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GENERALITAT VALENCIANA
IVACE
INSTITUT VALENCIÀ DE COMPETITIVITAT EMPRESARIAL
UNIÓN EUROPEA
Fondo Europeo de Desarrollo Regional
Una manera de hacer Europa

1 GOALS

Obtaining additives of natural origin and their use in toy sector products by recovering agricultural waste.

Obtaining extracts from different waste from the agri-food industry with the following **functionalities**:

- NATURAL COLOURANTS
- FLAME RETARDANTS
- ANTIMICROBIAL EFFECT

Incorporating the additives obtained into **biopolymers**

Scaling up and obtaining **demonstrators** for the **toy industry**

VALORISING OF AGRI-FOOD WASTE

Food waste is a big problem:

The **food and beverage industry** is the **first manufacturing branch** of the industrial sector

MORE INFORMATION

The **EU** generates

87,6 MMt/year

of **food waste**

= 178 kg/per capita

annually

MORE INFORMATION

In **Spain**

176 kg/per capita

are lost or wasted every year

MORE INFORMATION

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Worldwide,
vegetable,
fruit and tuber waste
represents

40-50%

of **food waste**

MORE INFORMATION

In **Spain**, from **food manufacturing industry** represents

39%

and in **commerce**

14%

In **catering and households** the percentages are

14% & 42%

respectively

The recovery of agri-food waste is a **SOLUTION** to this problem based on the action plan for the

circular economy

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*Data obtained from the Ministry of Agriculture, Fisheries and Food

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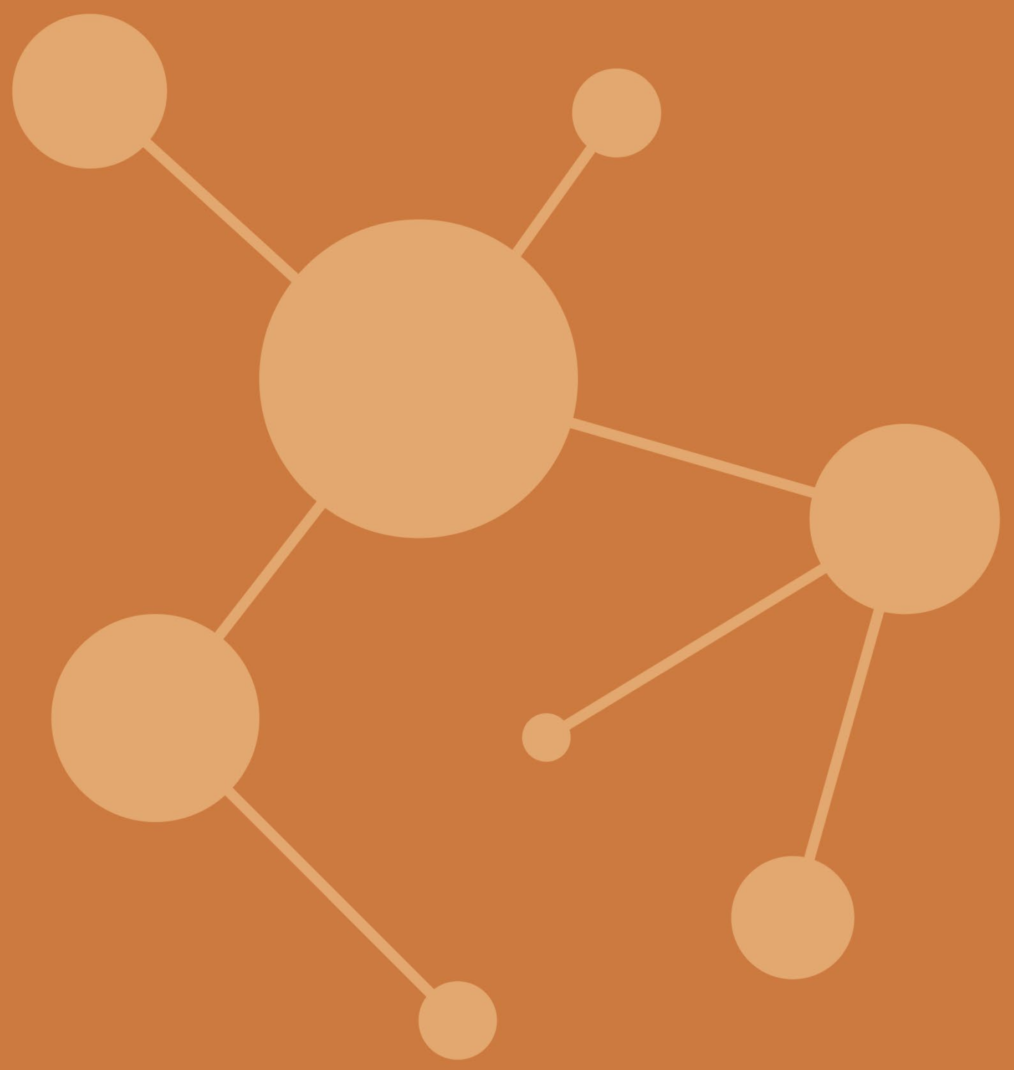
Classification

according to the role they provide or improve the polymeric matrices



Material that is added to other substances to give them qualities they lack or to improve those they have

ANTIOXIDANTS	LIGHT STABILIZERS	PLASTICIZERS	ANTISTATICS
Protect the polymer from thermooxidative degradation	Protect the polymer against UV rays to prevent ageing or colouring changes	Give the polymer flexibility and impact strength	Prevent static charge accumulation on the polymer

NUCLEATION	FLAME RETARDANTS	COLOURANTS	FOAMING AGENTS
Increase crystallinity of semicrystalline polymers by increasing polymer stiffness and thermal properties	Protect the polymer from ignition	Provide colouring to the polymer	Introduce air inside polymers to make them less dense

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Masterbatches

Most **additives** used in the **polymer processing industries** are found on the market in the form of **masterbatches**.

This is a format, in which **the additive is incorporated in the polymer matrix, as a concentrate, which is supplied in the form of pellets.**

This format **makes it easier to handle the additive and to incorporate it during processing.**

Additives for polymers can be **added**:

- During polymer **production**.
- In the **transformation processes** in the industries manufacturing plastic products.

Additives for biopolymers

The **UNE EN14995 regulation. Plastics. Evaluation of compostability**, determines that **biodegradation must be determined for each organic component** as long as this does not represent more than **1% of the dry weight of the material** and as long as the **sum of all the non-evaluated components does not exceed 5% of the weight*.**

*If it is desired to add an additive that has not been certified as compostable, these percentages must be taken into account when using the additive.

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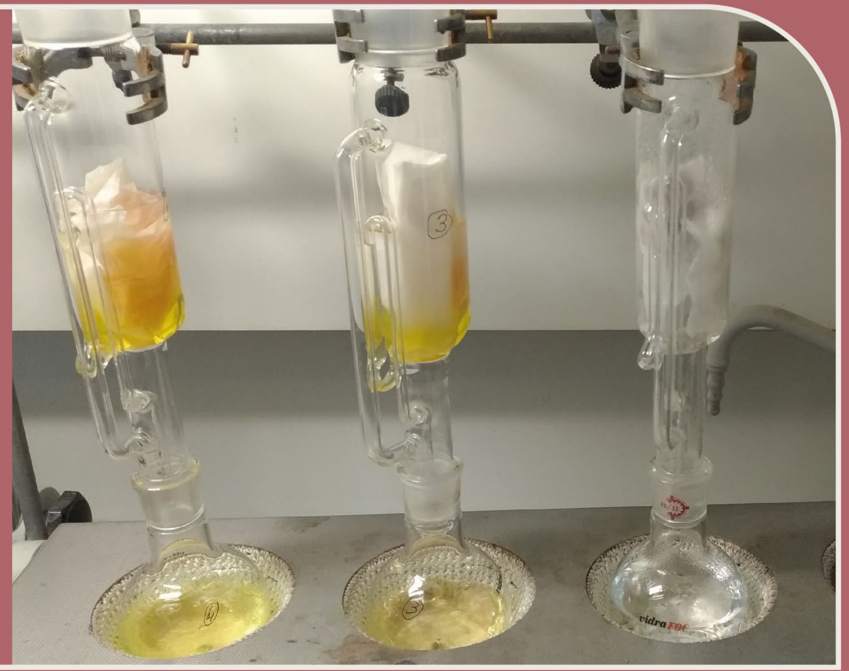
COLOURING

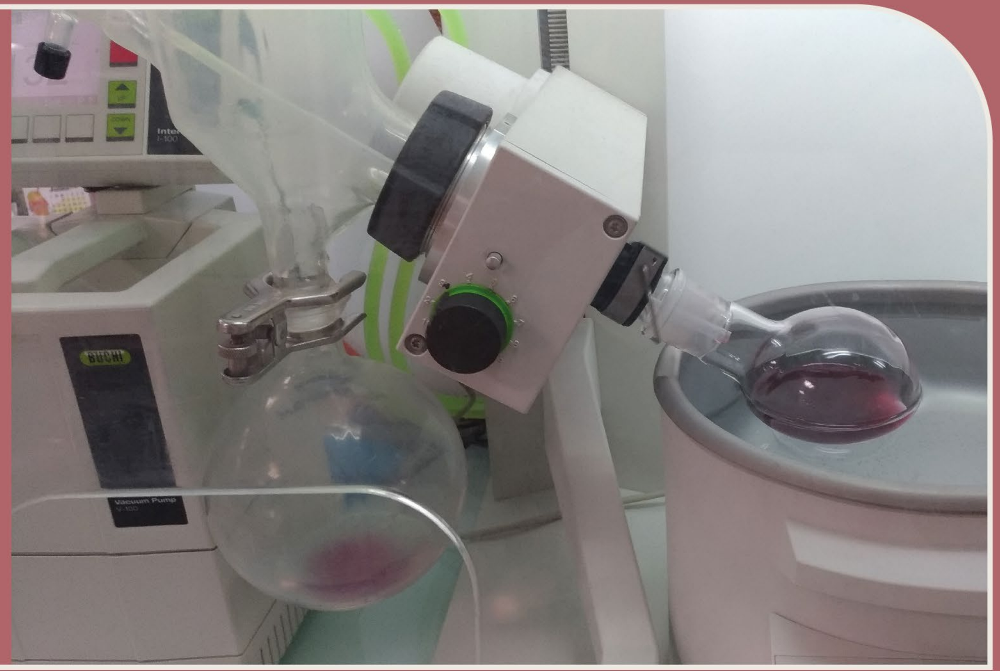
Obtaining extracts
from **agri-food residues**

- **Fruit waste:** peaches and cherries
- **Vegetable waste:** carrot leaves, spinach, chard, lettuce, broccoli and beetroot

Pigment extraction by Soxhlet method
Solvents:
Ethanol-Water



Evaporation of solvent with rotovap
Solvents:
Ethanol-Water



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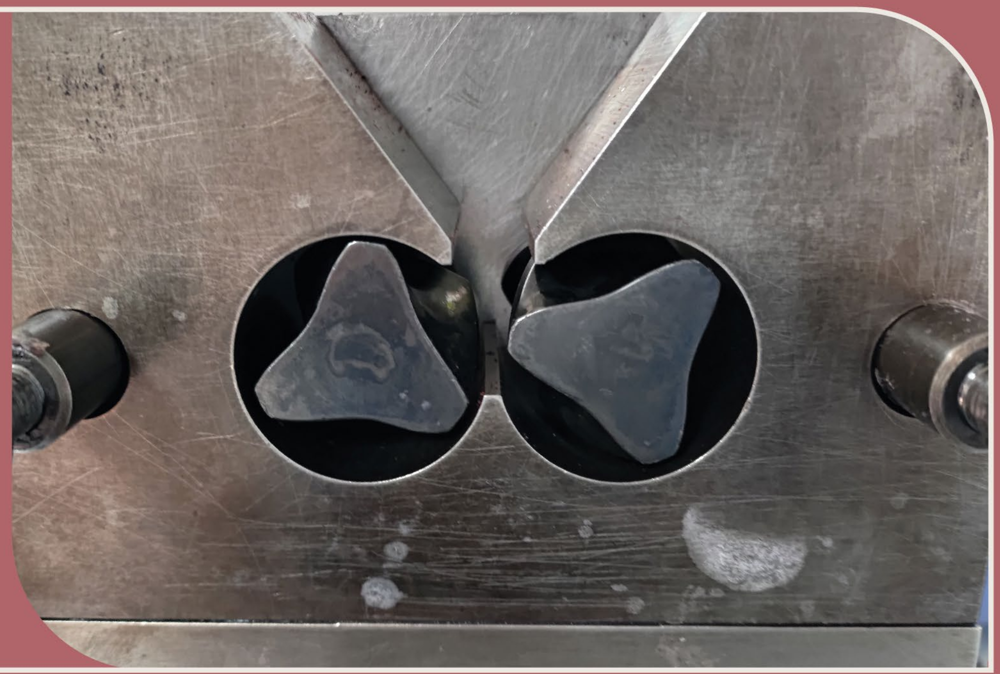
COLOURING

Incorporating extracts into the polymer matrix

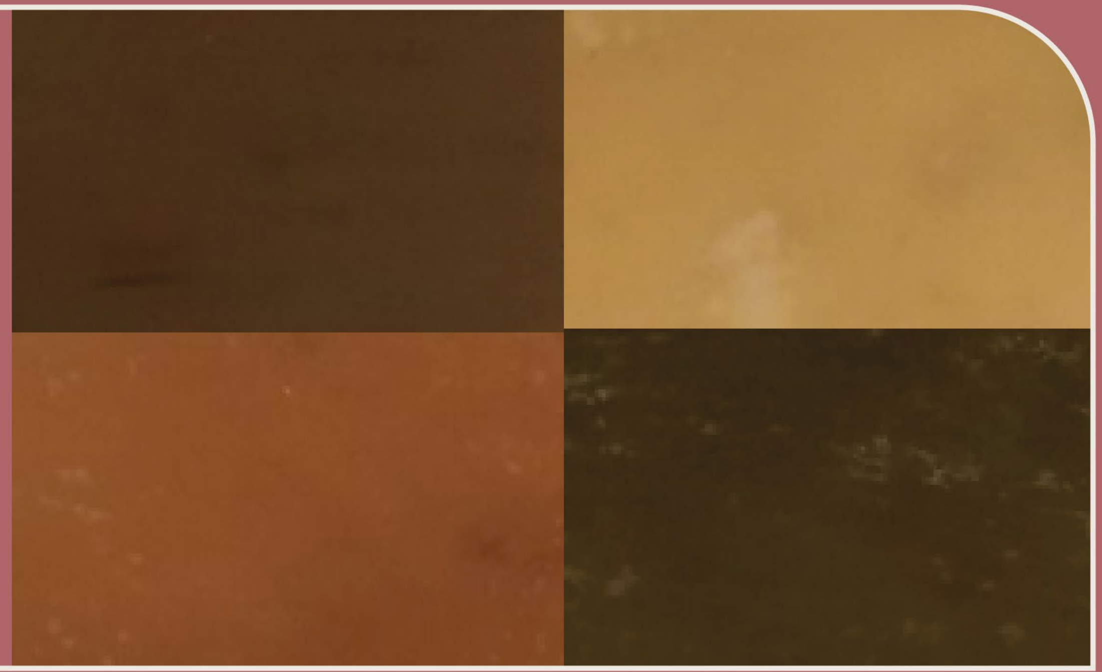
Material used:
PBS

Mixtures with **plastograph**



Hot plate press sheet production

Coloured bioplastics obtained*



*Extracts obtained from fruits (peach and cherry) cannot be processed because of their high sugar level.

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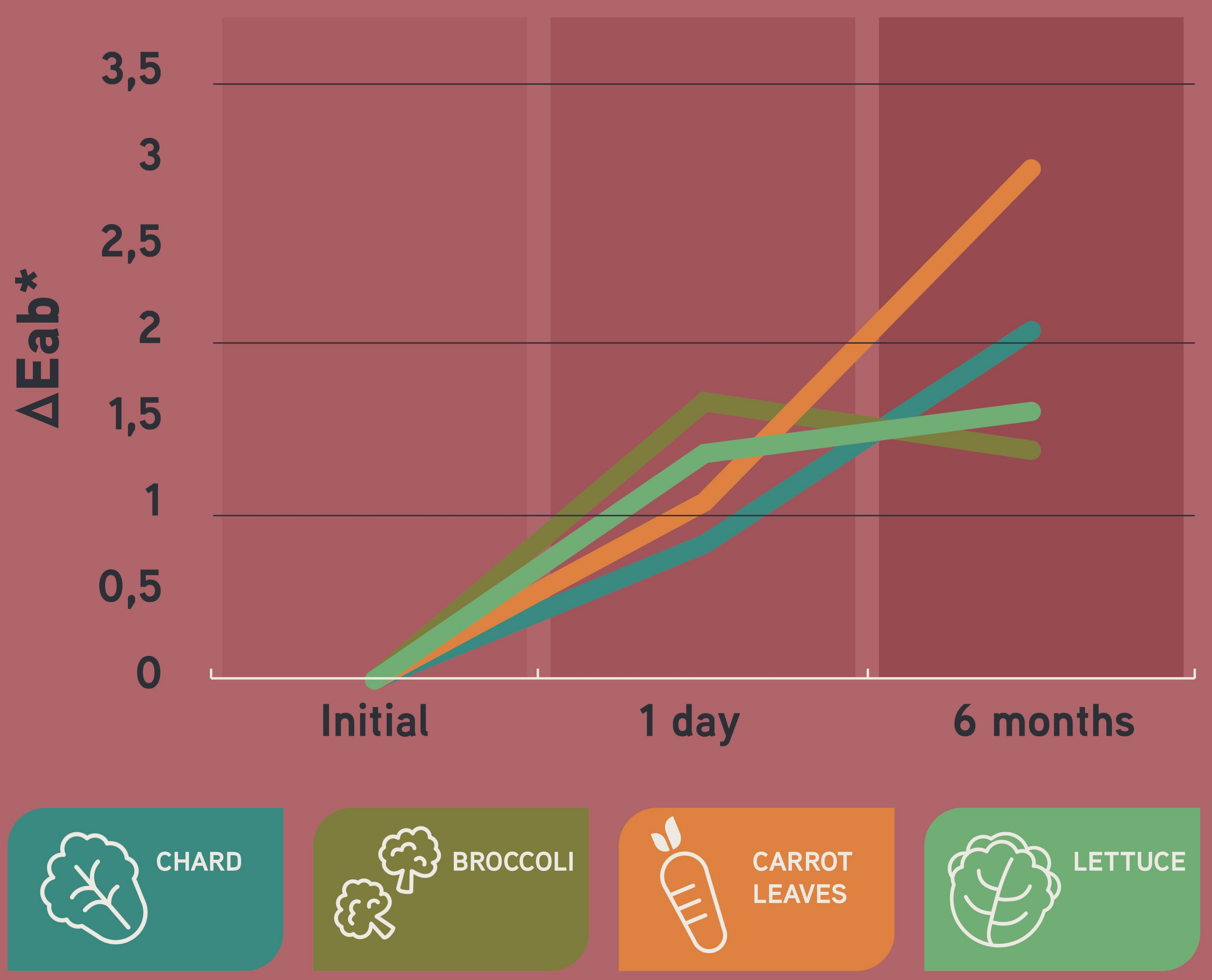
COLOURING

Colouring measurement

How does colour change over time?



Colour measurement by **CIELab System**

MORE INFORMATION

Insignificant variations for **broccoli extract** and **lettuce extract**

Minor variations for **chard extract** and **carrot leaves extract**

Colouring stability in time in the four developed formulations

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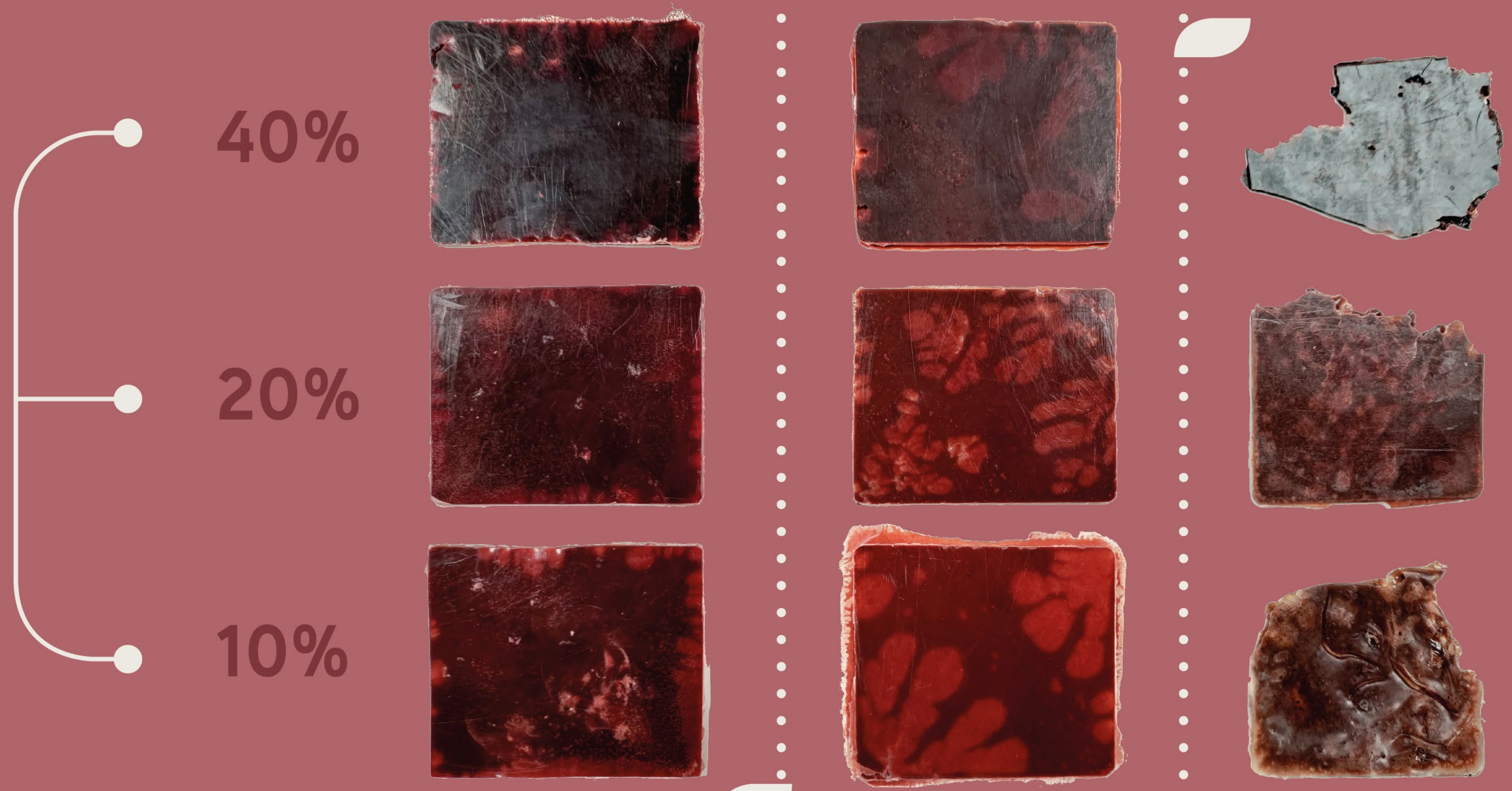
Introduction of natural beetroot pigment into biopolymeric matrices



Colour measurement by
CIELab System

MORE INFORMATION

PCL	L	a	b
PCL+10% col	23,67±0,78	17,45±0,35	3,55±0,06
PCL+20% col	21,5±0,68	12,57±0,34	1,73±0,07
PCL+40% col	21,88±0,15	7,68±0,71	0,52±0,06

PBS	L	a	b
PBS+10% col	26,77±0,28	23,10±0,35	7,91±0,14
PBS+20% col	24,48±0,54	15,52±0,19	5,65±0,16
PBS+40% col	24,50±0,42	9,63±1,34	2,56±0,36

PLA	L	a	b
PLA+10% col	28,72±2,47	9,68±0,23	5,43±0,55
PLA+20% col	27,62±2,61	11,48±1,10	5,26±0,82
PLA+40% col	25,24±1,30	5,03±0,38	1,67±0,38

RESULTS:

Thermal degradation of the pigment. Limitation if processed at high temperature.

Decrease in lightness (L) at higher pigment percentages. Formulations become darker.

Parameters **a and b decrease with increasing amount of colouring agent.**

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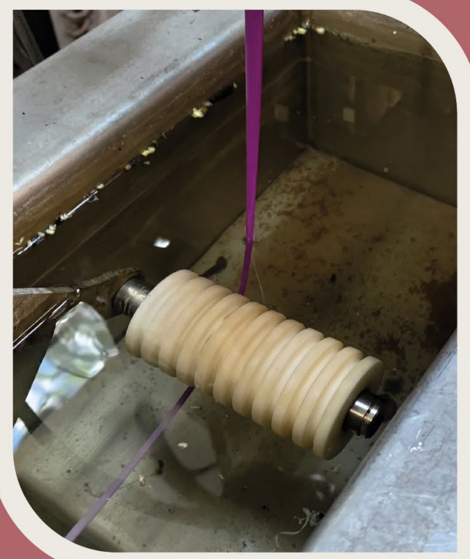
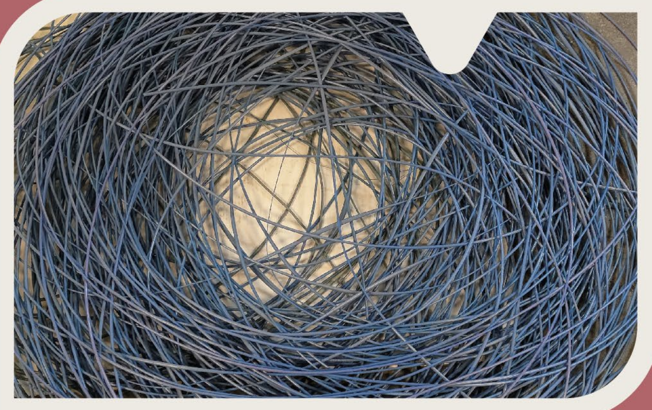
Commercial masterbatches of natural pigments and biopolymeric matrices

Colorimetry	L	a	b
PE+Blue	55,47±0,14	16,07±0,14	15,12±0,52
PE+Yellow	57,27±0,67	-1,11±0,12	-6,00±0,24
PLA+Pink	55,91±0,49	9,65±0,29	8,74±0,15
PLA+Red	55,47±1,08	16,07±0,10	15,12±0,31





ADVANTAGE:

Natural colouring of biopolymers in a direct way **without the need of previous processes.**

Useful in different transformation processes.

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FLAME RETARDANCY

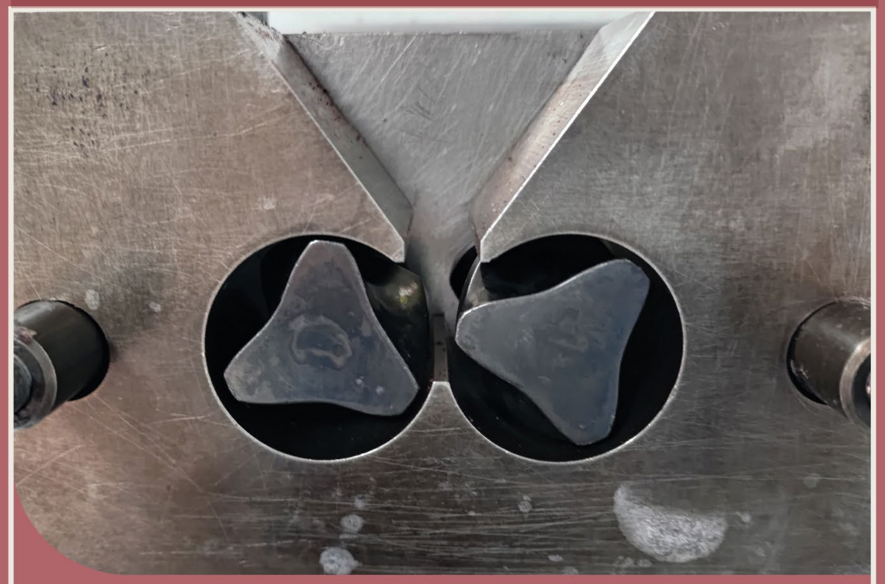
Incorporation of lignin into biopolymeric matrices

Lignin as a **flame retardant agent**

+

PLA and **PBS** polymeric matrices

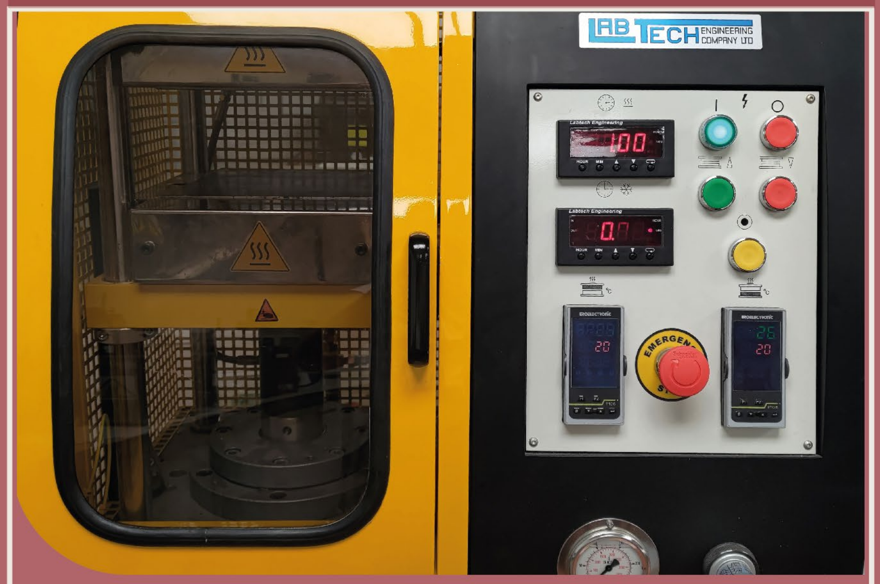
COMPONENT MIXING



Mixing with **plastograph**

Extrusion-compounding

PROCESSING OF MATERIALS



Compression molding

Injection moulding

FORMULATIONS MADE

PLA
- PLA+5% lignin
- PLA+10% lignin
- PLA+15% lignin

PBS
- PBS+5% lignin
- PBS+10% lignin
- PBS+15% lignin

PLA/PBS
- PLA/PBS+10% lignin
- PLA/PBS+15% lignin
- PLA/PBS+20% lignin

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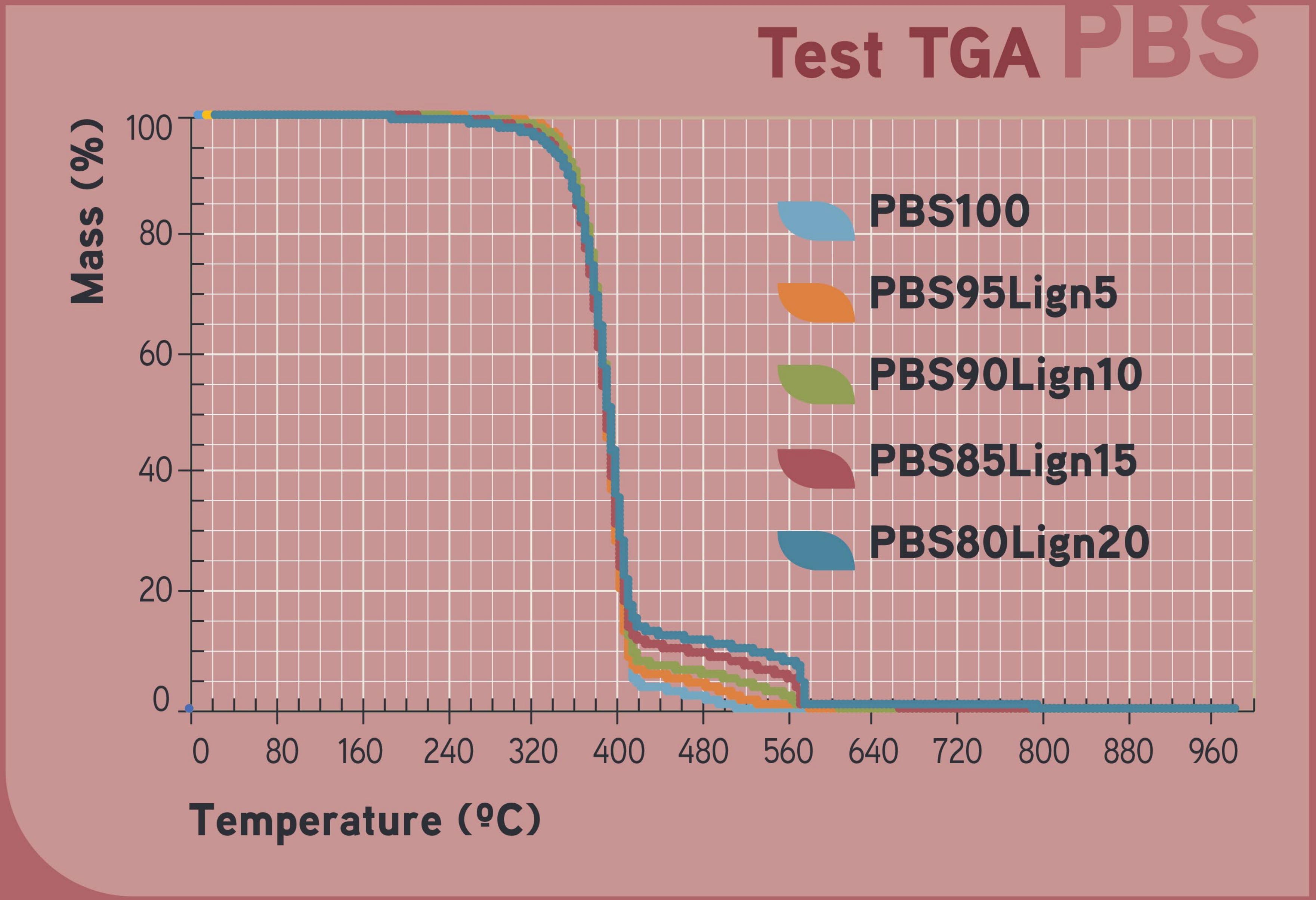
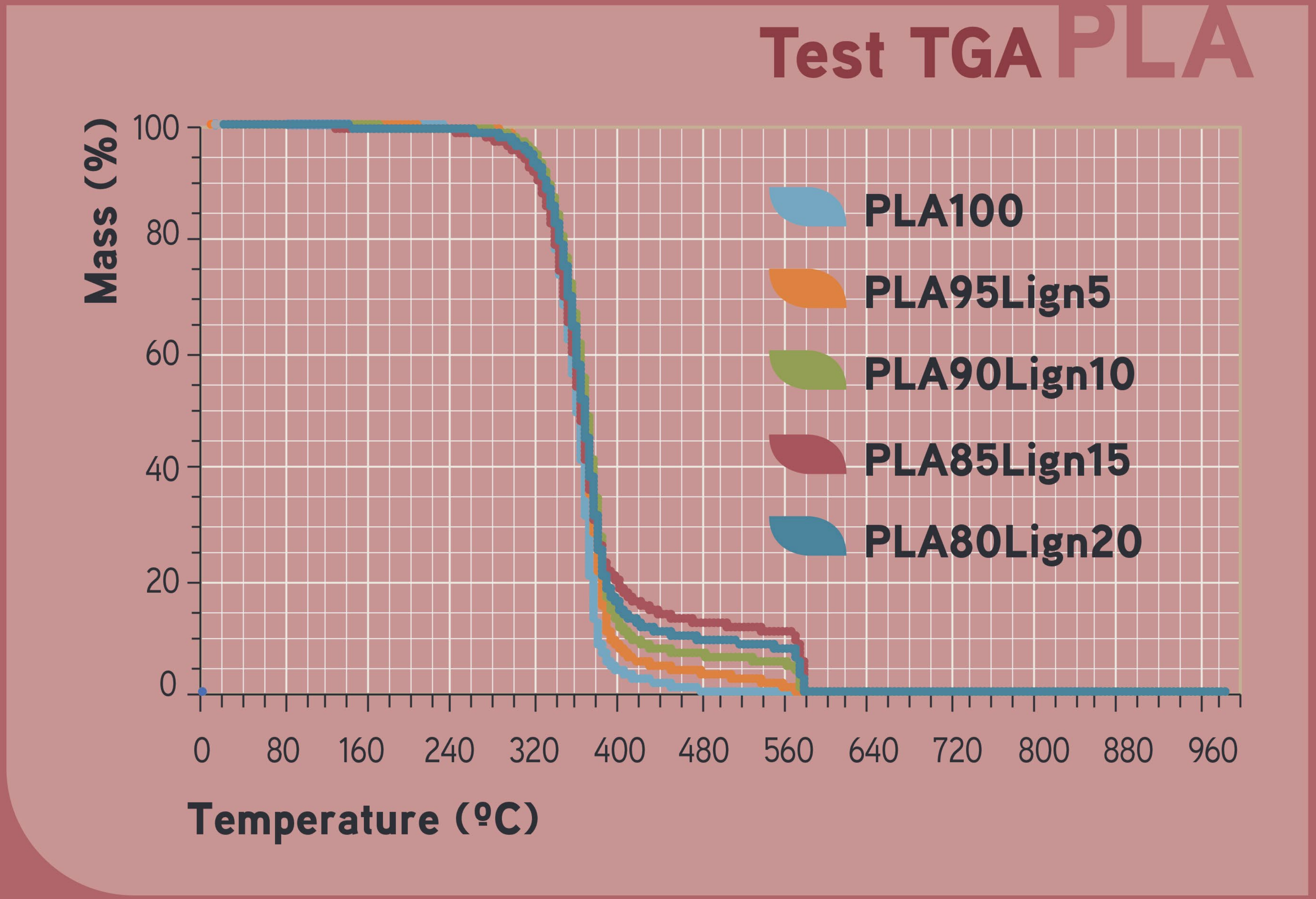
FLAME RETARDANCY

A study of the flame-retardant effect of lignin





The addition of lignin to PLA and PBS **increases the residue obtained at 550 ºC and helps to increase flame retardancy.**

The formulation with **the highest flame retardancy for PLA matrix is PLA85Lig15** (15% lignin content)

Flammability test according to toy standards

Flammability tests have been carried out in accordance with **EN 71-2:2020: Safety of Toys. Part 2 Flammability**, and according to **ASTM F-963-17 regulation, section 4.2 "Flammability"**, giving a **result of conformity for all formulations.**

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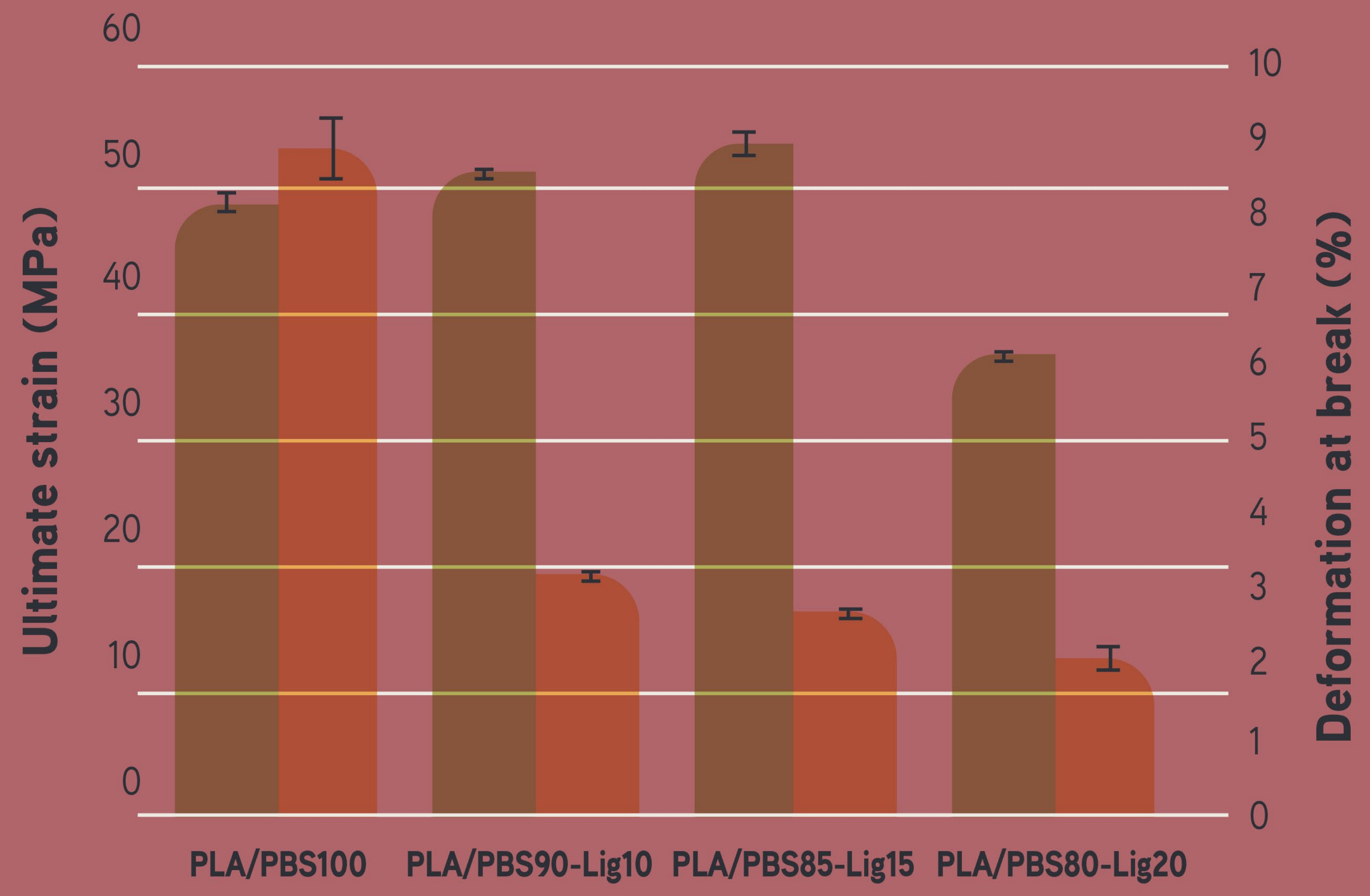
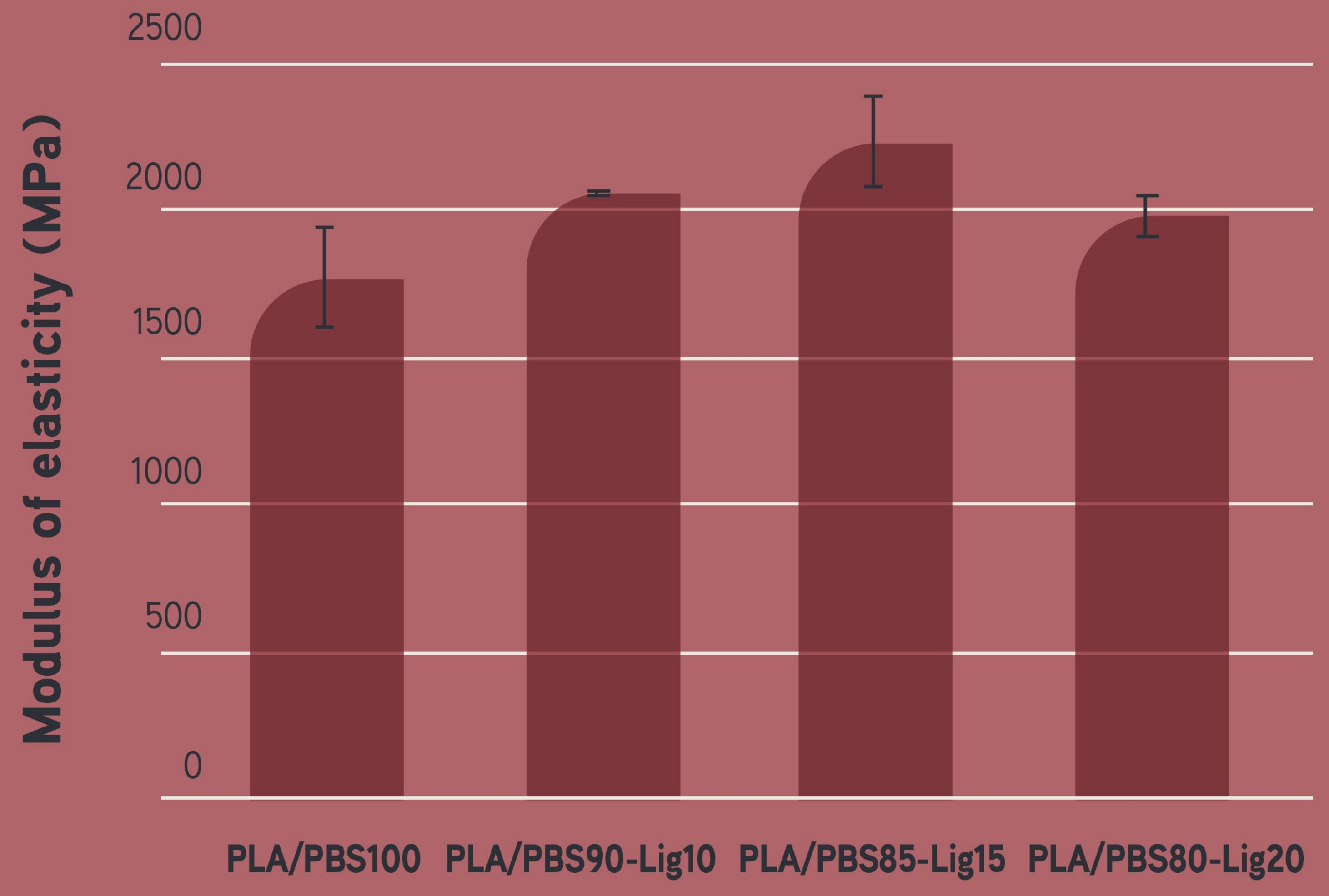
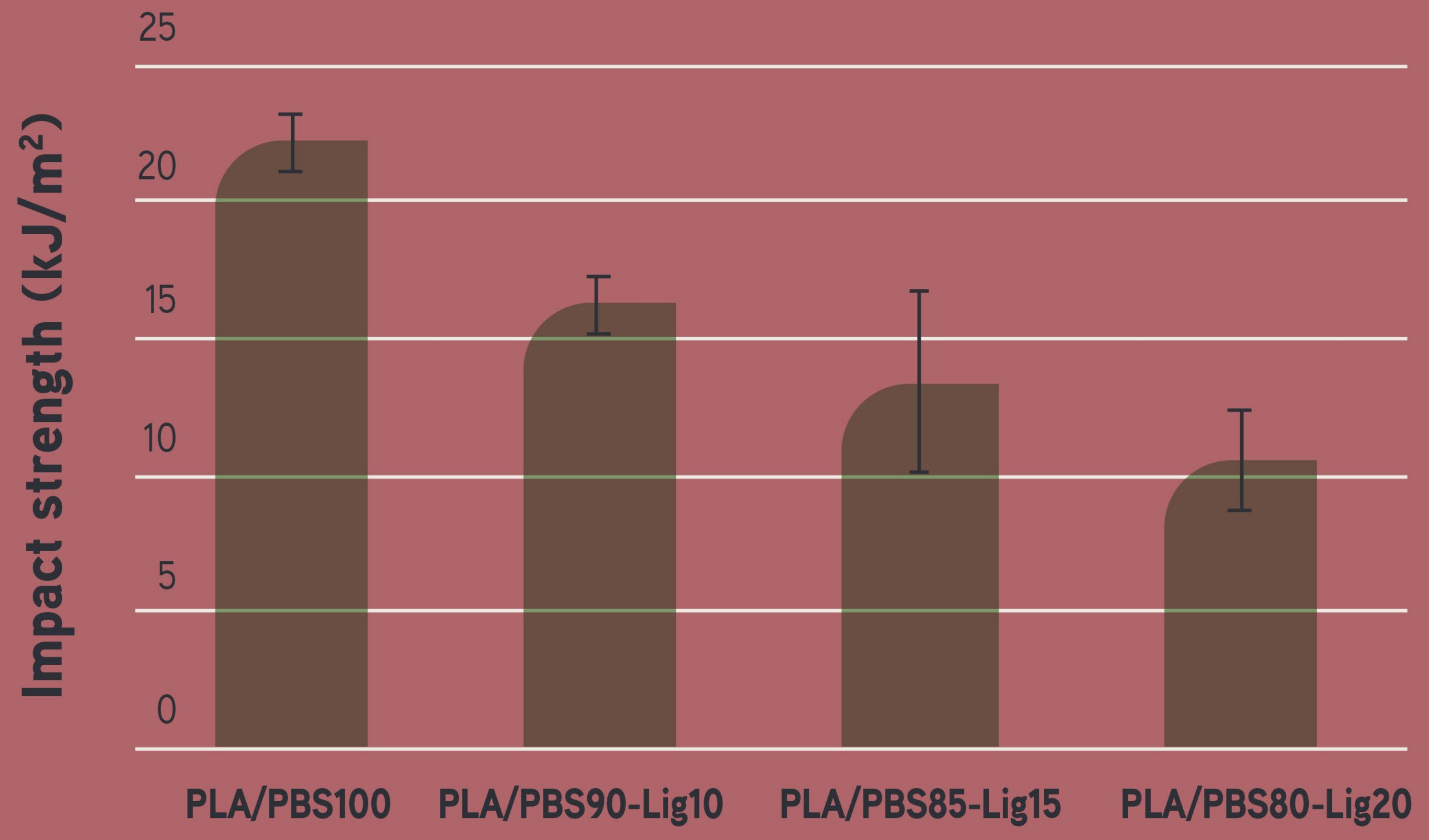
Mechanical properties of formulations with lignin







The addition of lignin makes the **material more rigid and fragile**:

- **Higher modulus of elasticity in traction and ultimate strain**
- **Lower impact strength and lower deformation**

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ANTIMICROBIAL

Incorporation of natural antimicrobial agent into biopolymeric matrices

PBS matrix

+

Orange and clementine essential oils obtained from orange and clementine peels (juice industry)

A good antimicrobial response to "Staphylococcus aureus" and "Klebsiella pneumoniae" bacteria

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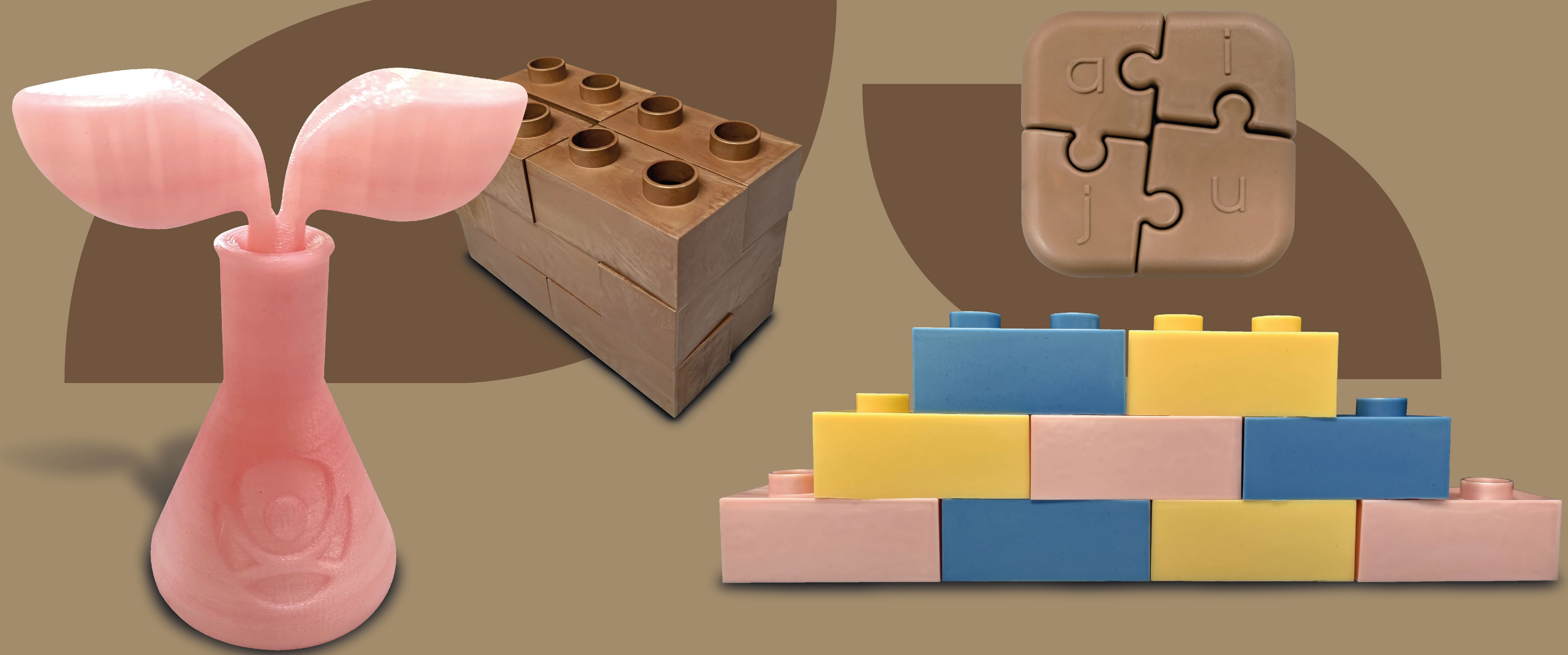
EXAMPLES OF USE IN TOYS



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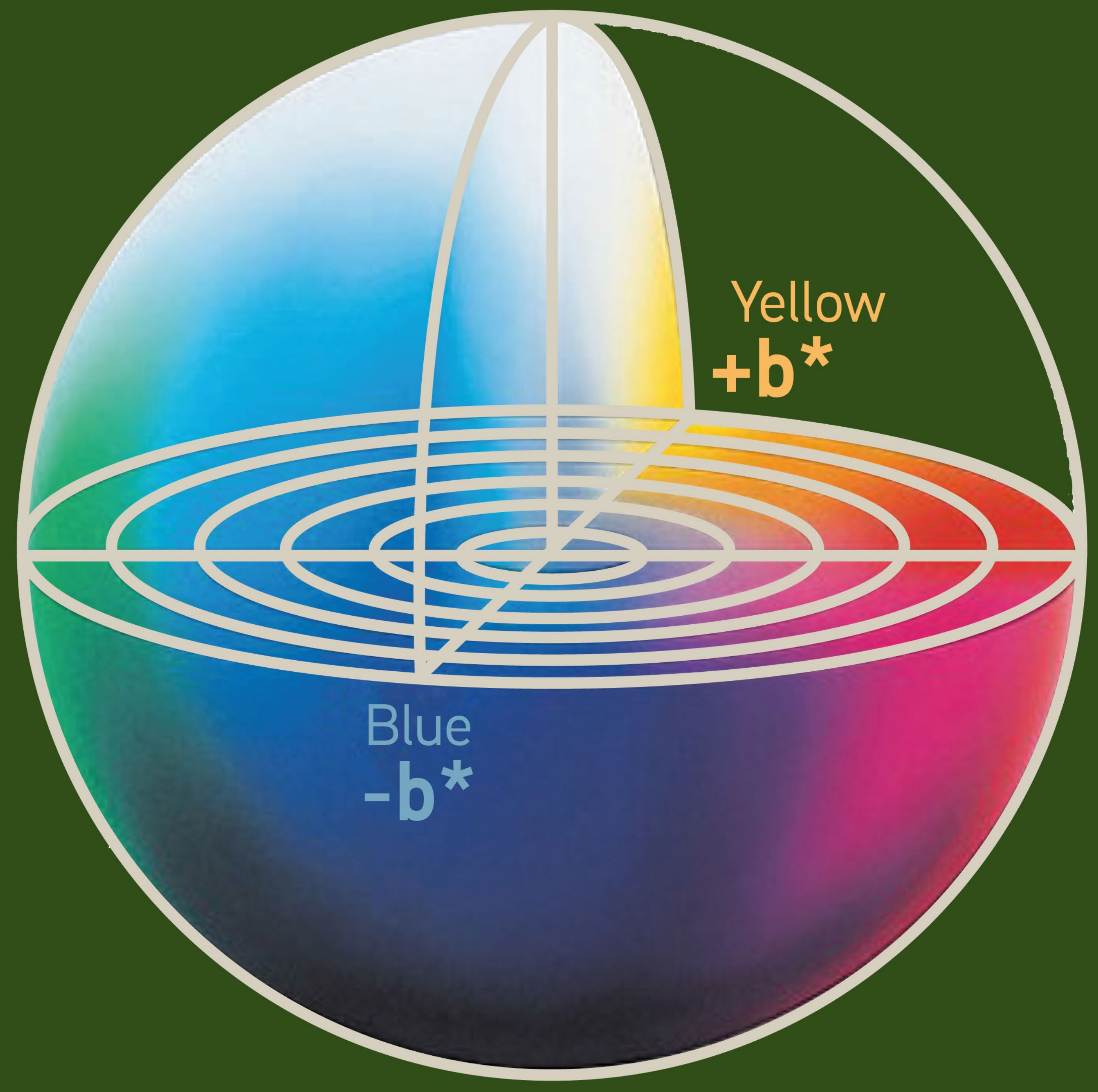
Proyecto cofinanciado por los fondos FEDER, dentro del Programa Operativo FEDER de la Comunidad Valencia 2014–2020

COLOUR MEASUREMENT: CIELAB SYSTEM

The CIELab measurement system is a system for quantitative measurement of colour and colour variations



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Three coordinates are used:

L* — **It measures the brightness** of the sample and can take values between 0 and 100. A value of 0 corresponds to **black** and 100 to **white**.

a* — **It measures the colour between green and red**, and can take negative and positive values. The higher the value of a*, the closer the colour of the sample is to red, and the smaller the value and with a negative sign, the closer the colour of the sample is to green.

b* — **It measures the colour between blue and yellow**, and can take negative and positive values. The higher the value of b*, the closer the colour of the sample is to yellow, and the smaller the value and with a negative sign, the closer the colour of the sample is to blue.

▼ Continue

The **colour difference between two samples** is shown by the variable

$$\Delta E_{ab}*$$

This variable considers the variations of L*, a* and b*, according to the equation:

$$\Delta E_{ab}* = \sqrt{(\Delta L*)^2 + (\Delta a*)^2 + (\Delta b*)^2}$$

The colour difference between two samples is affected by the differences in brightness, colour changes on the variable a* and b*.

The value of ΔEab* can be found in **different intervals:**:

ΔEab* < 1
Imperceptible
Values under 1: change imperceptible to the human eye

1 < ΔEab* < 2
Experienced observer
Between 1 and 2: colour changes perceptible by a highly experienced observer

2 < ΔEab* < 3,5
Inexperienced observer
Between 2 and 3.5: colour changes perceptible by less experienced observers

3,5 < ΔEab* < 5
Different colours are detected
Between 3.5 and 5: colour changes perceptible to any observer

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