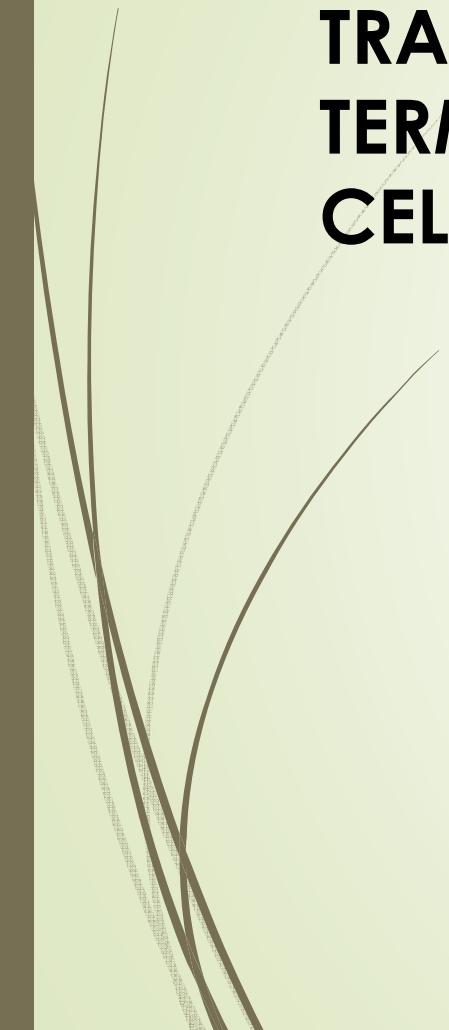




# **UMA ALTERNATIVA "VERDE" AOS COMPÓSITOS TRADICIONAIS: TERMOPLÁSTICOS REFORÇADOS COM FIBRAS DE CELULOSE, BIOCOMPÓSITOS**



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Instituto de Química – Unicamp  
Campinas, SP, Brasil**

# O que é um compósito tradicional?



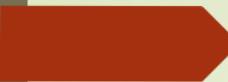
Compósito de fibra de carbono



Compósito de fibra de vidro e de carbono



Compósitos de fibra de vidro ou de carbono combinados com diferentes matrizes termofixas ou termoplásticas.



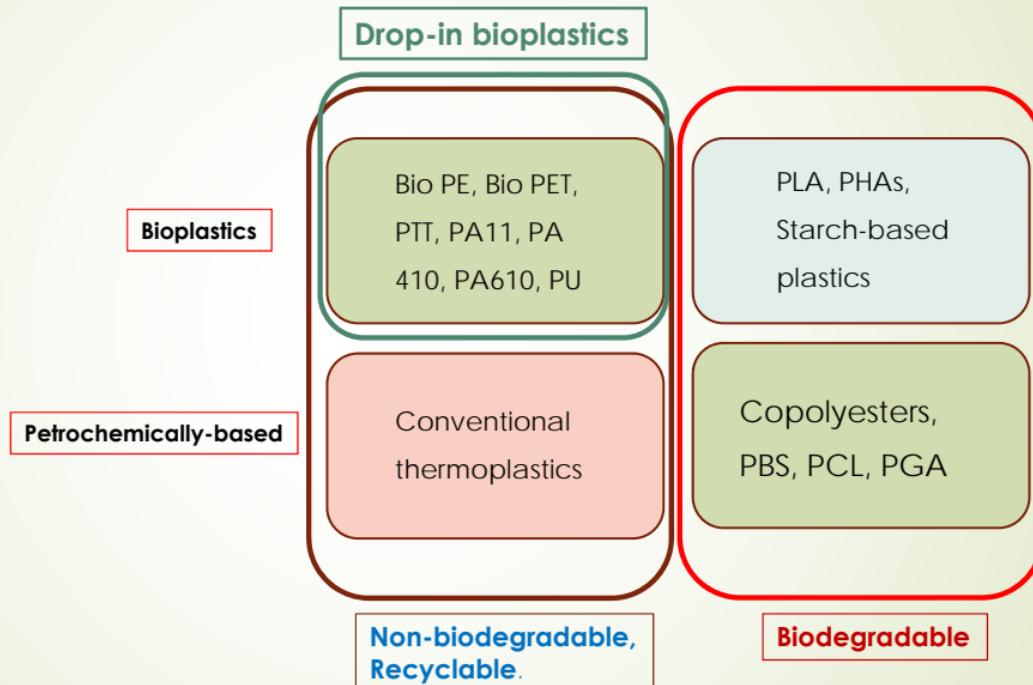
## Meanings, definitions:

- ▶ **Biodegradable**: bio-based or synthetic polymers that decompose to CO<sub>2</sub>, water and humus in municipal composting facilities for a maximum of 6 months.
- ▶ **Bioplastics**: biodegradable or non-biodegradable polymers obtained from biomass or renewable raw-materials.
- ▶ **Drop-in bioplastics**: non-biodegradable polymers, identical to their fossil fuel counterparts, obtained from renewable raw-materials; can be recycled.
- ▶ **Biocomposites**: composite materials where, at least, one of the components is obtained from a renewable raw-material.

Adapted from M. Hackett, "Ready to grow: the biodegradable polymers market", Plastics Engineering, March 2016,p. 1-4.



# The present situation:



PA= polyamide, PBS = polybutylene succinate, PCL=polycaprolactone, PE= polyethylene, PET= poly(ethylene terephthalate), PGA= polyglycolic acid, PHAs= polyhydroxyalkanoates, PLA= polylactic acid, PTT = poly(trimethylene terephthalate), PU = polyurethane. Adapted from M. Hackett, "Ready to grow: the biodegradable polymers market", Plastics Engineering, March 2016,p. 1-4.

## Why use renewable resources ?

“They (automobiles) will be lighter and much of them will be built of plastics developed from farm products”.

**Henry Ford**, from an article written by James Schweinhart published in The Detroit News of July, 30<sup>rd</sup>, 1942.



# Renewable resources:

- **Presently used for the following applications in the plastics industry:**
- **Monomers**: sugar cane ethanol (PE, PP and PET), castor oil (PU), glycerin (thermosets).
- **Biocides or antimicrobians**; chitosan, essential oils, etc.
- **Pigments**: several.
- **Bioplasticizers for PVC**: epoxidized soybean oil, citrates, castor oil, dioctyl succinate, sebacates (market share of US\$ 1,140 million by 2020).
- **Lubricants**: stearic and sebacic acid salts and vegetal oils.
- **Antistatic**: glycerol esters
- **Mold releases**; soybean, sunflower, castor oils.
- **Fillers and thermal insulation**: wood flour, agricultural residues, etc.
- **Reinforcing agents**: ligno-cellulosic fibers, cellulose.
- **Anti-oxidant**: lignin, vitamin E.

# Reinforcing agents and stabilizers.

**Reinforcing agents** are used to adjust the mechanical properties of polymers for very specific applications, such as structural parts or substitution of metallic parts.(predicted market share: for talc in 2021 US\$ 3.29 billion and for glass fibers in 2022 US\$ 2.7 billion<sup>2</sup>).

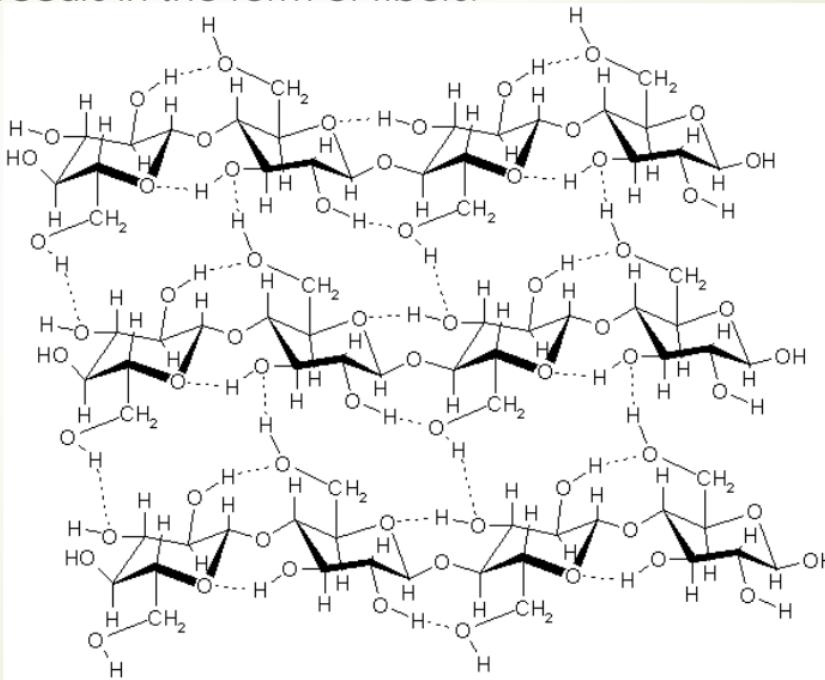
**Stabilizers** are needed to prevent the degradation of plastic parts, increasing their lifetime; antioxidants, photostabilizers, lubricants or antiacids.(market share of US\$ 3.6 billion in year 2000<sup>1</sup>).

1-<http://pubs.acs.org/cen/coverstory/7849/7849bus1.html>

2-<http://www.4spe.myindustrytracker.com/en/article/139030/recent-research-glass-fiber-in-the-global>

## Reinforcing agent.

- ▶ The most abundant polymers in our planet are **cellulose** and **lignin**:
- ▶ **Cellulose** occurs in the form of fibers.





## Vegetal fibers as reinforcing agent.

► **Advantages:**

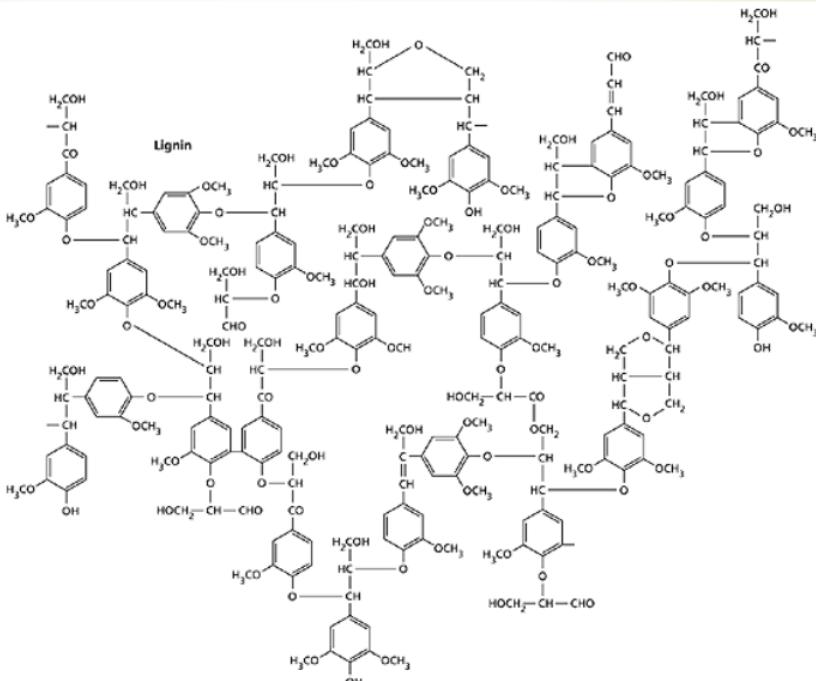
- May have a low cost.
- Availability.
- Low environmental impact, carbon credits.
- Lower density in comparison to talc and glass fibers ( $1.45 \times 2.50 \text{ g cm}^{-3}$ ).
- Lower abrasivity to the processing equipment in comparison to glass fibers and talc.

► **Challenges:**

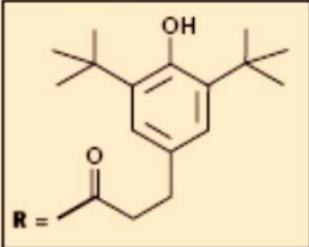
- Large scale production with reproducible properties.
- Development of the appropriate processing conditions.

## Stabilizer, anti-oxidant.

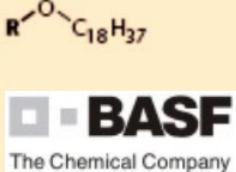
- **Lignin:** Amorphous polymeric resin found in the cell wall of plant cells, acts as a binder of cellulose fibrils, strengthening and stiffening the wall.



Commercial anti-oxidant:

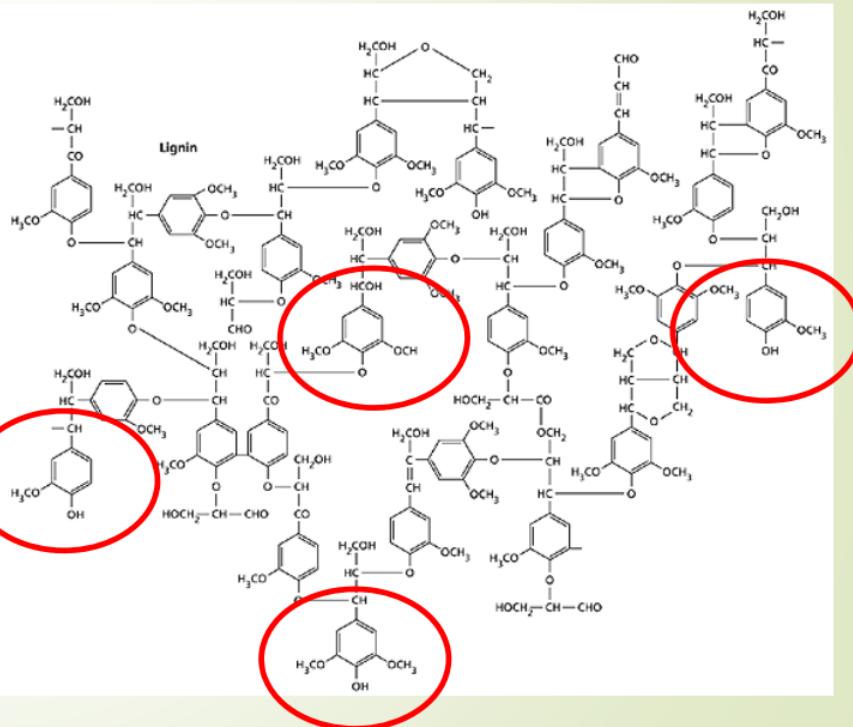


**IRGANOX 1076**  
CAS No. 2082-79-3  
Molecular Wt  
(g/mol) 531

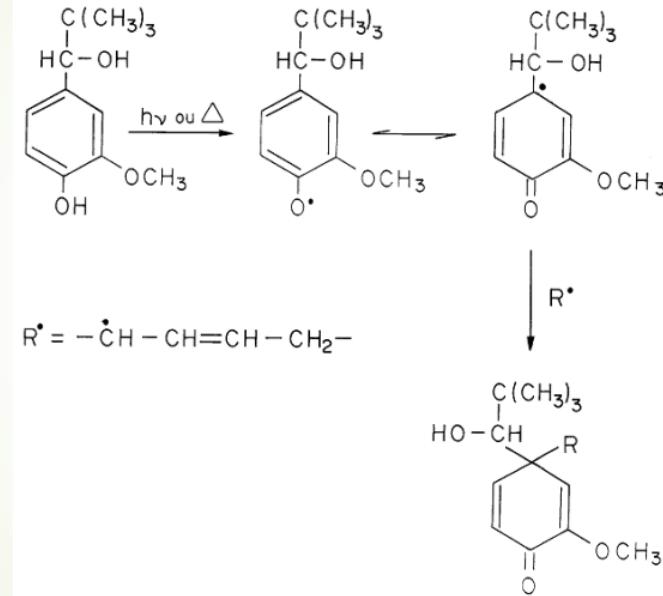


Antioxidant activity depends on the siringyl/guaiacyl rate of the lignin. Thus, on the vegetal species from which it was extracted.

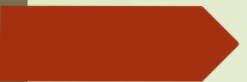
Lignin as anti-oxidant:



Free radical scavenging mechanism for guaiacyl units of lignin:  
Adapted from I. Forsskahl, J. Photochem. 27 (1984) 363.



M.A. De Paoli, L.T. Furlan, M.A. Rodrigues, "Lignin from sugar cane-bagasse as photostabilizer for butadiene rubber", Quim. Nova 6 (1983) 121.



## Lignin as anti-oxidant.

► **Advantages:**

- Low cost,
- Availability.
- May act as compatibilizing agent.
- No Volatile Organic Components, VOC.

► **Challenges:**

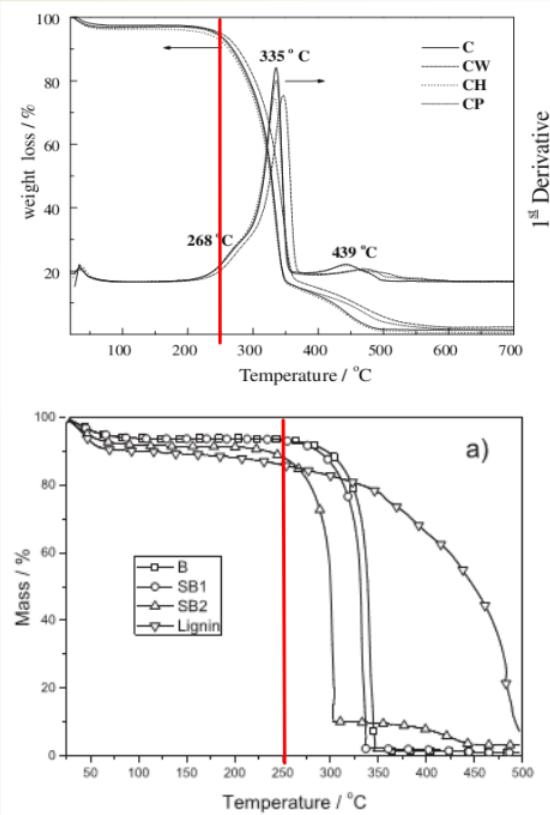
- Properties depend on the vegetal species from which it is obtained.
- They impart color to the material.
- Insoluble, processing conditions must achieve uniform dispersion.
- May be associated to a secondary anti-oxidant.

Polymer additives: vegetal fibers as reinforcing agent:  
adjusting processing conditions.

- ▶ **Twin-screw corotating intermeshing extruder, Coperion Werner Pfleiderer ZSK-26, L/D = 44, D = 26 mm with side-feeder. Screw profile and temperature profile adjusted according to polymer matrix and fiber.**
- ▶ **Injection molding, Arburg All-rounder M-250.**



Polymer additives: vegetal fibers as reinforcing agent: adjusting processing temperature.



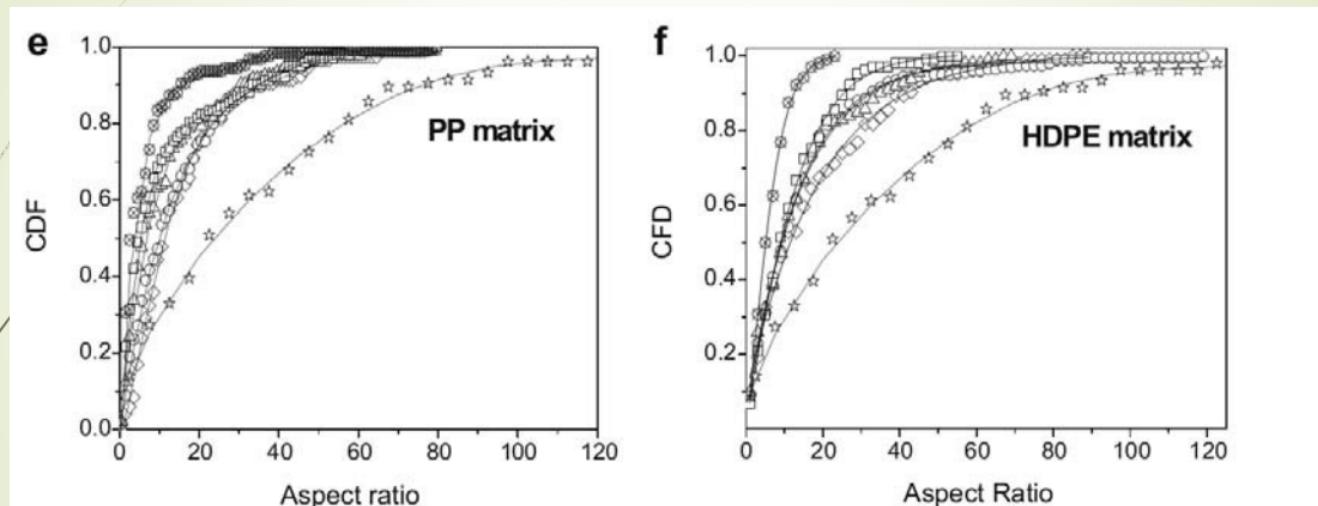
**Curauá fibers  
Ligno cellulosic material**

M.A.S. Spinacé et al. / Carbohydrate Polymers 77 (2009) 47–53

**Bleached and semi-bleached  
Cellulose fibers**

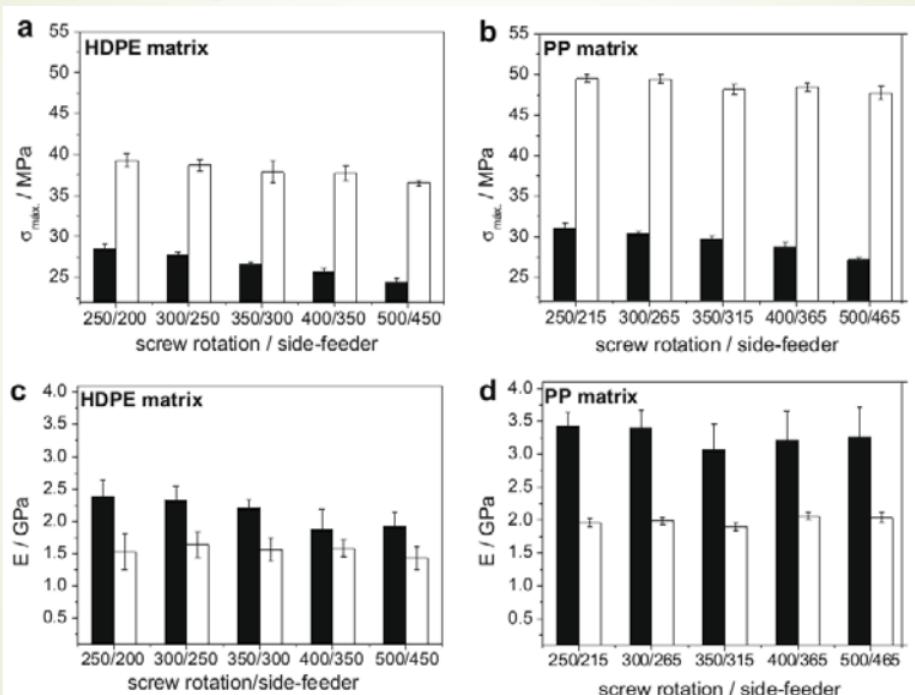
R. Gadioli et al. / Polymer Degradation and Stability 108 (2014) 23–34

**Curauá fibers (20 wt %) as reinforcing agent for PP and HDPE; adjusting screw rotation i.e. shear effect.**



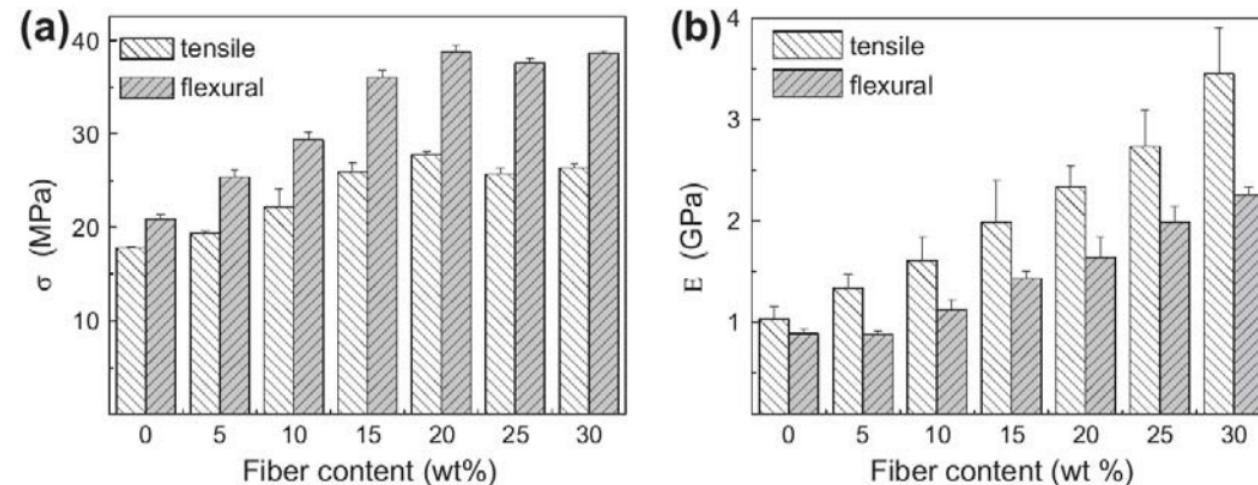
**Fig. 1.** Cumulative distribution function (CDF) of fibre length, diameter and aspect ratio for pristine fibre ( $\star$ ) and composites of PP (a, c, e) and HDPE (b, d, f), respectively, extruded at ( $\diamond$ ) 250, ( $\circ$ ) 300, ( $\triangle$ ) 350 ( $\square$ ), 400 and ( $\otimes$ ) 500 rpm.

# Curauá fibers (20 wt %) as reinforcing agent for PP and HDPE; adjusting screw rotation.



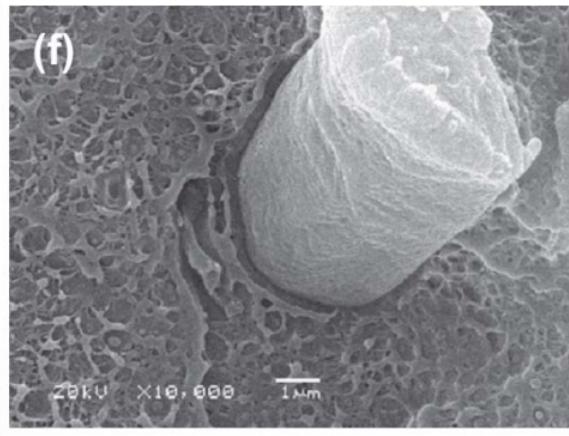
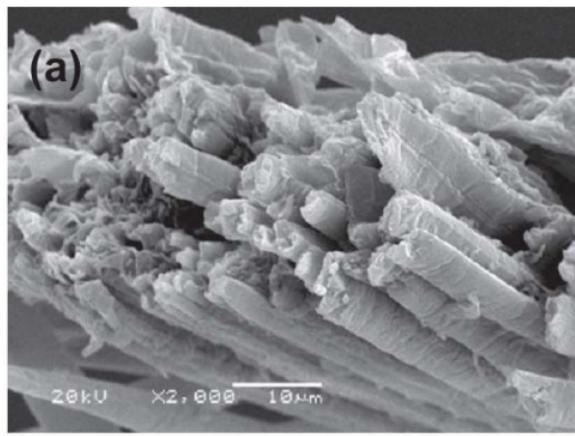
Yield stress, modulus in strain (■) and flexural (□) tests for HDPE (a, c, d) and PP (b, d, f).

## Curauá fibers as reinforcing agent for HDPE, processed at 300 rpm, 160 – 180 °C; adjusting fiber content.



**Fig. 2.** (a) Tensile strength and (b) elastic modulus of the composites, with increasing fiber content.

## Curauá fibers as reinforcing agent for HDPE, fibrillation and adhesion.



a) SEM of a single fiber tip and f) the HDPE composite with 20 wt % of Curauá fiber.

## Cellulose fibers and lignin from Eucaliptus Grandis



For each ton of CO<sub>2</sub> emitted during the cellulose production process, the Eucaliptus plantations absorb from the atmosphere 3.8 tons of CO<sub>2</sub>.

<https://visionbresil.wordpress.com/2011/02/24/environnement-fevrier-2011-le-business-vert/>

**Cellulose fibers** as reinforcing agent for PP: mechanical properties of injection molded test samples, PP with 30 wt % of fibers.

### Tensile

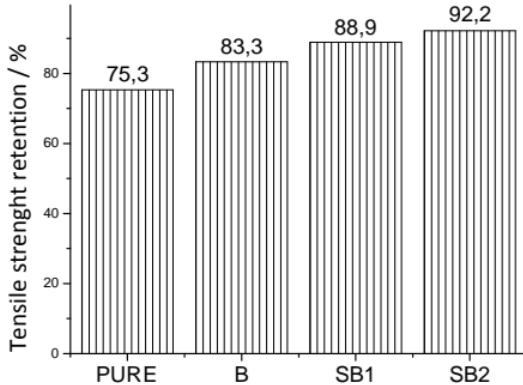
	PP	B	SB <sub>1</sub>	SB <sub>2</sub>
T. strength (MPa)	30.0 ± 0.2	49 ± 2	50 ± 1	54 ± 1
Modulus (MPa)	897 ± 247	1663 ± 136	1662 ± 422	1824 ± 86
Strain (%)	~ 21	9 ± 1	9 ± 1	8 ± 0.3

### Flexural

	PP	B	SB <sub>1</sub>	SB <sub>2</sub>
F. strength (MPa)	41.0 ± 0.3	67.0 ± 0.3	66 ± 3	71 ± 1
Modulus (MPa)	1409 ± 22	3091 ± 68	3150 ± 42	3464 ± 33

**B = bleached cellulose fibers, SB<sub>1</sub> and SB<sub>2</sub> = semi-bleached cellulose fibers with different lignin concentrations.**

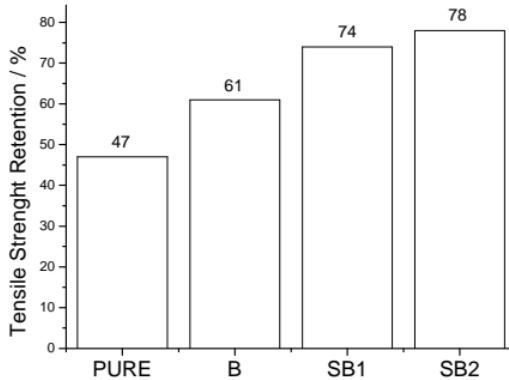
Accelerated aging, 500 h; effect of the lignin present in the cellulose fibers : PP with 30 wt % of cellulose fibers.



QUV test chamber

**Tensile strength retention after 500 h of accelerated aging (QUV test chamber) for pure PP and composites.**  
**Higher lignin content – higher properties retention**

Environmental aging, 360 days: effect of the lignin present in the cellulose fibers: PP with 30 wt % of cellulose fibers .

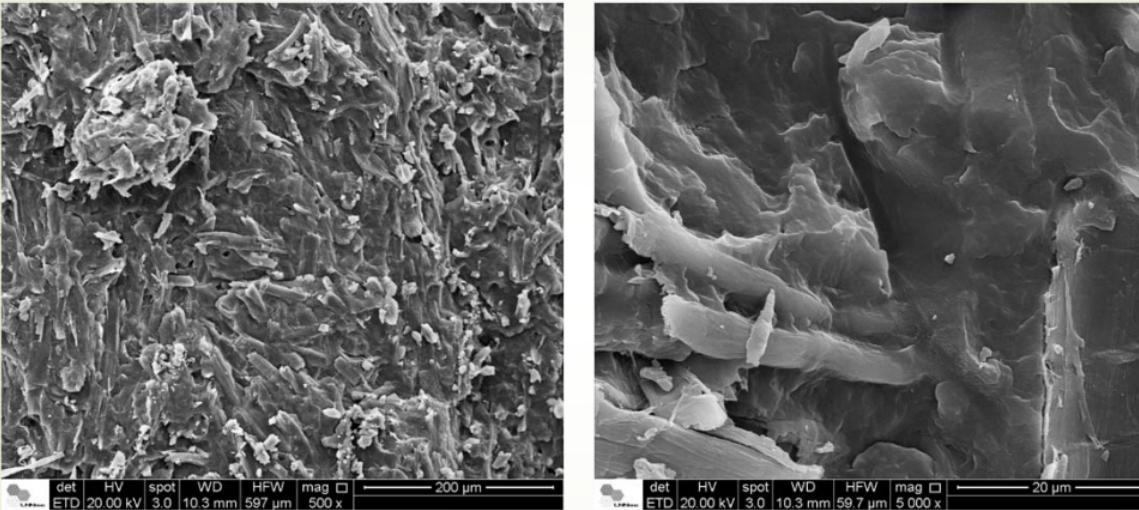


Sample's exposure site

**Tensile strength retention after 360 days of environmental aging for pure PP and composites.**

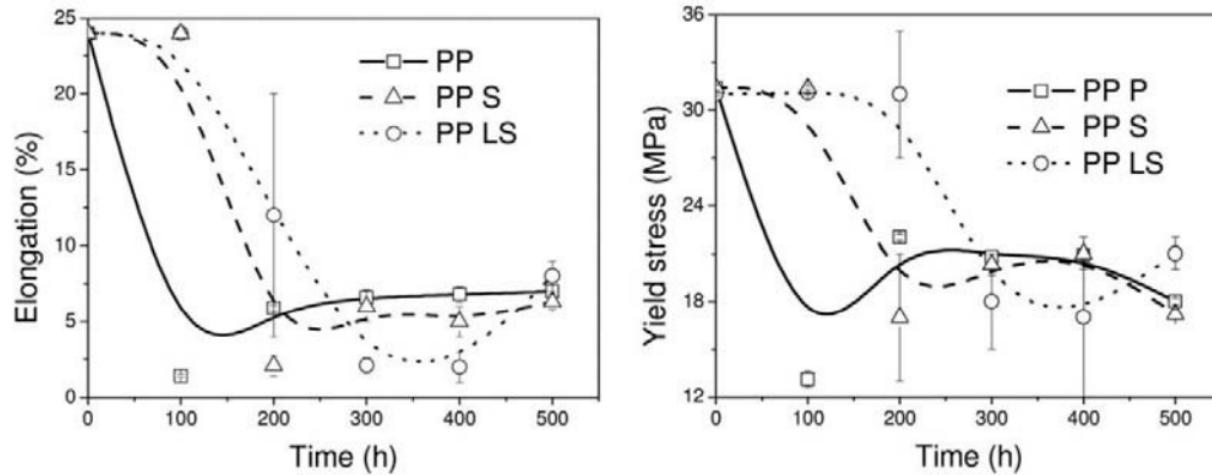
**Higher lignin content – higher properties retention**

# SEM micrographs: **PP30SB1** after environmental aging: retention of fiber/matrix interaction.



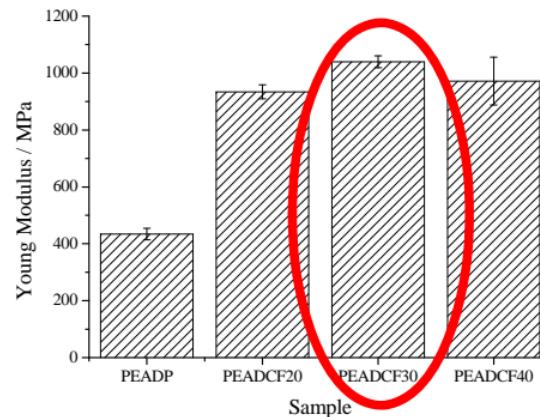
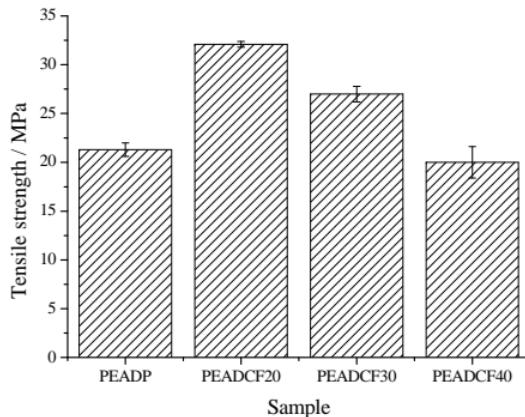
R Gadioli, J A Morais, W R Waldman, M.A. De Paoli, Polym. Degrad. Stab. 108 (2014) 23 – 34.

Lignin (0.09 wt. %) used as anti oxidant for PP: accelerated aging test.



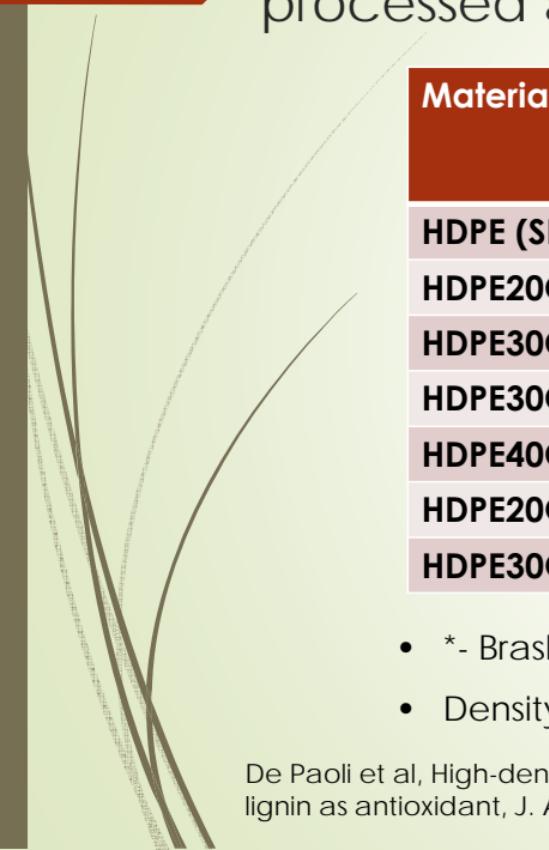
**Figure 4.** Variation of elongation and yield stress as a function of aging time for pure polypropylene (PP), PP stabilized exclusively with commercial stabilizers (PPS), and PP stabilized with lignin and secondary stabilizer (PPLS).

## Cellulose fibers as reinforcing agent for **greenHDPE™**, processed at 300 rpm; fiber content effect.



In this case 30 wt % was chosen because it provides the highest elastic modulus.

Fiber content determination by extraction, after processing: 30 – 33 wt %.

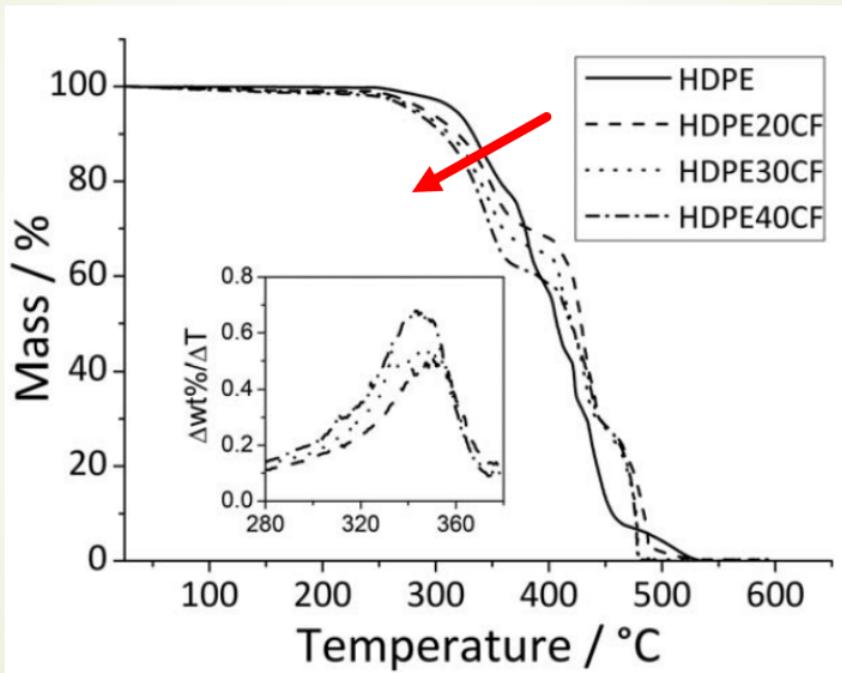


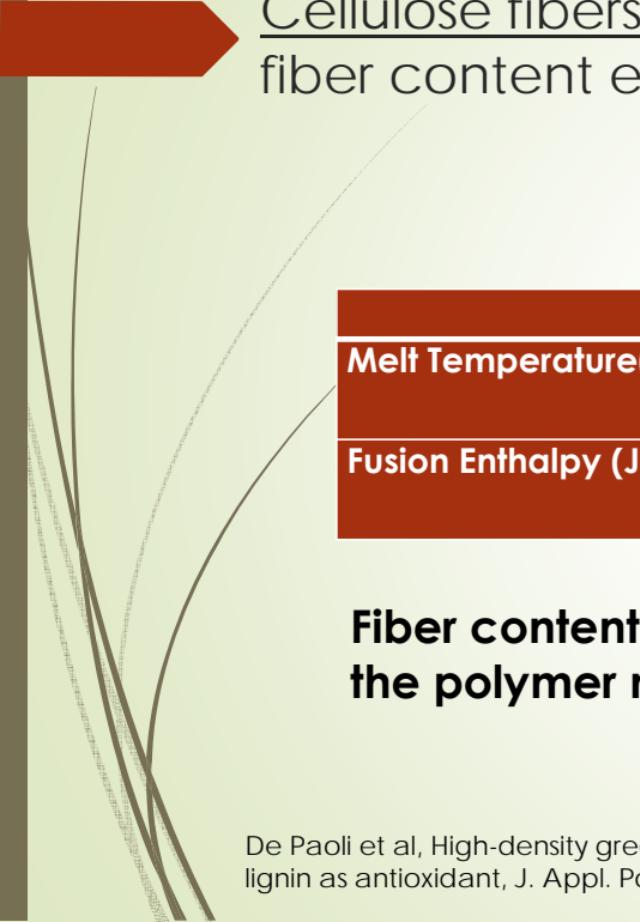
## Cellulose fibers as reinforcing agent for greenHDPE™, processed at 300 rpm; fiber content effect on density.

Material	Density (g cm <sup>-3</sup> )	$\sigma$ (tensile) MPa	$\sigma/\text{dens}$ MPa/(g cm <sup>-3</sup> )
HDPE (SHC7260) *	0.96	22.6 ± 0.4	23.5
HDPE20CF	1.04	32.5 ± 0.1	31.3
HDPE30CF	1.08	26.1 ± 0.3	24.2
HDPE30CF5L	1.03	22.5 ± 0.9	22.3
HDPE40CF	1.10	20.0 ± 0.6	19.1
HDPE20GF#	1.11	50	45
HDPE30GF#	1.30	57.5	46

- \* - Braskem data sheet, # Latene data sheet, GF = glass fibers.
- Density of CF fibers is *ca.* 1.45 and for GF is 2.50 g cm<sup>-3</sup>

## Cellulose fibers as reinforcing agent for greenHDPE™, fiber content effect on the onset mass loss temperature.



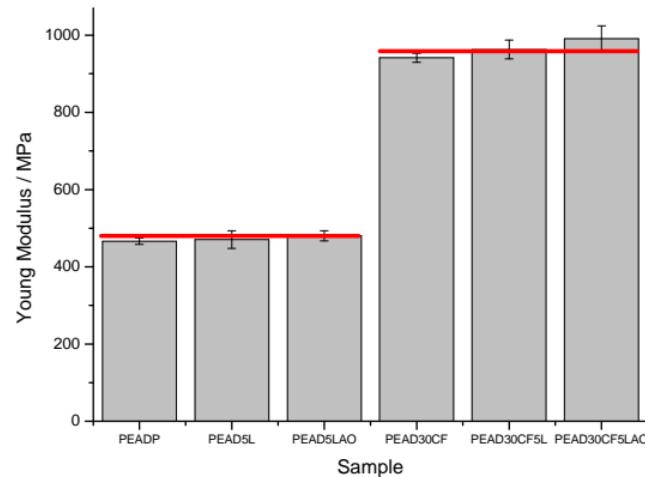
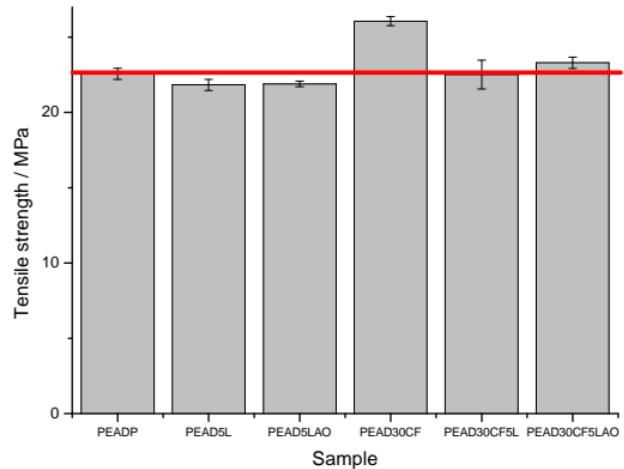


## Cellulose fibers as reinforcing agent for greenHDPE ™, fiber content effect on thermal parameters.

	HDPEP	HDPECF20	HDPECF30	HDPECF40
Melt Temperature(°C)	135	140	138	138
Fusion Enthalpy (J/g)	253	240	243	250

**Fiber content does not affect thermal properties of  
the polymer matrix**

# Cellulose fibers as reinforcing agent for greenHDPE™, lignin effect on mechanical properties.



**The lignin added did not affect the mechanical properties of the composites**

De Paoli et al, High-density green polyethylene biocomposite reinforced with cellulose fibers and using lignin as antioxidant, J. Appl. Polym. Sci., 2017, DOI: 10.1002/app.45219



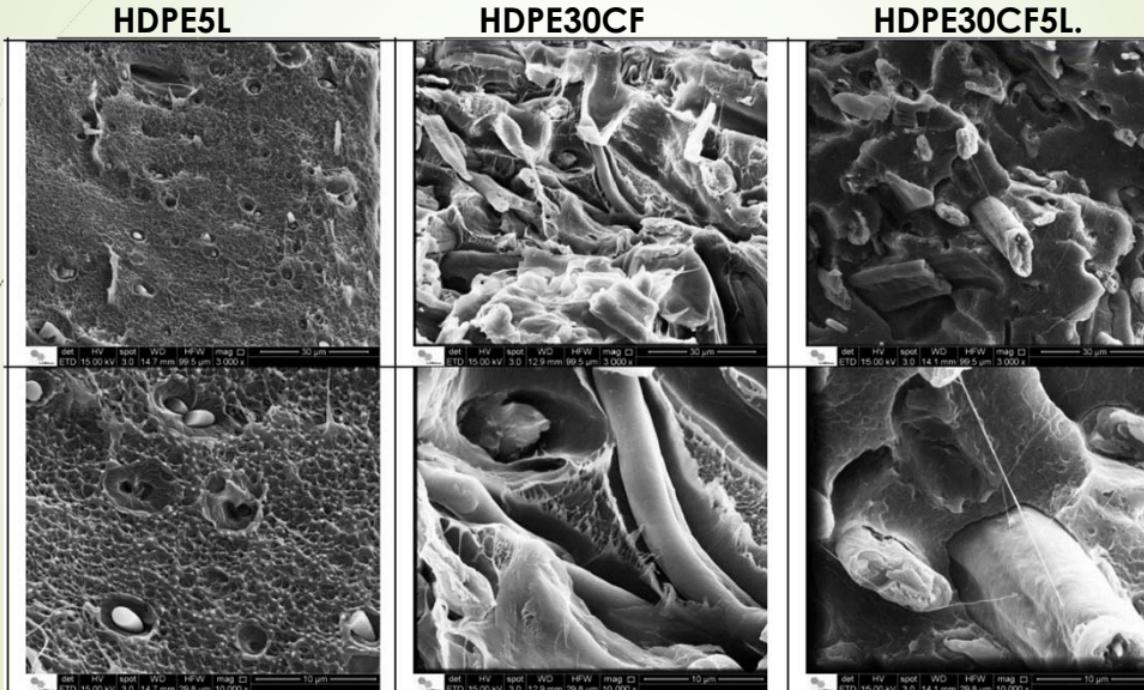
## Cellulose fibers as reinforcing agent for greenHDPE™, lignin effect on oxidation induction time, OIT.

	HDPE	HDPE5L	HDPE5LAO	HDPECF30	HDPECF305L	HDPECF305LAO
OIT (min)	17*	76.± 1	T > 90#	24 ± 0	78 ± 2	76 ± 2

\* - only one measurement, # - no exothermic process until 200 °C  
L = lignin, AO = secondary antioxidant.

**There is a large increase of OIT by adding lignin to HDPE and composites in comparison to pure HDPE and composites without lignin.**

## Cellulose fibers as reinforcing agent for greenHDPE™; lignin as anti-oxidant. **samples aged for 1000 h**



De Paoli et al, High-density green polyethylene biocomposite reinforced with cellulose fibers and using lignin as antioxidant, J. Appl. Polym. Sci., 2017, DOI: 10.1002/app.45219

**PA-6 is routinely processed at 220 – 240 °C !!**  
**Fibers degrade at 200 °C !!**

Is it possible to reinforce polyamide-6 with vegetal fibers ?



**NO, it is Impossible !**

**PA-6 is routinely processed at 220 – 240 °C !!**  
**Fibers degrade at 200 °C !!**

Is it possible to reinforce polyamide-6 with vegetal fibers ?



## Curauá fibers as reinforcing agent for polyamide-6: mechanical properties.

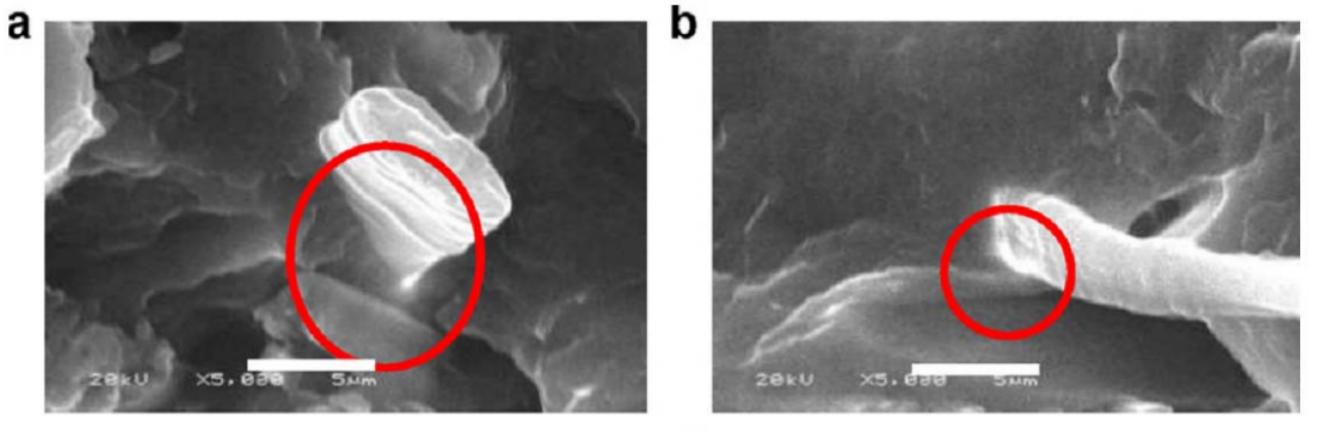
Specific values of tensile and flexural tests of composites of PA-6 with 20 wt% Curauá long fiber prepared using WP-25 extruder, PM-1004 and PF-1004 finished products [17]

Sample	Tensile tests		Flexural tests	
	$\sigma_{\max}$ (MPa/ g cm <sup>-3</sup> )	$E$ (GPa/ g cm <sup>-3</sup> )	$\sigma_{\max}$ (MPa/ g cm <sup>-3</sup> )	$E$ (GPa/ g cm <sup>-3</sup> )
WP3	70	4.3	98	3.1
PM-1004	57	5.3	90	3.5
PF-1004	80	5.1	126	3.9

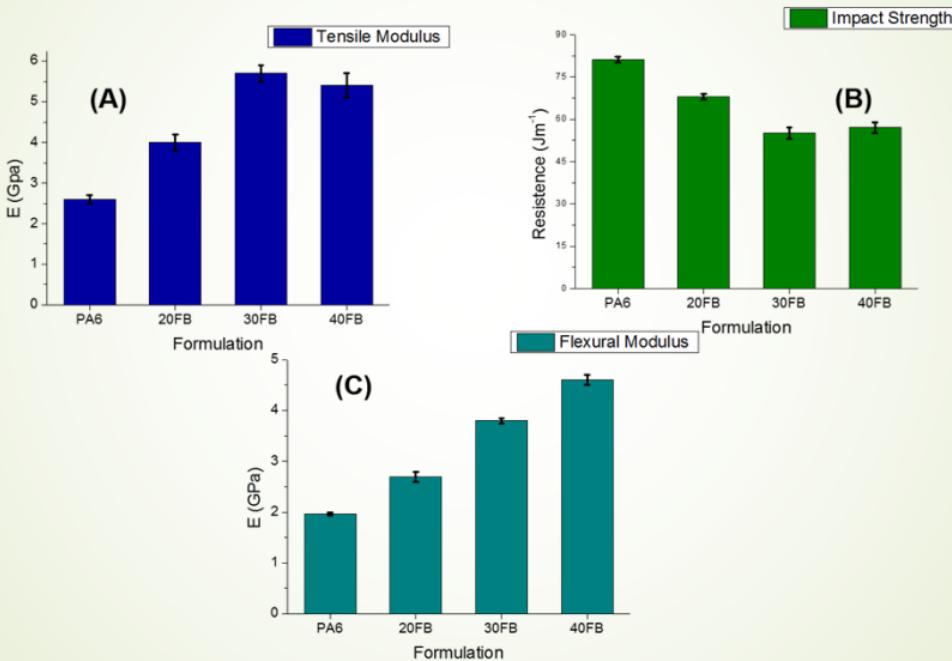
WP3 twin screw extruder

PM-1004 talc reinforced and PF-1004 glass fiber reinforced.

**Curauá fibers as reinforcing agent for polyamide-6:  
fiber matrix adhesion, non dried fibers.**



# Bleached **cellulose** fibers (FB) as reinforcing agent for polyamide-6: mechanical properties.

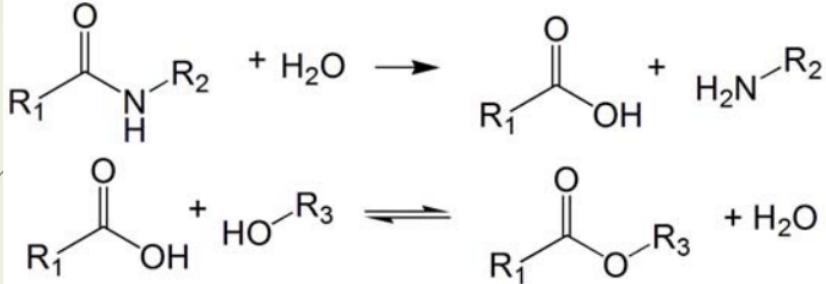




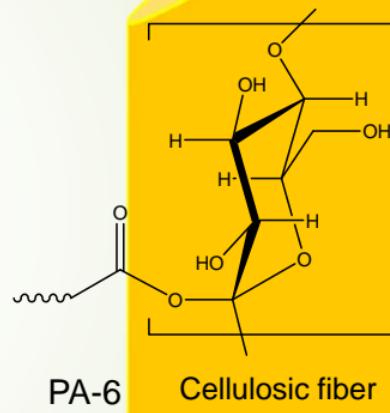
## Bleached cellulose fibers (FB) as reinforcing agent for polyamide-6: mechanical properties and density.

Formula	Density (g cm <sup>-3</sup> )	Specific E (GPa / g cm <sup>-3</sup> )
<b>PA6EBS</b>	1.099 ( $\pm 0.004$ )	2.37 ( $\pm 0.09$ )
<b>PA620FB</b>	1.139 ( $\pm 0.004$ )	3.5 ( $\pm 0.2$ )
<b>PA630FB</b>	1.182 ( $\pm 0.004$ )	4.8 ( $\pm 0.2$ )
<b>PA640FB</b>	1.207 ( $\pm 0.004$ )	4.5 ( $\pm 0.2$ )
<b>PA-6 + 20 wt. % Curauá Fiber*</b>	1.18 ( $\pm 0.01$ )	4.3 ( $\pm 0.3$ )
<b>PA-6 + 20 wt. % Talc*</b>	1.27 ( $\pm 0.01$ )	5.3 ( $\pm 0.5$ )
<b>PA-6 + 20 wt. % Glass Fiber*</b>	1.27 ( $\pm 0.01$ )	5.1 ( $\pm 0.4$ )

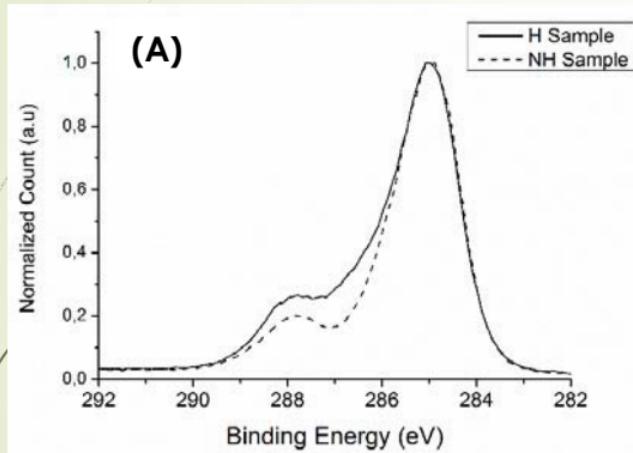
## Cellulose fibers as reinforcing agent for polyamide-6.



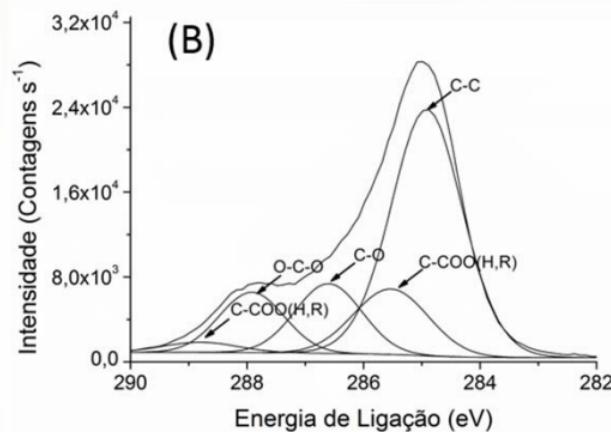
**PA-6 partial hydrolysis and  
esterification reaction with OH groups  
on fiber surface.**



## X-ray photoelectron spectroscopy, XPS, evidence for fiber/matrix interaction.

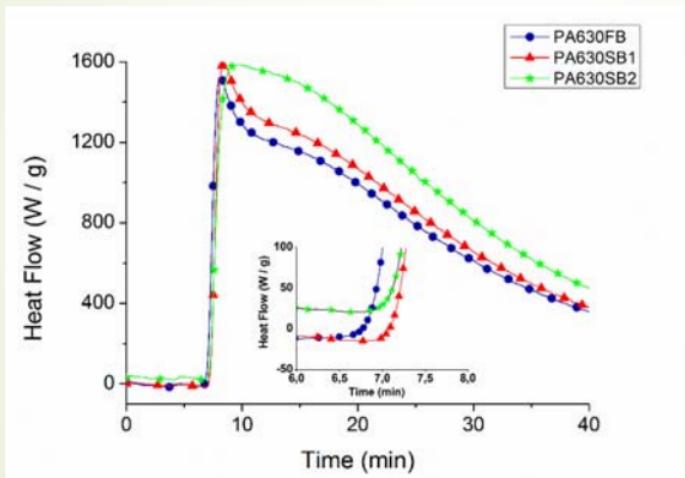


Overlapped and normalized high-resolution XPS spectra of C1s: non dried fiber(H-full line) and dried fiber (NH-dashed line).



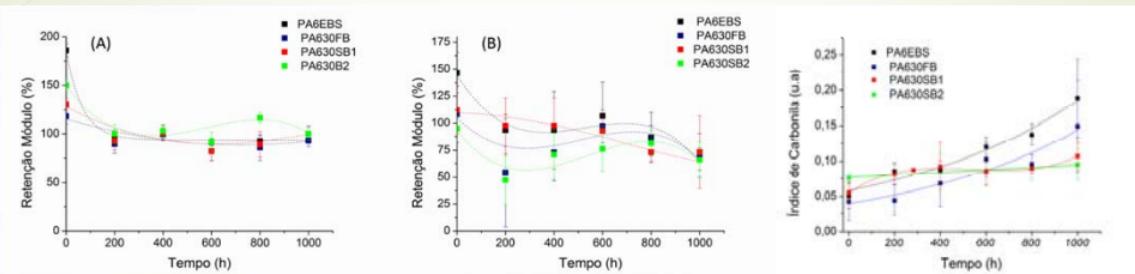
Deconvoluted curve for composite with non dried fibers, showing evidence for ester bond presence at the fiber-matrix interface.

## Lignin containing cellulose fibers as reinforcing agent for polyamide-6: stabilization effect, OIT.



material	OIT / min
PA630FB	6.76
PA630SB1	7.08
PA630SB2	7.01

# Lignin containing cellulose fibers as reinforcing agent for polyamide-6: 1000 h accelerated aging.



**Degradation localized on the surface, as evidenced by ATR-FTIR x mechanical props.**



Test samples, before and after aging  
(PA6EBS, PA630FB, PA630SB1 e PA630SB2)



## Conclusões.

- É possível desenvolver biocompósitos termoplásticos com alto desempenho, para substituir os compósitos usuais de fibra de vidro ou de talco, no entanto, é necessário investir muito em pesquisa para atingir essas propriedades de uma forma economicamente viável.

# Equipe:



e Jacqueline Alvarado.

# Agradecimentos:



Conselho Nacional de Desenvolvimento  
Científico e Tecnológico

Processo: 301933/2015-4  
Modalidade/Nível: PQ-Sr



Grant no.: 2010/17804-7



Petroquímica brasileira de classe mundial



## Lignin as primary anti-oxidant for rubbers and PP.

- M.-A. De Paoli, L.T. Furlan, M.A. Rodrigues, "Lignin from sugar cane-bagasse as photostabilizer for butadiene rubber", Quim. Nova 6 (**1983**) 121.
- M.-A. De Paoli e L.T. Furlan, "Sugar cane bagasse-lignin as photostabilizer for butadiene rubber", Polym. Degrad. Stab., 11 (**1985**) 327-337.
- M.-A. De Paoli e L.T. Furlan, "Sugar cane bagasse-lignin as stabilizer for rubbers II: butadiene rubber", Polym.Degrad.Stab., 13 (**1985**) 129- 138.
- M.-A. De Paoli, M.A. Rodrigues e L.T. Furlan, "Sugar cane bagasse-lignin as stabilizer for rubbers III: styrene- butadiene rubber and natural rubber", Polym.Degrad.Stab., 13 (**1985**) 337- 350.
- R Gadioli, J A Morais, W R Waldman, M.-A. De Paoli, "The role of lignin in polypropylene composites with semi-bleached cellulose fibers: mechanical properties and its activity as antioxidant", Polym. Degrad. Stab. 108 (**2014**) 23 – 34.
- R. Gadioli, W. R. Waldman, M. A. De Paoli, "Lignin as a green primary antioxidant for polypropylene", J. Appl. Polym. Sci., 133 (**2016**) doi: 10.1002/APP.43558

# Vegetal fibers as reinforcing agent: PP, HDPE, CA .

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