	33±0	39±0	18±1

was 85 % of the original sample height. Samples with a cross-sectional area of 25 × 25 mm and a thickness of 20 mm were tested at a strain rate of 2 mm/min. All samples were conditioned at 23 ± 1 °C and 50 % RH for 48 h prior to the test. The data were recorded and averaged from 3 measurements.

Thermal conductivity

The thermal conductivity was determined with a Hot Disk TPS 2500 S instrument (Hot Disk AB, Göteborg, Sweden) using a 20 mW output power and a 40 s measurement time in isotropic mode. A 6.4-mm Ni wire sensor was used, and the samples were probed in bulk mode to obtain values for the thermal conductivity at 23 °C. All samples were conditioned for 24 h at 23 °C and 50 % RH. The data were averaged from 3 replicates.

Results and discussion

Density

Table 2 shows the weight gain percentage of the coated insulating materials when MFC or fire retardants + MFC were coated on the thermal insulating materials. After coating, the weight increased by approximately 20 % for most of the samples except the nanoclay-coated sample. This could be due to a loss of high-viscosity nanoclay particles + MFC coating. No obvious density increase was observed when 1 % MFC was coated on the sample due to the limited dry mass of MFC. Additionally, the fire retardants + MFC-coated samples showed 20 % increased weight.

Scanning electron microscopy (SEM)

As shown in Figure 2, the coated surfaces had different microscopic structures. For example, 0.8 kg/m² of MFC coat-

ing did not cover the entire surface (Figure 2b) because the concentration of MFC suspension (1 %) was too low to cover the entire surfaces. Sulfonated kraft lignin + MFC coating (Figure 2c) resulted in a smoother sample compared with the other additives mixed with MFC. This could be due to a good film-forming ability of sulfonated kraft lignin in MFC, i. e., sulfonated kraft lignin readily dissolves in water and is well-compatible with MFC suspension due to the presence of the sulfonic group, leading to an improved surface activity (Ouyang et al. 2009).

The kraft lignin + MFC-coated samples (Figure 2d) showed a relatively rough surface; a few particles remained undissolved in the MFC solution. Nanoclay + MFC coating (Figure 2e) covered most of the surfaces and filled the voids between fibers, which may be related to the better dispersion of smaller particle size of nanoclay (10–1000 nm) in MFC. For the synergetic fire retardant + MFC and expandable graphite + MFC-coated samples, aluminum hydroxide particles (Figure 2f) and expandable graphite flakes (Figure 2g) were observed on the surfaces. The thickness of the MFC and nanoclay + MFC coating films were 0.02 mm and 0.03 mm, respectively, and the thicknesses of other fire retardants + MFC coatings were approximately 0.2–0.3 mm as measured by SEM software. MFC and nanoclay + MFC created a 10-times thinner film than other fire retardants + MFC because of the smaller particle sizes of MFC and nanoclay.

Thermogravimetric analysis (TGA)

TGA was used to explore the thermal degradation behaviors, thermal stability, and final char formation of the uncoated reference and coating films. The curves and data are presented in Figure 3 and Table 3.

$T_{\text{onset } 10\%}$ denotes the initial decomposition temperature at which 10 % material loss was reached. Nanoclay + MFC film had the highest onset decomposition temperature and final residue content (87 %) at 800 °C. The reference had the lowest residue yield due to a lower ther-

Figure 2: SEM images of the uncoated surfaces of reference and coated thermal insulating materials. (a) Reference; (b) MFC; (c) sulfonated kraft lignin + MFC; (d) kraft lignin + MFC; (e) nanoclay + MFC; (f) synergetic fire retardant + MFC; (g) expandable graphite + MFC.

mal stability of fibers consisting of 50 % recycled cotton denim and 50 % mechanical pulp fiber. Approximately 6 % of synthetic fibers (polyurethane and spandex) in the denim fibers increased volatile yields and decreased final char yields. MFC film showed a slightly higher content of residue than the reference, which could be due to its higher purity and quantity of crystalline cellulose (Moriana et al. 2016). Sulfonated kraft lignin + MFC coating film had a lower onset temperature and an increased residue yield than kraft lignin + MFC, which could be due to a relatively higher sulfur content (4–5 %) from sulfonation or the kraft pulping process in sulfonated kraft lignin; kraft lignin only contains 2–3 % sulfur (Han, Sophonrat et al. 2018). The higher sulfur content and introduction of sulfonate groups (SO_3^-) in the sulfonated kraft lignin catalyzes the dehydration of lignin, thus promoting the generation of esters and rearrangement and formation of condensed lignin structure. This results in a fabric more thermally stable than the unmodified kraft lignin (Ouyang

et al. 2009, Konduri and Fatehi 2015, Prieur et al. 2016, Han et al. 2018).

Compared with the commercially synergetic fire retardant + MFC and expandable graphite + MFC coating films, the nanoclay montmorillonite + MFC coating was the most thermally stable sample during the overall thermal degradation process. The only volatile detected during the thermal degradation of nanoclay was water at 300 °C (Cervantes-Uc et al. 2007). This indicated nanoclay can act as a good thermal insulator and a protective layer for cellulosic thermal insulating materials. T_{max} represents the temperature at which the rate of weight loss reaches a maximum in the derivative curves due to rapid volatilization and carbonaceous residue formation (Kopczyński et al. 2015). The derivative curves of sulfonated kraft lignin + MFC, nanoclay + MFC, synergetic fire retardant + MFC, and expandable graphite + MFC coating films showed multiple peaks (Figure 3b). This confirmed that more than two different thermal degradation events occurred. Compared

Figure 3: (a) TG and (b) DTG curves for the uncoated reference, MFC coating film, and fire retardants + MFC coating films.

Table 3: Thermalgravimetric analysis data of the uncoated reference and coating films.

Sample	$T_{\text{onset 10 \%}}$ (°C)	T_{max1} (°C)	T_{max2} (°C)	T_{max3} (°C)	Residue at 800 °C (%)
Reference	306±3	367±1	—	—	15±1
MFC	299±1	343±3	—	—	22±1
Sulfonated kraft lignin + MFC	270±1	284±0	690±0	—	52±0
Kraft lignin + MFC	295±6	356±0	—	—	40±2
Nanoclay + MFC	617±19	313±1	651±10	—	87±0
Synergetic fire retardant + MFC	263±3	245±3	297±2	—	45±3
Expandable graphite + MFC	265±6	128±1	176±1	272±4	74±2

with the reference without any coatings, similar trends (i. e., decreasing T_{max1} and increasing char yield) were observed with the fire-retardant coatings as a result of the decomposition and dehydration of fire retardants and the generation of char. This resulted in a shift of the maximum weight loss temperature (T_{max2}) to a higher temperature in the late stage. Similar results have been reported for different types of fire retardant lignocellulosic materials (Altun et al. 2016, Zheng et al. 2017a, Mandlekar et al. 2018).

Ignition ability

The standard single-flame source test was used to determine the ignition ability of the uncoated reference and coated cellulosic thermal insulating materials (CEN ISO 2010). The results showed that sulfonated kraft lignin + MFC, nanoclay + MFC, and two types of commercial fire retardants + MFC-coated samples met fire class E requirements in surface and edge exposure tests (Figure 4 and Figure 5). This indicated that the products can resist a small flame attack without substantial flame spread for short durations (CEN 2007). The burned areas on the surfaces of the sulfonated kraft lignin + MFC and nanoclay + MFC-

coated samples were similar to those of the two types of commercial fire retardants (synergetic fire retardant and expandable graphite) + MFC-coated samples. These commercial fire retardants + MFC coatings performed much better compared with the same quantity of fire retardants added to fiber suspensions in foaming processes (Zheng et al. 2017a). These coatings can provide more efficient fire protection and thermal insulation effects, resulting in the generation of effective char layers on the surfaces of insulating materials (Weil 2011). However, the reference and MFC-coated samples did not pass the fire test and were completely burned (Figure 4a,b and Figure 5a,b). Additionally, the kraft lignin-coated samples also failed to pass the fire tests (Figure 4d and Figure 5d) likely due to a low formation of protective char residue and large release of flammable volatiles during the thermal degradation of unmodified kraft lignin. These results were confirmed by TGA (Table 3).

Cone calorimetry

Using a standard cone calorimetry test, the burning properties of the uncoated reference and coated samples were

Figure 4: Single-flame source test (surface) results. (a) Reference; (b) MFC; (c) sulfonated kraft lignin + MFC; (d) kraft lignin + MFC; (e) nanoclay + MFC; (f) synergetic fire retardant + MFC; (g) expandable graphite + MFC. Note: burned areas are highlighted by dotted lines.

Figure 5: Single-flame source test (edge) results. (a) Reference; (b) MFC; (c) sulfonated kraft lignin + MFC; (d) kraft lignin + MFC; (e) nanoclay + MFC; (f) synergetic fire retardant + MFC; (g) expandable graphite + MFC. Note: burned areas are highlighted by dotted lines.

measured at a heat flux of 25 kW/m^2 , which simulates a heat flux below vertical spreading wall flames in typical fires (ISO 2012). The results, e. g., times to ignition and heat release rates, are shown in Figure 6 and Table 4.

The peak heat release rate of the sulfonated kraft lignin + MFC-coated sample decreased by 30 % (Figure 6) compared with the uncoated reference. A lower peak heat release rate indicates a reduced flammability and a decreased amount of oxygen consumed in a fire (Brohez 2005). Compared with the uncoated reference and other coated samples, the nanoclay + MFC-coated sample did not ignite under a heat flux of 25 kW/m^2 . This sample performed the best due to the generation of the most efficient char layer and a very limited production of flammable volatiles during nanoclay thermal decomposition. The improved fire retardancy resulted from the formation of a

protective char layer during the degradation of the surface coating. This char layer prevented the underlying substrate from further decomposing by reducing heat transfer and flammable volatile release, thereby decreasing heat release rates and improving fire retardancy (Marney et al. 2008, Laoutid et al. 2009). The results were consistent with the SEM, TGA, and single-flame source test results (Figure 2e, Figure 3, Figure 4e, and Figure 5e). As shown in Figure 7e and Figure 8e, the residues after cone calorimetry test and the SEM images showed that the nanoclay + MFC-coated sample had a compact and intact char layer on the surface, and the underlying cellulosic insulating materials were protected from thermal decomposition.

The expandable graphite + MFC-coated samples had a similar peak heat release rate compared with that for the same quantity of fire retardant added to the fiber sus-

Table 4: Cone calorimetry results for the uncoated reference and coated thermal insulating materials.

Sample	TTI (s)	Peak HRR (kW/m ²)	THR (MJ/m ²)
Reference	12±4	120.0±5.8	9.5±0.7
MFC	18±1	126.6±9	10.8±1.1
Sulfonated kraft lignin + MFC	12±1	84.9±3.9	8.4±2.0
Kraft lignin + MFC	14±2	126.6±8.0	11.1±0.8
Nanoclay + MFC	No Ignition	5.4±0.8	0.4±0.1
Synergetic fire retardant + MFC	34±2	47.2±5.6	4.2±0.2
Expandable graphite + MFC	26±8	47.0±0.5	7.0±0.4

Figure 6: Heat release rate (HRR) curves for the uncoated reference, MFC and fire retardants coated thermal insulating materials.

pension in the foaming process. However, the expandable graphite + MFC-coated sample had a 3-times longer time to ignition (Zheng et al. 2017a). This was due to the expansion of the expandable graphite into a worm-like char layer (Figure 8g) at 160–170 °C caused by redox reactions between H_2SO_4 and the layered graphite (Camino et al. 2001). The efficient intumescent effect of expanded graphite created a 3-mm thick char layer on the surface and thus, delayed the time to ignition (Figure 7g).

For the synergetic fire retardant + MFC-coated sample, the residue formed a shrunken char and could not maintain its original shape. This was due to stress changes during the catalytic dehydration of cellulosic fibers by polyphosphates produced during ammonium polyphosphate (APP) decomposition (Seefeldt et al. 2012), water release and formation of Al_2O_3 (Figure 8f) from aluminum hydroxide (ATH) decomposition at 180 °C (Musbah Redwan et al. 2015), and the evolution of diluted gases, such as NH_3 (Statheropoulos and Kyriakou 2000). Additionally, the generation of thermally stable char resulted in a higher T_{max} in the late stage, as evidenced by thermal gravimet-

Figure 7: Residues after cone calorimetry test. (a) Reference; (b) MFC; (c) sulfonated kraft lignin + MFC; (d) kraft lignin + MFC; (e) nanoclay + MFC; (f) synergetic fire retardant + MFC; (g) expandable graphite + MFC.

Figure 8: SEM images of samples after the cone calorimetry test. (a) Reference; (b) MFC; (c) sulfonated kraft lignin + MFC; (d) kraft lignin + MFC; (e) nanoclay + MFC; (f) synergetic fire retardant + MFC; (g) expandable graphite + MFC.

ric analysis (Figure 3). For the uncoated reference, MFC, and kraft lignin + MFC-coated samples, only loose residues and no char layer were observed (Figure 7a,b,d and Figure 8a,b,d). These results agreed with the results of the single-flame source tests. Samples with a peak heat release rate greater than 120 kW/m^2 did not pass the single flame source test. A large amount of oxygen was consumed when flammable volatiles were released. The thermal insulating materials reacted with fire when the surface broke up, leading to the second peak heat release rate in Figure 6 and increased flammability (Zheng et al. 2017a).

Thermal conductivity

The thermal conductivity values of samples before and after coating are shown in Table 5. Generally, in warm climates, thermal insulation can reduce the indoor temper-

Table 5: Thermal conductivity of the uncoated reference and coated thermal insulating materials.

Sample	Thermal conductivity (W/m/K)
Reference	0.041 ± 0
MFC	0.045 ± 0.001
Sulfonated kraft lignin + MFC	0.045 ± 0
Kraft lignin + MFC	0.043 ± 0
Nanoclay + MFC	0.045 ± 0.001
Synergetic fire retardant + MFC	0.045 ± 0.001
Expandable graphite + MFC	0.047 ± 0.001

atures and cooling energy use in hot summer. Requirements are stricter in colder climates than in warmer climates, even though the standards differ significantly between countries and regions. Thermal conductivity is a very important parameter used to evaluate the thermal insulating properties (Gibson et al. 2012). A lower thermal conductivity indicates a better thermal insulation capacity (Pfundstein et al. 2008). Increased density resulted in increased thermal conductivity; this was due to increased solid conductivity induced by increased heat transfer through a high-density surface. The thermal conductivity of the coated samples ($0.045\text{--}0.047 \text{ W/m/K}$, density 40 kg/m^3) was slightly lower than those of other pulp-fiber-based thermal insulating materials (0.048 W/m/K , density 30 kg/m^3) (Zheng et al. 2017b). This was due to reduced radiative heat transfer and thermal convection due to increased densities and thus, result in a lower total thermal conductivity (Scheiding 2000, Simmler et al. 2005, Pöhler et al. 2017). The thermal conductivity values meet the requirements of thermal insulating materials in buildings. If the thermal conductivity of a material is lower than 0.07 W/m/K , then this material can be considered a thermal insulating material (Dilmac and Kesen 2003).

Compressive strength

The compressive strength values of the uncoated reference sample and coated samples are presented in Table 6. The coated samples had higher compressive strengths (increased by 30 % to 170 %) than the uncoated reference sample. The coated samples had 3–4 times higher compressive strengths compared with similar cellulosic thermal insulating materials ($0.025\text{--}0.049 \text{ MPa}$, density $25\text{--}32 \text{ kg/m}^3$) reported in previous works (Zheng et al. 2017b). The coatings may fill the spaces between fibers and result in reinforcement effects, leading to increased compressive strengths of the coated cellulosic thermal insu-

Table 6: Compressive strength of the uncoated reference and coated thermal insulating materials.

Sample	Compressive strength (MPa)
Reference	0.069±0.005
MFC	0.103±0.043
Sulfonated kraft lignin + MFC	0.143±0.053
Kraft lignin + MFC	0.190±0.016
Nanoclay + MFC	0.096±0.017
Synergetic fire retardant + MFC	0.081±0.015
Expandable graphite + MFC	0.091±0.024

lating materials. The compressive strengths of the porous thermal insulating materials depended on their macroporosity, macropore sizes and geometry, and the strengths of the supports. Decreased surface macroporosity may induce the generation of struts from the coating that could increase the compressive strength. Similar results have been reported by Miao et al. (Miao et al. 2008).

Conclusion

Cellulosic thermal insulating materials were produced from recycled denim and mechanical pulp fibers using the foam-forming technique. Different types of bio-based fire retardants (sulfonated kraft lignin, kraft lignin, and nanoclay) and commercial fire retardants were combined with microfibrillated cellulose (MFC) binder to improve the thermal coating formulations. These formulations were coated on the cellulosic thermal insulating materials to improve their fire retardancy.

The effects of the coatings on reaction-to-fire properties, microscopic surfaces, thermal insulating performances, and mechanical properties of the thermal insulating materials were studied. Sulfonated kraft lignin + MFC and nanoclay + MFC coatings improved the fire retardancy of cellulosic thermal insulating materials and the coated samples met the requirements of fire class E according to single-flame source test results. This indicated that these products can resist a small flame attack without substantial flame spread for a short period of time. Sulfonation of kraft lignin promoted the generation of protective char layers, leading to greater fire retardancy compared with unmodified kraft lignin. The nanoclay + MFC-coated materials performed the best among the bio-based fiber retardants, i. e., no ignition was observed under a heat flux of 25 kW/m². Furthermore, the compressive strengths of the fire retardants + MFC-coated cellulosic thermal insulating materials significantly increased due to reinforcement ef-

fects. The thermal insulating capacity of the coated samples indicates that the coating is a promising technique for improving the fire retardancy of thermal insulating materials. The coating technique combining green fire retardants, such as sulfonated kraft lignin and nanoclays, with MFC binder is a simple, affordable, and effective method for reducing the flammability of cellulosic thermal insulating materials.

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