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# **FIRE RESISTANCE CELLULOSIC FIBERS FOR BIOCOMPOSITES**

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## **ABSTRACT**

The incorporation of renewable resources in composite materials is a viable means to reduce environmental impact and support sustainability development in the composites industry. Cellulosic fiber polymer composites have received very much attraction for different industrial applications because of its low density and its renewable ability. However, the uses of cellulosic fibers in the composite are limited in many applications that require fire resistance due to their flammability and their low thermal resistance.

This chapter reports an innovative and sustainable treatment approach to retard the burning of cellulosic fibers for composite production in which a minimum amount of non-toxic and low cost inorganic chemicals have been used. Different types of reacting minerals and different treatment parameters have been investigated in order to determine the most cost-effective treatment solution. The cellulosic fibers obtained from this approach become self-extinguished while there is no negative effect on fiber strength. The composite with the treated cellulosic fibers also shows their good fire resistance with minor effect on the mechanical properties. Thus this solution will open the door for the use of the cellulosic fibers in composites for applications where fire resistance is an important issue, particularly in aerospace, transportation, and construction.

## **INTRODUCTION**

Cellulosic materials (natural and synthetic) in different forms (fiber, film, powder, particle, pellet, chip, etc) at different sizes (nano, micro or macro) are often flammable and have low thermal resistance. They can be burned and also can spread the fire in the presence of oxygen. Thus, their use either in direct or non-direct form is limited in applications requiring fire resistance. Due to their flammability, the use of cellulosic materials in polymer composites is also limited in certain applications.

Cellulosic materials are treated with different flame retardants depending on the application, for example in furniture, textiles or composites. The most commonly used flame retardants are based on halogen, phosphorous, boron, ammonium, graphite, alkaline-earth metallic compounds or mixtures thereof. To improve fire resistance of organic polymer composites, the incorporation of flame retardants based on halogen, phosphorous, metallic hydroxide (magnesium hydroxide, aluminum hydroxide, calcium hydroxide, layer double hydroxide), metallic oxide (antimony oxide, boron oxide), silicate (clay, talc), etc, in the polymer matrix has been widely used.

Among the compounds listed above, halogen based flame retardants are well known to be the most efficient as they can be used at a low concentration in the final composition thus limiting their impact on other properties of the product. However, halogen compounds are considered to be harmful to the environment. Boron compounds are supposed to be efficient, however, they tend to be washed off due to their good solubility in water. Less harmful flame retardants based on phosphorous, graphite or alkaline-earth metallic compounds are much less efficient, thus a large amount of those additives must be used in the formulation. The use of flame retardant incorporated in a polymer matrix alone does not satisfactorily resolve the flammability problem in cellulose-polymer composites, especially when the concentration of cellulose is quite significant in the formulation of the composite.

It is generally known that metal hydroxides, including barium hydroxide, can be used as a flame retardant for cellulosic materials [1-4] and for polymer materials [5]. Further, Herndon [6] used a flame retardant composition for cellulosic material comprising sodium hydroxide and a metal salt of boron among other ingredients. The metal salt of boron is defined as borax which is a sodium tetraborate. De Lissa [7] suggested a flame-proofing composition comprising potassium hydroxide and/or potassium carbonate and possibly a small amount of sodium

hydroxide and/or sodium carbonate and may include another potassium salt. Musselman [8] proposed inorganic additives to impart flame resistance to polymers. The additives include hydroxides and metal salts that evolve gas. One such metal salt is barium chloride dihydrate. The use of a mixture of a polycondensate of a halogenated phenol and an alkaline earth metal halide in a flame retarding composition has also been suggested [9].

Flame retardant compositions in which ancillary flame retardant additives may be used alone or in combination, such as metal hydroxides and metal salts, including alkaline earth metal salts, has also been reported [10].

Fukuba [11] discloses the use of "alkali compounds" for use in flame resistant plaster board. The "alkali compounds" are defined as at least one of an alkali metal hydroxide, alkali metal salt, alkaline earth metal hydroxide or alkaline earth metal salt. It is preferred to use a mixture of alkali metal salts and alkaline earth metal salts, for example a mixture of sodium and calcium formate.

Yan demonstrate the use of a flame retardant composition which initially involves the step of making magnesium hydroxide from the reaction of magnesium sulfate and sodium hydroxide [12].

It is known that treatment of cellulosic materials with alkaline earth metal carbonates (e.g. barium carbonate) imparts fire resistance to the cellulosic material [13]. Here, the alkaline earth metal carbonate is applied to the cellulosic material by first coating the cellulosic material with an alkaline earth metal chloride and then treating the so-coated material with sodium carbonate. It is also known to use both a clay and a metal hydroxide in a fire retarding composition comprising a polymer material [14, 15].

However, there is no disclosure treating a cellulosic material with an aqueous reaction mixture of an alkali metal hydroxide and alkaline earth metal salt simultaneously with or shortly after mixing the alkali metal hydroxide with alkaline earth metal salts.

There remains a need for an environmentally friendlier, effective approach to producing fire-resistant cellulosic materials. This chapter presents an innovative method for improving fire resistance of cellulosic materials, especially when the cellulosic material is to be used in polymer composites, which is simple, cost-effective and environmentally friendly.

## PRINCIPLE CONCEPT

In this method cellulosic material is treated with an aqueous mixture of alkali metal or ammonium hydroxide and alkaline-earth or aluminum metal salt simultaneously with or within a short period of time of preparing the mixture. The treated cellulosic material becomes self-extinguishing and may also have improved thermal stability, improved interfacial thermal resistance, improved resistance to damage by oxidants and other chemical agents, improved resistance to damage by ultra-violet light and/or reduced negative impact on fiber strength and/or modulus. The fire-resistant cellulosic material may also be treated with a layered nanoparticulate material either simultaneously with, subsequent to or prior to treatment with the aqueous mixture of alkali metal or ammonium hydroxide and alkaline-earth or aluminum metal salt to impart further fire resistance to the cellulosic material.

In principle, the mentioned chemicals attached on the cellulose surface to form a non flammable layer that can protect cellulose effectively from fire. Single or double or multiple layer can deposit on the cellulose surface as desired. Figure 1 describes the principle of the cellulosic fiber after the treatment.

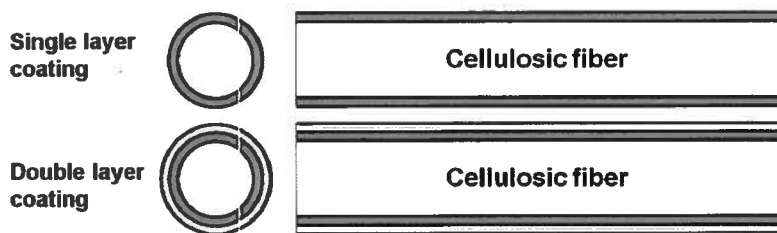
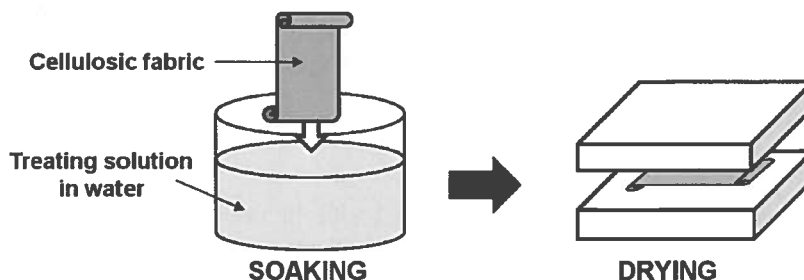


Figure 1. Description of the principle structure of the treated cellulose fiber

The treatment is very simple and easy to scale-up and it consists of the soaking of the cellulose in the aqueous chemical solution bath and drying as illustrated in Figure 2.



**Figure 2.** Illustration of the simplicity of the fiber treatment process

Polymer composites produced from cellulosic material treated according to this method have significantly improved fire resistance with minimum negative impact on the mechanical performance, and may have the added benefit of one or more of improved thermal stability and improved interfacial thermal resistance.

## EXPERIMENTAL

### Materials

Different cellulosic materials tested are shown in Table 1. The chemical products used in this work are summarized in Table 2.

**Table 1.** Description of Cellulosic Fibers

Sample	Fiber	Weight (g/m <sup>2</sup> )
C1	Flax fabric C 20M-2/2 twill from Moss Composites, Belgium, received in 2008	149
C2	Flax fabric C 20M-2/2 twill from Moss Composites, Belgium, received in 2010	149
C3	Flax fabric C10M-8H satin from Moss Composites, Belgium, received in 2010	258
C4	Canada woven flax fabric from JB Matin, Canada, received in 2010	240
C5	Hemp mat supplied by Composite Innovation Centre, Canada	350

**Table 2.** Description of Chemicals

Chemicals	Company	Information
CaCl <sub>2</sub> ·2H <sub>2</sub> O	Fisher	
Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	Aldrich	
MgCl <sub>2</sub>	Sigma Life Science	
MgSO <sub>4</sub>	Sigma-Aldrich	
Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Fluka	
Mg(OH) <sub>2</sub>	Alfa Aesar	
NaOH	Aldrich	
KOH	Sigma-Aldrich	
Al(OH) <sub>3</sub>	Aldrich	
AlCl <sub>3</sub>	Sigma-Aldrich	
NH <sub>4</sub> OH	Sigma-Aldrich	
BaCl <sub>2</sub>	Fisher	
Ba(OH) <sub>2</sub>	Aldrich	
Clay MMT	Southern Clay Products, Inc	Montmorillonite Cloisite Na <sup>TM</sup>
Clay LDH	AkzoNobel	Layered double hydroxides (LDH)

## **Solution Preparation**

Different aqueous solutions which can be single or bicomponents were used in this study. In a single component solution, only one chemical is dispersed in demineralized water. In a bi-component solution or a bi-component suspension, separate solutions or suspensions of each of the two chemicals were prepared in an equal amount of demineralized water and then they were mixed together.

## **Fiber treatment processes**

Prior treated with the chemical the celluloses were cleaned with the detergent at 80°C for 2 hours to remove the impurities and contaminants as much as possible then rinsed three times with demineralized water.

Two different fiber treatment processes were used. In one-step treatment processes (P1), cellulosic fiber was soaked in a prepared solution for a period of time. The fibers were then dried in air for 6 hours and then in an oven at 120°C for 2 hours prior to testing.

In the two-step treatment processes (P2) cellulosic fiber was soaked in a first solution for 5 to 300 seconds. The fibers were then removed from the treating medium and allowed to dry in air for 6 hours, and then dried in an oven at 120°C for 2 hours. The dried fibers were then soaked in a second solution for 5 to 300 seconds. Finally the fibers were dried in air for 6 hours and then in an oven at 120°C for 2 hours prior to testing.

## **Composite fabrication**

For phenolic (PF) composites, phenolic resin was then wetted on the fibers and dried in an oven to remove solvent from the resin and to let the resin transfer to stage B before compression. Wabash PC 100-2418-2TM compression was used to fabricate the composites under 100 psi pressure at 150°C. The amounts of resin and fiber in the final product were about 60 wt% and 40 wt%, respectively. The thickness of the composite plaque was about 3 mm.

Laminate epoxy composites were prepared by compression molding similar to the fabrication of phenolic composites but at 80°C. The amounts of resin and fiber in the final product were about 60 wt% and 40 wt%, respectively.

Laminate unsaturated polyester (UPE) composites were prepared by compression molding similar to the fabrication of phenolic composites but at 50°C. The amounts of resin and fiber used were about 70 wt% and 30 wt%, respectively. The UPE resin contains 20 wt% alumina trihydrate Hubert SB332.

## **Fiber Surface Observation**

JEOL JSM-6100 SEM at a voltage of 10 kV was used to observe the surface of fibers before and after treatment. This SEM was also used to observe the fracture surface of the composites after tensile test.

## **General Procedure for Burning Tests**

A Govmark UL94 chamber was used to conduct burning tests. For each example, results are provided using numbers and the terms “NB” and “G”. The term “NB” means “no burning” and is an indication that there was no flame and no glow after removing the flame. “NB” represents excellent fire resistance as the sample did not continue to burn after the external flame source was removed, thus the sample was self-extinguishing. The term “G” means “glow” and is an indication that the sample continued to glow after removal of the flame. The numbers are the time in seconds that the sample continued to glow after removal of the flame.

## **Horizontal Burning Test (HB)**

A minimum of five specimens of each fiber sample having width x length (WxL) of 0.5 x 6.0 inch (12.7x152.4 mm) were cut from bulk fiber. Specimens were held at one end in a horizontal position and tilted at 45° with marks at 1, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 inch from the free end. A flame was applied to the free end of the specimen for 30

seconds or until the flame front reached the 1 inch mark. If combustion continued, the duration was timed between each 0.5 inch mark. A thin metallic wire was inserted to support the specimen.

For the composite samples, five specimens having WxL of 0.5x6.0 inch (12.7x152.4 mm) were cut from the 3 mm thick composite plaque. Specimens were held at one end in a horizontal position and tilted at 45° with marks at 1, 2.0, 3.0, 4.0, 5.0 inch from the free end. A flame was applied to the free end of the specimen for 30 seconds or until the flame front reached the 1 inch mark. If combustion continued, the duration was timed between each 1.0 inch mark.

### **Vertical Burning Test (VC-2)**

A Govmark VC-2 chamber was used to conduct burning tests for some composites. This chamber is widely cited through out the USA and internationally to measure the ignition resistant properties of aircraft and transportation materials, tents and protective clothing.

For phenol formaldehyde composite samples, three specimens having width x length (WxL) of 3x12 inch (76.2x304.8 mm) were cut from the 3 mm thick composite plaque. Specimens were held at one end in the vertical position. The flame was applied for sixty seconds and then removed until flaming stopped. The combustion time and burning length was recorded. If the specimen has burning length and burning time less than 8 inch and 15 seconds, respectively, it is considered to be passed the standard (self-extinguished) Each separate set of specimens prepared for testing will consist of at least three specimens (multiple places).

### **Tensile Test**

Tensile tests on fibers were conducted on a tow (strand) disassembled from the fabric. The tows in the longitudinal direction in the fabric were separated from the ones in the orthogonal direction. Tests were carried out for both series separately. The tensile properties of the fiber tow were determined at room temperature and 50% relative humidity on an Instron 5548 micro-tester machine, with crosshead distance of 50 mm and speeds of 120 mm/min. The maximum load at break was recorded for each specimen. A minimum 10 specimens were tested for each type of sample.

The tensile properties of the composites were evaluated at room temperature and 50% relative humidity on an Instron 5500R machine, with crosshead speeds of 5 mm/min according to ASTM 3039-00. A minimum 5 specimens were tested for each type of sample.

## **RESULTS AND DISCUSSIONS**

### **Fiber Treatment**

#### ***Fibers Treated with Single Component Solutions***

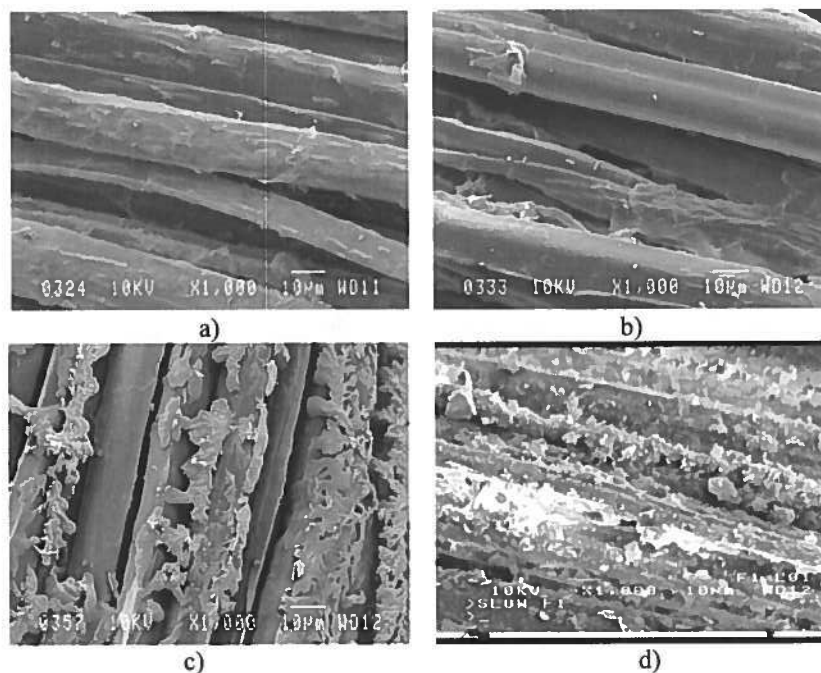
Flax fiber C1 and C2 as described in Table 2 was treated with different single component solutions as indicated in Table 3 for 120 s using the process P1. Burning tests were conducted in accordance with the general procedure described above and the results from the burning tests are also shown in Table 3. It is evident from Table 3 that all of the C1 fibers treated with various single component systems are not self-extinguishing, although these treatments slowed down flame propagation. Fibers treated with NaOH or KOH did not continue to burn but did continue to glow. Fibers treated with NaOH and then washed with water did continue to burn, demonstrating that any fire resistant effect afforded by an alkali metal hydroxide alone is easily removed if the fibers get wet. Collectively, Table 3 demonstrates that single component systems of metal hydroxides, metal salts or clays do not impart self-extinguishing properties on fibers treated with the systems.

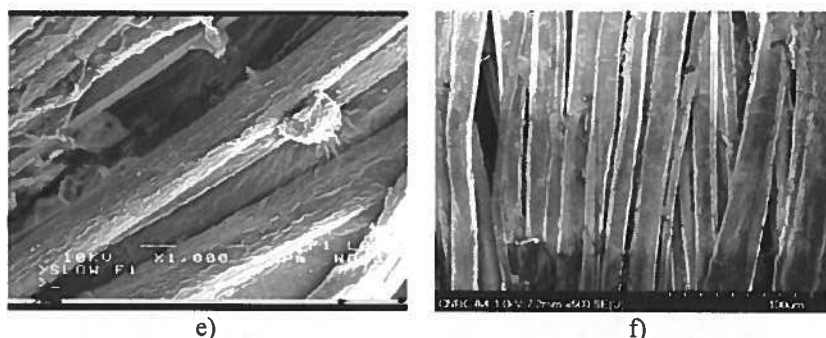
**Table 3.** C1 Fibers Treated with Single Component Solutions Using P1

Name	Description	Burning characteristics
C1	Untreated	Burned

C1-1	Clay MMT2%	Burned
C1-2	Clay MMT4%	Burned
C1-3	Clay LDH2%	Burned
C1-4	Clay LDH4%	Burned
C1-5	(BaCl <sub>2</sub> )2%	Burned
C1-6	(Ba(OH) <sub>2</sub> )2%	Burned
C1-7	(BaCl <sub>2</sub> )2% then washed with water	Burned
C1-8	(Ba(OH) <sub>2</sub> )2% then washed with water	Burned
C2	Untreated	Burned
C2-1	Ba(OH) <sub>2</sub>	Burned
C2-2	BaCl <sub>2</sub>	Burned
C2-3	BaCl <sub>2</sub> twice	Burned
C2-4	MgNO <sub>3</sub>	Burned
C2-5	MgCl <sub>2</sub>	Burned
C2-6	MgSO <sub>4</sub>	Burned
C2-7	Mg(OH) <sub>2</sub>	Burned
C2-8	Ca(NO <sub>3</sub> ) <sub>2</sub>	Burned
C2-9	CaCl <sub>2</sub>	Burned
C2-10	KOH	Glowed
C2-11	NaOH	Glowed
C2-12	NaOH twice	Glowed
C2-13	NaOH then washed with water	Burned
C2-14	AlCl <sub>3</sub>	Burned
C2-15	Al(OH) <sub>3</sub>	Burned

The difference in surface structure between the untreated and treated flax fibers are illustrated in Figure 3. In general the single component systems do not provide a good coating on the flax fiber surface. Among them LDH and MMT provide better coverage but the can be peeled off easily during handling the fibers. These can be the reason for its poor fire retardant performance.





**Figure 3.** SEM image of the flax fibers: treated with a) NaOH, b) BaCl<sub>2</sub>, c) Ba(OH)<sub>2</sub>, d) LDH, e) MMT and f) untreated

### ***Fibers Treated with Bi-component Solutions***

Flax fiber C1 and C2 were treated with different bi-component systems as indicated in Table 4. It is evident that all of the C1 fibers treated with bi-component systems involving the mixture of barium chloride and sodium hydroxide are self-extinguishing. Fibers treated with barium chloride alone then with clay or barium hydroxide alone then with clay are not self-extinguishing. Thus, single component systems are not self-extinguishing, even with the subsequent addition of clay. A mixture of both the alkaline metal salt and the alkali metal hydroxide is needed to make the fibers self-extinguishing. It is further clear that washing the fibers after treatment with a bi-component system does not remove the self-extinguishing properties imparted by the treatment. Further, the order in which clay is introduced into the bi-component does not affect the self-extinguishing properties of the fibers after treatment.

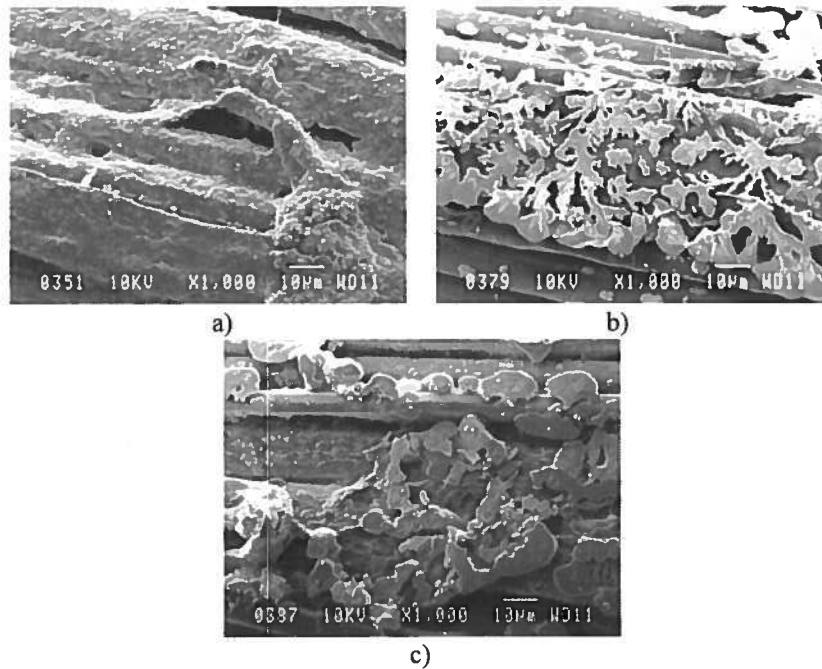
For the C2 series fibers treated with (MgCl<sub>2</sub>+NaOH) and with (CaCl<sub>2</sub>+NaOH) are self-extinguishing. Fibers treated with (Mg(NO<sub>3</sub>)<sub>2</sub>+NaOH) and with (Ca(NO<sub>3</sub>)<sub>2</sub>+NaOH) did not burn but continued to glow. Fibers treated with (MgSO<sub>4</sub>+NaOH) continued to burn, but at a slower rate than untreated fibers. The efficiency of the (MgCl<sub>2</sub>+NaOH) system is greater than the (Mg(NO<sub>3</sub>)<sub>2</sub>+NaOH) system, which is greater than the (MgSO<sub>4</sub>+NaOH) system. This is also similar for the calcium-containing systems where the efficiency of the (CaCl<sub>2</sub>+NaOH) system is greater than the (Ca(NO<sub>3</sub>)<sub>2</sub>+NaOH) system. Thus, chloride is the most preferred counter anion for the alkaline earth metal cation.

**Table 4.** C1 and C2 Fibers Treated with a Solution of Barium-containing Bi-component Systems

Name	Description	Burning characteristics
C1	Untreated	Burned
C1-9/P2	BaCl <sub>2</sub> then + clay MMT	Burned
C1-10/P2	Ba(OH) <sub>2</sub> then + clay LDH	Burned
C1-11/P1	BaCl <sub>2</sub> + NaOH	Self-extinguished
C1-12/P1	BaCl <sub>2</sub> + NaOH then washed	Self-extinguished
C1-13/P2	BaCl <sub>2</sub> + NaOH then + clay MMT	Self-extinguished
C1-14/P2	BaCl <sub>2</sub> + NaOH then + clay LDH	Self-extinguished
C1-15/P2	Clay MMT then + BaCl <sub>2</sub> + NaOH	Self-extinguished
C1-16/P2	Clay LDH then + BaCl <sub>2</sub> + NaOH	Self-extinguished
C2	Untreated	Burned
C2-16/P1	MgCl <sub>2</sub> + NaOH	Self-extinguished
C2-17/P1	Mg(NO <sub>3</sub> ) <sub>2</sub> + NaOH	Glowed
C2-18/P1	MgSO <sub>4</sub> + NaOH	Burned
C2-19/P1	CaCl <sub>2</sub> + NaOH	Self-extinguished
C2-20/P1	Ca(NO <sub>3</sub> ) <sub>2</sub> + NaOH	Glowed
C2-21/P1	AlCl <sub>3</sub> +NH <sub>4</sub> OH	Self-extinguished
C2-22/P2	AlCl <sub>3</sub> + NH <sub>4</sub> OH then clay MMT	Self-extinguished

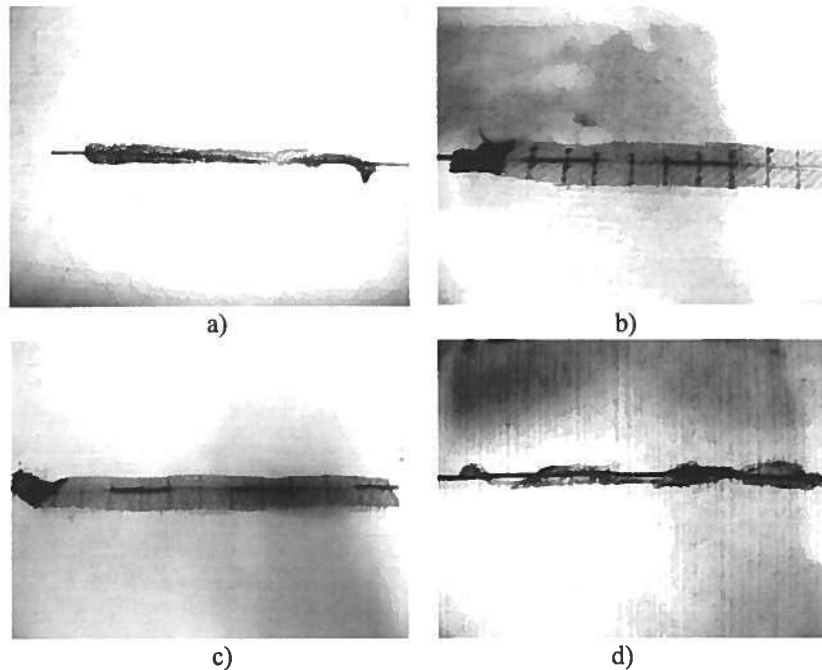


Figure 4 illustrates the fibers treated with the bi-component systems providing better coating and adhesion of the chemical on the fiber surface thus preventing the treated fiber from burning.



**Figure 4.** SEM image of the flax fibers treated with a) NaOH+MgCl<sub>2</sub>, b) NaOH+BaCl<sub>2</sub> and c) NaOH+BaCl<sub>2</sub>+MMT

Figure 5 illustrates the remains of the flax fiber after burning test. The non-treated flax burned completely to form the grey ash while the flax treated with BaCl<sub>2</sub> formed the black char and the fibers treated with (NaOH+BaCl<sub>2</sub>) or (NaOH+BaCl<sub>2</sub>+MMT) become self extinguishing.



**Figure 5.** Photo of the flax fibers after burning test: treated with a) BaCl<sub>2</sub>, b) NaOH+BaCl<sub>2</sub> c) NaOH+BaCl<sub>2</sub>+MMT, and d) untreated

### ***Different Fibers Treated with a Magnesium-containing Bi-component Systems***

Various fiber samples C2, C3, C4, C6 and C7 as described in Table 2 were treated with a magnesium-containing bi-component systems as indicated in Table 5. It is evident that all of the fibers were self-extinguishing after treatment with the (MgCl<sub>2</sub>+NaOH) system. It shows that the treatments are useful across a range of cellulose materials.

**Table 5.** Different Fibers Treated with a Magnesium-containing Bi-component Systems Using P1

Name	Description	Burning characteristics
C2	Untreated C2	Burned
C2-21	C2 + MgCl <sub>2</sub> + NaOH	Self-extinguished
C3	Untreated C3	Burned
C3-1	C3 + MgCl <sub>2</sub> + NaOH	Self-extinguished
C4	Untreated C4	Burned
C4-1	C4 + MgCl <sub>2</sub> + NaOH	Self-extinguished
C5	Untreated C5	Burned
C5-1	C5 + MgCl <sub>2</sub> + NaOH	Self-extinguished

### ***Tensile Properties of Fiber Tows***

Tensile properties of untreated various treated flax fiber samples were measured in accordance with the procedure described above. Table 6 lists the fiber tows that were tested as well as their tensile properties. The tows in the longitudinal direction in the fabric are denoted as parallel, whereas the ones in the orthogonal direction are denoted as perpendicular.

It is evident from Table 6 that the tensile properties did not change much for most of the systems indicating that the treatment did not generally have a detrimental effect on tensile properties. However, for fibers treated with alkali metal hydroxide alone (e.g. KOH and NaOH), there is a significant loss in tensile properties. It is clear, therefore, that cellulose materials treated with both alkaline earth metal salt and alkali metal hydroxide are advantageously fire retardant, often self-extinguishing, while retaining good tensile properties, in contrast to fibers treated only with alkali metal hydroxide or treated with another metal salt.

**Table 6.** Tensile Force of Tows of Treated C2 Fibers

Fiber	Description	Max load pounds force (N)	
		Parallel	Perpendicular
C2	Untreated C2	4.6 (20.4)	5.4 (23.8)
C2-1/P1	Ba(OH) <sub>2</sub>	4.9 (21.7)	5.4 (24.1)
C2-2/P1	BaCl <sub>2</sub>	4.7 (21.1)	5.6 (25.1)
C2-4/P1	Mg(NO <sub>3</sub> ) <sub>2</sub>	5.4 (23.8)	5.7 (25.5)
C2-7/P1	Mg((OH) <sub>2</sub>	4.3 (19.2)	5.3 (23.6)
C2-10/P1	KOH	3.6 (15.8)	4.5 (20.2)
C2-11/P1	NaOH	3.6 (15.8)	4.3 (19.0)
C2-13/P1	NaOH then washed	3.0 (13.2)	4.1 (18.4)
C2-15/P1	Al(OH) <sub>3</sub>	5.1 (22.8)	5.3 (23.6)
C2-17/P1	MgCl <sub>2</sub> + NaOH	4.8 (21.3)	5.3 (23.7)
C2-18/P1	MgSO <sub>4</sub> + NaOH	5.2 (23.0)	5.8 (25.8)
C2-19/P1	CaCl <sub>2</sub> + NaOH	4.4 (19.5)	5.6 (24.9)
C2-20/P1	Ca(NO <sub>3</sub> ) <sub>2</sub> + NaOH	5.5 (24.4)	5.6 (24.8)

### **Biocomposites**

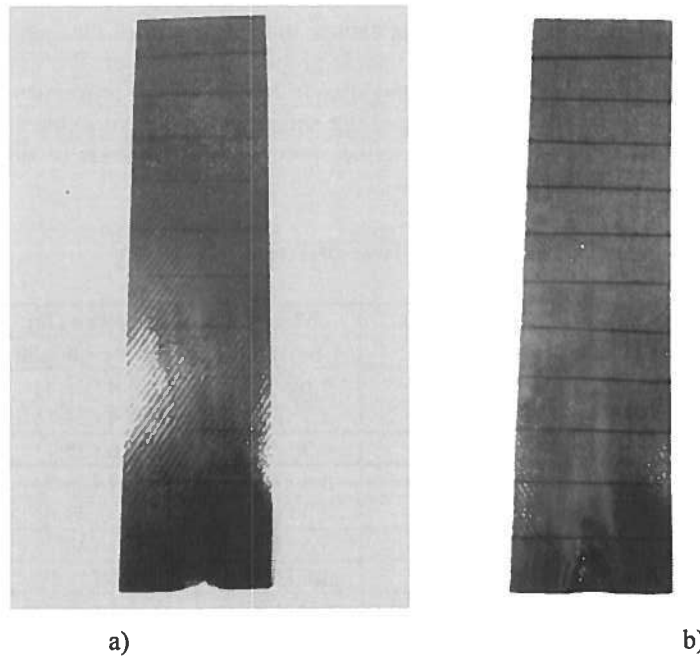
#### ***PF/flax fiber composites***

Vertical VC-2 burning tests were conducted on the PF composites and the results are shown in Table 7. Sample PF-C2 is a comparative example of a PF composite containing untreated flax fiber. PF-C2-21/P2 is PF composite containing flax fibers treated with a bi-component aluminum-containing system. Burning time is the time it takes for the sample to self-extinguish after the external flame is removed. Thus, a shorter burning time is indicative of a more fire resistant sample. PF is a thermoset resin which itself has considerable resistance to fire. Because of the fire resistance of phenol formaldehyde, it is the flax fiber that primarily burns during the burning test. As is evident from Table 8, fire-resistant flax fibers of this approach provide a tremendously significant greater resistance to burning in the PF matrix than untreated flax fibers that allows the obtained composite with the treated flax fibers to be classified as self-extinguished (Figure 6).

**Table 7. PF/Flax Fiber Composites**

Sample	Composition	Max flame time (s)	Max burn length (inches)	Glow	Pass VC-2 test
PF-C2	Phenol formaldehyde matrix Flax fabric C2 (untreated)	$35.8 \pm 8.2$	$1.3 \pm 0.1$	No	No
PF- C2-21/P1	Phenol formaldehyde matrix Flax fabric C2-34/P1 (C2+(AlCl <sub>3</sub> +NH <sub>4</sub> OH))	$7.5 \pm 5.6$	$0.5 \pm 0.1$	No	Yes

Figure 6 illustrates the remains of the PF composite flax fabric after burning. The PF composite with non-treated flax fabric has burned very much before stop while the PF composite with treated flax behaves very differently.



**Figure 6.** Photos after burning of PF composites made with a) untreated and b) treated flax fibers

The SEM observation of the fracture composite specimens demonstrates a good fiber-matrix in both the untreated and treated flax composites. Figure 7 illustrates the resin sticks on the fracture fibers.



**Figure 7.** SEM image of fractured PF composites made with a) untreated and b) treated flax fibers

Mechanical properties of the phenol formaldehyde/flax fiber composite samples are shown in Table 8. It is evident that PF composites containing fibers treated with a bi-component aluminum-containing system at 2% have comparable flexural properties with the reference.

**Table 8.** Mechanical Properties of PF/Flax Fiber Composites

Sample	Composition	Flexural strength (MPa)	Flexural modulus (GPa)
PF-C2	Phenol formaldehyde matrix Flax fabric C2 (untreated)	$129.8 \pm 8.2$	$10.2 \pm 0.3$
PF- C2-34/P1-2%	Phenol formaldehyde matrix Flax fabric C2-34/P1-2% (C2+(AlCl <sub>3</sub> +NH <sub>4</sub> OH)2%)	$118.1 \pm 4.2$	$10.1 \pm 0.8$

#### *Epoxy/flax fiber composites*

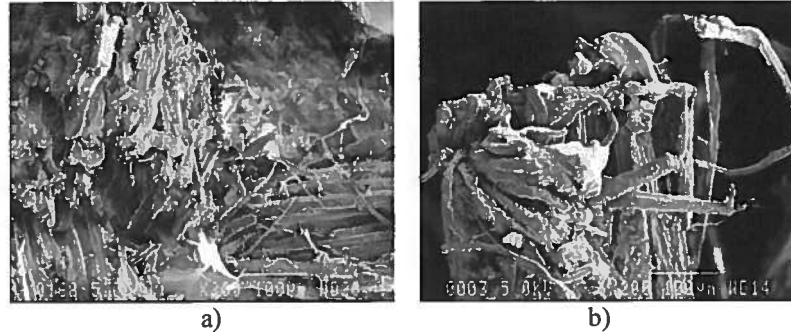
The glass transition temperature of the epoxy-flax fiber composite samples is about 80-82°C (as determined by differential scanning calorimetry) and there is no significant difference between them, indicating that the treatment has no effect on the degree of curing of the epoxy matrix.

Horizontal burning tests were conducted in the composites and the results are shown in Table 9. It is clearly seen that the conventional flax composite is flammable while the treated flax fibers have stopped the composites from burning.

**Table 9.** Burning Test Results of Epoxy/Flax Composites

Sample	Burning characteristics
Epoxy-C2	Burned
Epoxy-C2-21/P1	Self-extinguished
Epoxy-C2-22/P2	Self-extinguished

The SEM observation of the fracture composite specimens demonstrates a good fiber-matrix in both the untreated and treated flax composites. Figure 8 illustrates the resin sticks on the fracture fibers.



**Figure 8.** SEM image of fractured epoxy composites made with a) untreated and b) treated flax fibers

Mechanical properties of the epoxy/flax fiber composite samples are shown in Table 10. The epoxy composites containing treated flax fibers have very slightly reduction in tensile strength and modulus while improving the energy to break which represents the composite toughness.

**Table 10.** Mechanical Properties of Epoxy Composites

Sample	Tensile stress (MPa)	Tensile modulus (GPa)	Energy to break (J)
Epo-C2	117.7 $\pm$ 4.0	9.8 $\pm$ 0.6	33.7 $\pm$ 2.0
Epo-C2-21/P1	106.4 $\pm$ 1.0	7.2 $\pm$ 0.3	36.7 $\pm$ 2.6
Epo-C2-22/P2	103.7 $\pm$ 4.2	8.4 $\pm$ 0.2	36.7 $\pm$ 2.6

#### ***UPE/flax fiber composites***

Sample UPE-C2 is a comparative example of an epoxy composite containing untreated flax fiber. UPE-C2-21/P1 is a comparative example of UPE composite containing flax fibers treated only with a bi-component aluminum-containing system. Horizontal burning tests were conducted as shown in Table 11 that the fire-resistant treated flax fibers have stopped the composites from burning.

**Table 11.** Burning Tests on UPE/Flax Fiber Composites

Sample	Burning length (inches)					
	0.0	1.0	2.0	3.0	4.0	5.0
	Burning Time (seconds)					
UPE-C2	0	114	-	-	421	522
UPE-C2-21/P1	0	NB	NB	NB	NB	NB

#### **Conclusions**

Coating of a layer of effective chemicals on the cellulosic fibers significantly improves its fire resistance. The treated cellulosic material becomes self-extinguishing and has no negative impact on fiber strength and/or modulus. The fire-resistant cellulosic material may also be treated with a layered nano-particulate material either simultaneously with, sub-sequent to or prior to treatment with the effective chemicals to impart further fire resistance to the cellulosic material. Fire-resistant flax fibers provide a tremendously significant greater resistance to polymer matrix than untreated flax fibers. This will allow the production of green composites from cellulosic fibers with improved fire resistance.

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