BIODEGRADABILITY: THE PRINCIPLES BEHIND THE STANDARDS

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Since 1991 research, development and production of biodegradable plastics
Headquarter: Novara, Italy (Milan area)
Main product : Mater-Bi

- The methodology for the biodegradability of plastics has been taken from the Guidelines of the **Organisation for Economic Cooperation and Development** (OECD) for the degradability of chemicals (OECD, 2006).

- The fundamental concepts introduced by the OECD are:

- "**ultimate biodegradation**" : the level of degradation achieved when the test compound is totally utilised by micro-organisms resulting in the production of carbon dioxide, water, mineral salts and new microbial cellular constituents (biomass).

- "**Ready biodegradability**" is determined by subjecting the substance in question to laboratory tests in which ultimate mineralisation into CO2 and H2O is measured.

BIODEGRADATION UNDER AEROBIC CONDITIONS

$C_{polymer}$ is assimilated by microorganisms $C_{biomass}$ and then it is either fast **mineralized** into CO_2 and H_2O or used for growth and reproduction (again as $C_{biomass}$).

Also $C_{biomass}$ is in the long term mineralized as a result of the subsequent turnover of the soil microbial community or storage polymers leading to the production of CO_2.

HOW TO MEASURE BIODEGRADATION AT LAB SCALE

REAGENT AND PRODUCT OF RESPIRATION

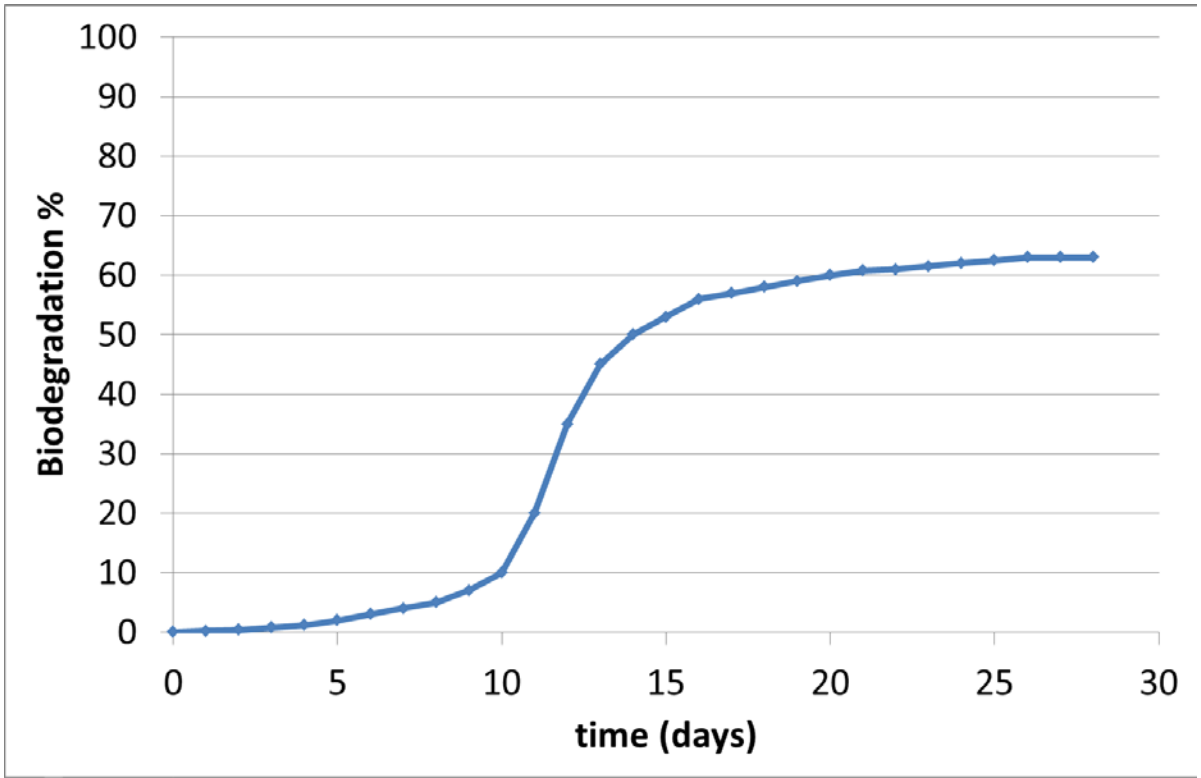
$$C_{polymer} + O_2 \rightarrow C_{biomass} \rightarrow CO_2 + H_2O$$

OECD TEST METHODS

- Non-specific analytical methods are used to follow the course of biodegradation.
- The methods are applicable to any organic substance and there is no need to develop specific analytical procedures.
- Since these methods also respond to any biodegradation residues or transformation products, an assessment of the extent of ultimate biodegradation is provided.

“READY BIODEGRADABILITY”

- Those substances demonstrating a minimum mineralisation level of 60% are considered to be "**readily biodegradable**“.
- Such requirements practically represents **complete and ultimate degradation** of the test substance since the remaining 30-40% is assumed to be assimilated as biomass.

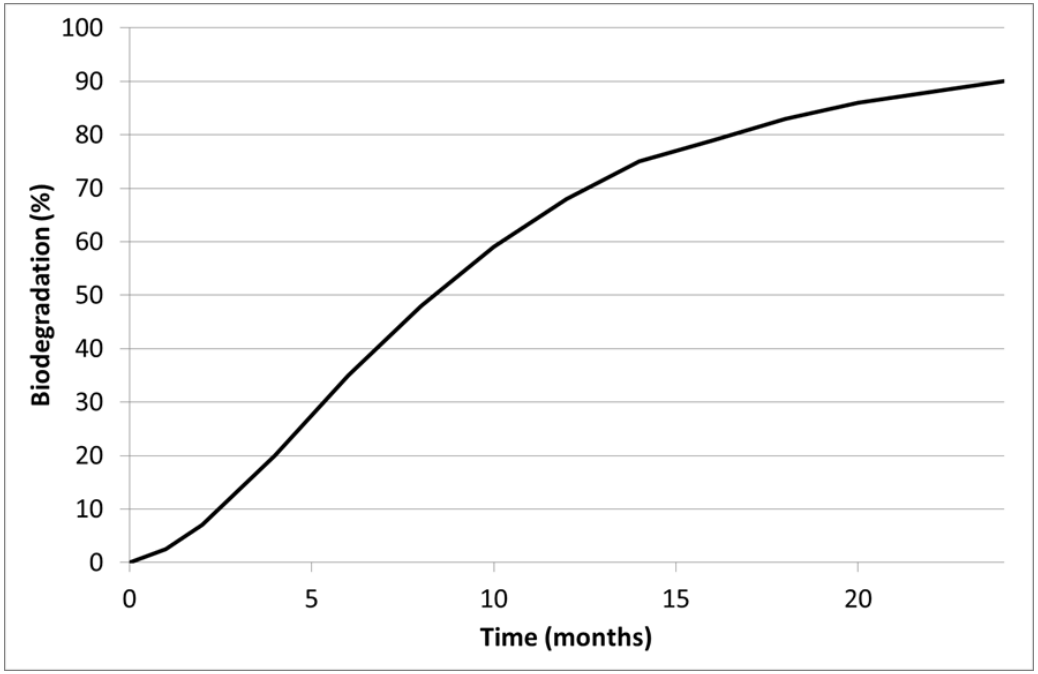


- Moreover, whenever a substance satisfies the “ready biodegradability” test requirements, it can be assumed it will undergo rapid and ultimate biodegradation in any biologically-active environment.

- For such reasons, according to the REACH evaluation scheme (REACH, 2006) once the “ready biodegradability” of a substance is confirmed there is no need for further investigation.

BIODEGRADABLE MULCH FILM

- A European standard on biodegradable mulch films has recently been approved (EN 17033, 2018).
- Biodegradation requirement: 90% (absolute or relative to the reference material) in less than 24 months.
- The high biodegradation threshold is in line with the requirements of the OECD guideline

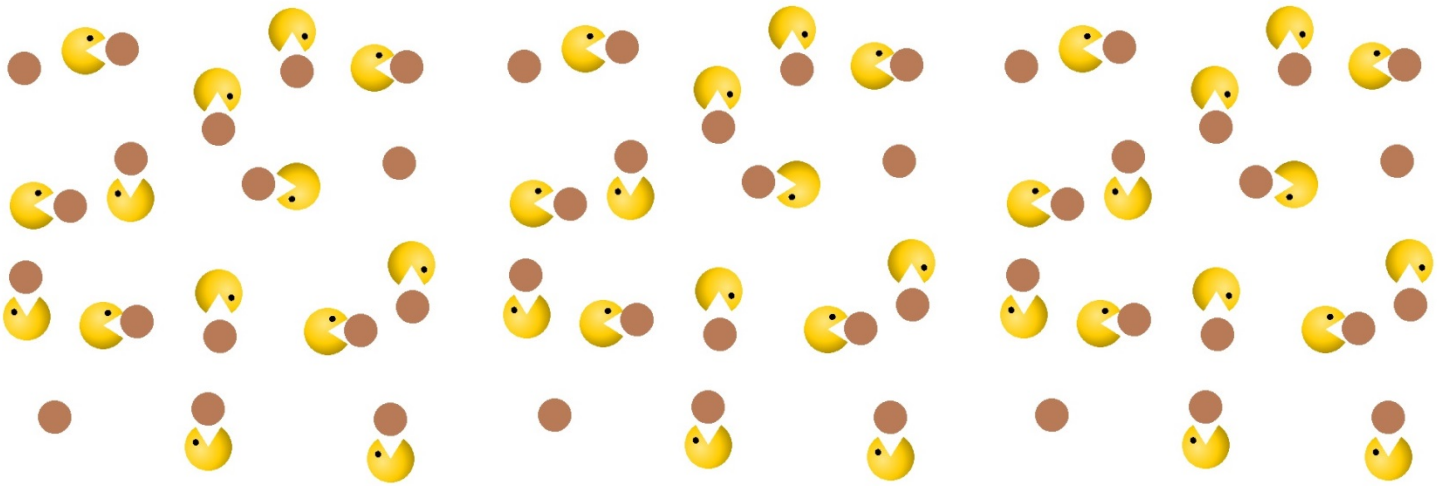


BIODEGRADABILITY OF MULCH FILMS

- The test duration is 2 years, vs 28 days.
- Thus biodegradable plastics cannot be classified as "readily biodegradable"
- Slow biodegradation suggests a complicated biodegradation process with the formation of relatively recalcitrant biodegradation intermediates, which only achieve total biodegradation after a whole 2 years of treatment under laboratory conditions, that is optimised conditions.
- *This does not sound as an indication of harmlessness to the environment.*
- *However….*

HOMOGENEOUS REACTIONS

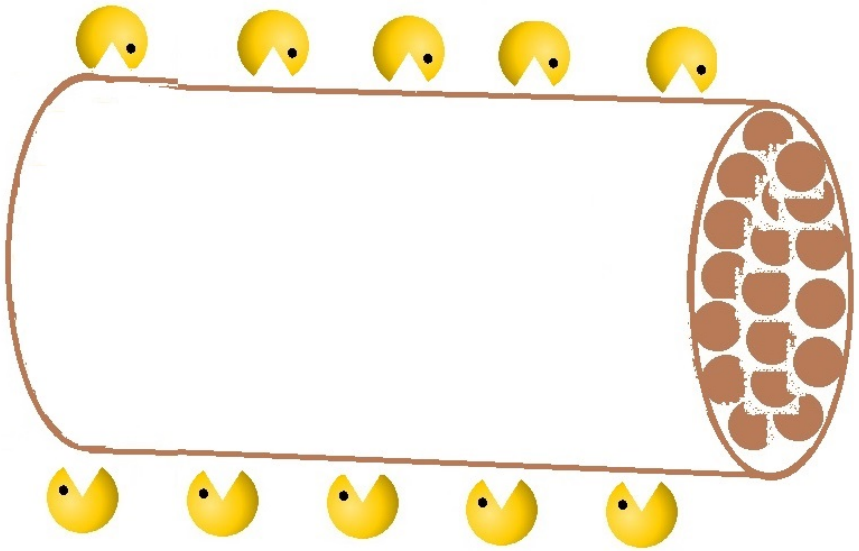
- The OECD test is applied to small molecules which are wholly available to enzymes and microorganisms present in the test environment (bioavailability).
- The reaction is homogeneous, in that the reagents and enzymes are present in the same phase.
- At any time the measured production of CO2 can be correlated with the quantity of C present in the system (the ThCO2) and therefore the rate of CO2/ ThCO2 is effectively an indication of the rate of biodegradation of the substance in question.



HETEROGENEOUS REACTIONS

- In biodegradation tests on bioplastics the reaction is heterogeneous, in that the substrate is in the solid phase while the enzymes and microorganisms are in the liquid phase . The reaction can only take at the interface.

- The CO2 released and counted when determining percentage biodegradation (CO2/ThCO2) comes only from the surface, which is a small fraction of the substance under test.



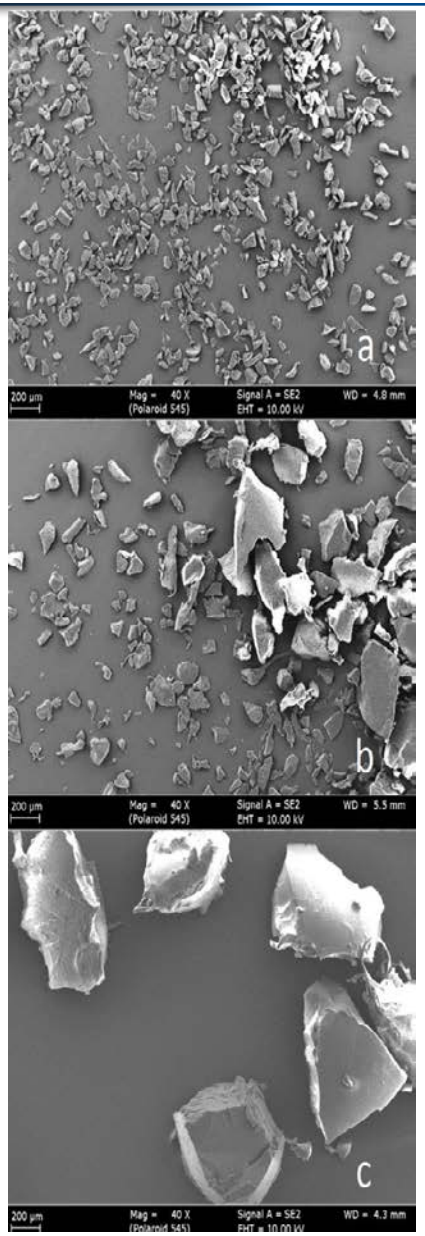
THE BIODEGRADATION RATE OF SOLID POLYMERS

A STUDY TO DETERMINE THE EFFECT OF PARTICLE SIZE ON BIODEGRADATION RATE

Polybutylene sebacate (PBSe), a biodegradable aliphatic polyester produced in the form of pellets has been milled and sieved obtaining different fractions.

Samples with different size particles have been tested for soil biodegradation.

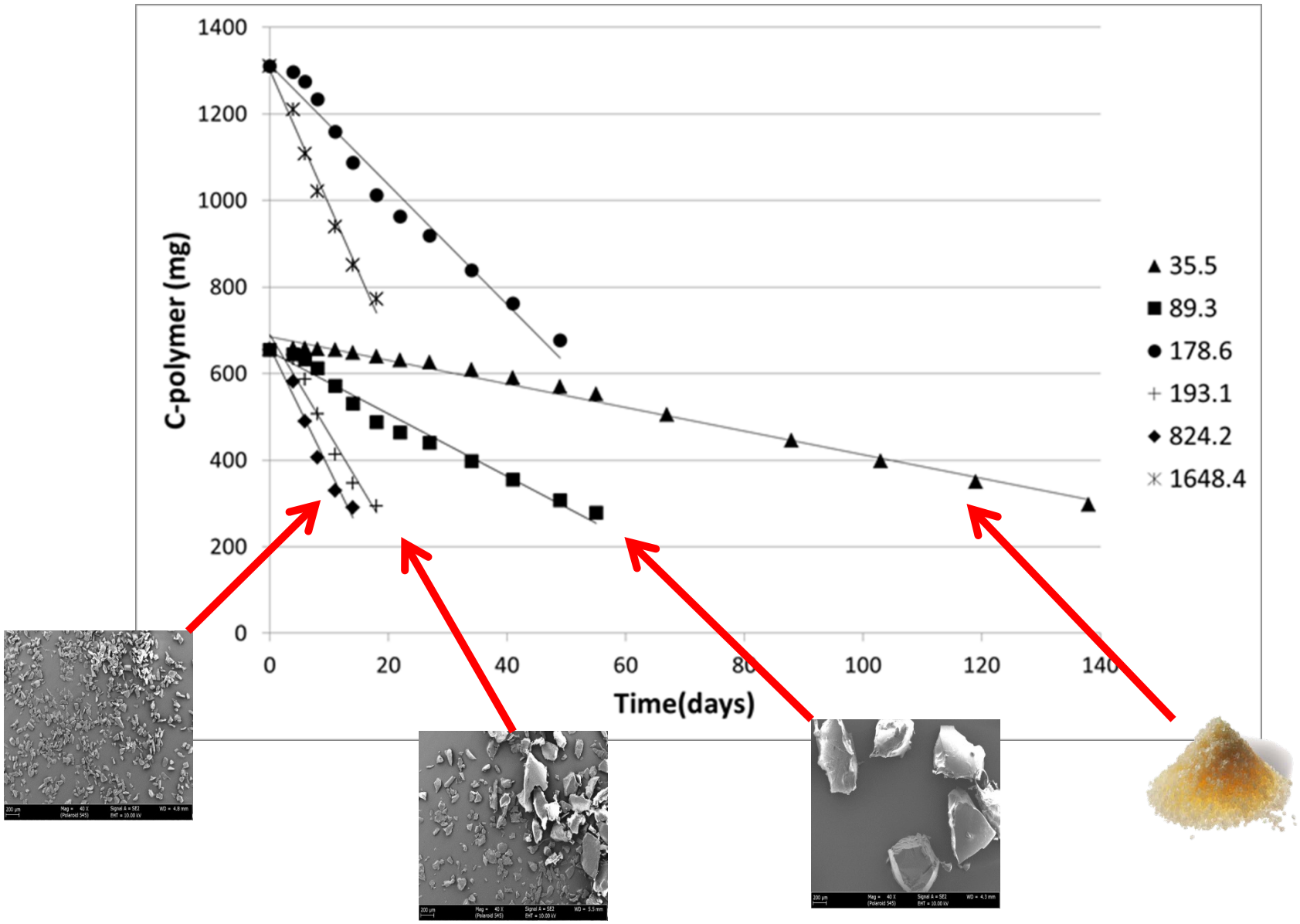
Biodegradation rate is affected by the available surface area.



S. Chinaglia, M. Tosin, F. Degli-Innocenti (2018) Biodegradation rate of biodegradable plastics at molecular level. Polymer Degradation and Stability 147: 237-244

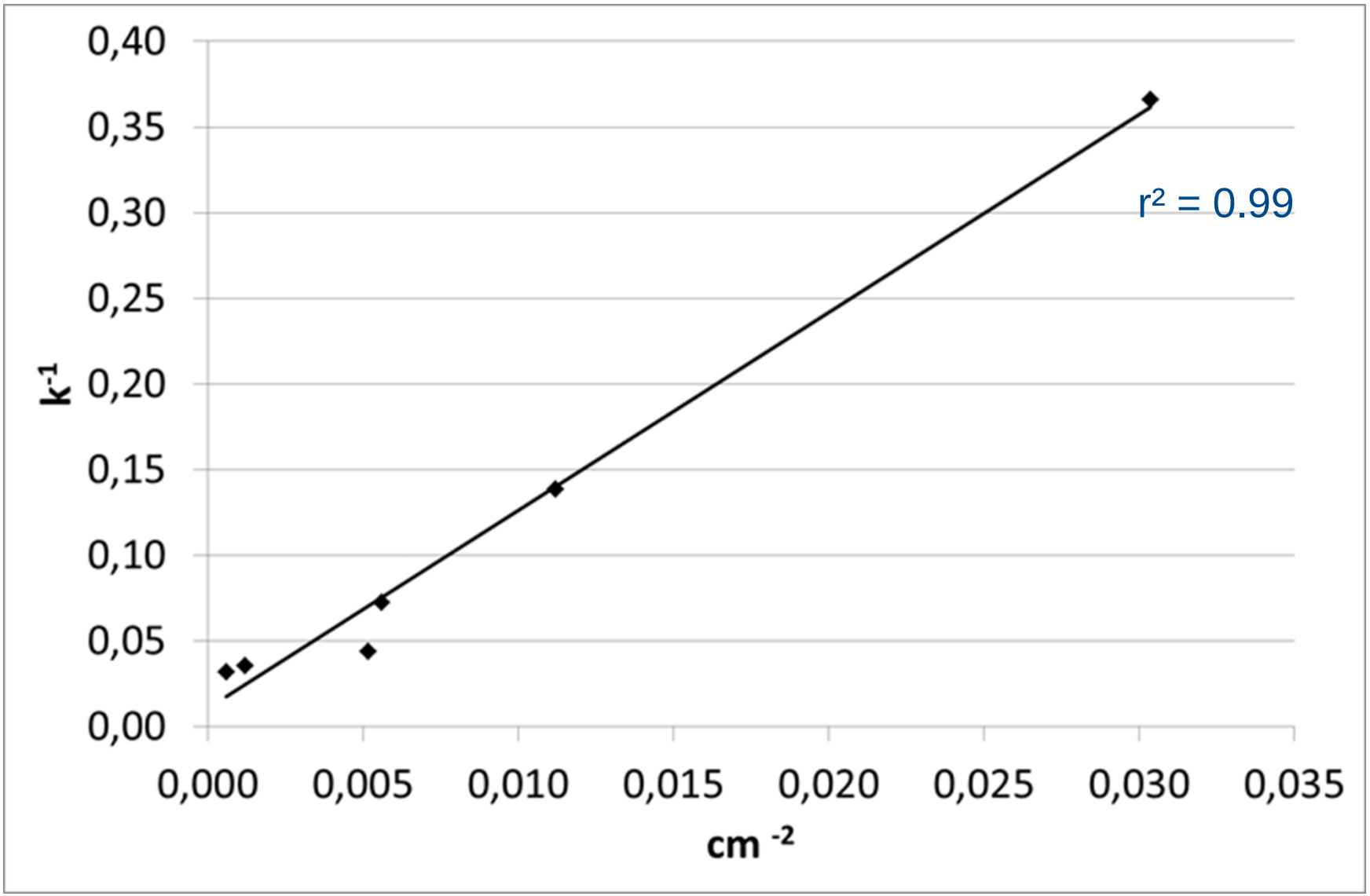
MINERALISATION RATE OF DIFFERENT SAMPLES

REGRESSION LINES HAVE BEEN DETERMINED AND THUS THE REACTION RATE (K).



LINEWEAVER-BURK (THE DOUBLE RECIPROCAL PLOT)

RELATIONSHIP BETWEEN THE SURFACE AREA AND THE REACTION RATE



- The various biodegradation rates of samples of different particle size are well correlated with their respective initial surface areas when a double reciprocal plot (that is the Lineweaver-Burk approach) is used.

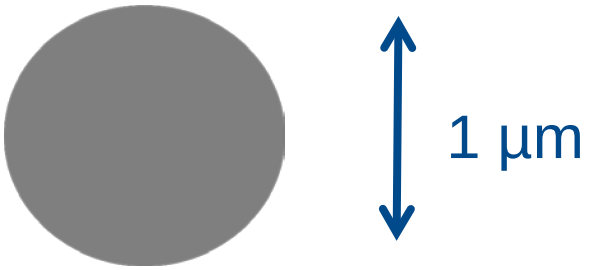
- The maximum achievable rate in the system studied can be determined by extrapolation. This value can be regarded as the biodegradation rate at molecular level, that is to say when the available surface area does not limit biodegradation (unlimited surface area).

THE BIODEGRADATION RATE AT MOLECULAR LEVEL

IF WE COULD TEST NANOPOLYMERS

If the polymer could be converted into microplastics (nanopolymeric particles), e.g. in the form of spheres of 1 µm of diameter, this surface would allow the 90% biodegradation threshold to be reached **in less than 7 days**, if constant for the whole biodegradation process.

THE PBSe NANOPOLYMER COULD POSSIBLY EVEN SATISFY THE OECD CRITERIA OF "READY BIODEGRADABILITY"



THE BIODEGRADATION RATE AT MOLECULAR LEVEL

- Biodegradation rate of a plastics is affected by particle size.
- The rate of CO2 evolution does not provide the true biodegradation rate at a given moment.
- In reality, if CO2 release is related to the available surface area of the polymer it will be seen that the rate is fairly high.
- Biodegradable polymers do not represent an environmental problem from the point of view of chemical permanence.
- However, the physical permanence of any product made using a biodegradable polymer will be influenced by its thickness (that is by the effective surface area) and environmental conditions (temperature, activity of the water, availability of nutrients, microbial population, etc.).

““The challenge of our millennium is in the balance between the technical means that humanity possesses and the wisdom in how we will make use of them”

UMBERTO COLOMBO

THANK YOU FOR YOUR ATTENTION


Francesco Degli Innocenti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