49th CEEES General Assembly

Modelling Aliphatic Polyesters Biodegradation

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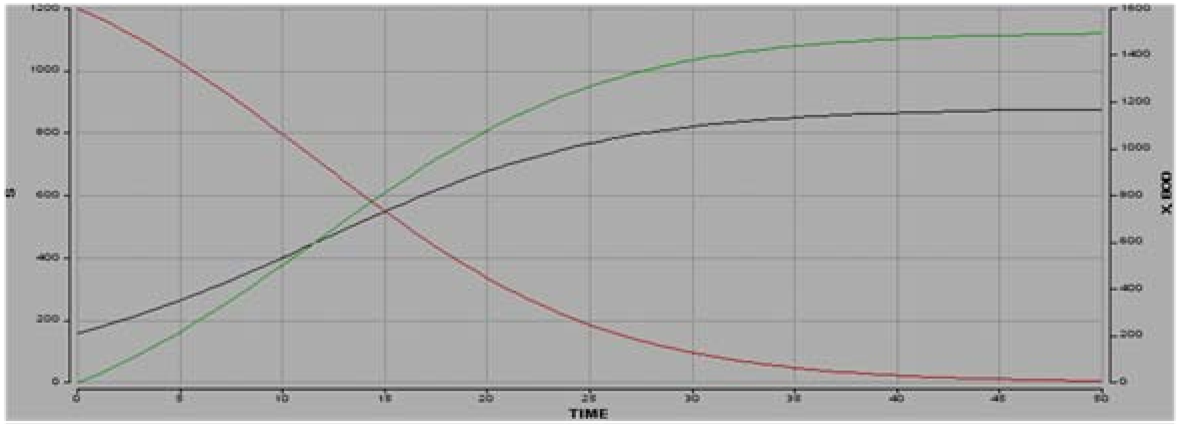

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Biodegradable Plastics

NATURAL BIODEGRADABLE PLASTICS

- Based on renewable resources
- Can be either naturally produced or synthesised from renewable resources

NON-RENEWABLE SYNTHETIC BIODEGRADABLE PLASTICS

- Petroleum-based

BIODEGRADABLE PLASTICS ARE BLENDED WITH SYNTHETIC POLYMERS TO PRODUCE PLASTICS WHICH MEET FUNCTIONAL REQUIREMENTS

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RANGE OF POTENTIAL APPLICATIONS

MAJOR POTENTIAL DISPOSAL ENVIRONMENTS

SOME ADVERSE ENVIRONMENTAL RISKS

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RANGE OF POTENTIAL APPLICATIONS

- Film including overwrap, shopping bags, waste and bin liner bags, composting bags, mulch film, silage wrap, landfill covers, packaging - including O_2 and H_2O barriers, bait bags, nappy backing sheet, and cling wrap
- Flushable sanitary products
- Sheet and non woven packaging
- Bottles
- Liquid paper board
- Planter boxes and fishing nets
- Food service cups, cutlery, trays, and straws

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MAJOR POTENTIAL DISPOSAL ENVIRONMENTS

- Composting facilities or soil burial
- Anaerobic digestion
- Wastewater treatment facilities
- Plastics reprocessing facilities
- Landfill
- Marine and freshwater environments
- General open environment as litter

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SOME ADVERSE ENVIRONMENTAL RISKS …

- Pollution in waterways due to high biochemical oxygen demand concentrations
- Migration of plastic degradation by-products to groundwater and surface water bodies
- Trauma and death of marine species
- Soil and crop degradation resulting from the use of compost that may have unacceptably high organic and or metal contaminants

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***ASTM* DEFINES BIODEGRADABLE AS**

capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds, or biomass in which **the predominant mechanism is the enzymatic action of microorganisms**, that can be measured by standardized tests, in a specific period of time, reflecting available disposable conditions

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Experimental design

POLYMERS	COMPOUNDING	BLENDS
HDPE PE-g-MA PLA PCL Mater-Bi®	REACTIVE EXTRUSION	PLA60 PCL60 SPLA50 SPLA70 SPCL50

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Experimental design

Blend	HDPE	PE-g-MA	PLA	PCL	Mater-Bi®	Chemical formula
PLA 60	30	10	60	0	0	C_3H_5O
PCL 60	30	10	0	60	0	$C_5H_{10}O$
SPLA 50	30	10	0	0	60 (50 TPS + 50 PLA)	C_5H_9O
SPLA 70	30	10	0	0	60 (30 TPS + 70 PLA)	C_3H_4O
SPCL 70	30	10	0	0	60 (30 TPS + 70 PCL)	C_3H_7O

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Specific standard for biodegradable plastics

ISO 14851 (1999)	Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium	Conversion to carbon dioxide, water and biomass via microbial metabolism

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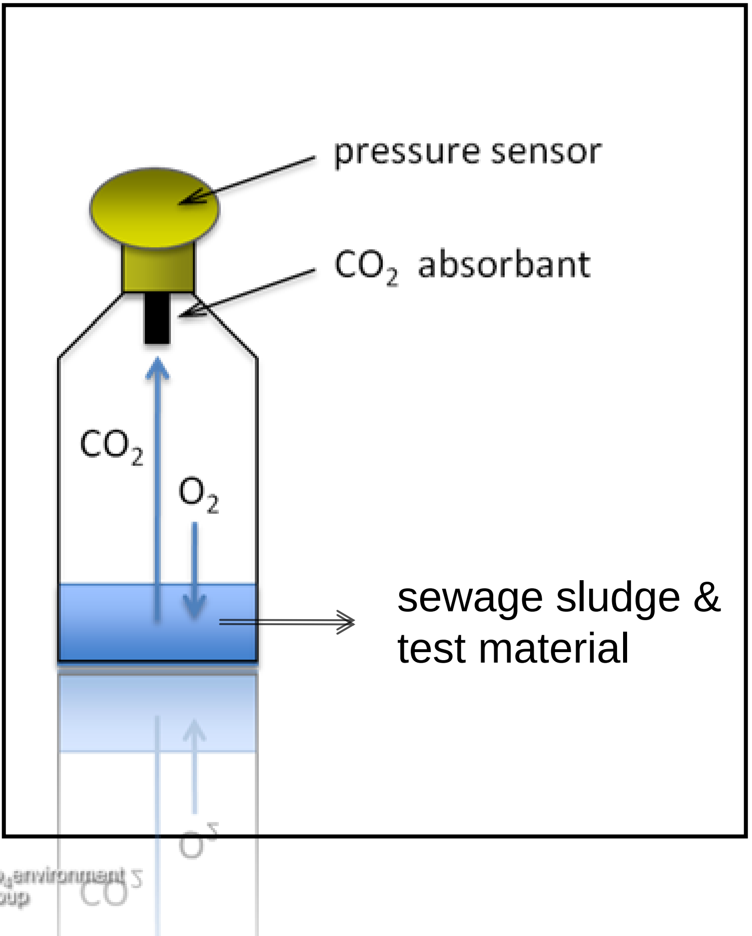
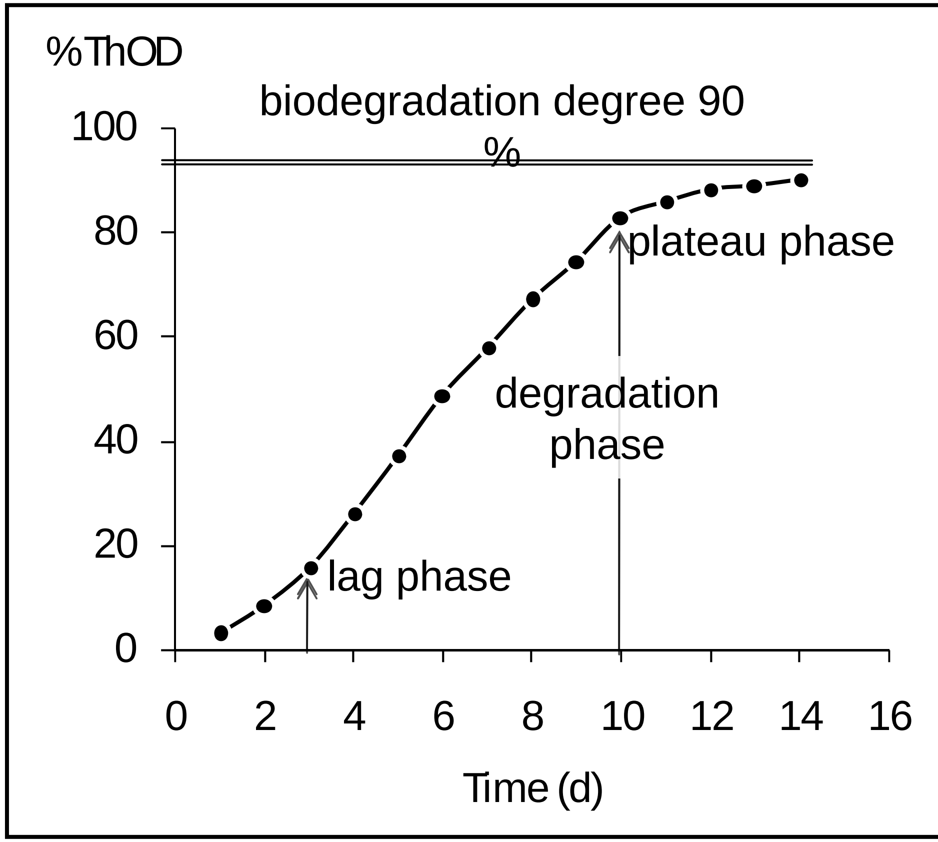
Oxygen consumption as a quantitative measure of biodegradation

Oxitop®



Biodegradation curve



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Saturation type mathematical model

STATE VARIABLES	• X - biomass concentration • BOD - biochemical oxygen concentration
MODEL PARAMETERS	• μ_{max} - maximum specific growth rate • k_s - affinity constant • Y - biomass yield • Z - conversion factor polymer to oxygen

RATE EQUATIONS

Rate of microbial growth

$$r_X = \frac{dX}{dt} = \mu_{max} \frac{P}{k_s + P} X$$

Rate of polymer consumption

$$r_P = \frac{dP}{dt} = -\frac{1}{Y} r_X = -\frac{\mu_{max}}{Y} \frac{P}{k_S + P} X$$

Rate of BOD formation

$$r_{BOD} = \frac{1}{Z} r_P = \frac{\mu_{max}}{Y\,Z} \frac{BOD}{k_s + BOD} X$$

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First order mathematical model

STATE VARIABLE	• BOD – biochemical oxygen concentration
MODEL PARAMETERS	• k_1 – first order rate constant • BOD_u – ultimate BOD
RATE EQUATION	$\frac{dBOD_t}{dt} = k_1 \left(BOD_u - BOD_t \right)$

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Mathematical model

METHOD	non linear regression analysis
SOFTWARE	Berkeley Madonna

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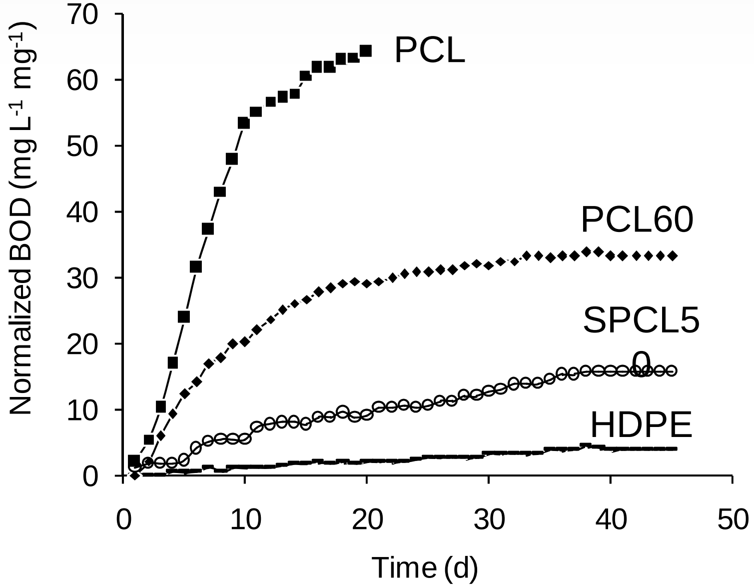
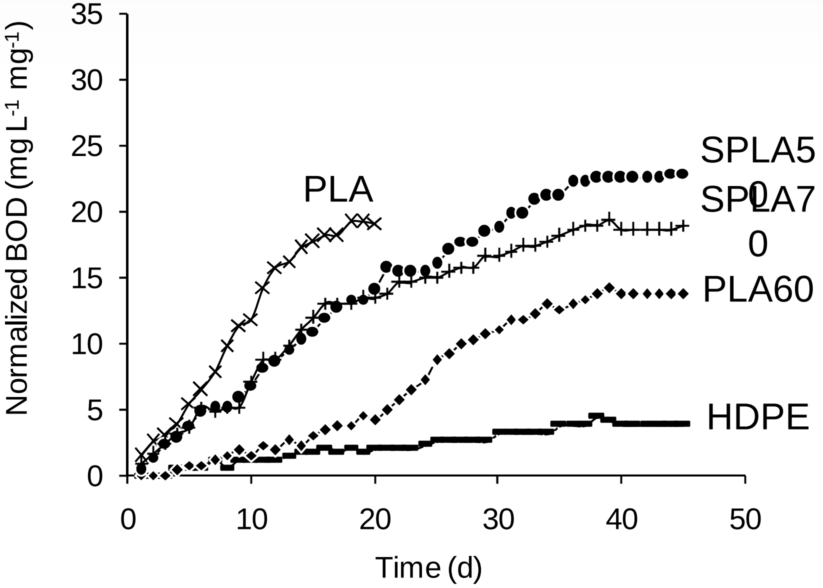
Biodegradation kinetics





- PCL and PCL60 blend are more biodegradable than PLA and PLA60 blend
- Starch increased biodegradability of PLA blend; the same was not observed for the of PLC blend

THE BIODEGRADABILITY TEST SUGGESTS THAT STARCH IS MORE BIODEGRADABLE THAN PLA BUT LESS THAN PCL

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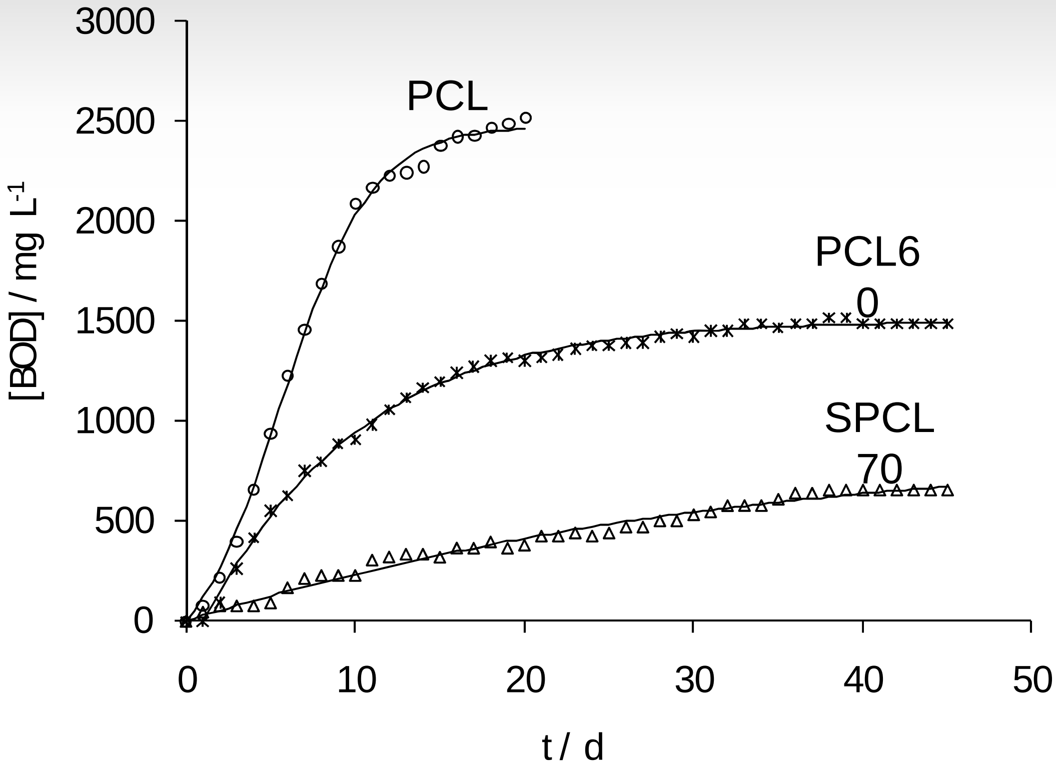

Sigmoidal curve	Parabolic curves	
PCL	**PCL60**	**SPCL70**
100 % ThOD μ_{max} = 0.43 d^{-1}	48 % ThOD k_1= 0.11 d^{-1}	24 % ThOD k_1= 0.03 d^{-1}

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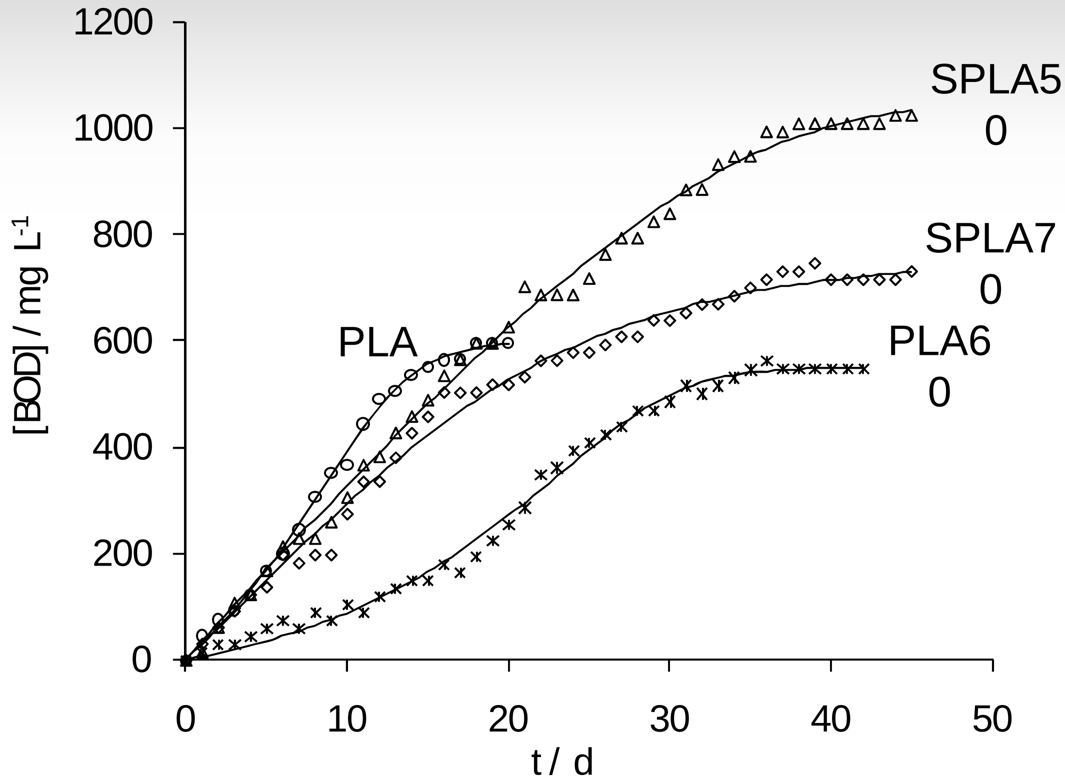

Sigmoidal curve		Parabolic curves	
PLA	**PLA60**	**SPLA50**	**SPLA70**
37 % ThOD μ_{max} = 0.17 d^{-1}	22 % ThOD μ_{max} = 0.08 d^{-1}	34 % ThOD k_1= 0.02 d^{-1}	25 % ThOD k_1= 0.03 d^{-1}

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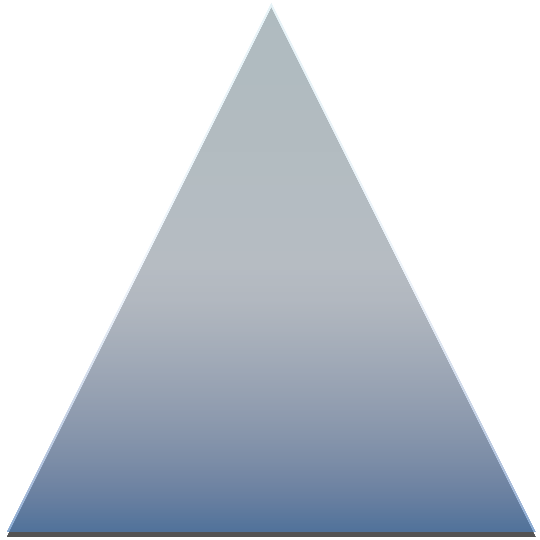
Testing biodegradability (OECD)

TESTS		LEVELS OF BIODEGRADABILITY
Ready biodegradability		Readily biodegradable
Inherent biodegradability		Inherently biodegradable
Simulation		Persistent



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Testing biodegradability (OECD)

READILY BIODEGRADABLE

- lag phase - 10 % of the chemical is consumed
- degradation phase - extent of degradation exceeds 60 % for ThOD within 10 d window

The blends did not pass the “ready”-level test because degradation occurs too slow

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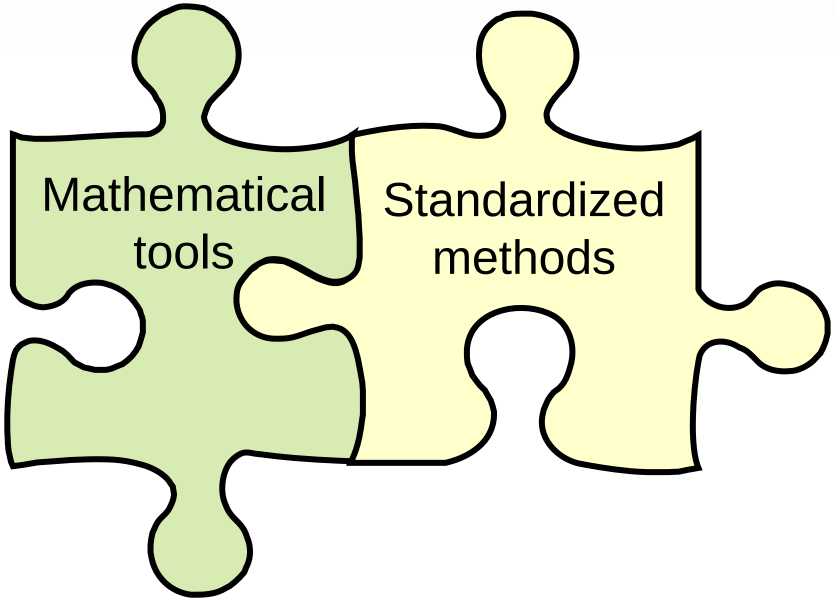

- The first-order kinetic model could be used instead of the 10-day-window to describe degradation kinetics
- The saturation model could be appropriate in estimating the lag phase as well as the final extent of degradation