Complexité des plastiques : mélanges, formulations et additifs

Vincent Verney

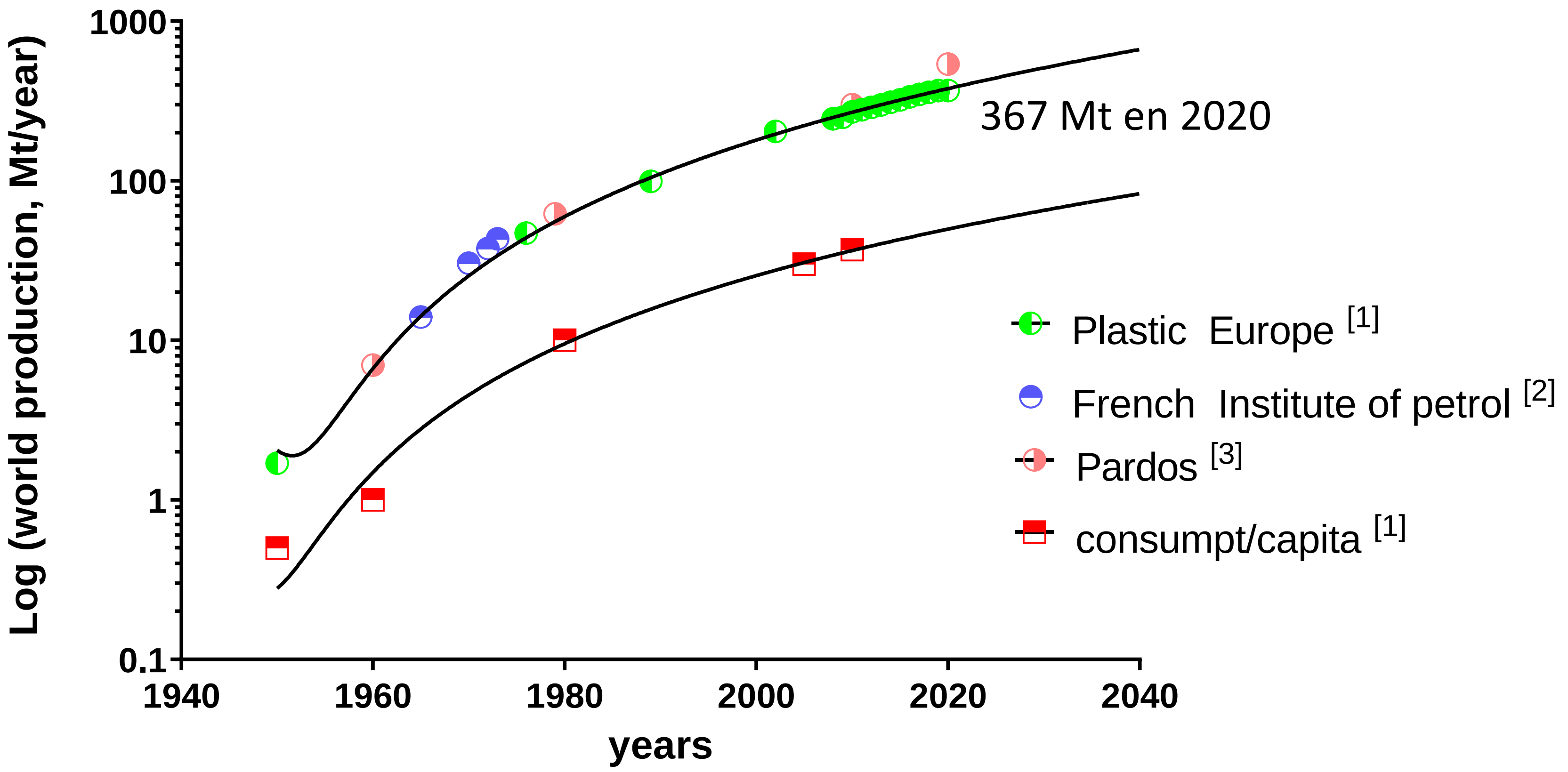
Vincent.Verney@naturadds.com

NaturAdds

Adebiotech - Biodégradabilité, Recyclages et Valorisation organique des plastiques, Mardi 16 novembre 2021

Les Matières Plastiques?

Un matériau du 20ème siècle (> 1950)



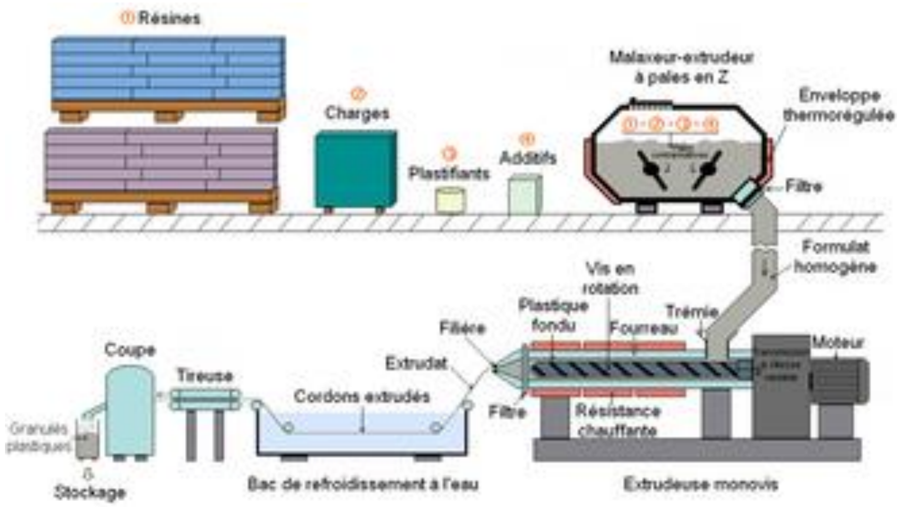
> 9 Mt produites de 1950 à 2020

Les Matières Plastiques (suite)?

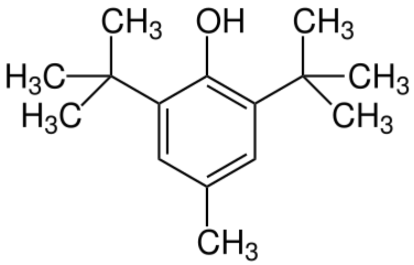
- Une matière plastique est un mélange qui associe de très grandes molécules (macromolécules) avec des petites molécules (additifs)
- Un plastique sans additifs n'existe pas
- Les additifs peuvent représenter entre 1000 ppm et 50% en masse de la matière
  - antioxydants
  - Absorbeurs UV
  - Plastifiants, lubrifiants
  - Colorants, azurants
  - Anti statiques
  - …..

Ils assurent la fonction requise pour le matériau

Les Matières Plastiques?



Antioxydant : *hydroxytoluène butylé*, BHT



Mise en forme et fabrication de l'objet

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Plastiques et additifs:
➔ Un mariage difficile!

- Issus de la chimie de synthèse

- Compatibilité chimique (Thermodynamique, hydrophile vs hydrophobe)
    - Efficacité de la fonction recherchée

- Compatibilité physique
    - Viscosités différentes
        - Diffusion, migration!

Additifs/Environnement et impacts?

SCIENCE ADVANCES | RESEARCH ARTICLE

PLASTICS

Production, use, and fate of all plastics ever made

Roland Geyer,[1]* Jenna R. Jambeck,[2] Kara Lavender Law[3]

Plastics have outgrown most man-made materials and have long been under environmental scrutiny. However, robust global information, particularly about their end-of-life fate, is lacking. By identifying and synthesizing dispersed data on production, use, and end-of-life management of polymer resins, synthetic fibers, and additives, we present the first global analysis of all mass-produced plastics ever manufactured. We estimate that 8300 million metric tons (Mt) as of virgin plastics have been produced to date. As of 2015, approximately 6300 Mt of plastic waste had been generated, around 9% of which had been recycled, 12% was incinerated, and 79% was accumulated in landfills or the natural environment. If current production and waste management trends continue, roughly 12,000 Mt of plastic waste will be in landfills or in the natural environment by 2050.

R. Geyer, J. R. Jambeck, K. L. Law, Production, use, and fate of all plastics ever made.
Sci. Adv. 3, e1700782 (2017)

2050 : 12 Mt dans l'environnement ➔ Additifs > 1 Mt??

Additifs/Environnement et impacts?

Contents lists available at ScienceDirect
Science of the Total Environment
journal homepage: www.elsevier.com/locate/scitotenv
ELSEVIER

Plastic additives as tracers of microplastic sources in Japanese road dusts

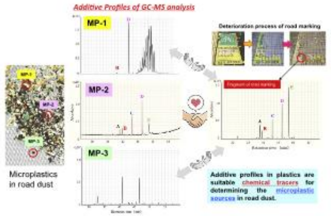
Ken-Ichi Kitahara, Haruhiko Nakata *

Faculty of Advanced Science and Technology, Kumamoto University, 2-39-1 Kurokami, Chuo-ku, Kumamoto 860-8555, Japan

HIGHLIGHTS

- The occurrence of microplastics (MPs) was investigated in Japanese road dusts.
- The abundance of MPs in road dusts was high in urban area, due to high population and traffic density.
- The same five additives were identified in both MPs in road dusts and a fragment of road marking.
- The additive profiles in MPs are suitable tracers for determining their potential sources.

GRAPHICAL ABSTRACT



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ABSTRACT

Plastic waste and microplastic pollution has been reported around the world. Up to 80% of marine plastic debris is derived from land, thus it is important to identify the terrestrial sources of microplastics to reduce their environmental impact. In this study, the abundance and polymer type of microplastics were characterized for road dusts collected from Kumamoto, Okinawa, and Tokyo, Japan. In addition, the profiles of additives in plastic products on the road and in road dust microplastics were determined to evaluate the potential use of additives as chemical tracers of microplastic sources. The abundance of microplastics in road dusts was 96 ± 85 pieces/kg (dry wt.) ($n = 16$), 68 ± 77 pieces/kg ($n = 12$), and 230 ± 50 pieces/kg ($n = 8$) in Kumamoto, Okinawa and Tokyo, respectively. In Kumamoto and Okinawa, significant correlations were observed between total microplastic abundance in road dusts and daily vehicle traffic. In Tokyo, high population and traffic density may account for the greater abundance of microplastics in road dusts than in the other cities. Polymer analysis shows that poly (diallyl phthalate), polyvinyl chloride, polymethyl methacrylate and polyester accounted for 60% to 70% of the total microplastics analyzed. To determine the potential sources of microplastics, plastic additives were analyzed in road dusts and fragments of road marking from the study area. Five common additives including plasticizers and flame retardants were identified in both road dusts and road markings. This suggests that road markings are a significant source of microplastics in Japanese road dust, and that additive profiles in plastic samples may be suitable tracers for determining the sources of microplastics in road dust.

Science of the Total Environment 767 (2021) 144345

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ELSEVIER

You are what you eat: Microplastics in the feces of young men living in Beijing

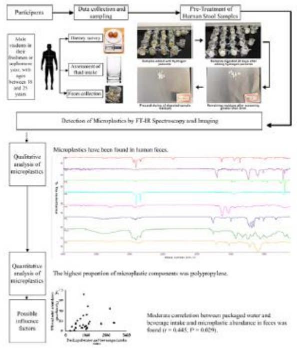
Na Zhang, Yi Bin Li, Hai Rong He, Jian Fen Zhang, Guan Sheng Ma *

Department of Nutrition and Food Hygiene, School of Public Health, Peking University, 38 Xue Yuan Road, Hai Dian District, Beijing 100191, China
Laboratory of Toxicological Research and Risk Assessment for Food Safety, Peking University, 38 Xue Yuan Road, Hai Dian District, Beijing 100191, China

HIGHLIGHTS

- Microplastics have been found in human feces.
- The highest proportion of microplastic components was polypropylene.
- Sources of water intake may one of the influencing factors on the content of microplastics in the human gastrointestinal tract.
- More attention should be paid to the widespread existence of microplastics and its health effects.

GRAPHICAL ABSTRACT



Additifs/Environnement et Impacts?

Journal of Hazardous Materials 344 (2018) 179–199

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Review

An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling

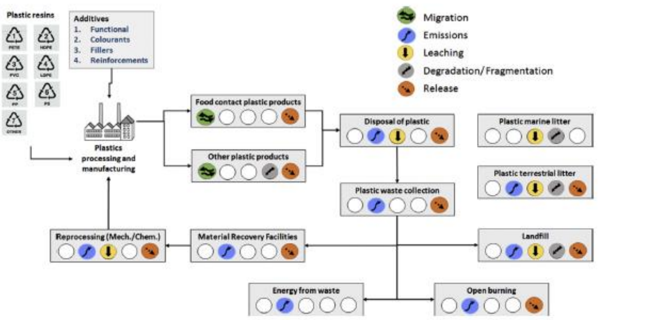
John N. Hahladakis[a,*], Costas A. Velis[a,*], Roland Weber[b], Eleni Iacovidou[a], Phil Purnell[a]

[a] School of Civil Engineering, University of Leeds, Woodhouse Lane, LS2 9JT, Leeds, United Kingdom
[b] POPs Environmental Consulting, Lindenfirststr. 23, D.73527, Schwäbisch Gmünd, Germany

H I G H L I G H T S

- Plastics are important in our society providing a range of benefits.
- Waste plastics, nowadays, burden the marine and terrestrial environment.
- Additives and PoTSs create complications in all stages of plastics lifecycle.
- Inappropriate use, disposal and recycling may lead to undesirable release of PoTSs.
- Sound recycling of plastics is the best waste management and sustainable option.

G R A P H I C A L   A B S T R A C T



Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Microbial capability for the degradation of chemical additives present in petroleum-based plastic products: A review on current status and perspectives

Carmen Sánchez

Laboratory of Biotechnology, Research Centre for Biological Sciences, Universidad Autónoma de Tlaxcala, Ixtacuixtla, C.P.90120, Tlaxcala, Mexico

A R T I C L E   I N F O

Editor: A. Daugulis

Keywords:
Bacterial degradation
Fungal degradation
Microbial enzymes
Plastic additives

A B S T R A C T

Plastic additives are present as pollutants in the environment because they are released from plastics and have been reported to be toxic to mammals. Due to this toxicity, it is crucial to develop ecofriendly tools to decontaminate the environment. Microorganisms are a promising alternative for efficient and effective plastic additive removal. This review describes the current knowledge and significant advances in the microbial degradation of plastic additives (i.e. plasticizers, flame retardants, stabilizers and antioxidants) and biotechnological research strategies that are being used to accelerate the biodegradation process of these additives. It is expected that further research supported by advances in genomics, proteomics, gene expression, enzyme immobilization, protein design, and nanotechnology can substantially increase our knowledge to enhance the enzymatic degradation efficiency, which will accelerate plastic additive degradation and establish successful and cost-effective bioremediation processes. Investigations should also address the identification of the enzymes involved in the degradation process and their catalytic mechanisms to achieve full metabolization of organo-pollutants (i.e. plastic additives) while avoiding harmful plastic additive biodegradation products. Microorganisms and their enzymes undoubtedly represent a potential resource for developing promising environmental biotechnologies, as they have the best systems for pollutant degradation, and their actions are essential for decontaminating the environment.

Additifs/Environnement et impacts?

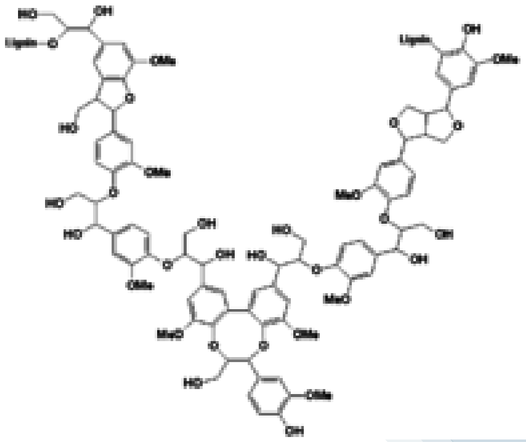
➔ On peut se poser absolument les mêmes questions pour les additifs que celles que l'on se posent pour les matrices:

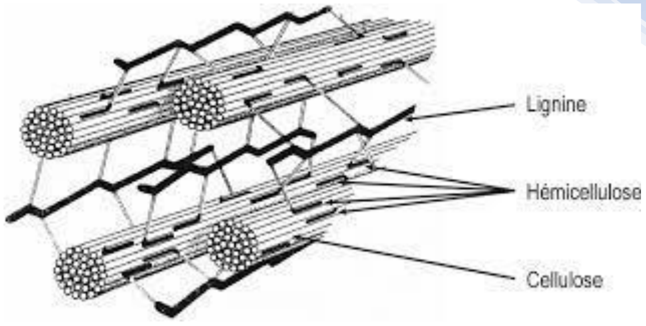
1. Quid du carbone biosourcé ?
   - **Additifs d'origine naturelle?**
2. Quid de leur biodégradation ?
   - En particulier pour les plastiques biodégradables!
3. Quid du recyclage des déchets et des additifs hérités?
   - Legacy additives

Additifs Naturels?

Les additifs sont utilisés en premier lieu:

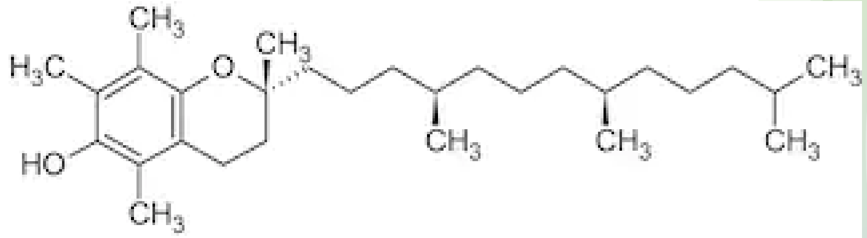
- Pour protéger la matière des agressions environnementales
    - Oxygène, Température, radiations UV,…
    - Il y a dans la nature un grand nombre de molécules pouvant répondre à ces questions : Exemple de la lignine





Additifs Naturels?

Antioxydant: Vitamine E (Alpha tocophérol)

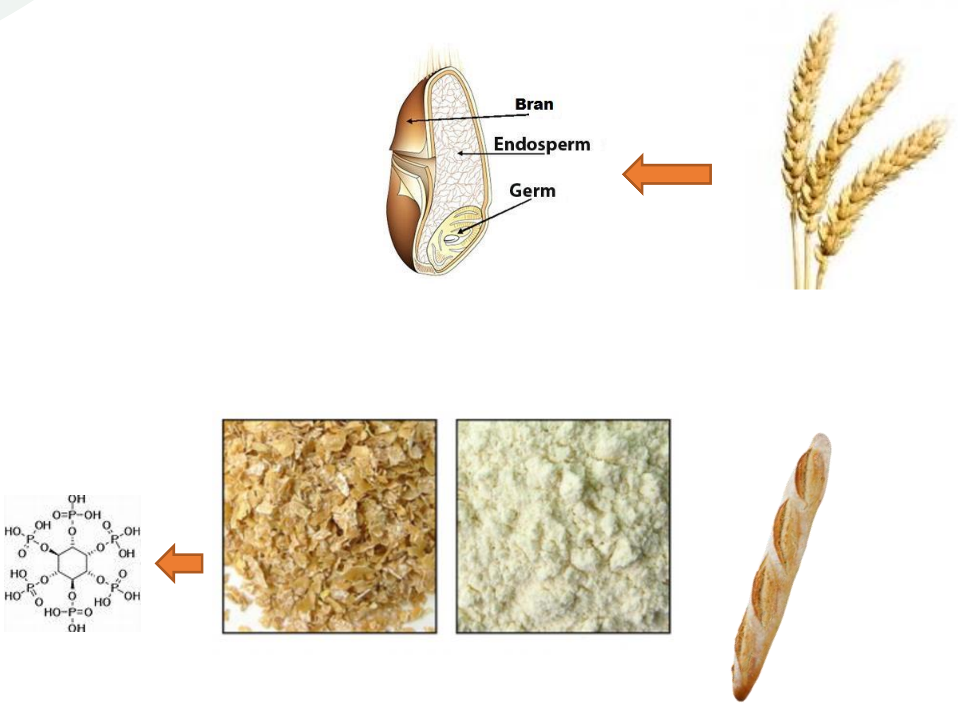


➔ En second lieu pour apporter (ou améliorer) une fonction que la matière ne possède pas (ou peu)

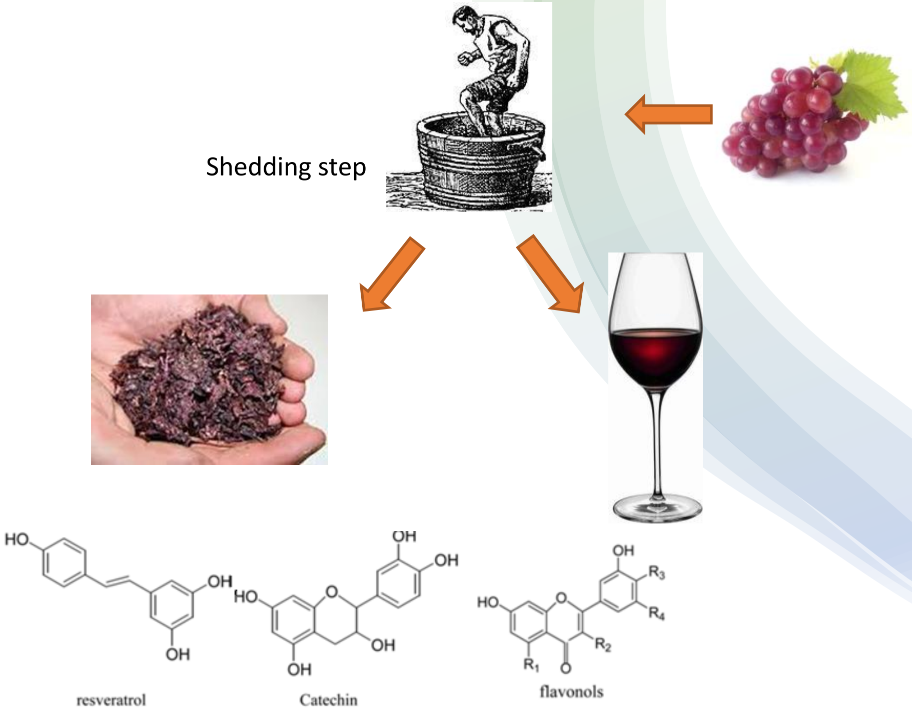
Dans la nature les températures maximales rencontrées par ces molécules ne sont pas aussi élevées que celles que peuvent rencontrer des molécules d'additifs lors de la mise en œuvre des plastiques (100 - < 300 °C)

➔ Stratégie de protection lorsque cela est nécessaire

Additifs Naturels?

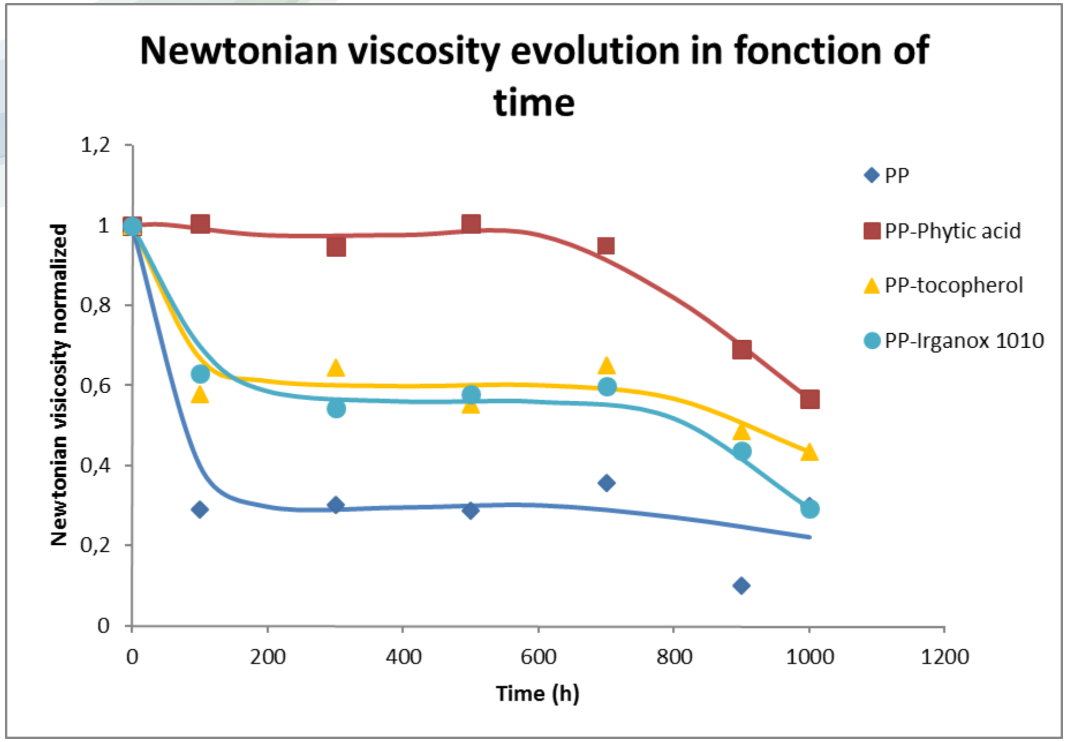


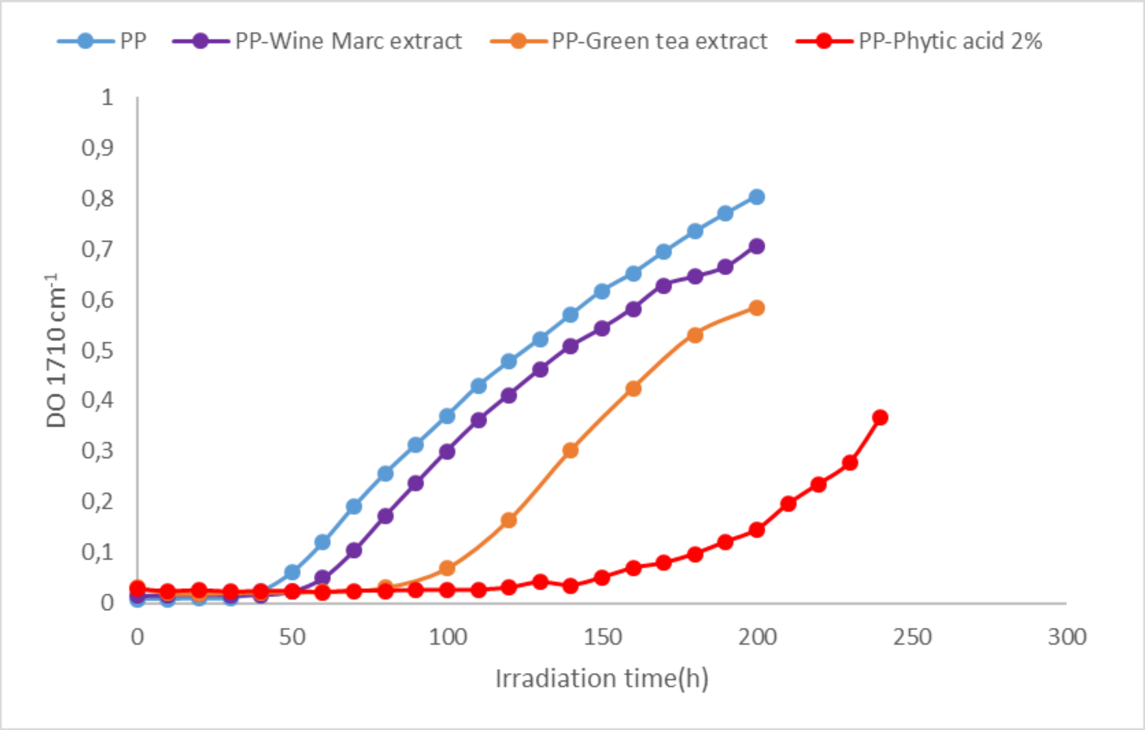
Molécule isolée



Molécules en cocktail

Additifs Naturels?





Thermo oxydation du PP

Photo oxydation du PP

Audrey Diouf-Lewis, SophieCommereuc, VincentVerney
Toward greener polyolefins: Antioxidant effect of phytic acid from cereal waste
European Polymer Journal, 96, November 2017, Pages 190-199

Diouf-Lewis, A., Commereuc, S. and Verney, V. (2018), Biowastes from wine as natural additive of polyolefins: Thermo- and photo-oxidation efficiency. *J. Appl. Polym. Sci.*, 135, 46607. doi: 10.1002/app.46607

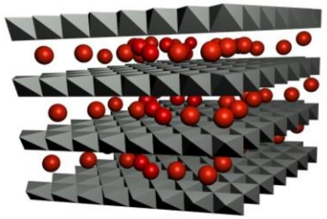
Solution proposée

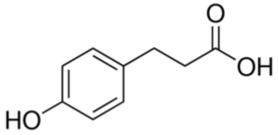
Dans le but de pallier ces inconvénients

➔ **Hydroxyde double lamellaire (HDL)**

Anionic nanoclays

Modifié avec de nombreuses molécules organiques (screening 30 molécules) , principalement le **3-(4-Hydroxyphenyl)propionic acid (HPPA)**





Brevet commun CNRS-ICCF / Université de Bologne

FR1554649 + WO 2016/189228 Al

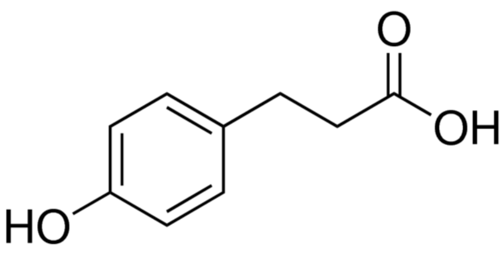
Melt mixing HDL-HPPA + PBS

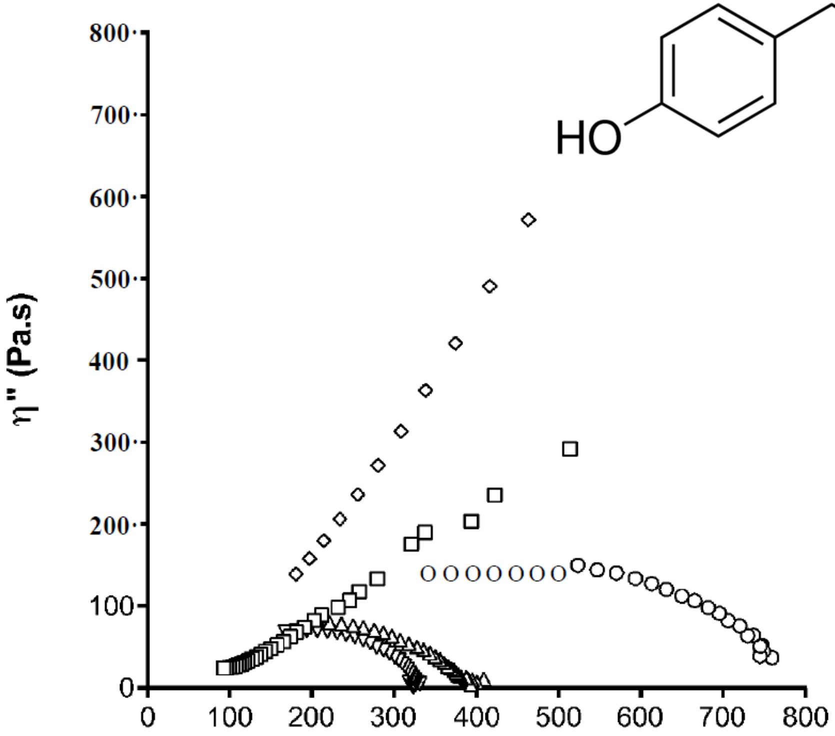
In-situ polycondensation HDL-HPPA + butanediol-succinic acid

Additifs Naturels: Stratégie de protection

(54) Title : ORGANO-MODIFIED LAYERED DOUBLE HYDROXIDES AND COMPOSITE POLYMER MATERIALS COMPRISING SAME

(54) Titre : HYDROXYDES DOUBLES LAM ERIAUX POLYMERES COMPOSITES LES COMPRENANT





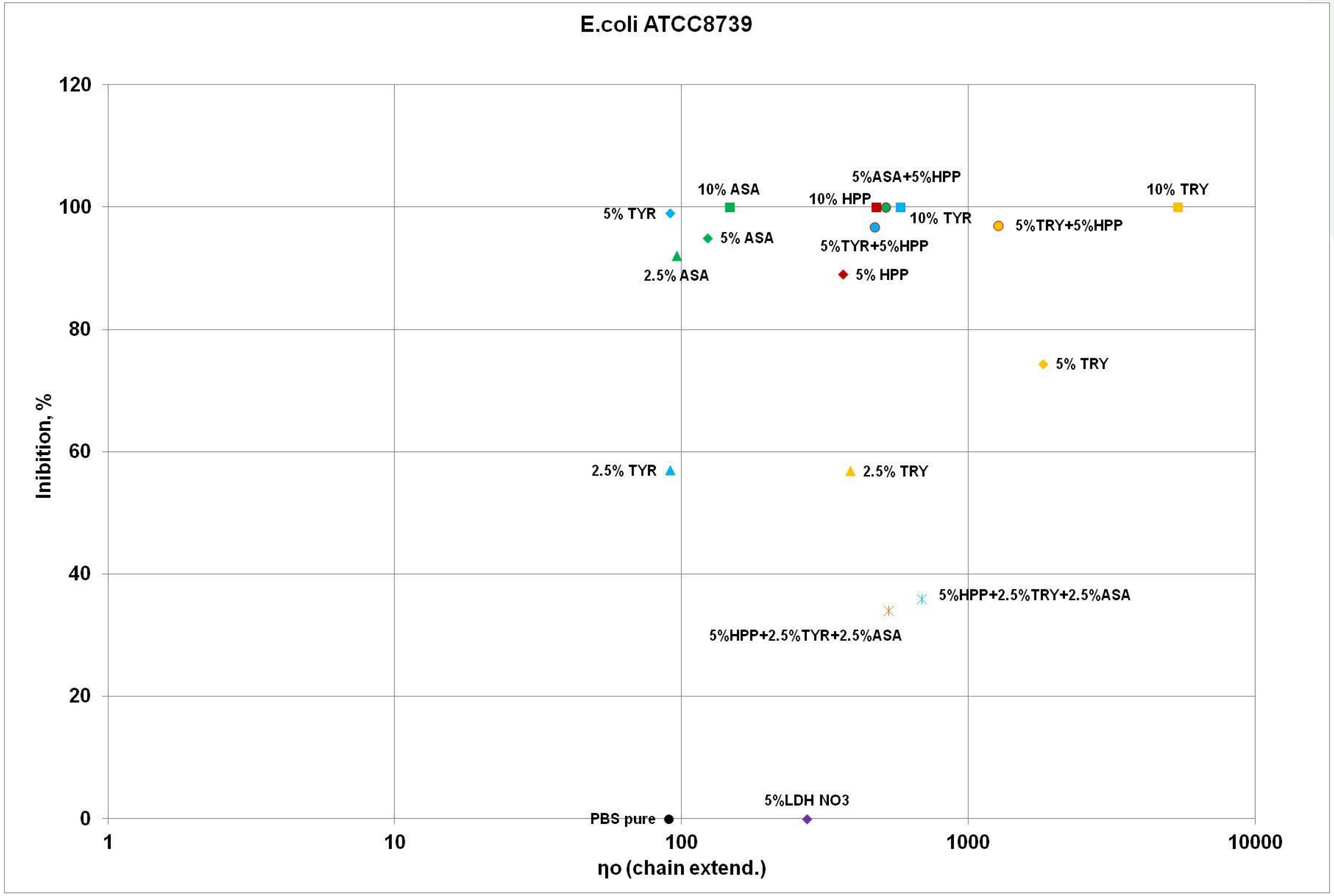
The invention relates to layered s organo-modified by 3-(4-hydroxy- acid (HPPA), by 2-(4-hydroxyphe- acid or by a hydroxyphenylprope- composite polymer materials com- e composite materials are advantageously made of biosourced polymers such as poly(butylene succinate). Thèse composite materials have improved properties over the polymers that make up the composition thereof, and over the composites of the prior art.

(57) Abrégé : Hydroxydes doubles lamellaires organo-modifiés par l'acide 3-(4- hydroxyphényl)propio - nique (HPPA) par l'acide 2-(4-hydroxyphényl)éthyl-sulfbnique ou par un acide hydroxyphénylpropè- noïque, et matériaux polymères composites les com - prenant. Les matériaux composites sont avantageuse - ment à base de polymères biosourcés comme le poly(butylène succinate). Ces matériaux composites présentent des propriétés améliorées par rapport aux polymères entrant dans leur composition, et par rap - port aux composites de l'art antérieur.

Brevet Europe/ Japon/ US

Additifs Naturels: Vers la multifonctionnalité

- Anti-bacterial properties related to chain extending



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Additifs Naturels: Vers la multifonctionnalité

Stratégie:

- Intercalation de molécules uniques puis mélanges de charges
- Intercalation de cocktails de molécules

- Propriétés:
  - Antioxydants/ Absorbeurs UV/Barrières/ Antimicrobiennes

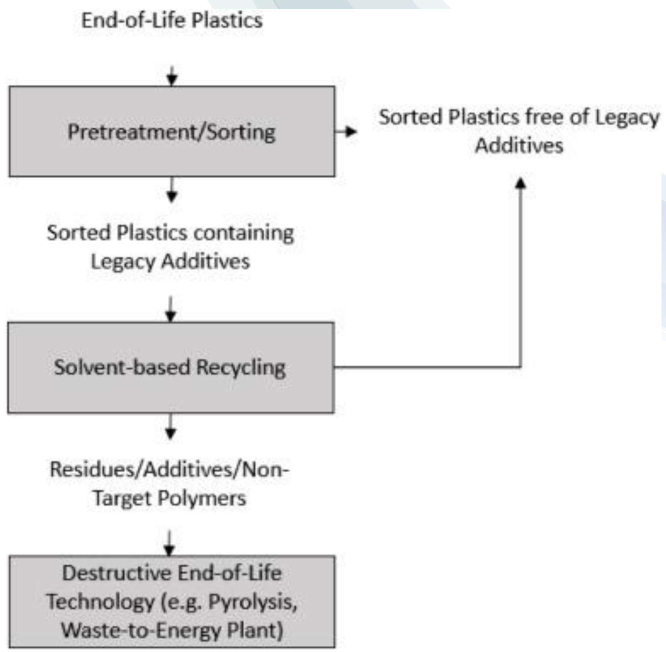
Les Additifs Hérités:

Ce sont des additifs qui ont été utilisé dans le passé mais qui sont dorénavant interdits:
- Phtalates / Ignifugeants bromés

Polymère	Taux [%]	Substances ignifugeantes
Mousse de polystyrène	0,8–4	HBCD
Polystyrène choc	11–15	DécaBDE, polystyrène bromé
Résine époxyde	0-0,1	TBBPA
Polyamides	13–16	DécaBDE, polystyrène bromé
Polyoléfines	5–8	DécaBDE, propylène dibromo styrène
Polyuréthanes	?	?
Polytéréphtalate	8–11	Polystyrène bromé
Polyesters insaturés	13–28	TBBPA
Polycarbonate	4–6	Polystyrène bromé
Copolymères styréniques	12–15	Polystyrène bromé

https://fr.wikipedia.org/wiki/Agent_ignifuge_brome

Recyclage chimique ou procédés d'extractions
- Solvatation/régénération
- Extraction (scCO2 , Solvants eutectiques,…)
- Upcycling
- Remplacer les additifs hérités par de nouveaux additifs pour permettre le recyclage de déchets qui ne pourraient pas l'être



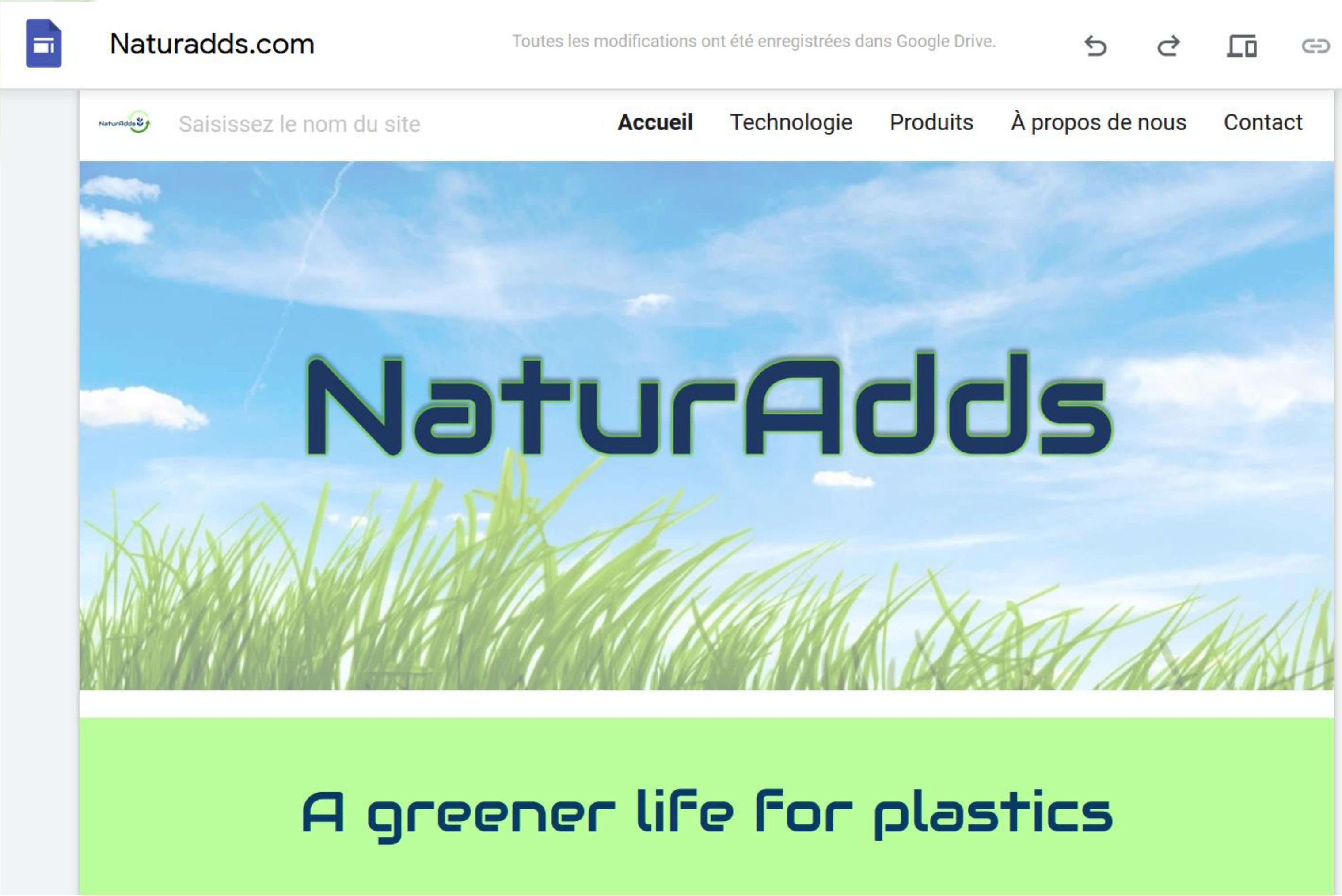
Additifs : encore des sujets de recherche

On a beaucoup étudié le vieillissement des matrices plastiques, mais les additifs eux-mêmes vieillissent.

Quid de leur sous-produits?

Quid des interactions Produits de dégradation ed la matrice : Produits de dégradations des additifs??

➔ C’est toute la complexité du vieillissement!



MERCI DE VOTRE ATTENTION