

NRC Publications Archive Archives des publications du CNRC

Fire resistance cellulosic fibers for green polymer composites

Ton That, Minh Tan; Ngo, Tri-Dung; Hu, Wei

NRC Publications Archive Record / Notice des Archives des publications du CNRC :

<https://nrc-publications.canada.ca/eng/view/object/?id=ac7d3b3b-17f1-4fc8-90fe-bf9e7e7617c2>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=ac7d3b3b-17f1-4fc8-90fe-bf9e7e7617c2>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

Fire Resistance Cellulosic Fibers for Green Polymer Composites

by

Minh-Tan Ton-That, Tri-Dung Ngo, and Wei Hu
Industrial Materials Institute, National Research Council
of Canada
75 De Mortagne Blvd., Boucherville, QC, Canada J4B
6Y4

Abstract

Cellulosic fiber polymer composites have received very much attraction for various industrial applications because of the low density, the cost-effectiveness and the renewable ability of cellulosic fibers. However, it is well known that cellulosic fibers are very flammable hence their composites are also often flammable. Thus it limits the use of these composites in many applications that require fire resistance.

This paper reports an innovative and sustainable treatment approach for retarding the burning of cellulosic materials for composite production in which a minimum amount of low cost and non-toxic inorganic chemicals have been used. The treatment can be carried out in aqueous solutions and in the same step of fiber cleaning either in batch or continuous process so no additional investment and equipment are really required. In addition, different types of reacting minerals and different treatment parameters have been investigated in order to determine the most cost-effective treatment process. The cellulosic fibers obtained from this approach become self-extinguished while there is no negative effect on fiber strength.

Introduction

Cellulose materials (fiber, film, powder, particle, pellet, chip, etc) are often flammable and have low thermal resistance. They can be burned easily and can also spread the fire rapidly in the presence of oxygen. Thus, their use either in direct or non-direct forms are limited in applications requiring fire resistance. Due to their flammability the use of cellulose materials in polymer composites is also limited in certain applications.

Cellulose materials are treated with different flame retardants depending on the application, some examples of those applications are in furniture, textiles or composites. The most commonly used flame retardants are based on halogen (1), phosphorous (2-9), boron (4, 10, 11), ammonium (3, 4, 8), graphite (12), alkaline-earth metallic compounds (13) 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, magnesium layer double hydroxide), metallic oxide (antimony oxide, boron oxide), silicate (clay, talc), etc, either alone or in combination with others in the polymer matrix has been widely used. All the compounds listed above have different drawbacks, such as negative impact on the environment as halogen based flame retardants, be washed off due to their good solubility in water as Boron, less effectiveness as flame retardants based on phosphorous, graphite or alkaline-earth metallic compounds, etc. 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.

This present work investigated a new approach for improving fire resistance of cellulose materials to be used in polymer composites, by coating cellulose fibers with a layer of effective chemicals. The focus of this development was to not negatively affect the mechanical properties of the obtained composite. This paper will report the work on improving fire resistance of cellulosic fibers without any negative effect on the fiber mechanical strength.

Experimental

Materials

The chemicals used in this work are summarized in Table 1. The cellulosic materials have been tested are shown in Table 2. 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 except the Whatman paper and the Govmark cotton pads.

Solution preparation

Different aqueous solutions which can be single or bicomponents were used in this study. In single component solutions, only one chemical is dissolved in demineralized water. In bi-component solutions separate solutions of each of the two chemicals were prepared in an

equal amount of demineralized water and then they were mixed together.

Table 1. Description of Chemicals

Chemicals	Company	Description
CaCl ₂ .2H ₂ O	Fisher	-
Ca(NO ₃) ₂ .4H ₂ O	Aldrich	≥ 99%
Ca(OH) ₂	Aldrich	≥ 96%
MgCl ₂	Sigma Life Science	-
MgSO ₄	Sigma-Aldrich	≥ 99.5%
Mg(NO ₃) ₂ .6H ₂ O	Fluka	≥ 99%
Mg(OH) ₂	Alfa Aesar	95-100.5%
NaOH	Aldrich	≥ 98%
KOH	Sigma-Aldrich	≥ 90%
Al(OH) ₃	Aldrich	Reagent grade, Al ₂ O ₃ : 50-57%
AlCl ₃	Sigma-Aldrich	98%
NH ₄ OH	Sigma-Aldrich	ACS reagent, NH ₃ : 28-30%
BaCl ₂	Fisher	Lab grade
BaCl ₂ .2H ₂ O	JTBaker Chemical	100.5%
Ba(OH) ₂	Aldrich	~95%
Clay MMT	Southern Clay Products, Inc	Montmorillonite Cloisite Na TM clay (CEC:92 meq/100 g)
Clay LDH	Akzo-Nobel	Layered Double Hydroxides (LDH)-anionic clay

Table 2. Description of Cellulose Fibers

Sample	Fiber	Weight oz/ft ² (g/m ²)	Weight oz/yd ² (g/m ²)
C1	Flax fabric C 20M-2/2 twill from Moss Composites, Belgium		4.5 (150)
C2	Flax fabric C 20M-2/2 twill from Moss Composites, Belgium		4.5 (150)
C3	Flax fabric C10M-8H satin from Moss Composites, Belgium		7.5 (250)
C6	Canada woven flax fabric from JB Matin, Canada		7.0 (240)
C7	Hemp mat 1 supplied by Composites Innovation Centre (CIC), Canada	1.00 (300)	

Fiber Surface Observation

JEOL JSM-6100 SEM at a voltage of 10kV was used to observe the surface of fibers before and after treatment.

Treatment processes

Two different fibre 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.

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 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 polypropylene composite samples, five specimens having width x length (W x L) of 0.5 x 6.0 inch were cut from the 0.11811 inches thick composite plaque prepared as described in Example 3. 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.

Results and Discussion

The quality of deposition of BaCl_2 and clays on the flax fiber surface is given Figure 1. Ba(OH)_2 forms a particle parts on the fiber surface. Both clays, MMT and LDH, provide very good coatings on the fibers. However, MMT forms a very smooth layer on the fibers while the LDH generate a very rough one. As the clays and the fibers are very hydrophilic and many hydroxyl groups are available on their surface, it can be expected that certain hydrogen bonding between the two materials can be formed at the interface thus allowing a good adhesion of these clay layers on the fiber.

Fibers Treated with Single Component Solutions

Belgium flax fiber samples C1 as described in Table 2 were 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.

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

Name	Description	Burning Length (inches)			
		1.0	2.0	3.0	3.5
		Burning Time (s)			
C1	Untreated	7	14	21	25
C1-1	Clay MMT2%	9	18	26	31
C1-2	Clay MMT4%	9	18	27	31
C1-3	Clay LDH2%	9	20	30	34
C1-4	Clay LDH4%	13	25	38	44
C1-5	$(\text{BaCl}_2)_2\%$	7	15	22	26
C1-6	$(\text{Ba(OH)}_2)_2\%$	8	18	27	32
C1-7	$(\text{BaCl}_2)_2\%$ then washed with water	7	14	21	25
C1-8	$(\text{Ba(OH)}_2)_2\%$ then washed with water	8	18	26	31

Belgium flax fiber samples C2 as described in Table 2 were treated with different single component systems as indicated in Table 4 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 4. It is evident

from Table 4 that all of the fibers treated with a single component system, including a barium hydroxide system (C1-6/P1), are not self-extinguishing. 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.

Table 4. C2 Fibers Treated with Single Component Solutions Using P1

Name	Description	Burning Length (inches)				
		1.0	2.0	3.0	4.0	4.5
		Burning Time (s)				
C2	Untreated	5.4	10.1	15.2	20.1	22.5
C2-1	Ba(OH)_2	6.1	11.9	17.6	23.3	26.5
C2-2	BaCl_2	5.0	9.1	13.3	17.5	19.8
C2-3	BaCl_2 twice	7.3	12.6	17.8	22.4	25.2
C2-4	MgNO_3	4.8	9.4	14.0	18.1	20.3
C2-5	MgCl_2	6.1	11.7	18.2	24.6	27
C2-6	MgSO_4	5.2	9.5	14.0	18.1	19.5
C2-7	Mg(OH)_2	6.2	10.1	14.6	18.8	20.6
C2-8	$\text{Ca(NO}_3)_2$	4.8	8.7	12.6	16.3	18.1
C2-9	CaCl_2	5.1	9.5	14.3	19.0	21.0
C2-10	KOH	G	G	G	G	G-250
C2-11	NaOH	G	G	G	G	G-250
C2-12	NaOH twice	G	G	G	G	G-280
C2-13	NaOH then washed	5.5	10.0	14.5	19.7	22.0
C2-14	AlCl_3	6.5	12.3	18.4	24.8	27.8
C2-15	Al(OH)_3	5.3	10.2	14.7	18.6	20.9

Collectively, Tables 3 and 4 demonstrate that single component systems of metal hydroxides, metal salts or clays do not impart self-extinguishing properties on fibers treated with the systems.

Fibers Treated with Bi-component Solutions Containing Barium Salts

Belgium flax fiber samples C1 as described in Table 2 were treated with different barium-containing bi-component systems as indicated in Table 5 for 120 s using the processes P1 and P2-1. Burning tests were conducted in accordance with the general procedure described above and the results from the burning tests are also shown in Table 5. It is evident from Table 5 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.

Table 5. C1 Fibers Treated with a Solution of Barium-containing Bi-component Systems

Name	Description	Burning Length (inches)			
		1.0	2.0	3.0	3.5
		Burning Time (s)			
C1	Untreated	7	14	21	25
C1-9/P2	BaCl ₂ then +clay MMT	8	17	26	31
C1-10/P2	Ba(OH) ₂ then +clay LDH	11	20	30	35
C1-11/P1	BaCl ₂ +NaOH	NB	NB	NB	NB
C1-12/P1	BaCl ₂ +NaOH then washed	NB	NB	NB	NB
C1-13/P2	BaCl ₂ +NaOH then +clay MMT	NB	NB	NB	NB
C1-14/P2	BaCl ₂ +NaOH then +clay LDH	NB	NB	NB	NB
C1-15/P2	Clay MMT then +BaCl ₂ +NaOH	NB	NB	NB	NB
C1-16/P2	Clay LDH then +BaCl ₂ +NaOH	NB	NB	NB	NB

Fibers Treated with Bi-component Systems Containing Different Magnesium and Calcium Salts

Belgium flax fiber samples C2 as described in Table 2 were treated with bi-component systems containing different magnesium and calcium salts of the hydroxide product of the alkaline earth metal salt and hydroxide as indicated in Table 6 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 6. It is evident from Table 13 that fibers treated with (MgCl₂+NaOH) and with (CaCl₂+NaOH) are self-extinguishing. Fibers treated with (Mg(NO₃)₂+NaOH) and with (Ca(NO₃)₂+NaOH) did not burn but continued to glow. Fibers treated with (MgSO₄+NaOH) continued to burn, but at a slower rate than untreated fibers. The efficiency of the (MgCl₂+NaOH) system is greater than the (Mg(NO₃)₂+NaOH) system, which is greater than the (MgSO₄+NaOH) system. This is also similar for the calcium-containing systems where the efficiency of the (CaCl₂+NaOH) system is greater than the (Ca(NO₃)₂+NaOH) system. Thus, chloride is the most preferred counter anion for the alkaline earth metal cation.

Table 6. Fibers Treated with a Solution of Mg- and Ca-containing Bi-component Systems Using P1

Name	Description	Burning Length (inches)				
		1.0	2.0	3.0	4.0	4.5
		Burning Time (s)				
C2	Untreated	5.4	10.1	15.2	20.1	22.5
C2-16	MgCl ₂ +NaOH	14.0	NB	NB	NB	NB
C2-17	Mg(NO ₃) ₂ +NaOH	G	G	G	G	G
						180-260
C2-18	MgSO ₄ +NaOH	10.6	19.5	29.5	38.7	43.4
C2-19	CaCl ₂ +NaOH	NB	NB	NB	NB	NB
C2-20	Ca(NO ₃) ₂ +NaOH	G	G	G	G	G
						50-300

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 15 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 7. It is evident from Table 7 that all of the fibers were self-extinguishing after treatment with the (MgCl₂+NaOH)% system. It shows that the treatments are useful across a range of cellulose materials.

Table 7. Different Fibers Treated with a Magnesium-containing Bi-component Systems Using P1

Name	Description	Burning Length (inches)				
		1.0	2.0	3.0	4.0	4.5
		Burning Time (s)				
C2	Untreated C2	5.4	10.1	15.2	20.1	22.5
C2-21	C2+ MgCl ₂ +NaOH	14.0	NB	NB	NB	NB
C3	Untreated C3	8.5	15.5	22.9	30.2	34.1
C3-2	C3+ MgCl ₂ +NaOH	G	NB	NB	NB	NB
		80-110				
C6	Untreated C6	4.8	8.4	12.0	15.6	18.0
C6-2	C6+ MgCl ₂ +NaOH	G	NB	NB	NB	NB
		35-215				
C7	Untreated C7	5.7	10.0	14.8	19.6	22.6
C7-2	C7+ MgCl ₂ +NaOH	NB	NB	NB	NB	NB

Tensile Properties of Fiber Tows

Tensile properties of untreated Belgium flax fiber samples C2 as described in Table 2 and of various treated C2 fiber samples were measured in accordance with the procedure described above. Table 8 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 8 that the tensile properties did not change much for most of the systems indicating that 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 very 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 8. 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) ₂	4.9 (21.7)	5.4 (24.1)
C2-2/P1	BaCl ₂	4.7 (21.1)	5.6 (25.1)
C2-4/P1	Mg(NO ₃) ₂	5.4 (23.8)	5.7 (25.5)
C2-7/P1	Mg(OH) ₂	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) ₃	5.1 (22.8)	5.3 (23.6)
C2-17/P1	MgCl ₂ +NaOH	4.8 (21.3)	5.3 (23.7)
C2-18/P1	MgSO ₄ +NaOH	5.2 (23.0)	5.8 (25.8)
C2-19/P1	CaCl ₂ +NaOH	4.4 (19.5)	5.6 (24.9)
C2-20/P1	Ca(NO ₃) ₂ +NaOH	5.5 (24.4)	5.6 (24.8)

Figure 2 illustrates the remains of the flax fiber after burning. The nontreated flax burned completely to form the grey ash while the treated flax formed the black char after burning such as treated with Ba(OH)₂ or the fiber becomes self extinguishing such as treated with CaCl₂+NaOH. This can be explained by the fact that the char formation on the surface by the presence of clays limits the diffusion of oxygen to the fiber during the burning process. Thus the fire is somehow retarded.

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 nanoparticulate material either simultaneously with, subsequent to or prior to treatment with the effective chemicals to impart further fire resistance to the cellulosic material.

This will allow the production of green composites from cellulosic fibers with improved fire resistance.

References

1. WO 2004/1097088 (Nov. 11, 2004)
2. U.S. Pat. 3,899,483 (Aug. 12, 1975) R. B. Le Balnc, R. I. Wickford (Cotton Inc. New York)
3. U.S. Pat. 6,524,653 (Feb. 25, 2003) W. H. Jones (NiPoNi, LLC, State College, PA (US))
4. U.S. Pat. 4,228,202 (Oct. 14, 1980) Bo O. E. Tjännberg (Box 5140, 421 05, Västra Frölunda, Sweden)
5. U.S. Pat. 5,238,464 (August 24, 1993) J. R. Johnson, R. L. Finley (Burlington Industries, Inc. (Greensboro, NC))
6. U.S. Pat. 2005/0215152 (Sep. 29, 2005) Y. Ahluwalia (Desoto, TX (US), Elkc corp)
7. U.S. Pat. 2004/0094279 (May 20, 2004) S. Myatt (Yorkshire (GB))
8. WO 2002/1044470 (June 6, 2002) S. Myatt
9. U.S. Pat. 6,352,786 (Mar. 5, 2002) R. P. Arshinova, E. J. Griffith (Astaris LLC (St. Louis, MO))
10. WO 2005/1042840 (May 12, 2005) W. Christ, K. Schmalfuss, H.-J. Knapp, M. Roth-Wangl
11. U.S. Pat. 2009/0156073 (June 18, 2009) Schubert D. M. (Lone Tree, Co (US))
12. E. Pat. 0735187 (Dec. 5, 2001) R. A. Mercuri, B. M. Brian, T. W. Weber (Ucar Carbon Technology Corporation)
13. U.S. Pat. 5,434,200 (July 18, 1995) W. R. Kolker (Pyrotite Corporation (Seattle, WA))

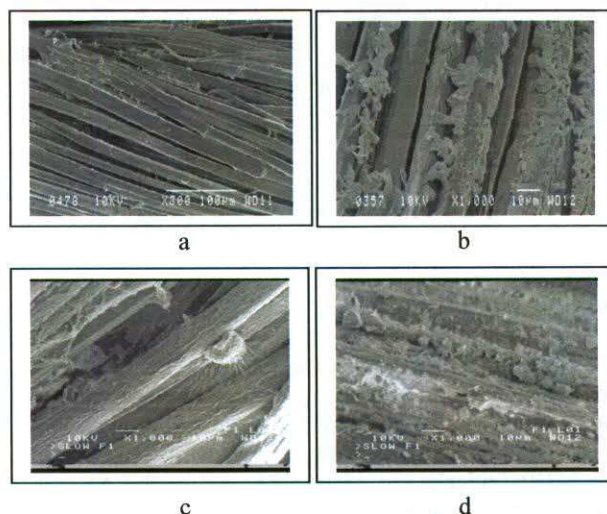


Figure 1. SEM images of the a) C1 fiber, C1 fibers coated with b) Ba(OH)₂, c) MMT and d) LDH

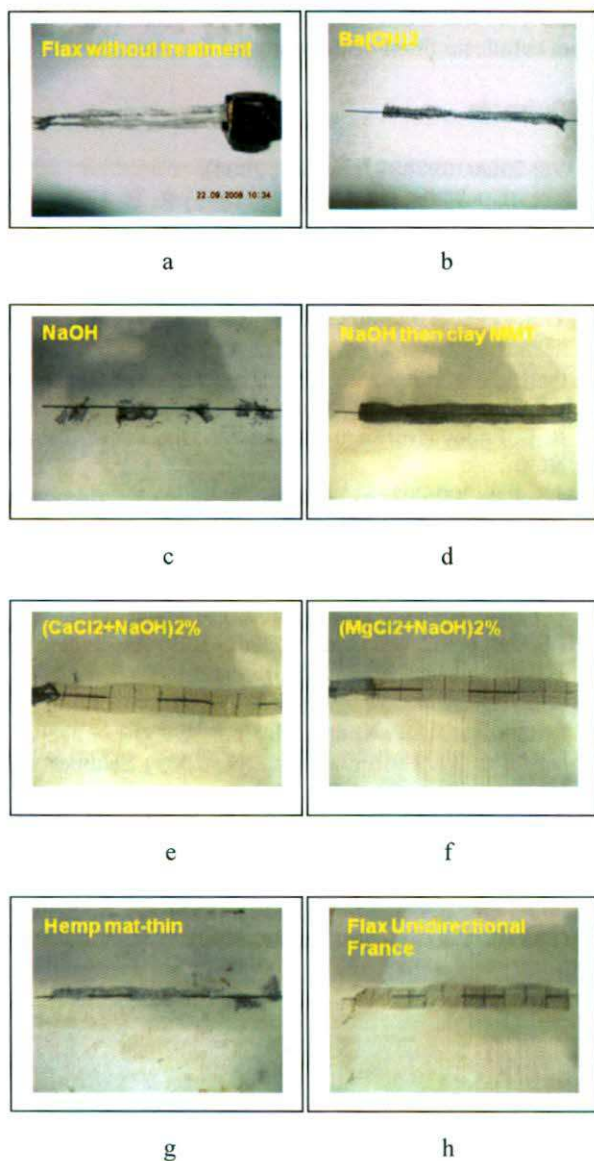


Figure 2. Specimens after burning

Acknowledgments

The authors would like to thank the financial support from different research programs of the Canadian Government via the National Bioproduct Program - Project 2 of the National Research Council of Canada, and the ABIP-Triticale and ABIP-NAFGEN of the Agriculture Agri-Food Canada.

Author biography

Dr. Ton-That has over 17 years of experience in interface and formulation of polymer composites/biocomposites. He holds 15 patents and inventions, wrote 121 technical reports and published over 180 pa-

COMPOSITES 2012 (Footer must be in Times New Roman, Italics, 9 point)

pers in international journals and conference proceedings.