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Cost-effect biocomposite solutions

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Why change to bioproducts?

Advantages of cellulosic fibre composites

- Low cost
- Low density
- Acceptable mechanical properties
- Renewable and non-food grade

Challenges

- Flammability
- Sensitivity to humidity
- Odor and VOC

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Objectives of this presentation

How to address issues of moisture sensitivity, flammability and odor/VOC of cellulosic fibres in biocomposites?

Solutions that are:

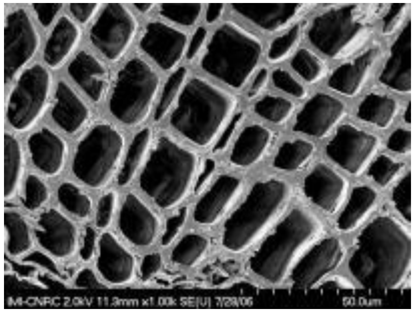
- Inexpensive
- Practical and effective
- Less harmful to the environment

Why are cellulosic fibres so flammable and moisture sensitive?

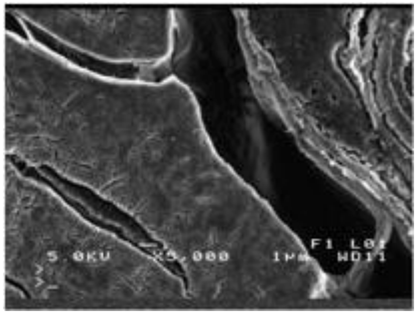
Highly flammable :

- The weak ether bond in the structure → quickly forms gassy molecules to feed the fire
- Fluffy and hollow material that stores oxygen readily supplied to the fire

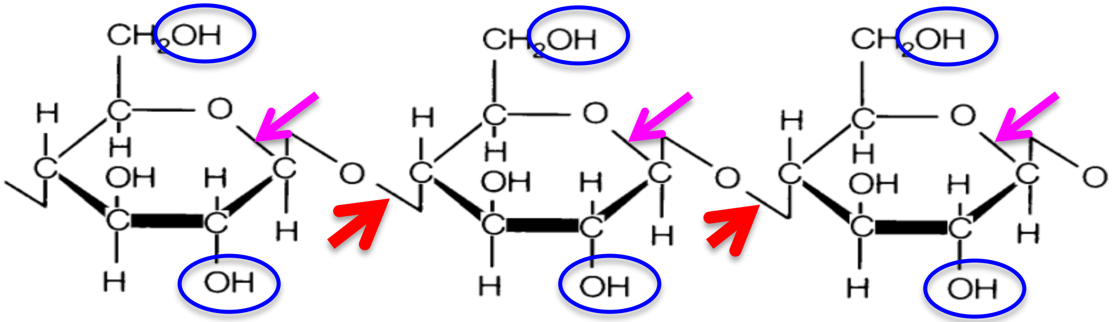
Highly sensitive to moisture: hydroxyl group in the molecules



Wood



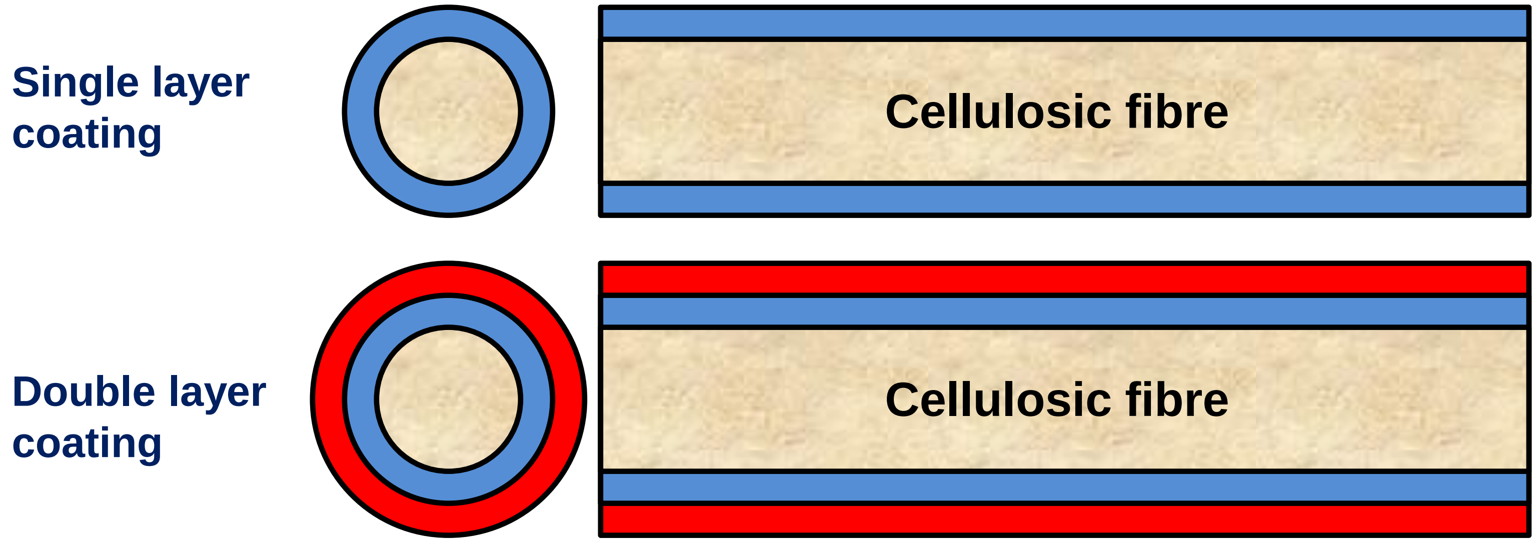
Flax



Flammability and moisture sensitivity: Solutions

NRC's innovative concept on cellulosic fibre surface treatment

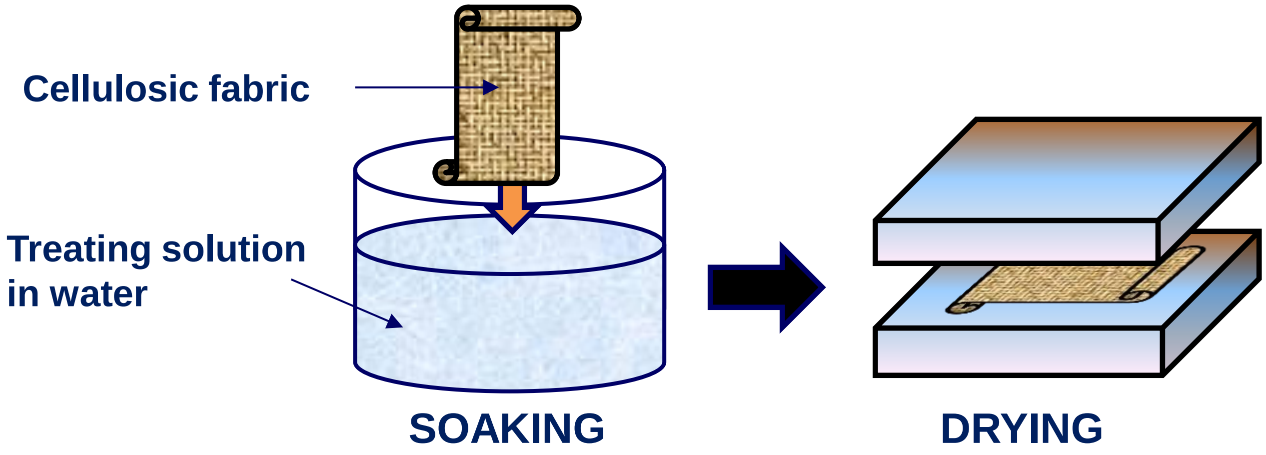
- Coating the cellulosic surface by a layer of inexpensive and non-toxic compounds to protect cellulosic fibres from fire or from moisture
- Single, binary of multiple component systems



Patent pending

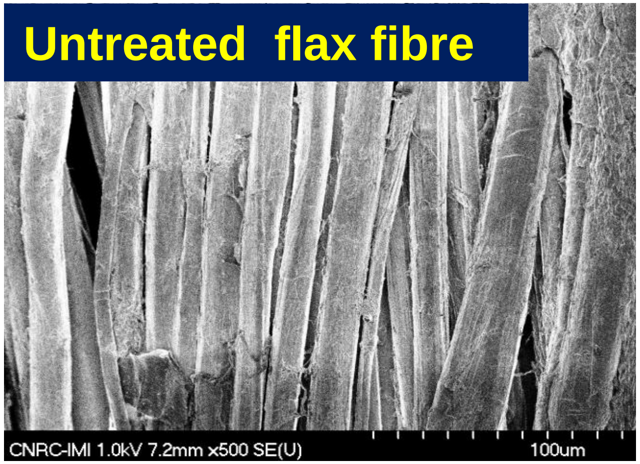
NRC's innovative concept

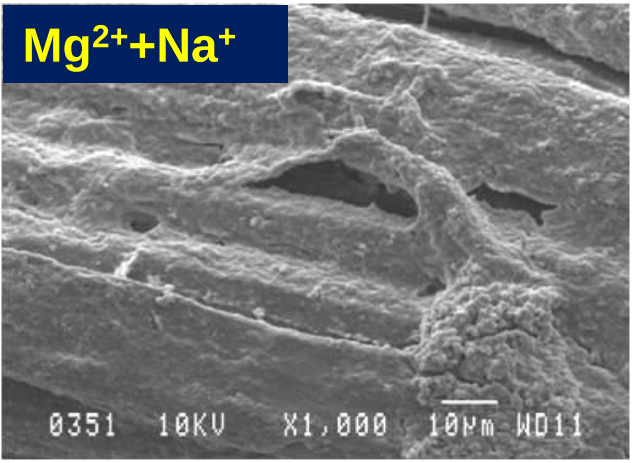
- Works with any form of cellulose: particle, mat or fabric
- Effective chemicals: low cost and non toxic (no halogen/phosphours)
- Easy and practical process: in water
- Good control of the morphology of the coating layer
- Good adhesion of the coating layer on the fibre surface

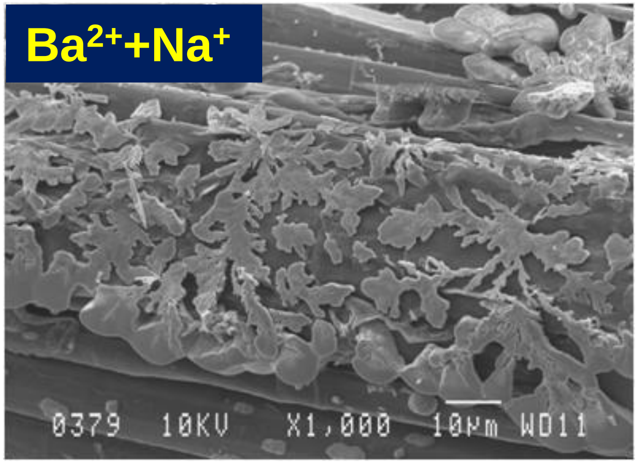


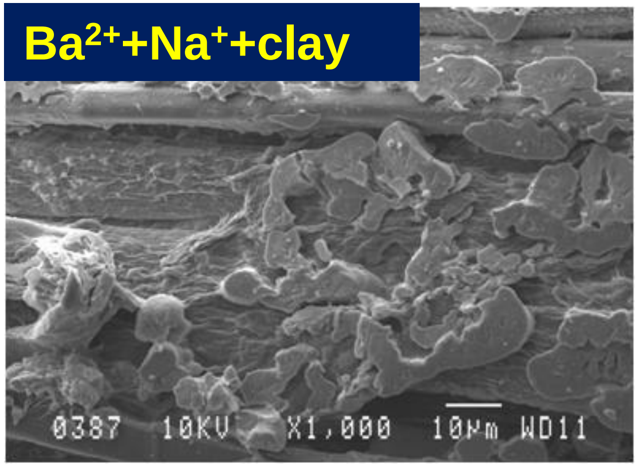
Patent pending

Example of flax fibre surface morphology

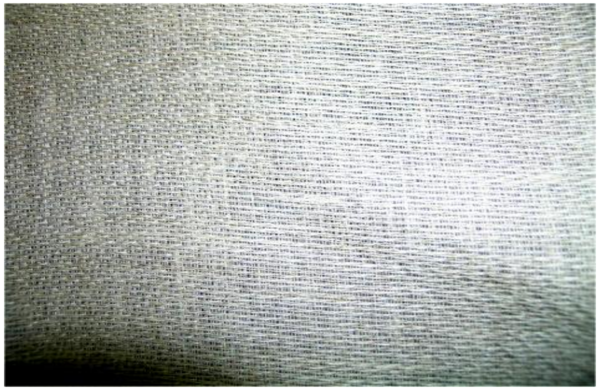


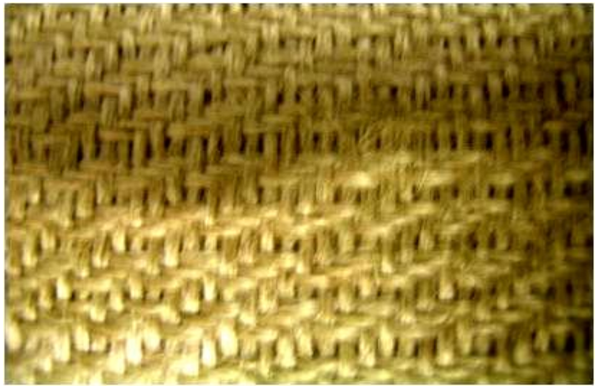






Applicable in various cellulosic materials


Flax satin plain weave


Flax roving woven


Flax mat


Hemp satin plain weave


Flax unidirectional


Chopped wheat straw

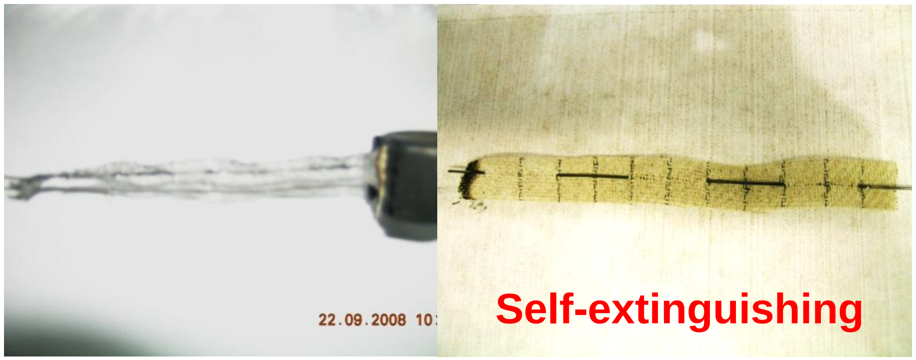
Self-extinguishing status for various celluloses

Name	Description	Burning Length (inches)				
		1.0	2.0	3.0	4.0	4.5
		Burning Time (s)				
Flax 1	Untreated	5.4	10.1	15.2	20.1	22.5
Treated Flax 1	Flax 1+(Mg^{2+}+Na^{+})-1	14.0	**NB**	**NB**	**NB**	**NB**
Flax 2	Untreated	8.5	15.5	22.9	30.2	34.1
Treated Flax 2	Flax 2+(Mg^{2+}+Na^{+})-1	G (80-110)	**NB**	**NB**	**NB**	**NB**
Flax 3	Untreated	4.8	8.4	12.0	15.6	18.0
Treated Flax 3	Flax 3+(Mg^{2+}+Na^{+})-1	G (35-215)	**NB**	**NB**	**NB**	**NB**
Hemp	Untreated	5.7	10.0	14.8	19.6	22.6
Treated Hemp	Hemp+(Mg^{2+}+Na^{+})-1	**NB**	**NB**	**NB**	**NB**	**NB**

G: glow **NB**: no burn

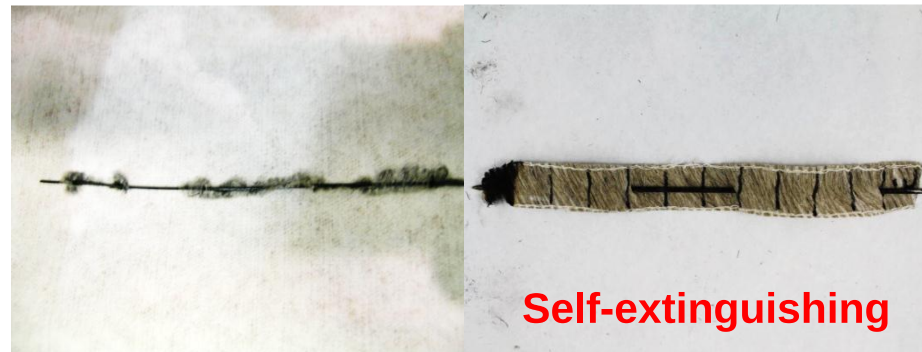
Burn tests for various cellulosic sources

C2-Flax fabric (Belgium)



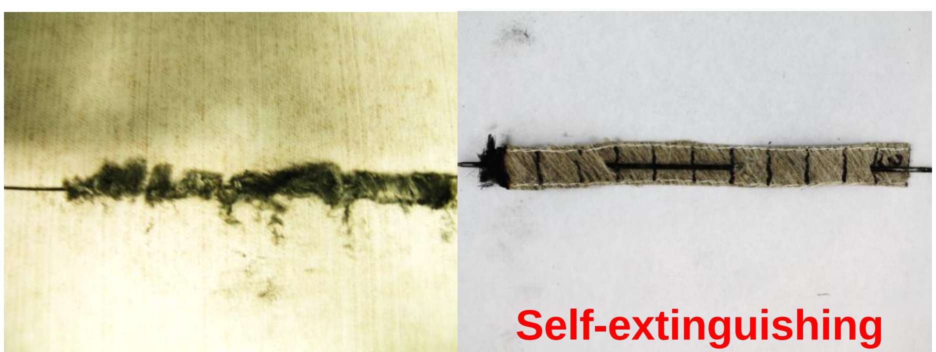
Untreated | Treated

C4-Hemp fabric (France)



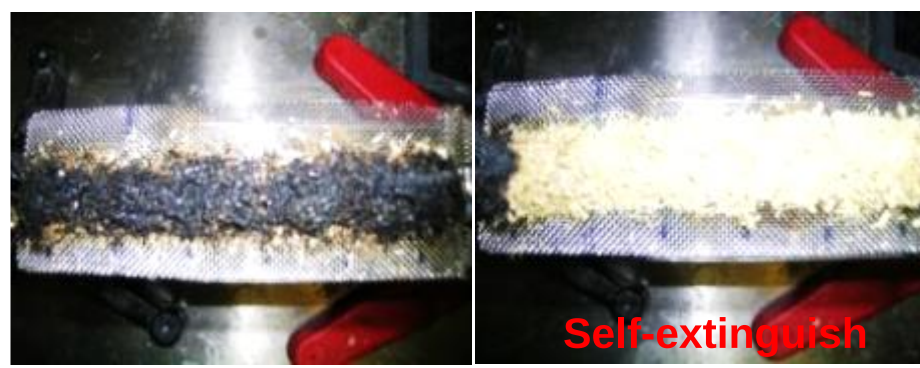
Untreated | Treated

C5-Flax Unidirectional (France)



Untreated | Treated

Chopped rice straw



Untreated | Treated

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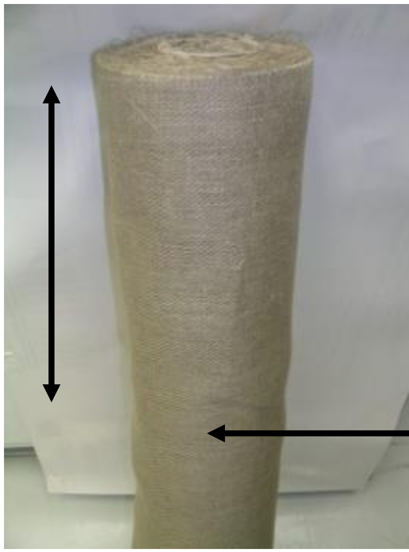
Excellent tensile properties after treatment



Tensile force of treated flax fibres

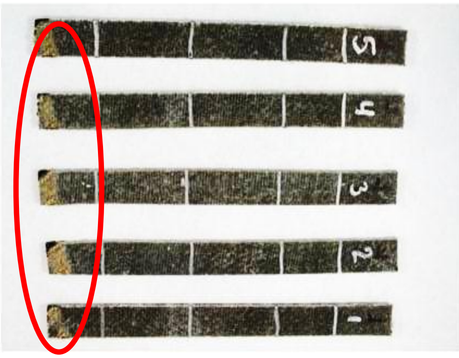
Fiber	Description	Max load pound force (or in N)	
		Parallel	Perpendicular
Untreated		4.6 (20.4)	5.4 (23.8)
Treated	Mg^{2+}+Na^{+}	4.8 (21.3)	5.3 (23.7)

SD < 10%

Tensile properties of flax-epoxy composites

Sample	Tensile stress (MPa)	Energy to break (J)
Untreated flax-Epoxy	117.7 ± 4.0	33.7±2.0
Treated flax-Epoxy	106.4 ± 1.0	36.7±2.6

Self-extinguishing treated fibres

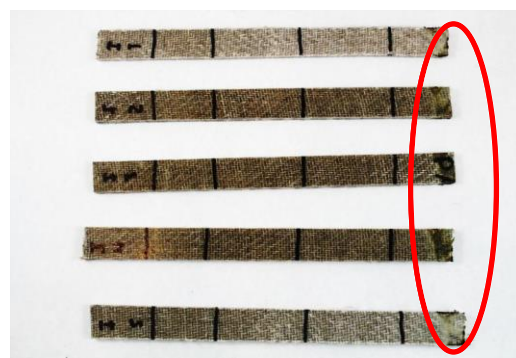


Treated flax -
Epoxy composite

Name	Burning Length (inches)				
	1.0	2.0	3.0	4.0	4.5
	Burning Time (s)				
Untreated fibre	5.4	10.1	15.2	20.1	22.5
Treated fibre	NB	NB	NB	NB	NB
Untreated fibre-Epoxy	111	218	321	425	542
Treated fibre-Epoxy	NB	NB	NB	NB	NB

NB: not burn

Treated flax -
Phenolic composite



Treated flax - UPE
composite

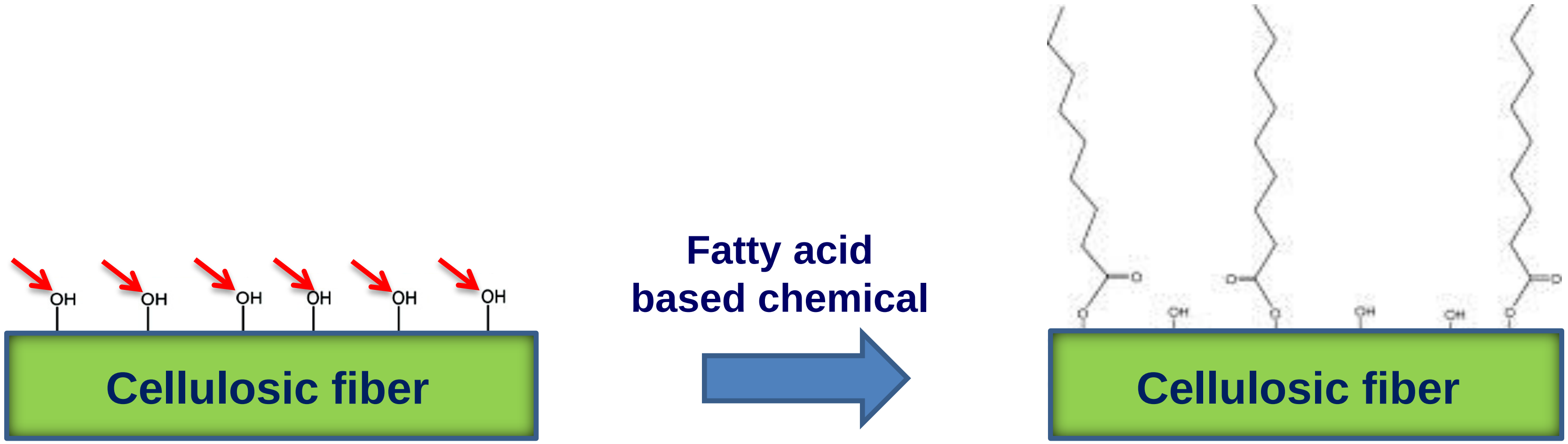
Moisture absorption in cellulose

Challenge

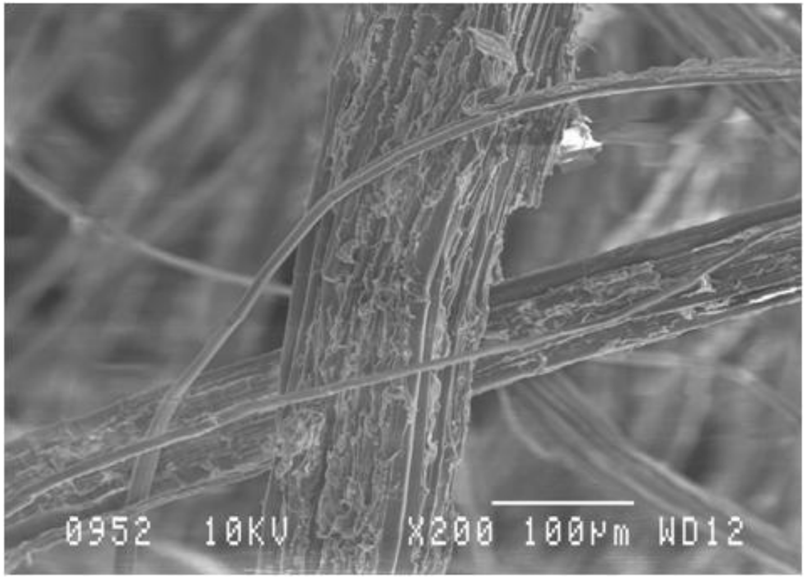
The hydrophilic nature of cellulose surface due to hydroxyl group leads to high moisture absorption

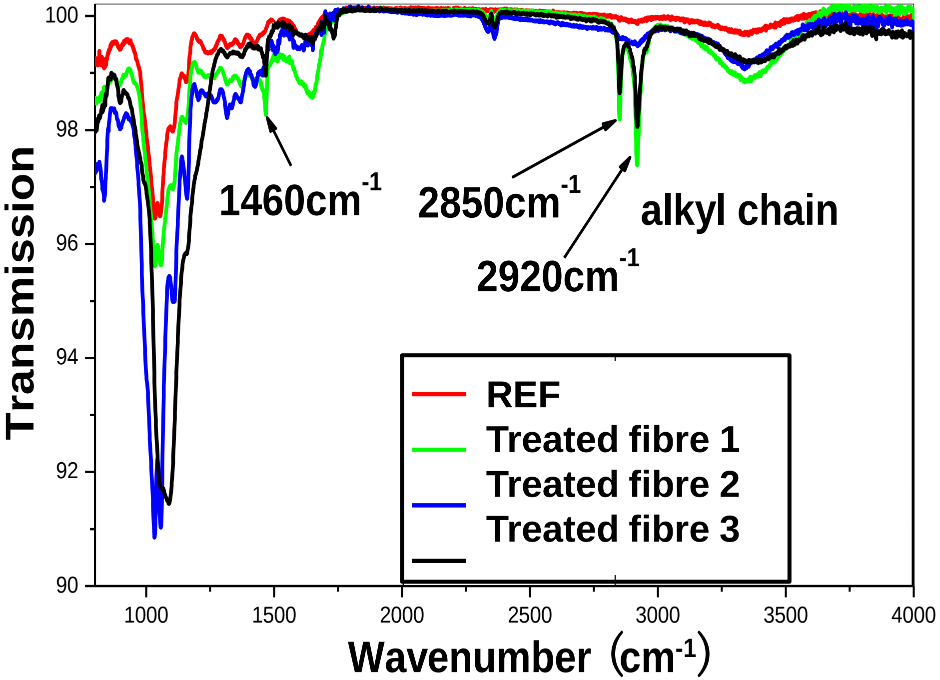
Solution

Transform the hydrophilic nature of cellulose fibre surface into hydrophobic for reducing moisture absorption by grafting fatty acid on the fibre surface via hydrophilic hydroxyl group



Fatty acid grafted on fibre surface





- SEM: a deposition of a layer of fatty on flax fibre surface
- FTIR: increased peak intensity at 2920 and 2850cm^{-1} associated with alkyl chain of fatty acid

From hydrophilic to hydrophobic

No wetting | Improved wetting | Complete wetting

HYDROPHILIC → HYDROPHOBIC

Reducing moisture absorption

Sample	Flax fibre REF	Treated fibre 1	Treated fibre 2
Moisture determined by TGA (%)	6.5	4.4	2.3
Moisture determined by weighting (%)	12.1	10.3	6.4

50% reduction of moisture absorption in the treated flax fibre

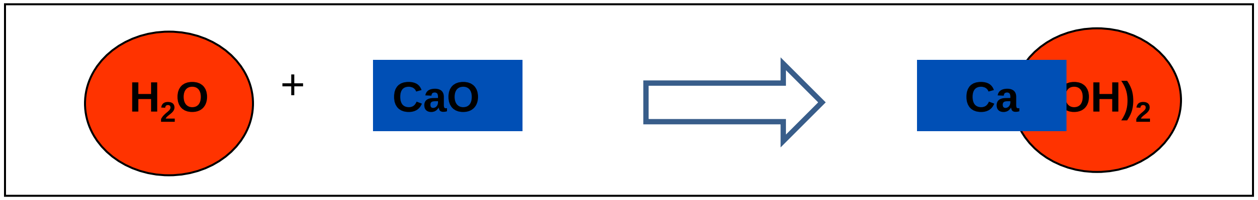
Removing moisture in cellulose prior to compounding

Challenge

The hydrophilic nature of cellulose surface due to hydroxyl group leads to high moisture absorption that must be removed prior to compounding

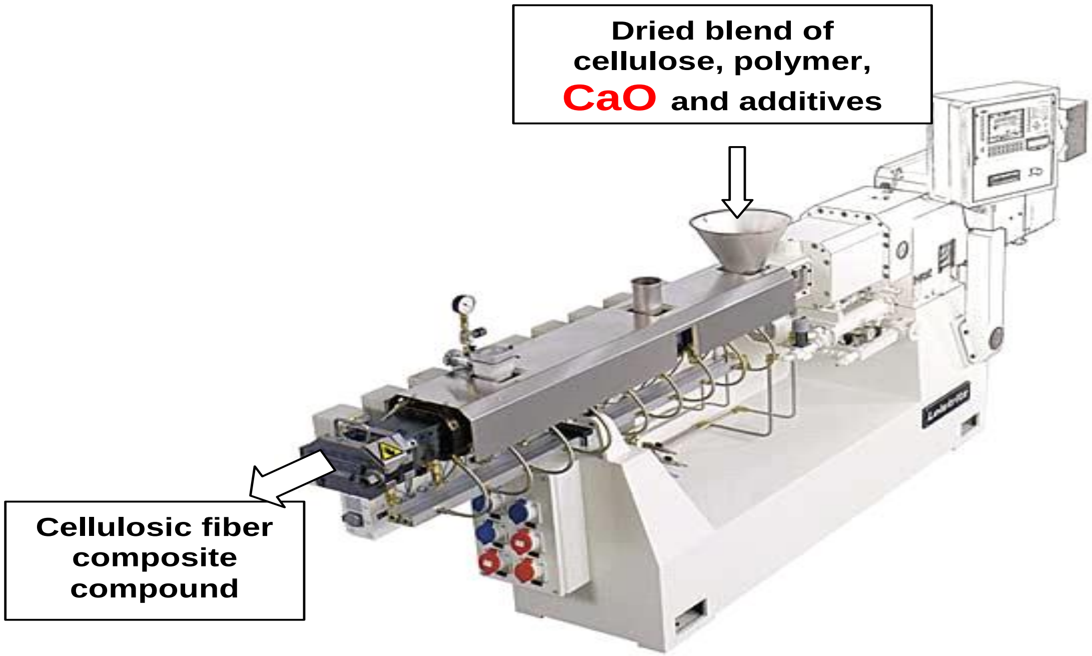
Solution

Using low cost reactive filler, CaO, which can chemically react with moisture in cellulose thus eliminating the need for drying cellulose prior to compounding



Canadian Patent 2,435,129 ***US 7,041,716 B2*** ***EP 1,646,685***

Risk-free and cost-effective solution



- Freedom of operation: patent granted in three continents
- Cost-effective solution :
  - Cost reduction: CaO is the cheapest among all components in the WPC (0.1U$/lb)
  - Energy savings: elimination of drying of cellulose
  - No additional fibre treatment or new investment

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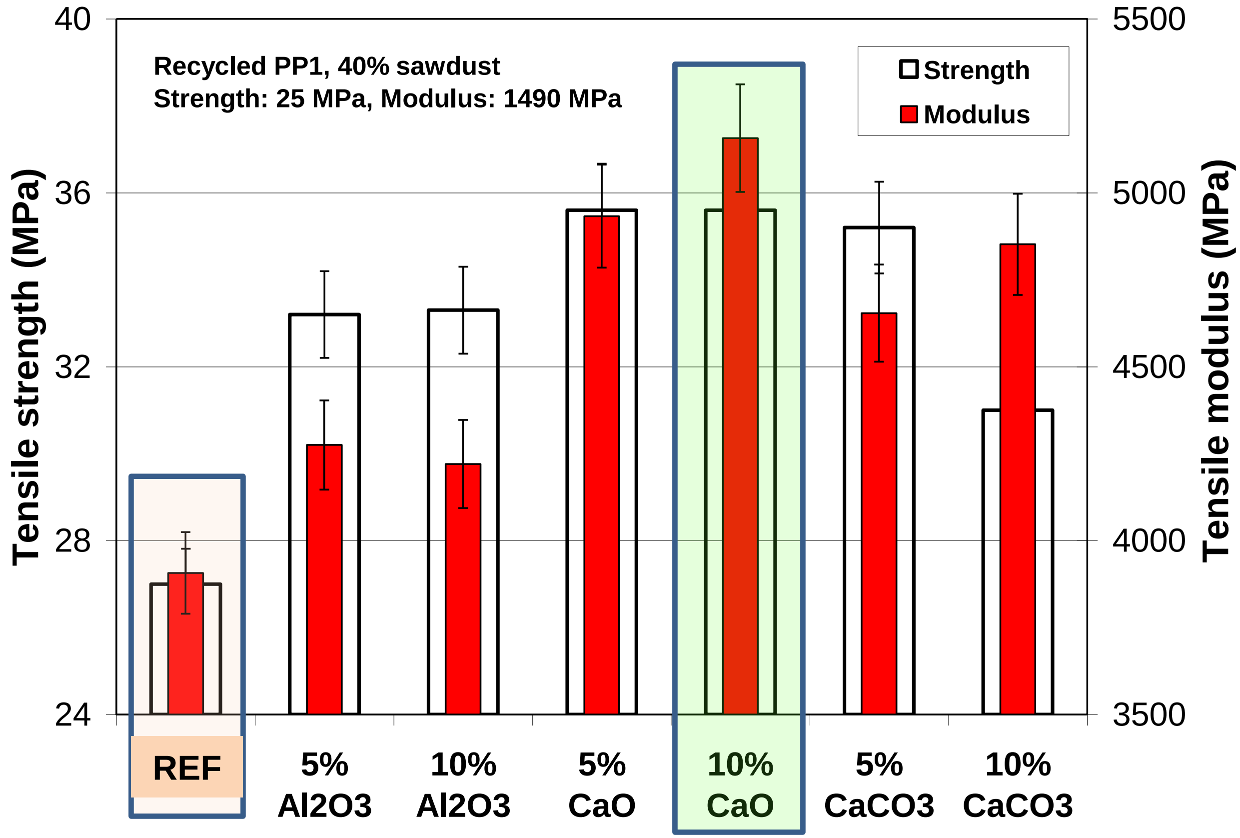
Improved performance

- **Recycled PP**
- **Wood sawdust with 16% moisture content**



- As compared with the composite reference the presence of 10wt% CaO increases: >30% in tensile strength and >40% in tensile modulus

VOC and odor test methods for automotive

Challenges

- Many standard methods for VOC
  - In ventilated test chambers at elevated temperature
  - In sealed bags, containing the tested product
  - In micro-chamber
  - In small glass vials
- Each company has their own way of testing
- Very few quantitative methods for odor

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VOC/odor test methods!

Specification:	Test Method:	VOC Test Description:
Hyundai-Kia	MS300-55	3L bag-DNPH & VOC Analysis
Nissan	NES M0402	Method #2 - 10L bag- DNPH & VOC analysis - 1 part & 1 background
Nissan	NES M0402	Method #1 - 2000L bag- DNPH & VOC Analysis - 1 part & 1 background
Toyota	TSM 0508G	Various size bag - DNPH & VOC analysis - 1 part & 1 background
Honda	DWG 0094Z SNA 0000	3 day bag prep - DNPH & VOC analysis
Mazda	MES CF 080 B	20L pot - DNPH & VOC analysis - Blank & test part
GM	GMW8081	VOC analysis by Headspace GCMS
GM	GMW3205	Resistance to odor propagation of interior materials
European	VDA-275	Formaldehyde release by modified flask / UV Vis Spec method
European	VDA-277	VOC analysis by Headspace GC
European	VDA-278	VOC and FOG emissions by thermal desorption GCMS
European	VDA-270	Determination of the odour characteristics of trim materials in motor vehicles
Daimler	PB VWL 709	Analysis of the emission of volatile and condensable substances from vehicle interior materials by thermodesorption
VW	PV 3341	Emissions of organic compounds by headspace GCMS
VW	PV 3900	Odor test
VW	PV 3015	Condensable constituents
VW	PV 3925	Measuring emissions of formaldehyde by bottle/UV-Vis Spec.
GM	GMW15654	Full vehicle air sampling, VOC and SVOC analysis by GCMS (analysis only)
GM	GMW15600	Full vehicle air sampling, aldehydes/ketones DNPH-HPLC (analysis only)
GM	GMW15634	Interior materials VOC and SVOC by TD-GCMS (direct sampling) Thermodesorption
GM	GMW15635	Interior materials aldehydes/ketones by ottle/DHPH-HPLC (lab sampling)

Even more VOC/odor test methods!

Specification:	Test Method:	VOC Test Description:
JEITA	PC-VOC-G-2005	23 C - 0.5 to 1 air change per hour - Background & 5 hr VOC analysis
CARB	CARB310	Determination of VOC in consumer products and reactive organic compounds in aerosol coating products
Paint/coat	D3960	Determining volatile organic compound (VOC) content of paints and related coatings (better for water based)
EPA	Method 24	Determination of volatile matter content, water content, density, volume solids and weight solids of surface coatings (better for solvent based paint)
Paint/coat	D6886	Speciation of the volatile organic compounds (VOCs) in low VOC content waterborne air-dry coatings by GC
EPA	Method 8260c	Volatile organic compounds by GC/MS (sampled by EPA 5021) USING EQUILIBRIUM HEADSPACE ANALYSIS)
SCAQMD	313-91	Determining volatile organic compound by GC/MS (Headspace or direct liquid injection GC/MS)
VOLVO	VCS 1027, 2739	Formaldehyde emissions by Bottle/Spectrometer method
VOLVO	VCS 1027, 2749	VOC analysis by Headspace GC
BMW	GS97014-2	SHED test, HC emission by FID, 1-6 parts in Micro-SHEDS (small parts)
BMW	GS97014-2	SHED test, HC emission by FID, 1 part in Mini-SHED (larger parts)
E2/BLDNG Mat.	EN-120	Wood based Panels, Determination of Formaldehyde Content. - Extraction Method called the perforator method. (reflux, UV/Vis spectrophotometry)
SCAQMD	304	Determining volatile organic compound in various materials (method 303 is a subtest)
Air	D5466	Determination of volatile organic chemicals in atmospheres (Canister sampling methodology)
SAE	J1756	Fogging (like PV 3015)

NRC can help you to address VOC/odor?

Identify the source of problem and provide solutions

- Provide science related to the determination of VOC and odor substances in your products
- Suggest/develop complementing testing methods/techniques adapted to your specific needs
- Develop practical solutions to address VOC and odor in your products covering from the raw materials to compounding, molding and post-treatment as necessary

Example: Lignin-thermoplastic blends

What is lignin?

- A composition important of wood and straw: 20-35% lignin (65-8% cellulose)
- A natural biothermoplastic → can blend with conventional TP
- Most of VOC and odor of cellulose source come from lignin

VOC and odor issue: no basic science for lignin-based products

- What type of VOCs in lignin and lignin thermoplastic blends?
- What the most possible odor substances among the VOCs?
- How these VOC and odor substances behave?
- How to control the VOC and odor in the final product?

Odor threshold

Table 2 Odor thresholds measured by the triangle odor bag method (ppm,v/v)

Substance	Odor Threshold	Substance	Odor Threshold
Formaldehyde	0.50	Hydrogen sulfide	0.00041
Acetaldehyde	0.0015	Dimethyl sulfide	0.0030
Propionaldehyde	0.0010	Methyl allyl sulfide	0.00014
n-Butylaldehyde	0.00067	Diethyl sulfide	0.000033
Isobutylaldehyde	0.00035	Allyl sulfide	0.00022
n-Valeraldehyde	0.00041	Carbon disulfide	0.21
I sovaleraldehyde	0.00010	Dimethyl disulfide	0.0022
n-Hexylaldehyde	0.00028	Diethyl disulfide	0 0020
n-Heptylaldehyde	0.00018	Diallyl disulfide	0.00022
n-Octylaldehyde	0.000010	Methyl mercaptane	0.000070
n-Nonylaldehyde	0.00034	Ethyl mercaptane	0.0000087
n-Decylaldehyde	0.00040	n-Propyl mercaptane	0.000013
Acrolein	0.0036	Isopropyl mercaptane	0.0000060
Methacrolein	0.0085	n-Butyl mercaptane	0.0000028
Crotonaldehyde	0.023	Isobutyl mercaptane	0.0000068
Methanol	33	sec. Butyl mercaptane	0.000030
Ethanol	0.52	tert. Butyl mercaptane	0.000029
n-Propanol	0.094	n-Amyl mercaptane	0.00000078
I sopropanol	26	Isoamyl mercaptane	0.00000077
n-Butanol	0.038	n-Hexyl mercaptane	0.000015
I sobutanol	0.011	Thiophene	0.00056
sec.Butanol	0.22	Tetrahydrothiophene	0.00062
tert.Butanol	4.5	Nitrogen dioxide	0.12
n-Pentanol	0.10	Ammonia	1.5
Isopentanol	0.0017	Methylamine	0.035
sec.Pentanol	0.29	Ethylamine	0.046
tert. Pentanol	0.088	n-Propylamine	0.061
n-Hexanol	0.0060	Isopropylamine	0.025
n-Heptanol	0.0048	n-Butylamine	0.17
n-Octanol	0.0027	Isobutylamine	0.0015
Isooctanol	0.0093	sec. Butylamine	0.17
n-Nonanol	0.00090	tert. Butylamine	0.17
n-Decanol	0.00077	Dimethylamine	0.033
2-Ethoxyethanol	0.58	Diethylamine	0.048
2-n-Buthoxyethanol	0.043	Trimethylamine	0.000032
1-Butoxy-2-propanol	0.16	Triethylamine	0.0054
Phenol	0.0056	Acetonitrile	13
o-Cresol	0.00028	Acrylonitrile	8.8
m-Cresol	0.00010	Methacrylonitrile	3.0
p-Cresol	0.000054	Pyridine	0.063
Geosmin	0.0000065	Indole	0.00030
Acetic acid	0.0060	Skatole	0.0000056
Propionic acid	0.0057	Ethyl-o-toluidine	0.026
n-Butyric acid	0.00019	Propane	1500
Isobutyric acid	0.0015	n-Butane	1200
n-Valeric acid	0.000037	n-Pentane	1.4
Isovaleric acid	0.000078	Isopentane	1.3
n-Hexanoic acid	0.00060	n -Hexane	1.5
Isohexanoic acid	0.00040	2-Methylpentane	7.0
Sulfur dioxide	0.87	3-Methylpentane	8.9
Carbonyl sulfide	0.055	2, 2-Dimethylbutane	20

- The VOC family generates the strongest odor:
  - Mercaptane
  - Aldehyde
  - Carboxylic acid
  - Ester

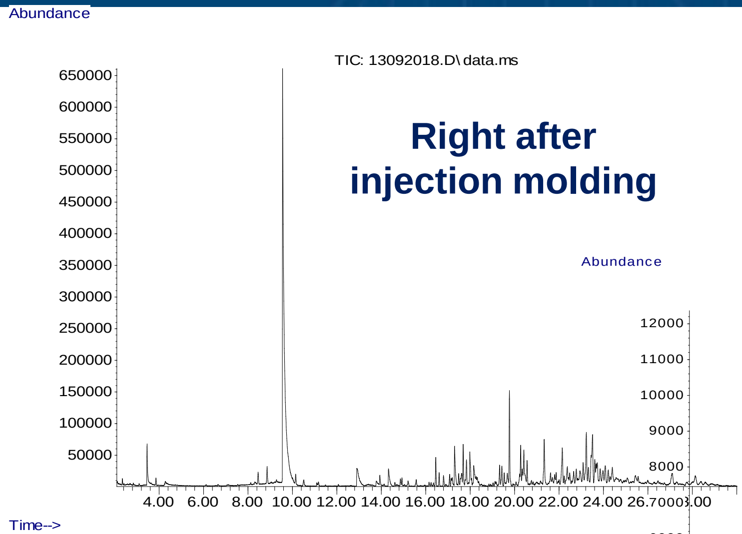
Typical VOC and odor in lignin

Chemical	CAS	Concentration at 50^{o}C (ng/L)/g	Concentration at 180^{o}C (ng/L)/g
Disulfide, dimethyl	000624-92-0	106	682415
Toluene	000108-88-3		1261
Cyclotrisiloxane, hexamethyl-	000541-05-9	2353	52395
Furfural	000098-01-1	172	388024
Styrene	000100-42-5	3879	502477
Cyclotetrasiloxane, octamethyl-	000556-67-2	4888	217197
Phenol, 2-methoxy-	000090-05-1	38406	3995316
4-Hydroxymandelic acid, ethyl ester, di-TMS	1000071-53-3	517	85009
Phenol, 4-ethyl-2-methoxy-	002785-89-9	573	2803296
Vanillin	000121-33-5		1121963
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	000498-02-2		6840544
Total VOC		**58921**	**71211429**

Typical VOC and odor of lignin-PP blend

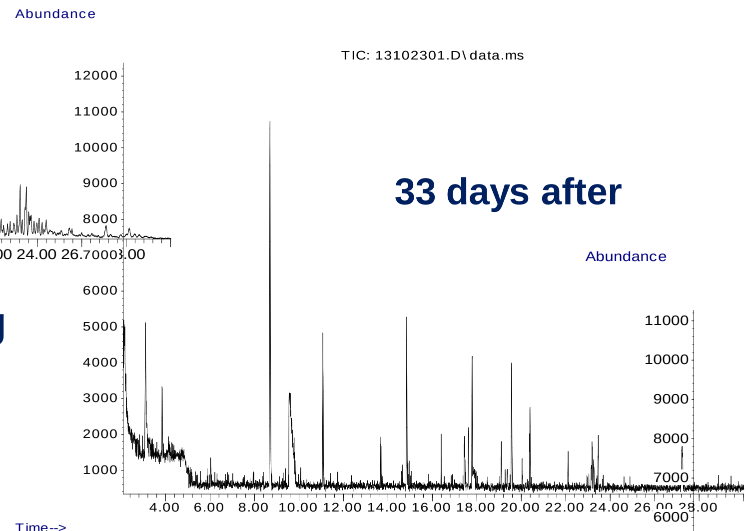
Chemical	CAS	Concentration (ng/L)/g
Acetic acid	000064-19-7	347.96
Cyclotrisiloxane, hexamethyl-	000541-05-9	23.52
Furfural	000098-01-1	3556.64
Ethanol, 2-butoxy-	000111-76-2	75.65
2-Furancarboxaldehyde, 5-methyl-	000620-02-0	39.76
Phenol	000108-95-2	10.41
Cyclotetrasiloxane, octamethyl-	000556-67-2	8.74
C13 branched hydrocarbon		33.35
Pentanoic acid, 4-oxo-, ethyl ester	000539-88-8	66.85
Phenol, 2-methoxy-	000090-05-1	21.63
Nonanal	000124-19-6	53.05
Benzoic acid, ethyl ester	000093-89-0	118.36
Oxiniacic Acid	002398-81-4	48.46
Octanoic acid, ethyl ester	000106-32-1	74.92
Decanal	000112-31-2	29.44
Vanillin	000121-33-5	22.06
Total VOC		**4893.31**

Evolution of VOC in lignin-PP with time



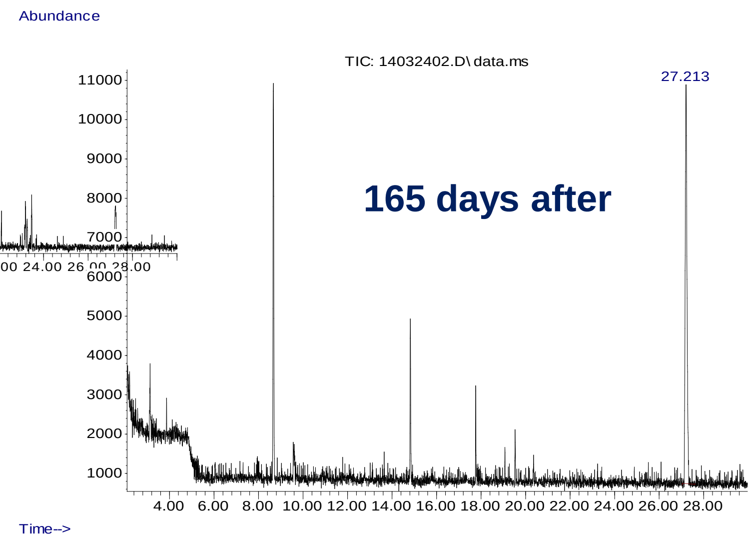
Right after injection molding

VOC = 4,893 (ng/L)/g



33 days after

VOC = 95 (ng/L)/g



165 days after

VOC = 84 (ng/L)/g

Conclusions

- NRC has developed a number of technologies at various technology readiness levels, that can be benefit for your product development and optimisation in terms of flammability, moisture sensitivity, VOC and odor with cellulosic composites
- NRC can complement with your in-house R&D expertise/capabilities
- By working with NRC, you can bring your products to market faster

For further information, please contact

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