Formation Mechanism(s) of Micro and Nanoplastics

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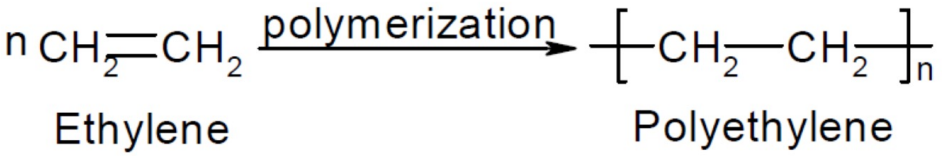
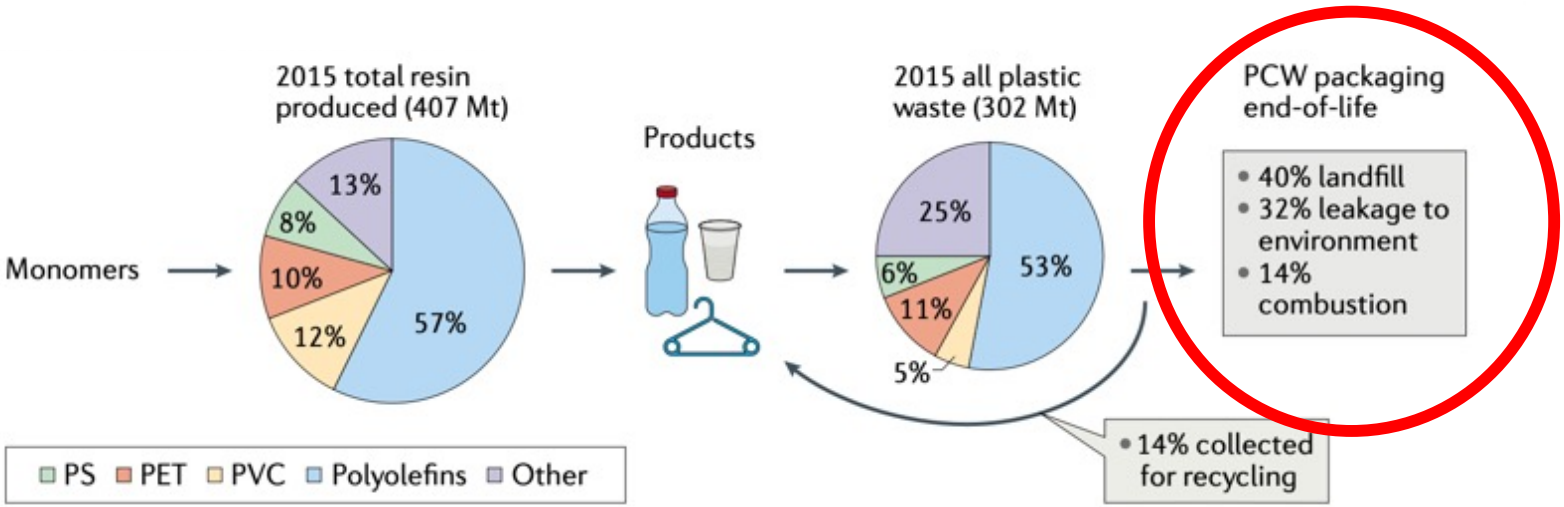
Department of Chemical Engineering, Columbia University

Ghosh, Kumaraswamy, Kumar Soft Matter (in press)
Mendez, Kumaraswamy, Kumar, Nat Comm (in press)
Singh, Kumaraswamy, Kumar - submitted

Vivek Sharma,
Guru Kumaraswamy

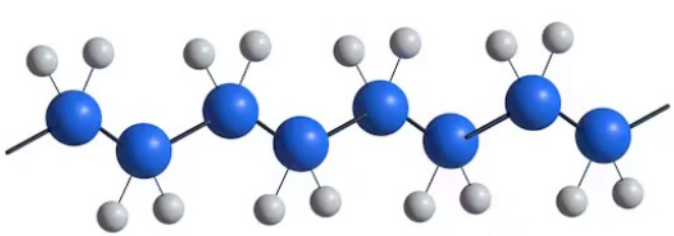
Linear plastic economy





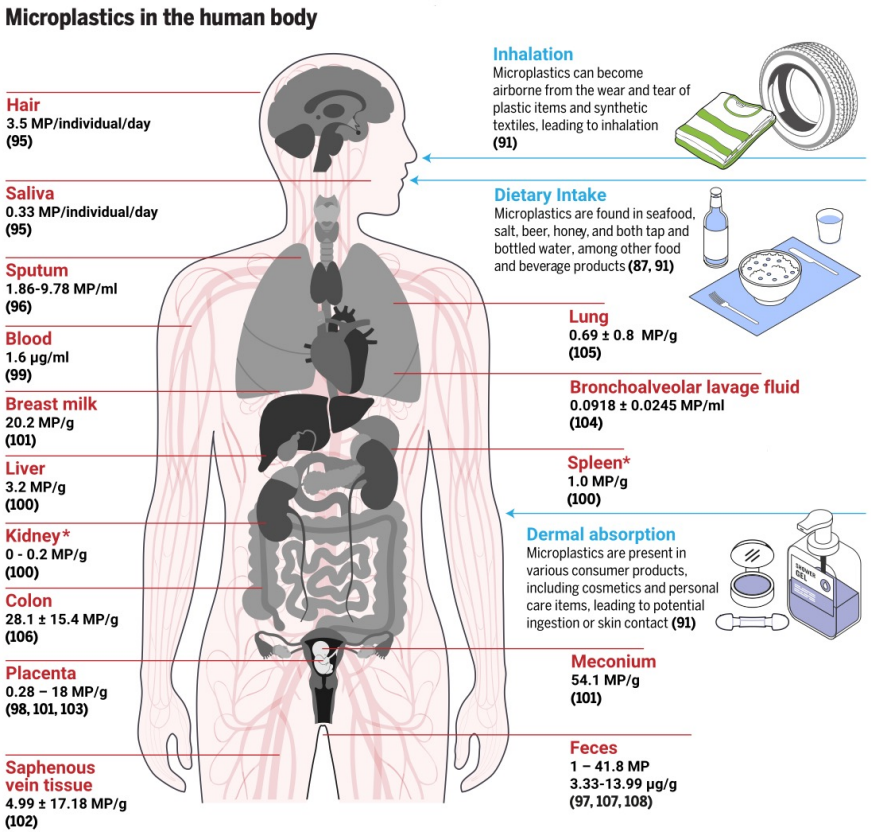
14% polymers collected – 2% recycled

Coates et al., 2015



Microplastics – 1 μm- 3mm

Nanoplastics - 1 nm -1 μm

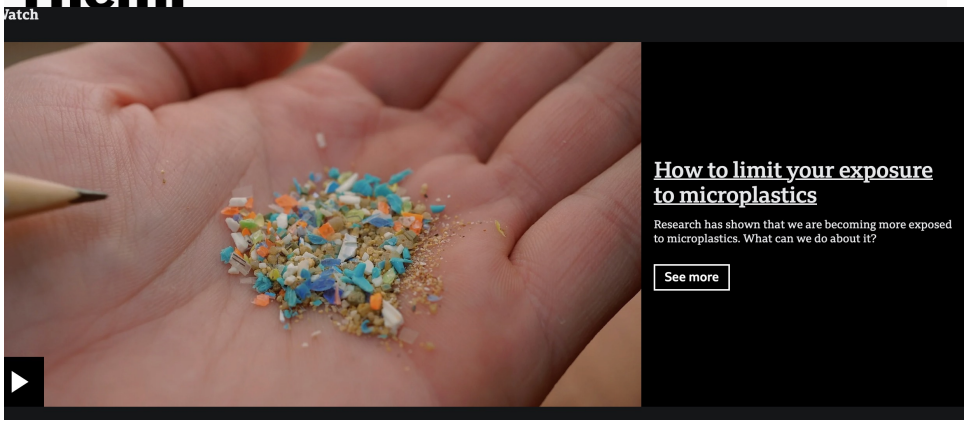


SUSTAINABILITY

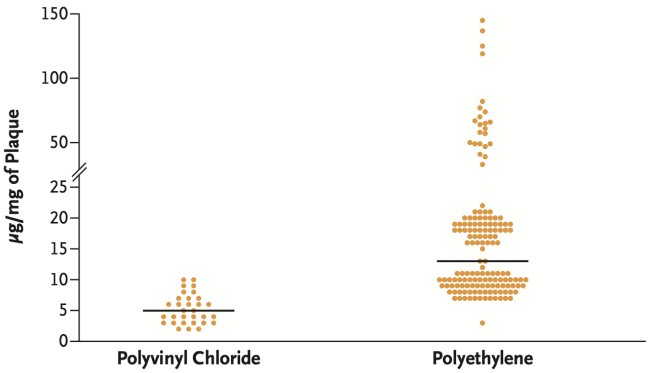
NY Times Wirecutter Piece

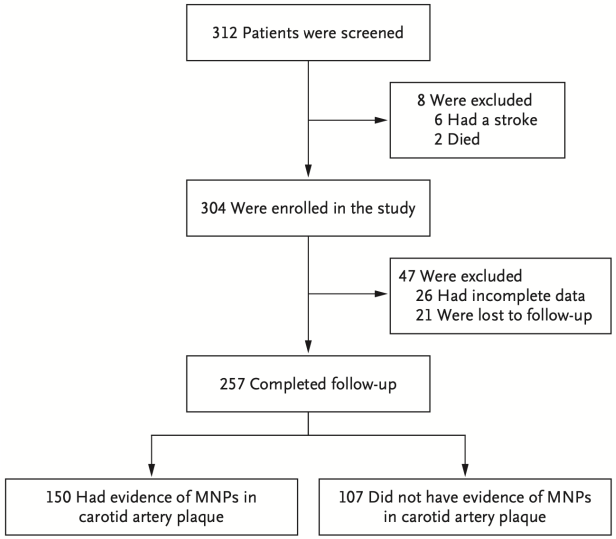
Microplastics Are Everywhere. Here's How to Avoid Eating Them.

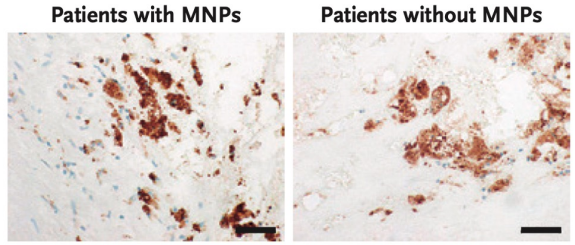
BBC

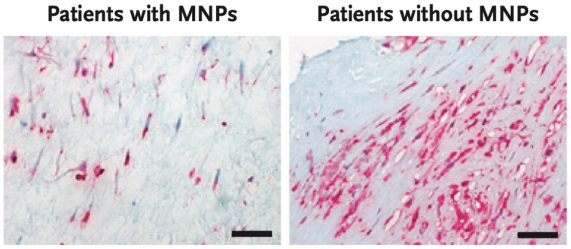


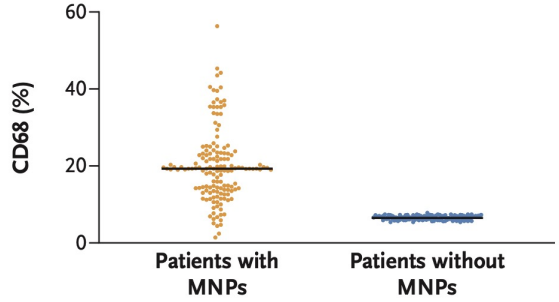
Microplastics and Nanoplastics in Atheromas and Cardiovascular Events

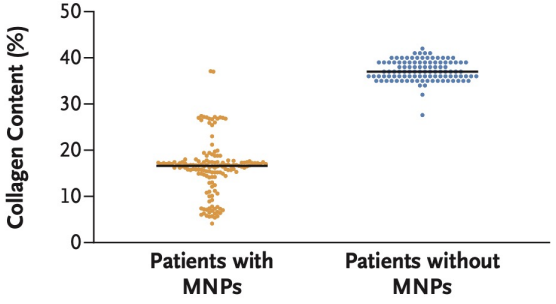










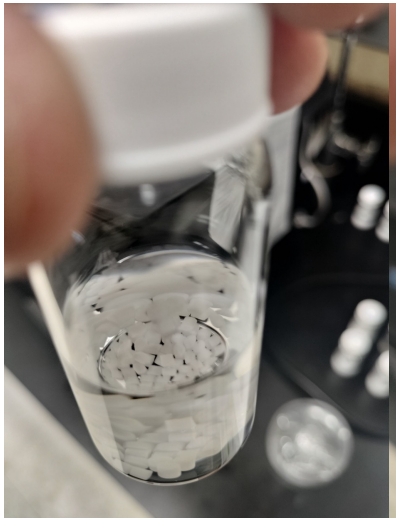


Micro/nanoplastic formation

1. Cut back on bottled water

Bottled water is a significant source of microplastics. In fact, it's the most concentrated source, according to a study from 2019.

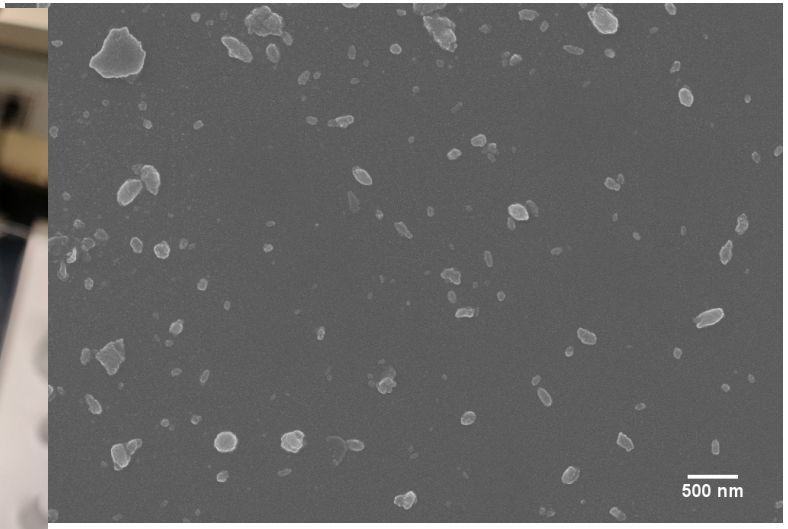
Researchers believe that bottled water contains many more microplastics than tap. The evidence is mounting: A study published in 2024 suggests that the typical plastic bottle of water contains two to three times the plastic than previously thought.

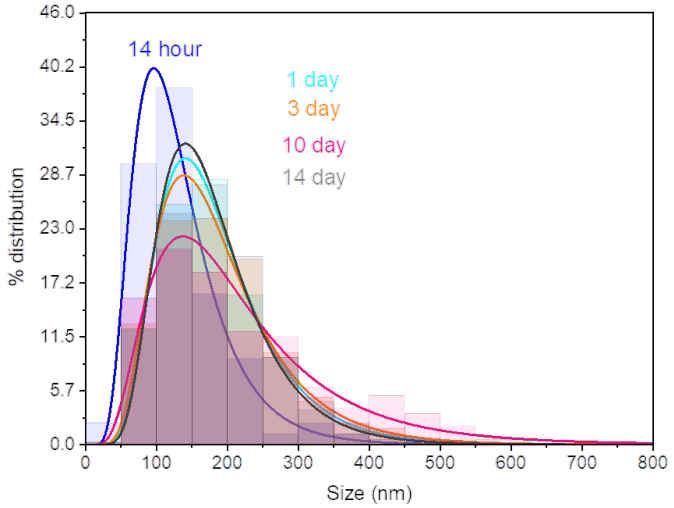


Control

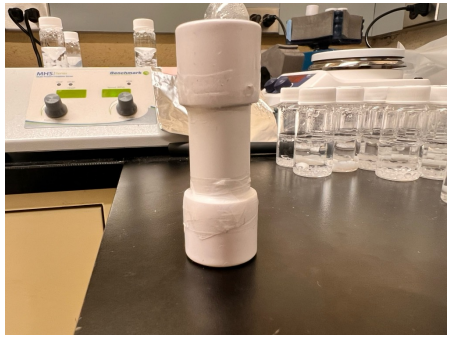
3 days

21 days

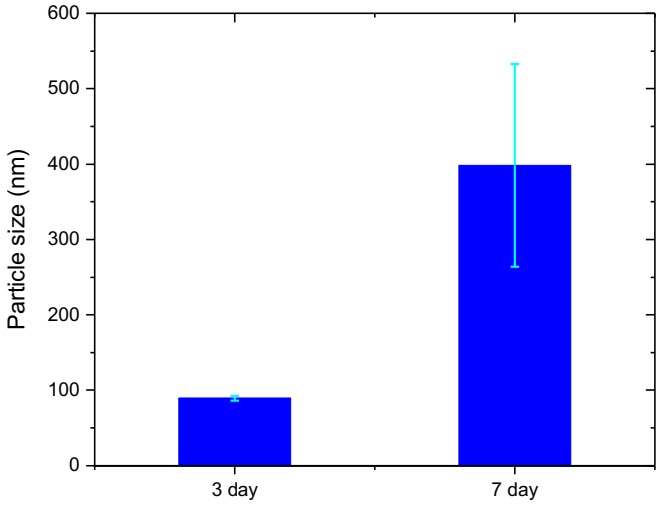




PVC pipes

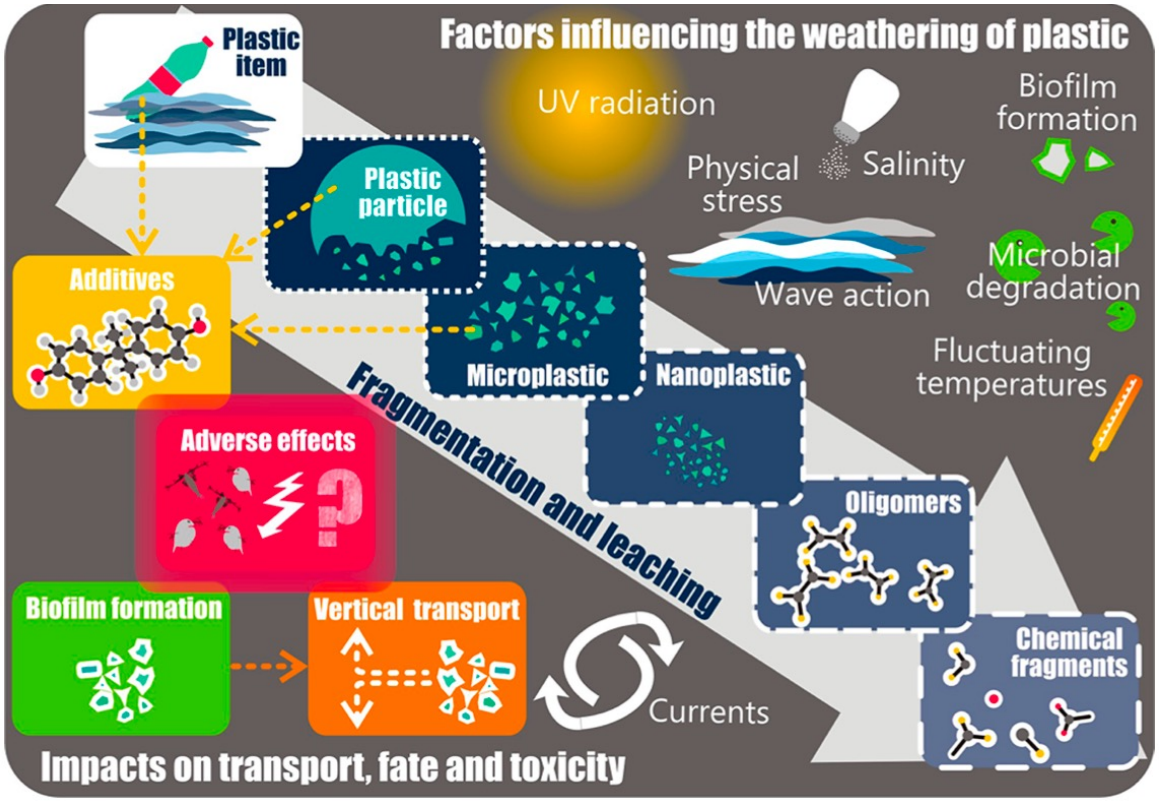


PVC pipe shaken



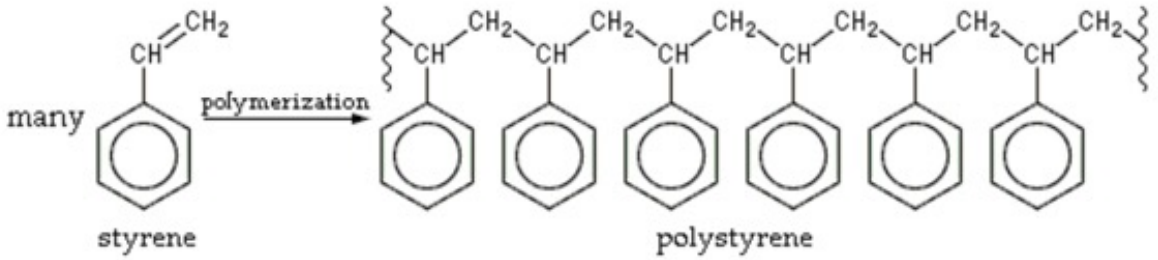
Nanoplastics From Tire Wear

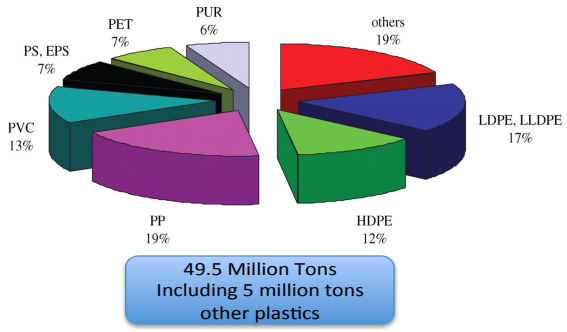
MNP Formation under Quiescent Conditions



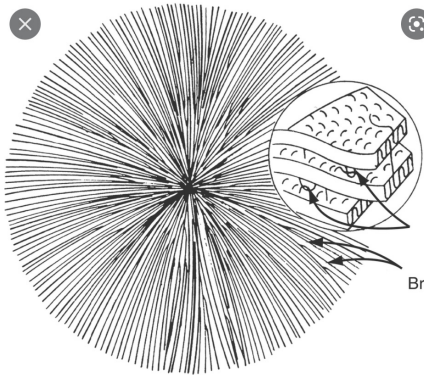
UV, O_2, Water,
leads to chain scission

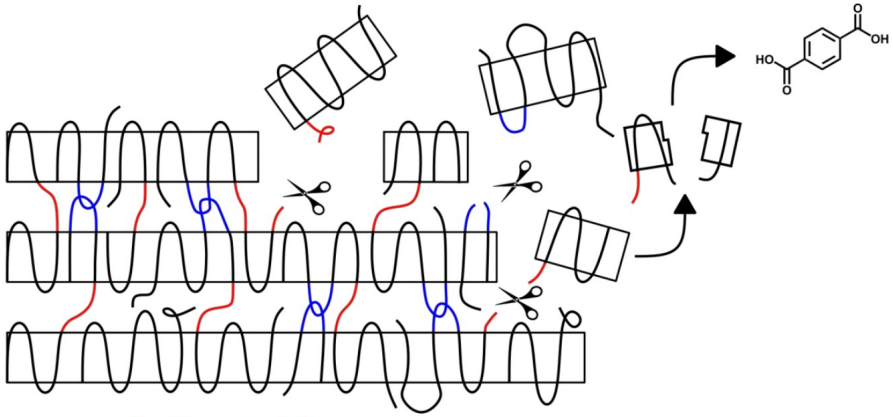
Chain Microstructure: Morphology

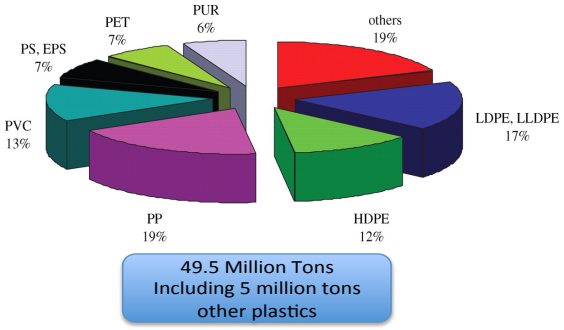


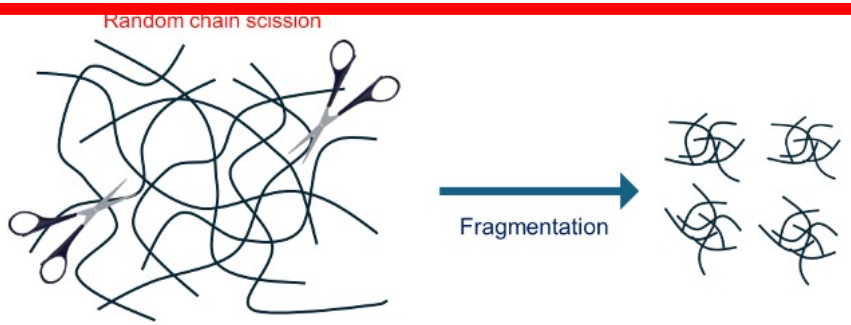


Hypothesis: Semicrystalline vs Amorphous

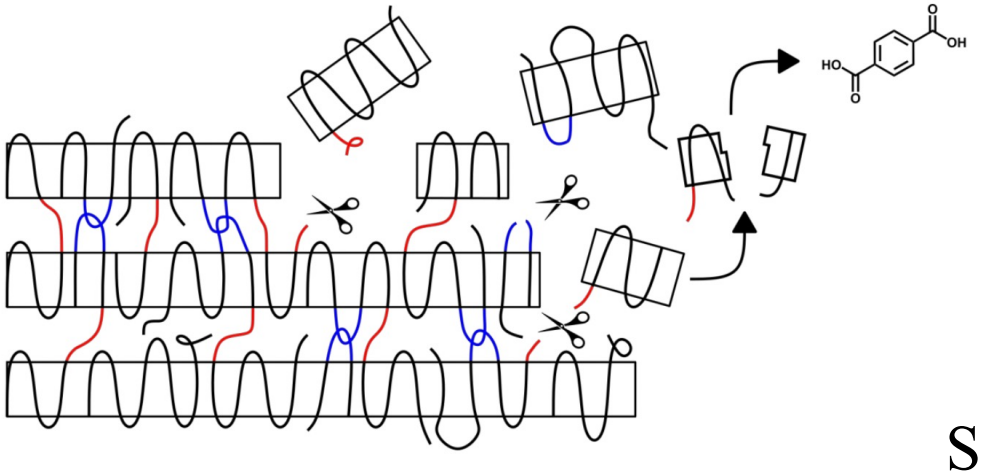






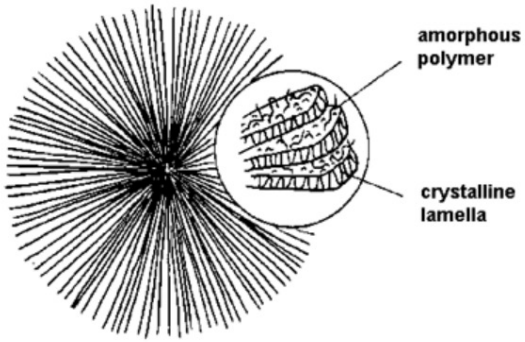


Amorphous Glassy Polymers: Entanglement Spacing
3 nm– 10K



Persistence of Nanoplastics

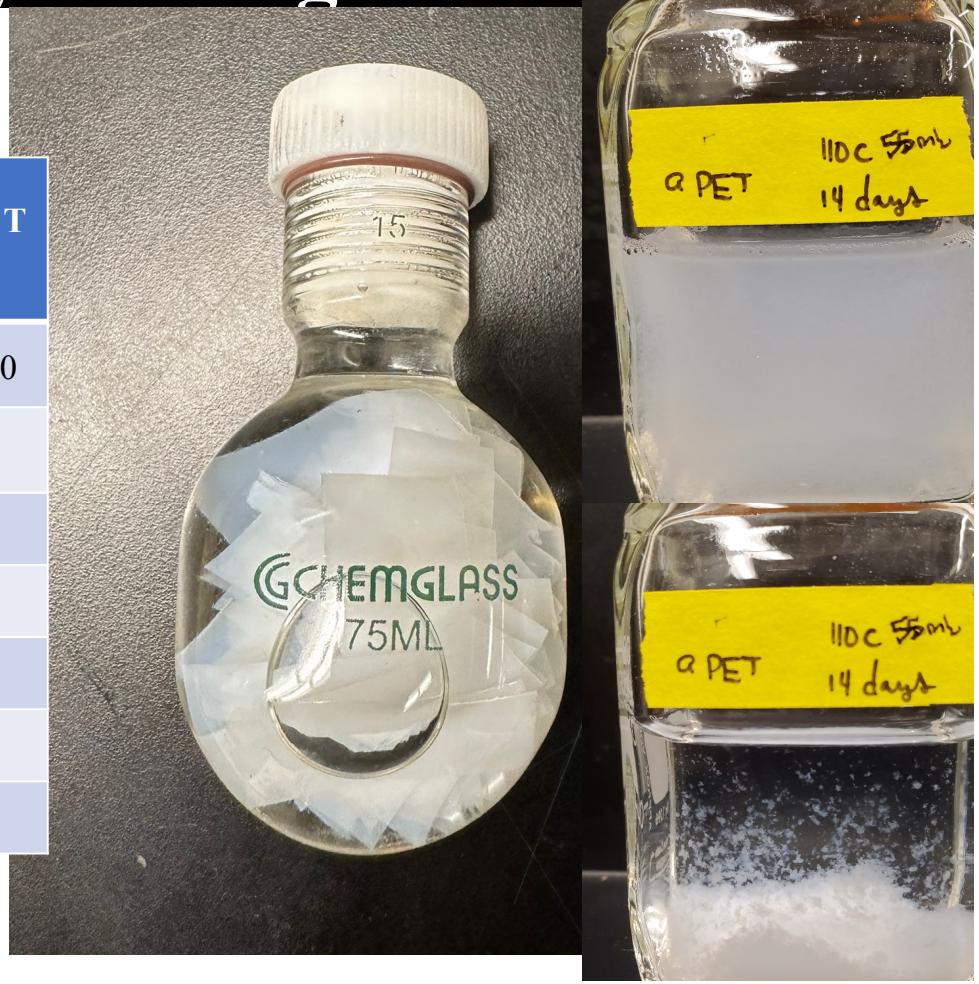
Semicrystalline: Ties Break
Embrittlement
lamellae “peel” off



Amorphous -- oligomers

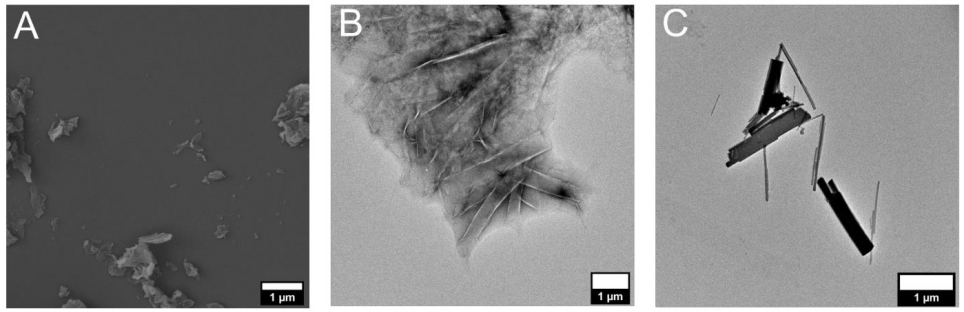
Quiescent Polymer Degradation

	Polymer	T_g [°C]	T_m [°C]	Aging T [°C]
Crystalline	PET (hydrolysis)	78	245	100, 110
	PET (glycolysis)	78	245	180
Amorphous	iPP	-5 [70]	161	70
	aPP		-	70
Amorphous	sPS	100 [71]	247	70
	aPS		-	70
	Nylon 6			35

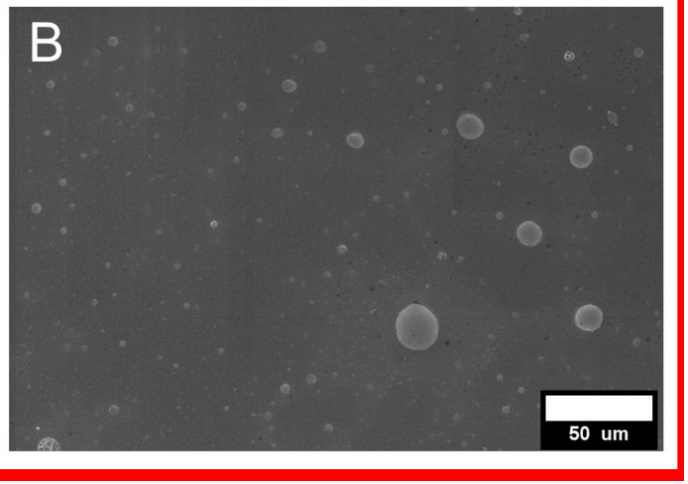


Role of Morphology

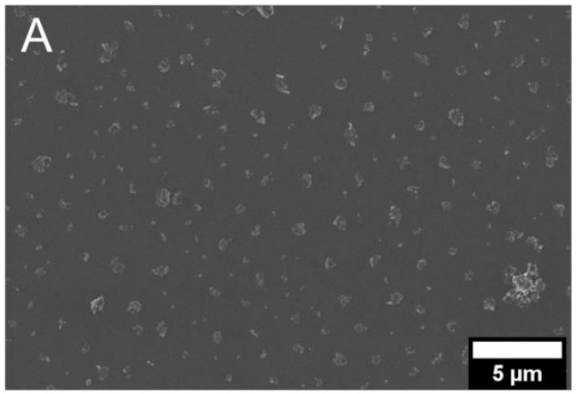
PET



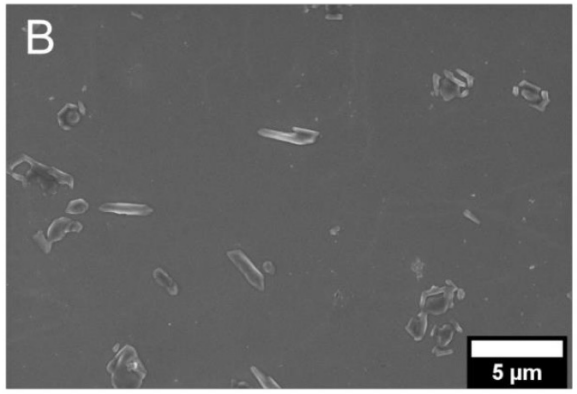
aPP



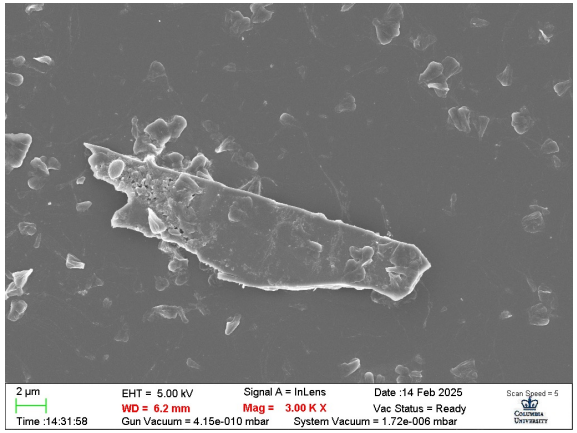
iPP



sPS



Nylon 6

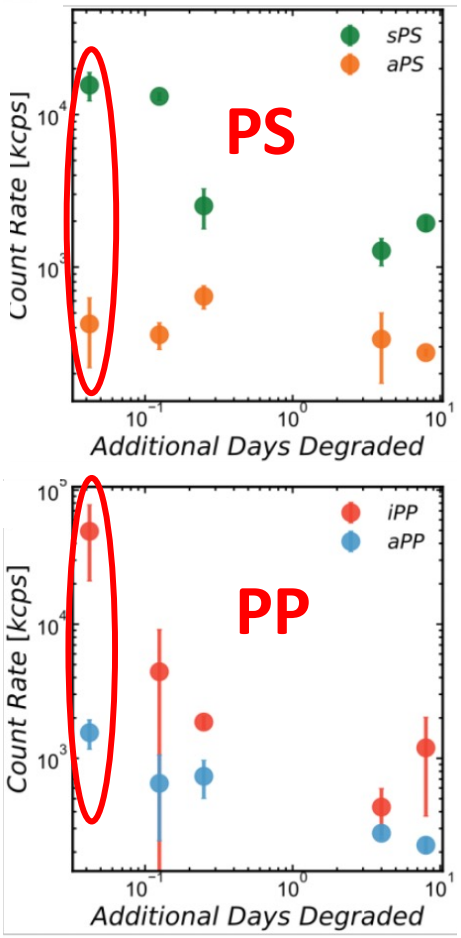


Dynamic Light Scattering

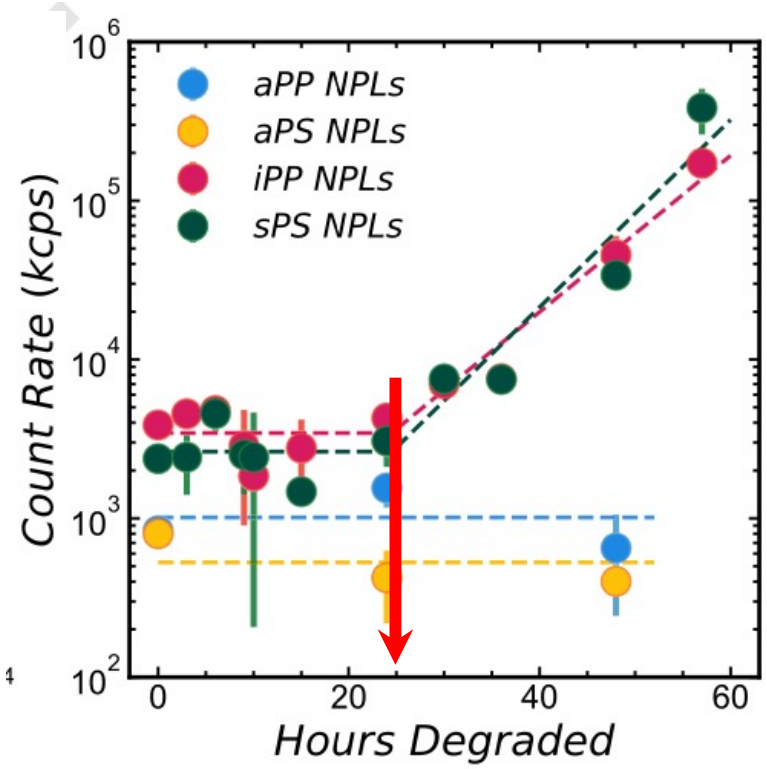
2 days oxidative degradation

$$K_2S_2O_8 + 2H_2O \rightarrow K_2SO_4 + H_2SO_4 + 2[OH]^{\cdot -}$$

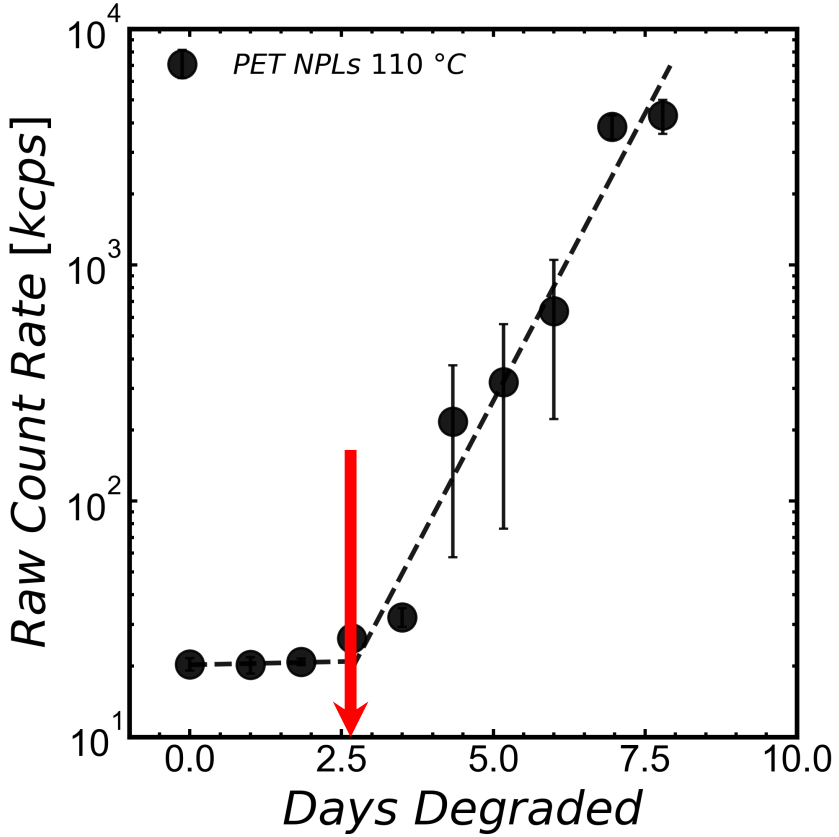
Crystal samples
much higher scattering



Induction Time

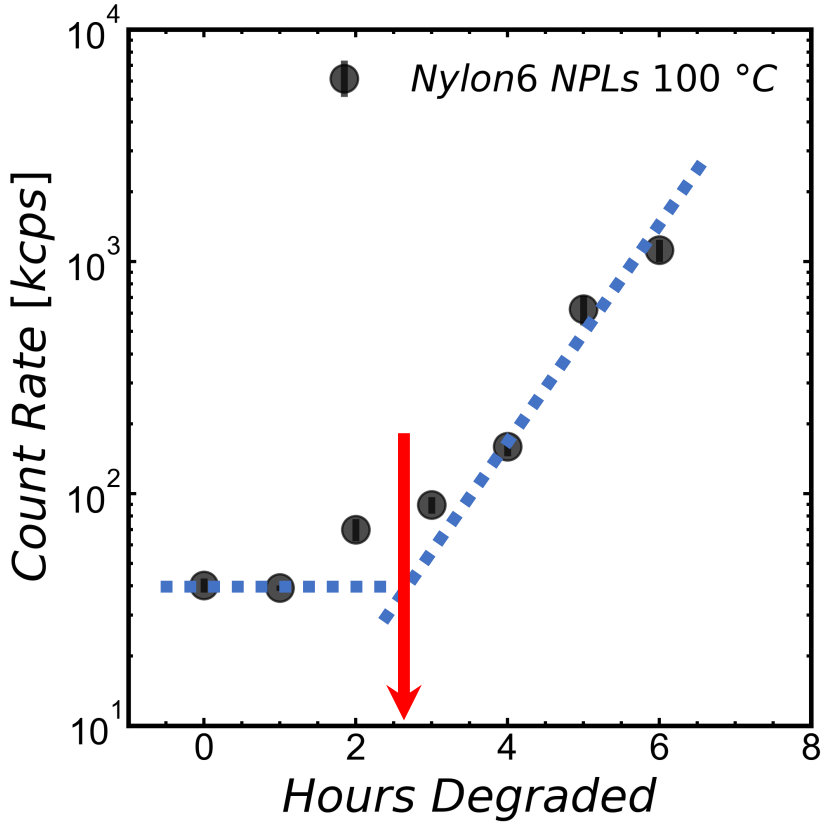


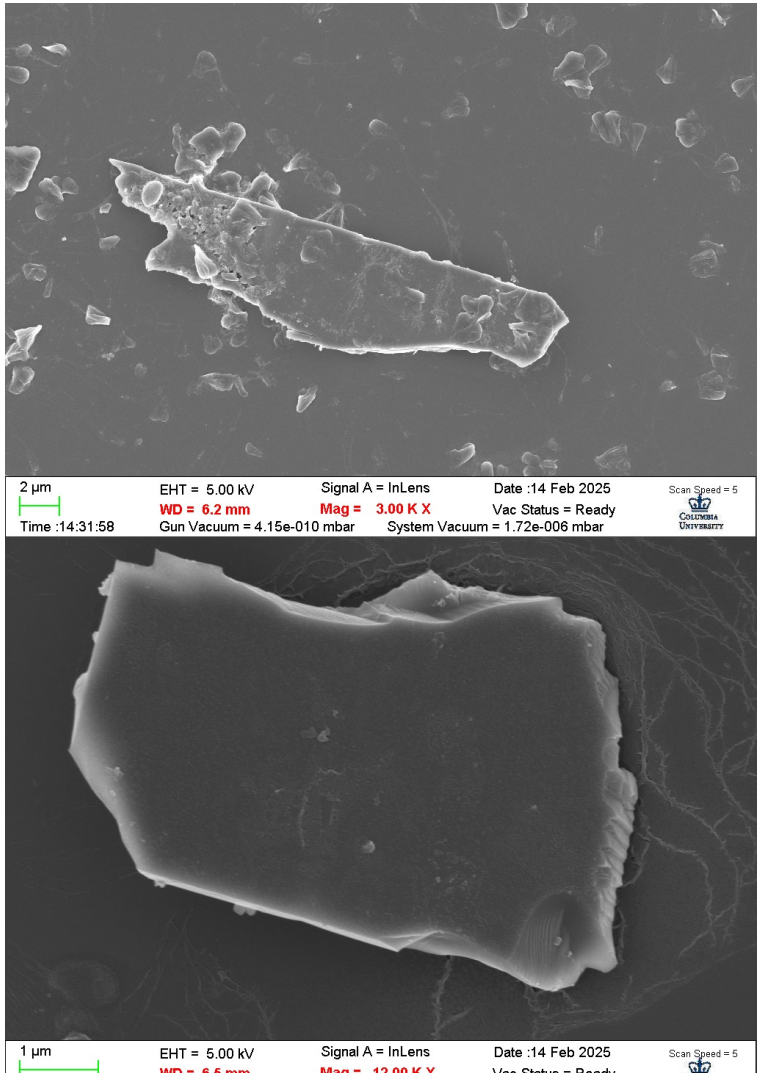
PET Hydrolysis



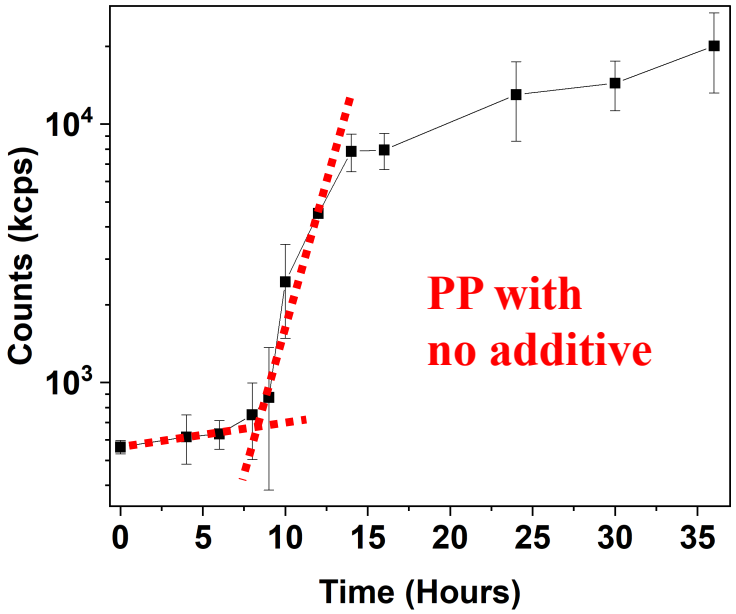
$$K_2S_2O_8 + 2H_2O \rightarrow K_2SO_4 + H_2SO_4 + 2[OH]^{\cdot -}$$

Nylon 6 + 2M HCl

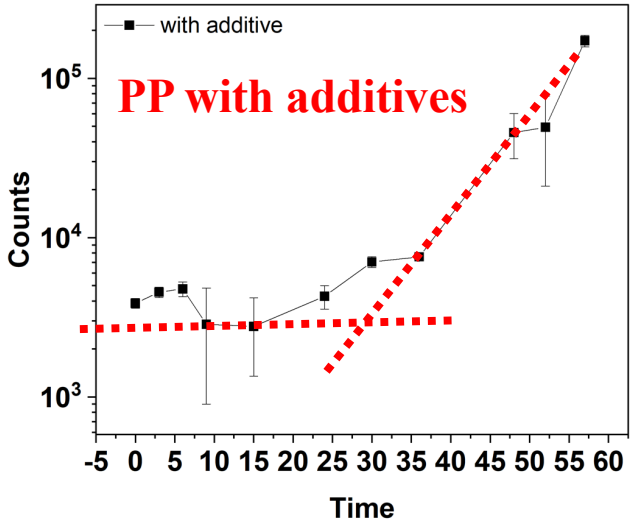




Role of Additives



Induction time reduced by
almost 1/3 in additive-free sample

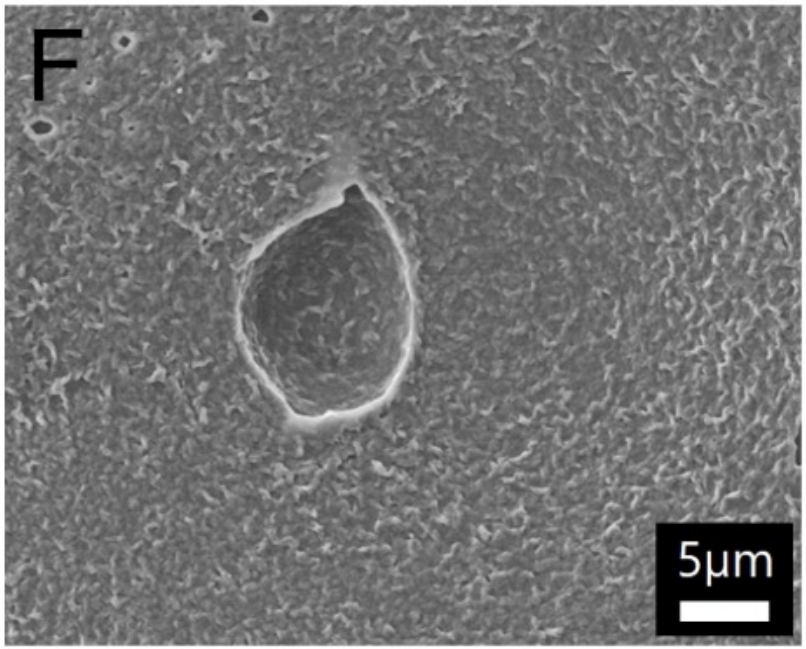


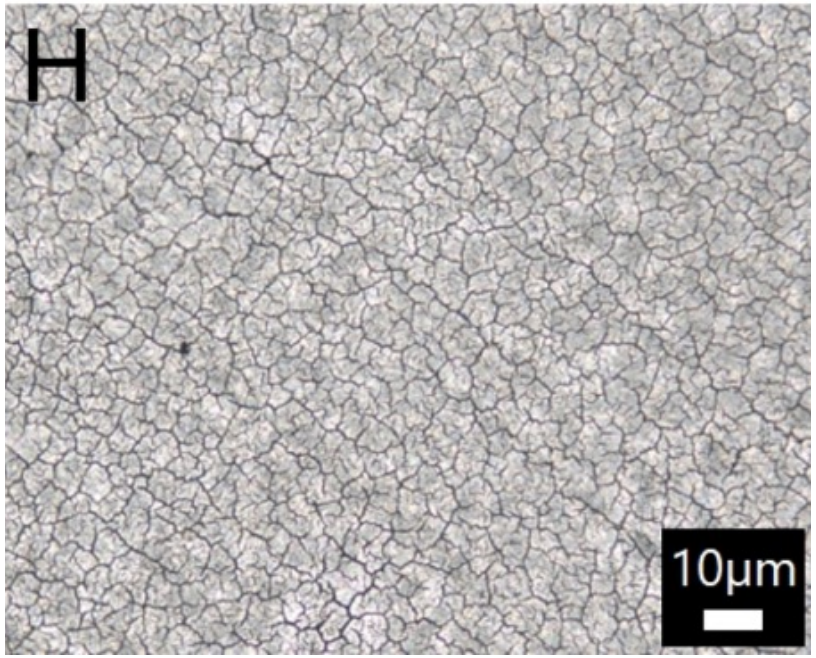
Additives

(i) **Stabilizers/anti-oxidants– affect fragmentation**

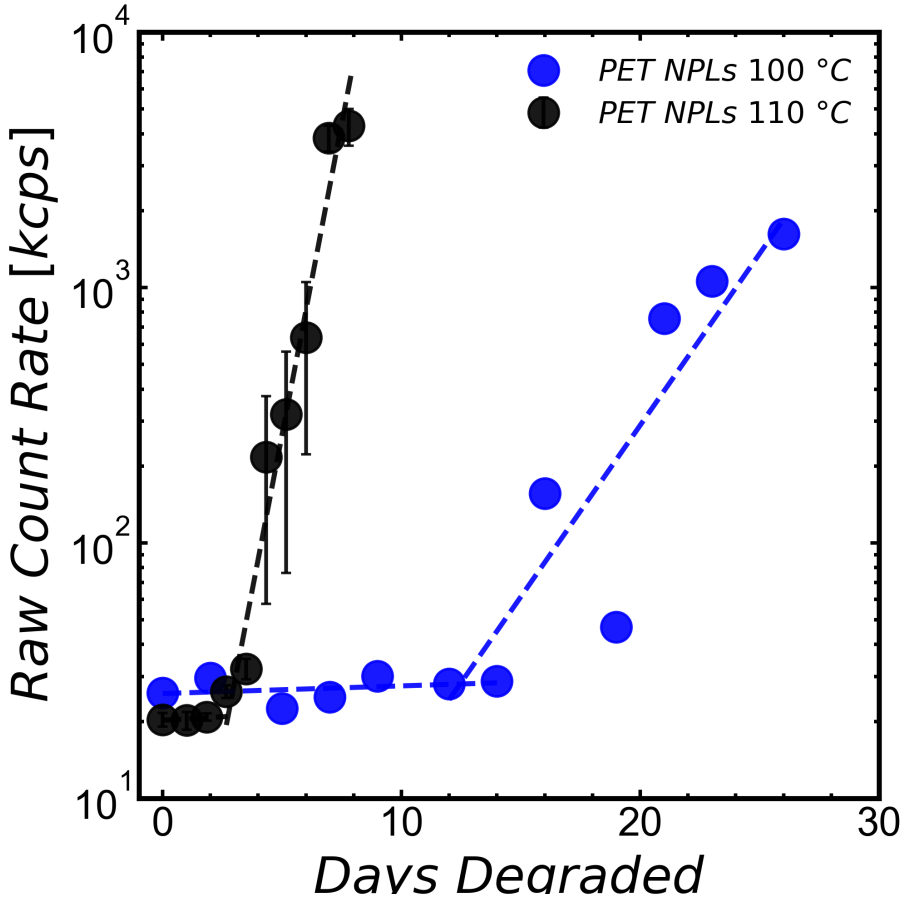
Surface Images

PET **iPP**

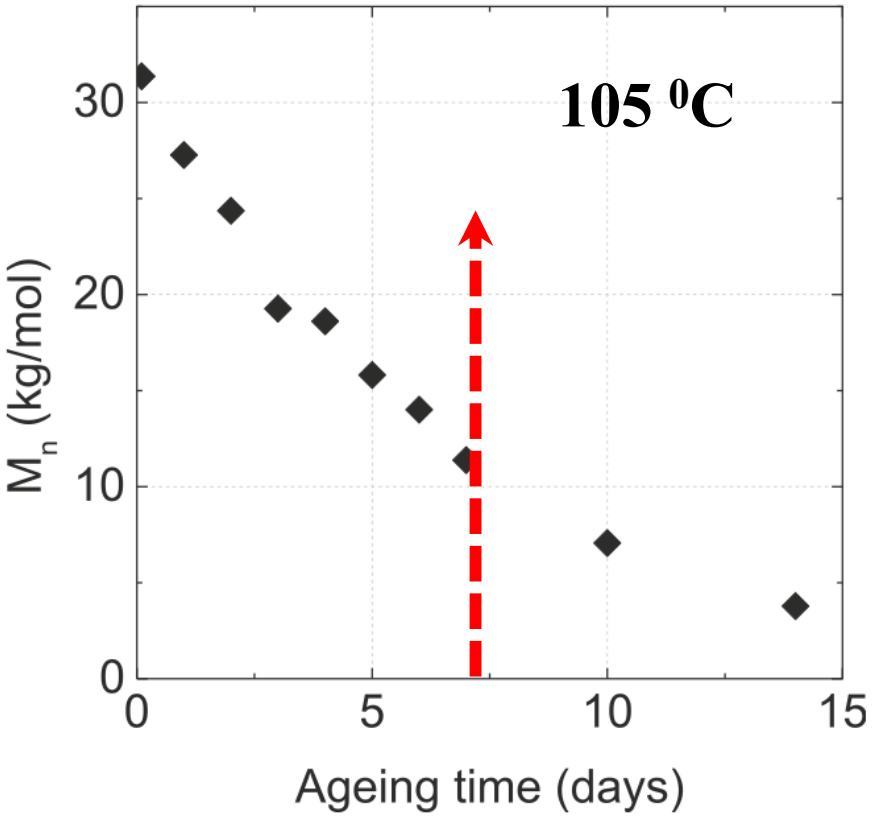




Temperature Dependence (PET)

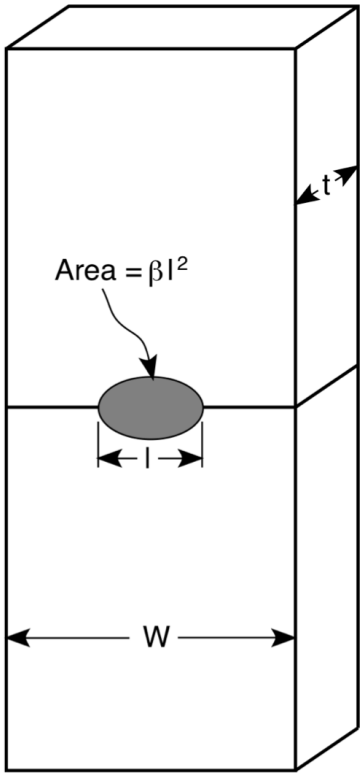


$M_e \sim 3.5$Kg/mol

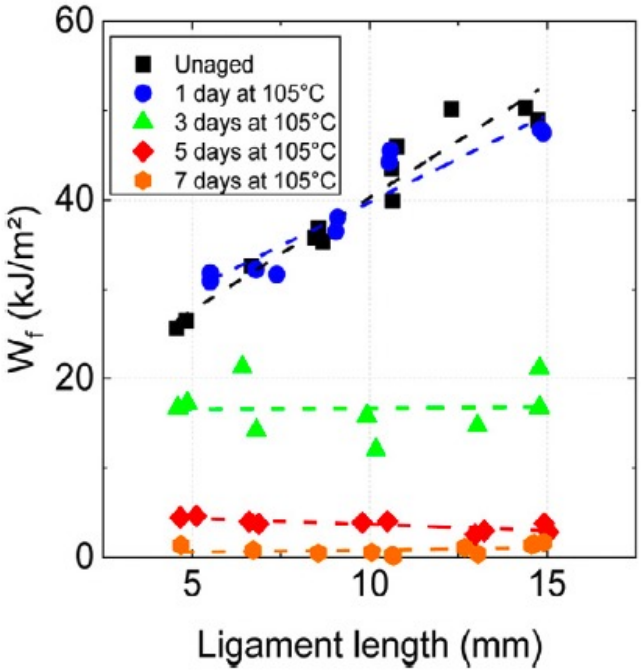


Fracture Mechanics

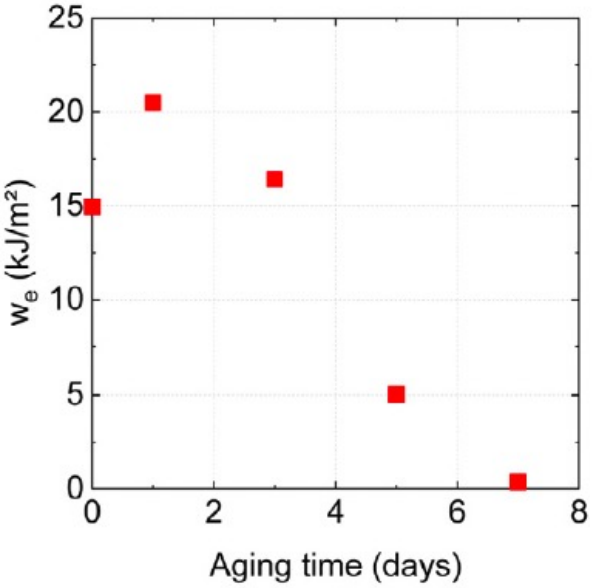
$$w_{total} = w_e lt + \beta w_p l^2 t$$

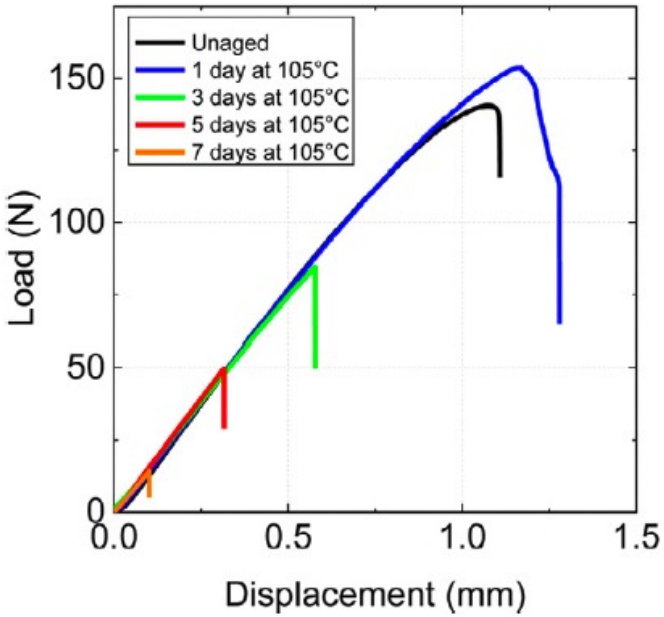


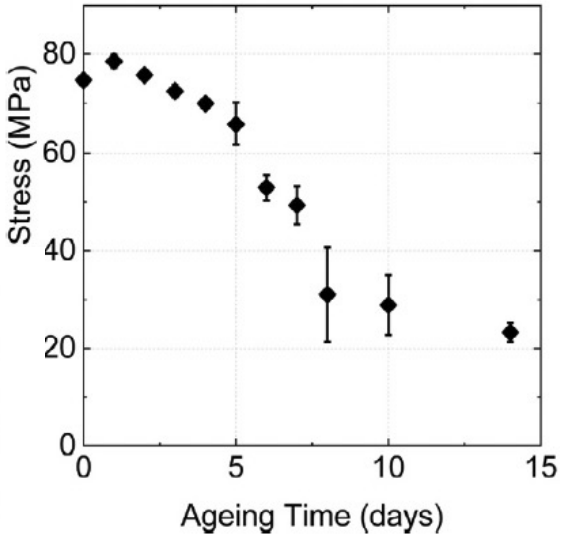
$$w_f = \frac{w_{total}}{lt} = w_e + \beta w_p l$$



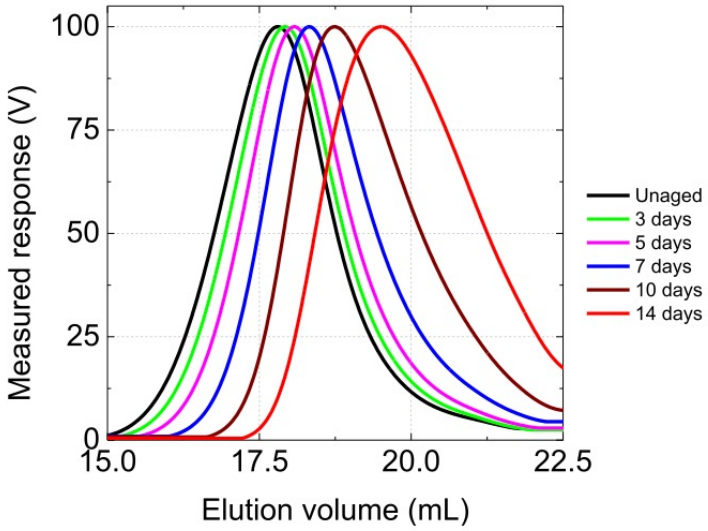
Fracture Mechanics: PET

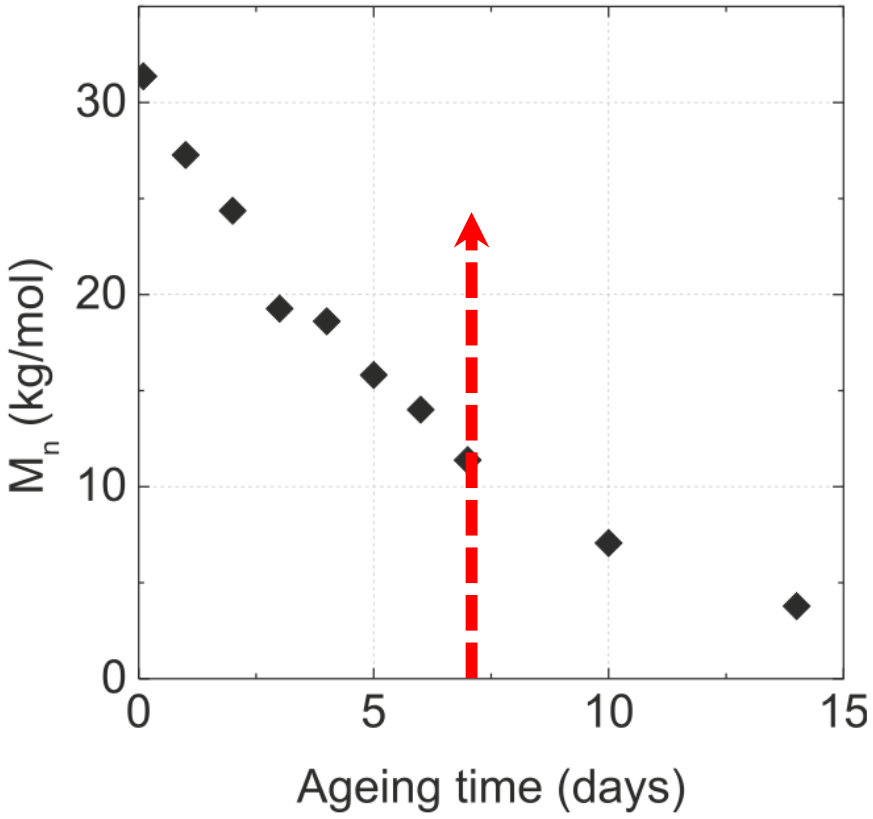






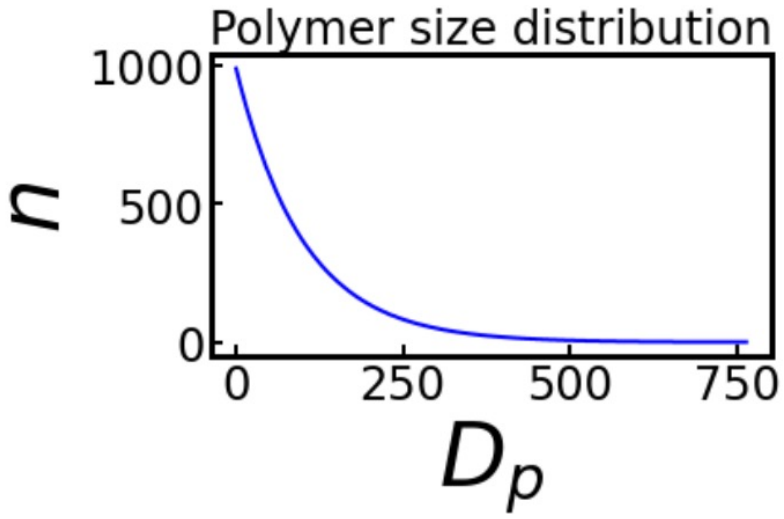
Random Chain Scission

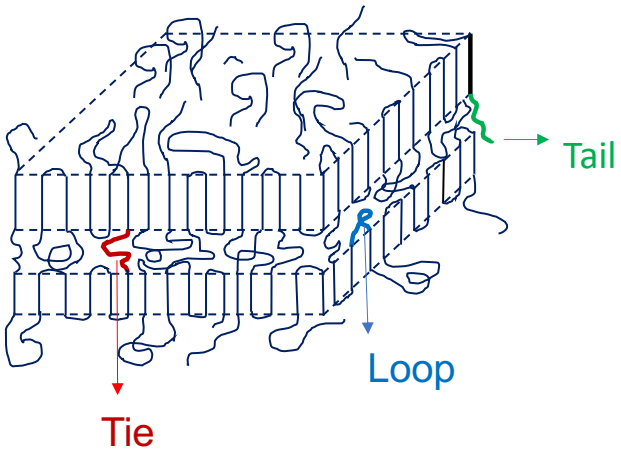


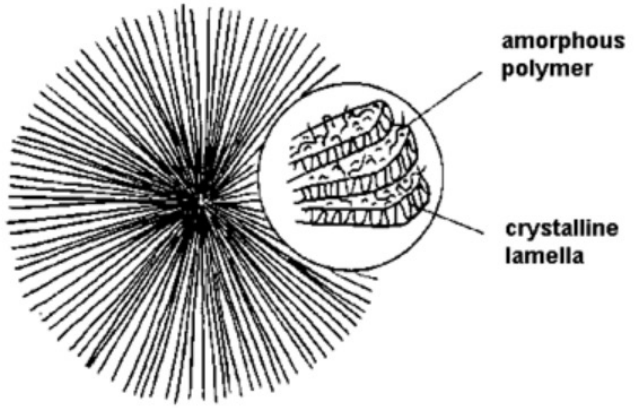


1.7 cuts per chain.
Each chain length ~ 105

ϕ~ 1.7/(105x0.73) ~ 0.02







Polymer Spherulite

www.doitpoms.ac.uk

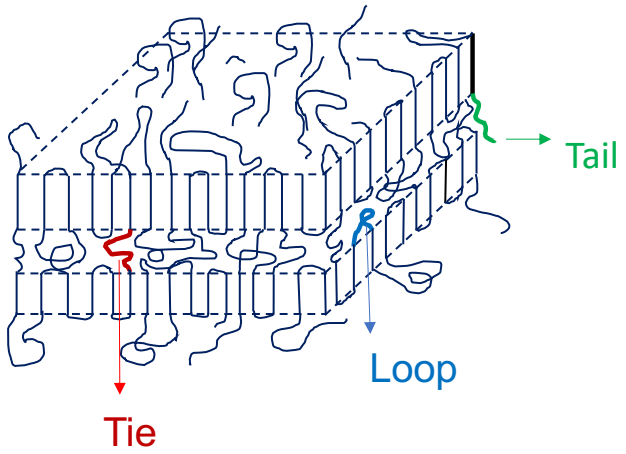
Decomposition reaction Kinetics:

Amorphous region alone

Failure creates nanoplastics

$$\frac{dN_{ties}}{dt} = -kN_{ties}l_{ties} \qquad \frac{dN_{mono}}{dt} = -kN_{mono}$$

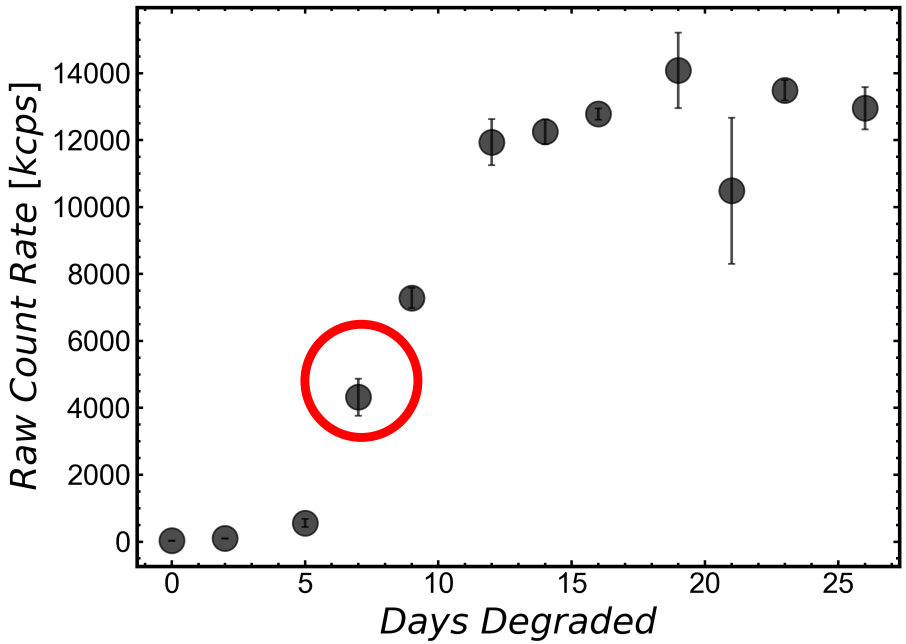
$$\frac{N_{ties}}{N_{ties,0}} \approx e^{-\phi l_{ties}}$$



$$l_{ties} \sim 15 \Longrightarrow \frac{N_{ties}}{N_{ties,0}} \sim 0.5$$

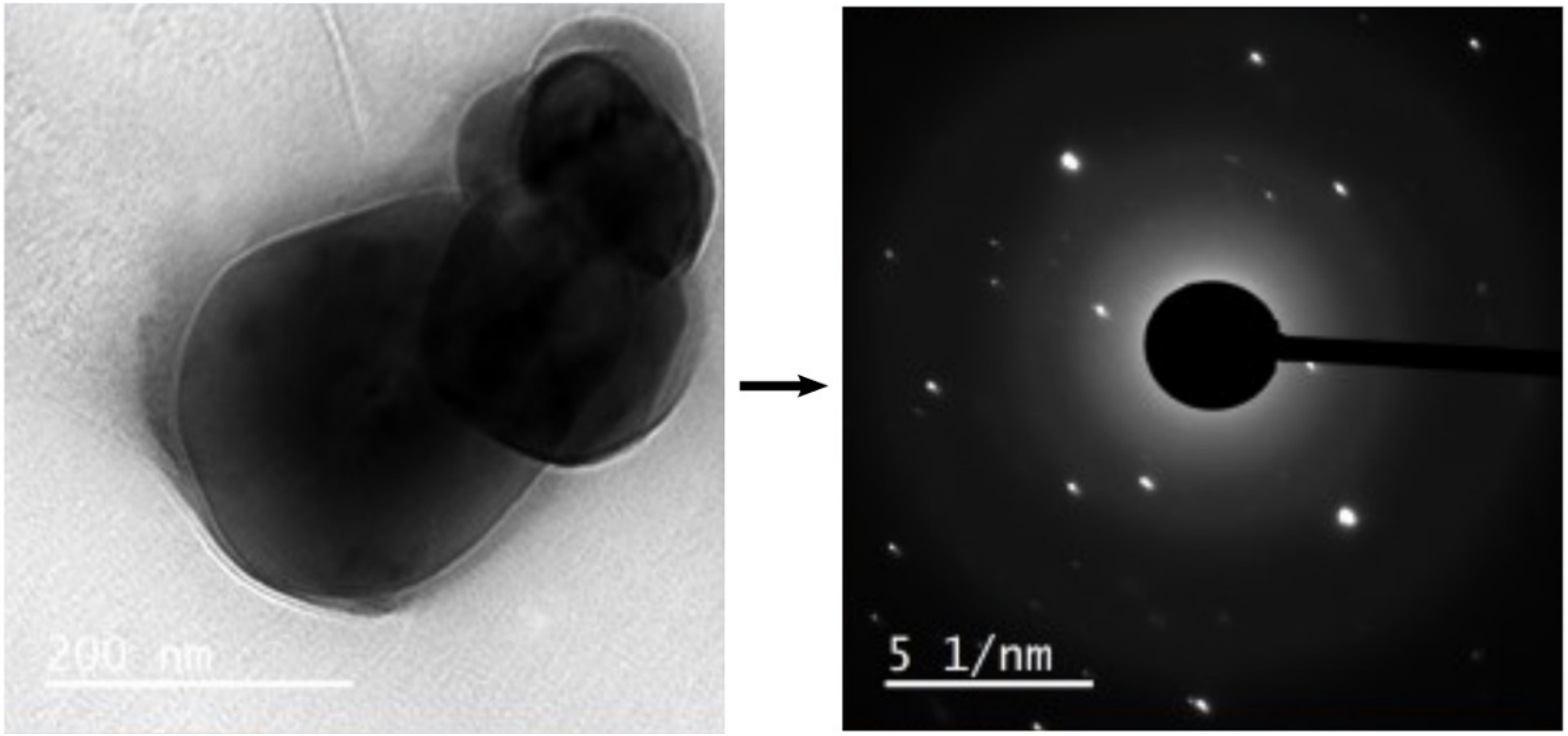
Separate NPL creation from continued degradation

- PET Film +Water 110 C
- After 7 days remove film
- 12 days further degradation



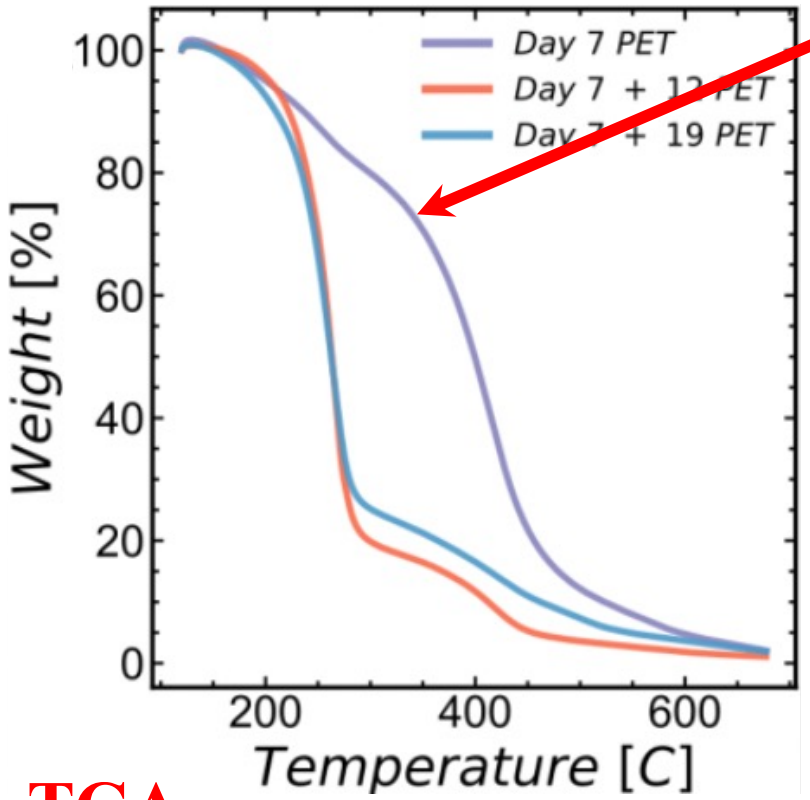
Only the crystals survive

PET glycolysis

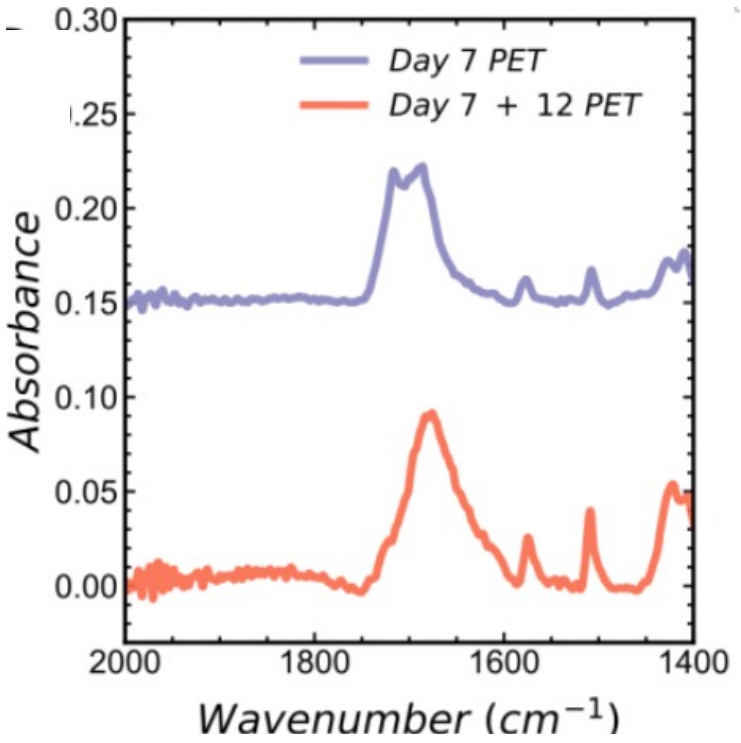


PET – continued hydrolysis

$\phi \sim 0.26$

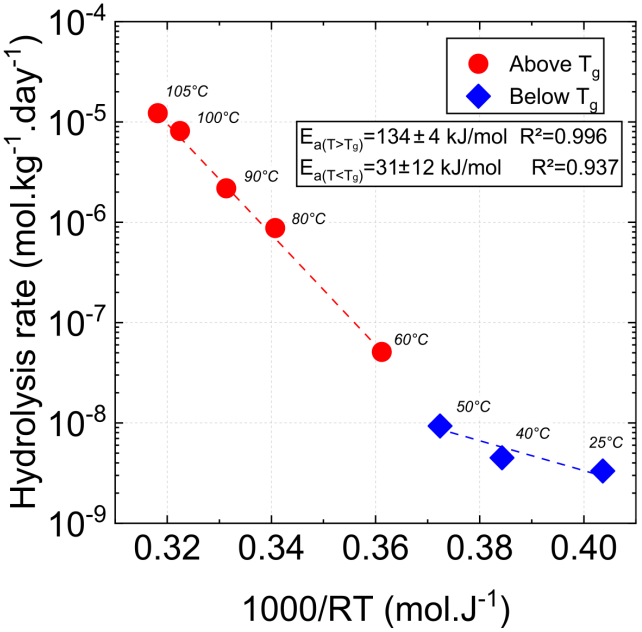


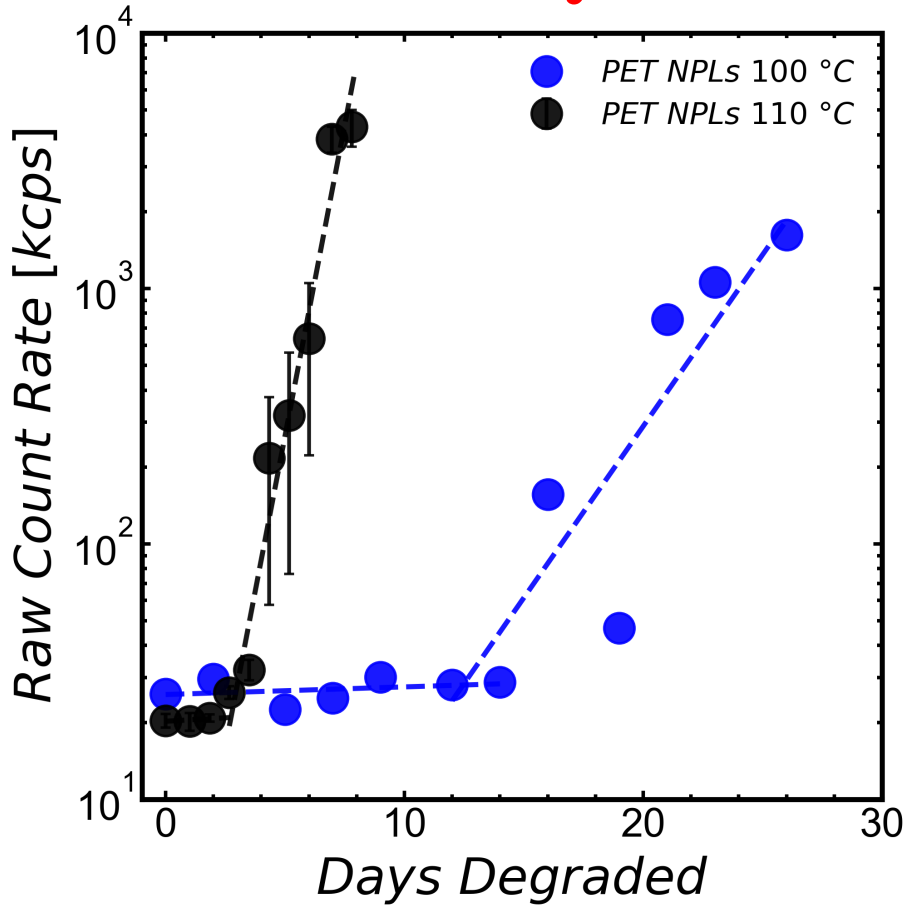
TGA



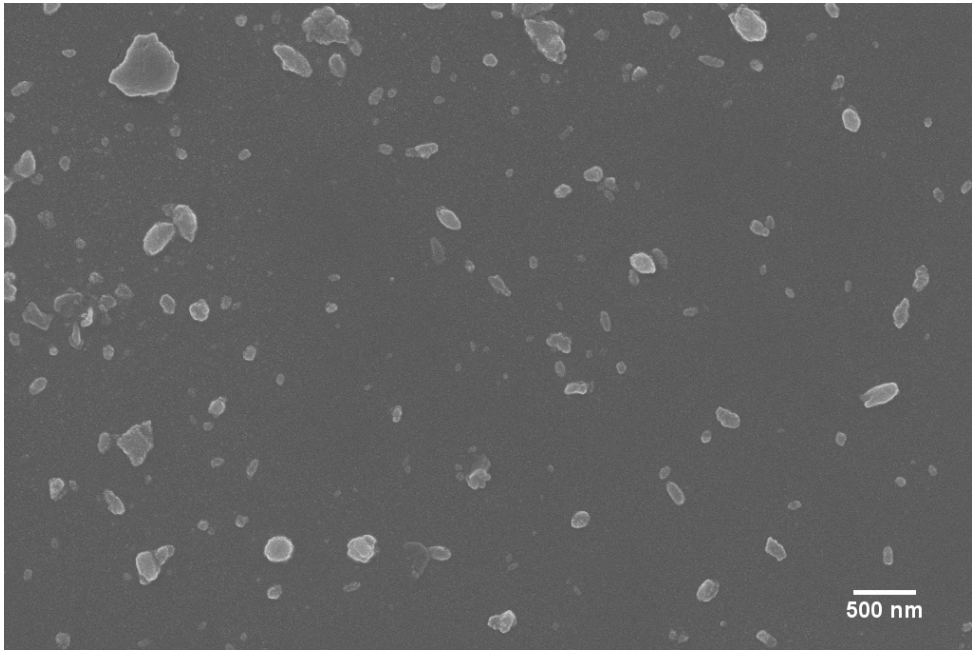
FTIR

Hydrolytic PET Degradation - 50-100 years !



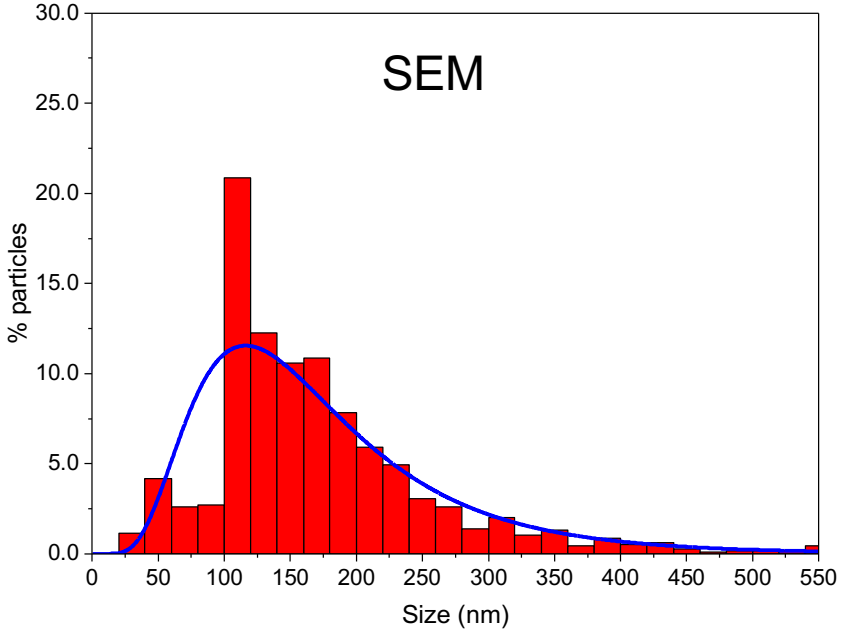


Mechanical fragmentation of plastics

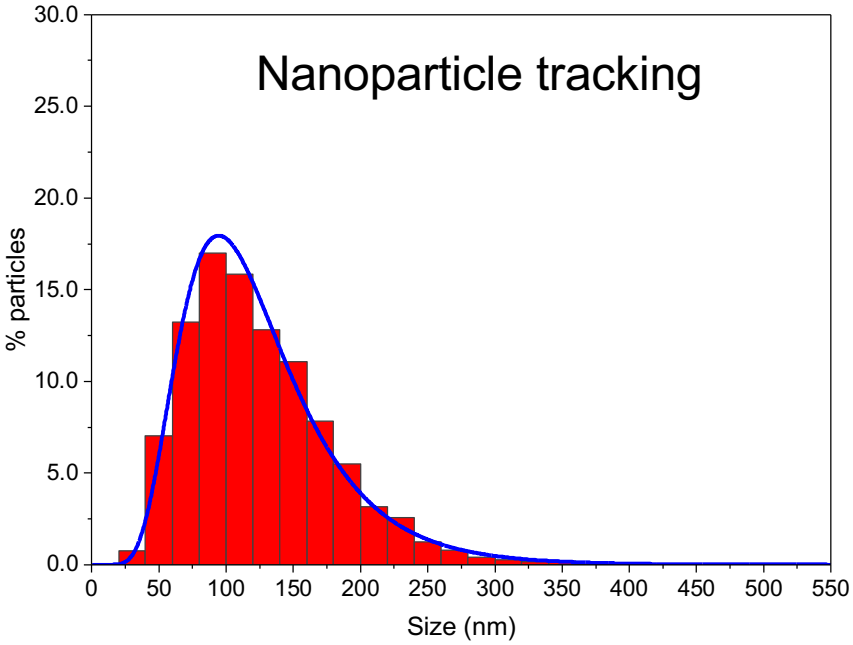


Particle distribution

PET – 7 days

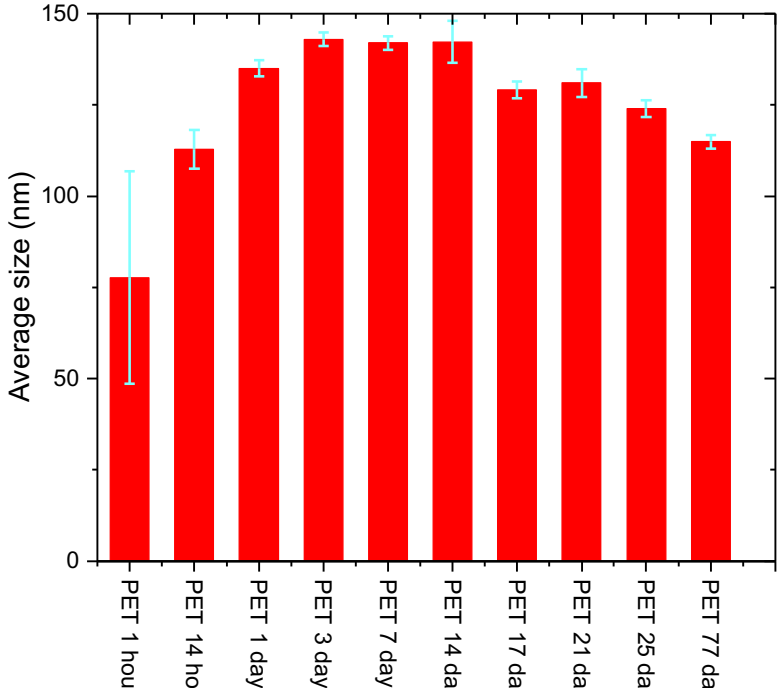


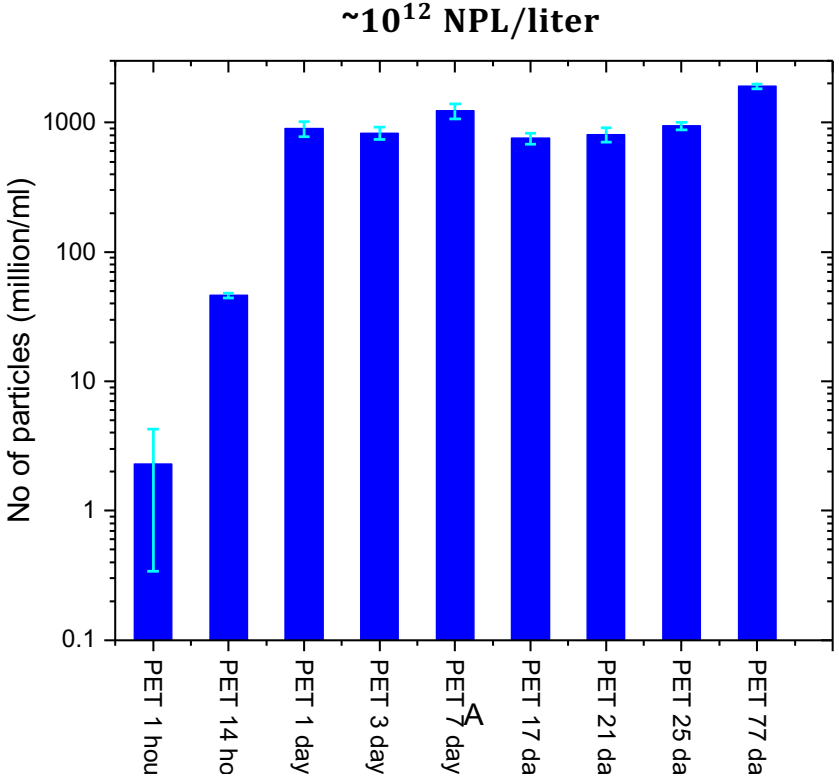
Average size from SEM: 151 nm



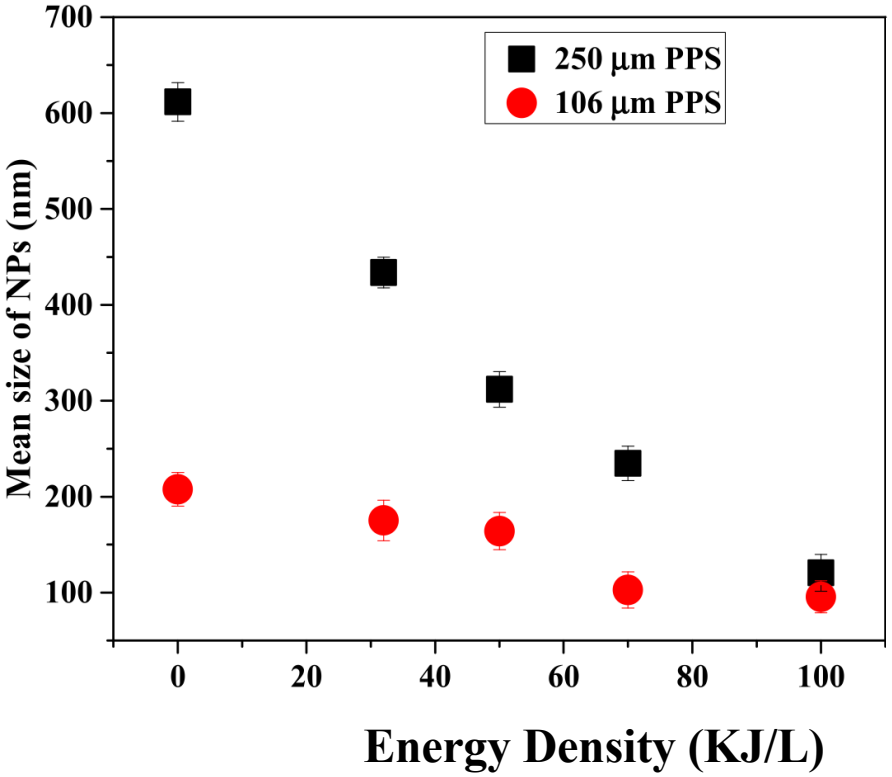
Average size from nanoparticle tracking : 124 nm

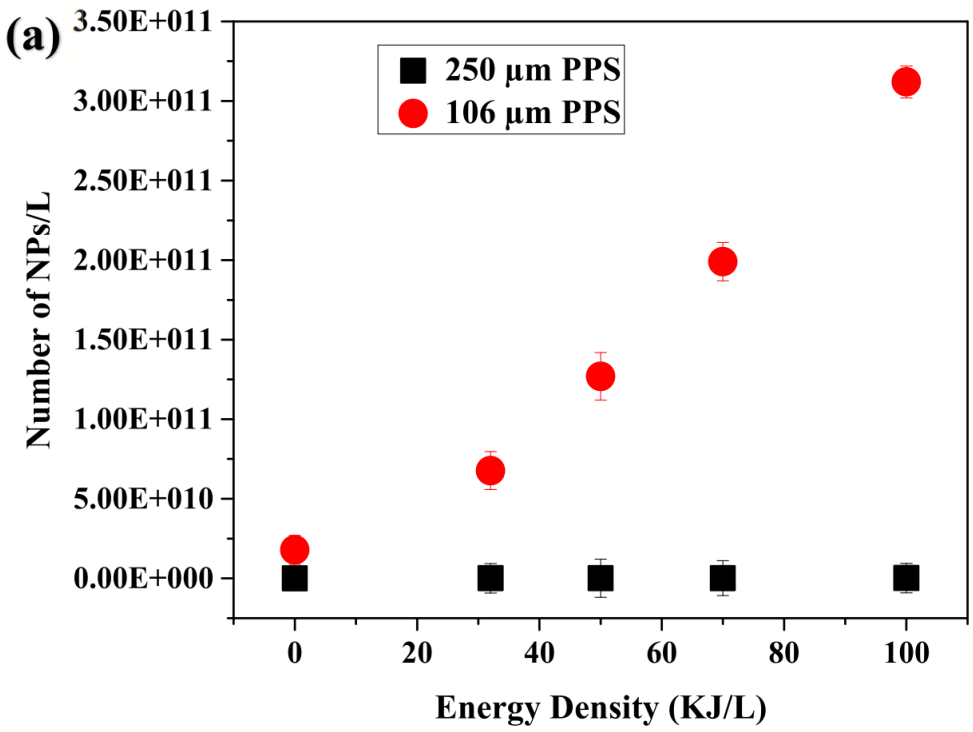
PET nanoplastic size, number vs time





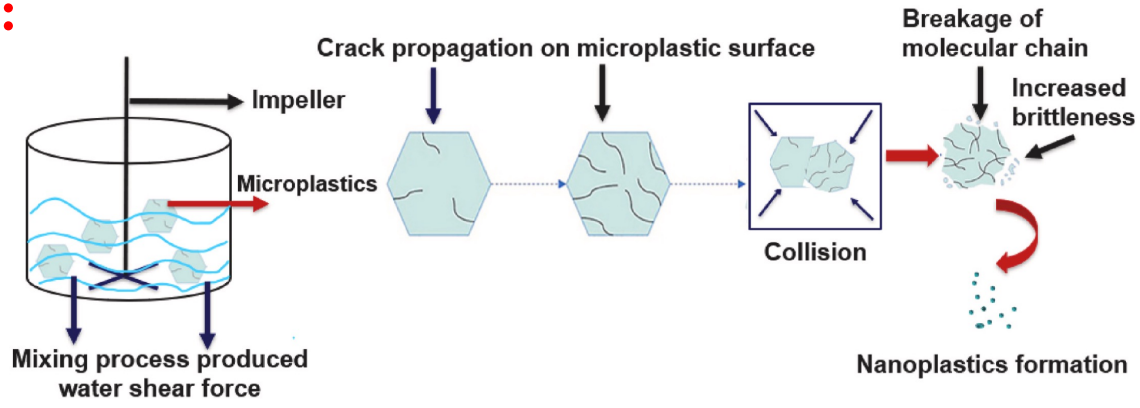
Literature Data

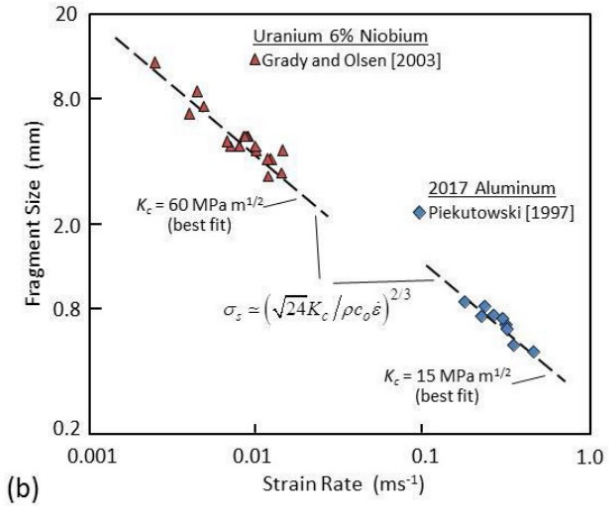


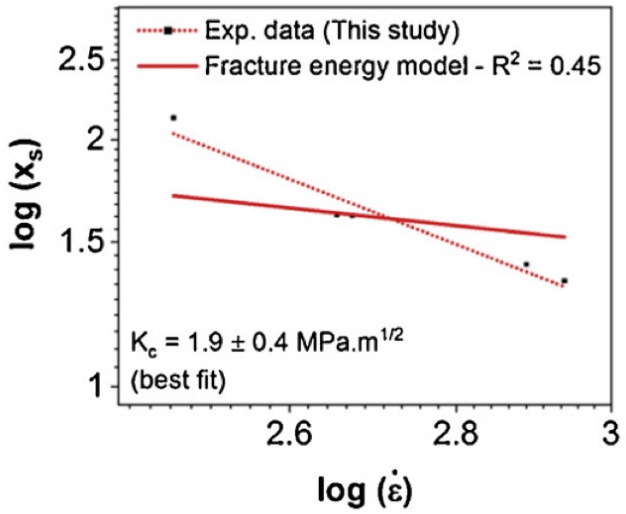


Current "Understanding": Fracture Energy Model

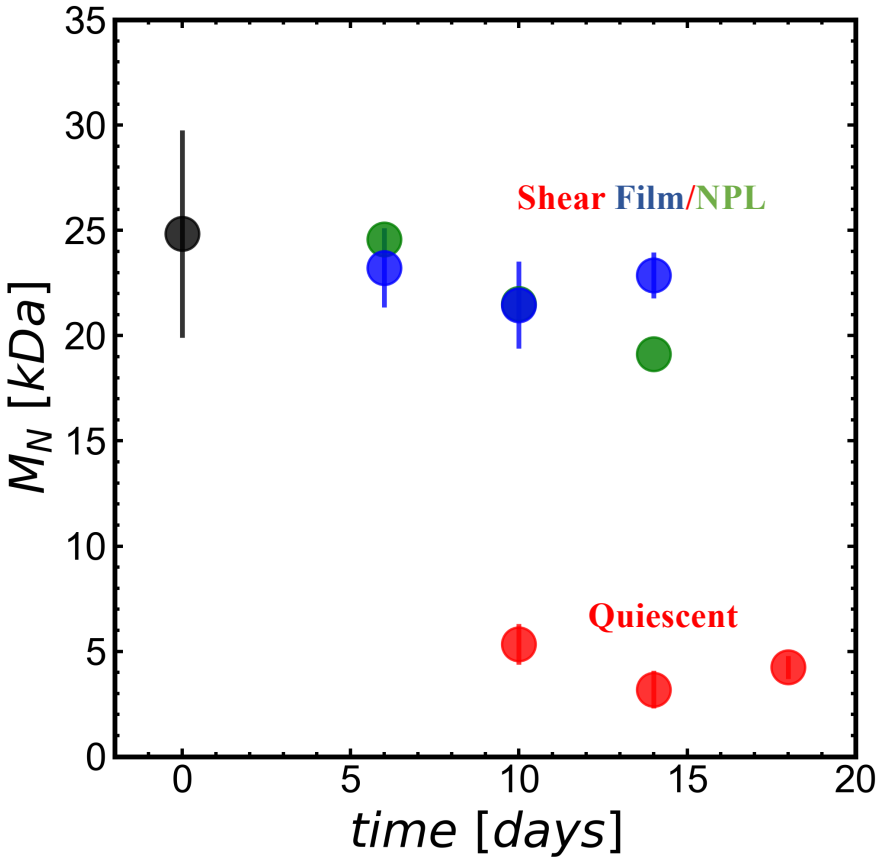
$$x_s = \left(\frac{K_c\sqrt{24}}{\rho c_0 \dot{\varepsilon}}\right)^{\frac{2}{3}}$$

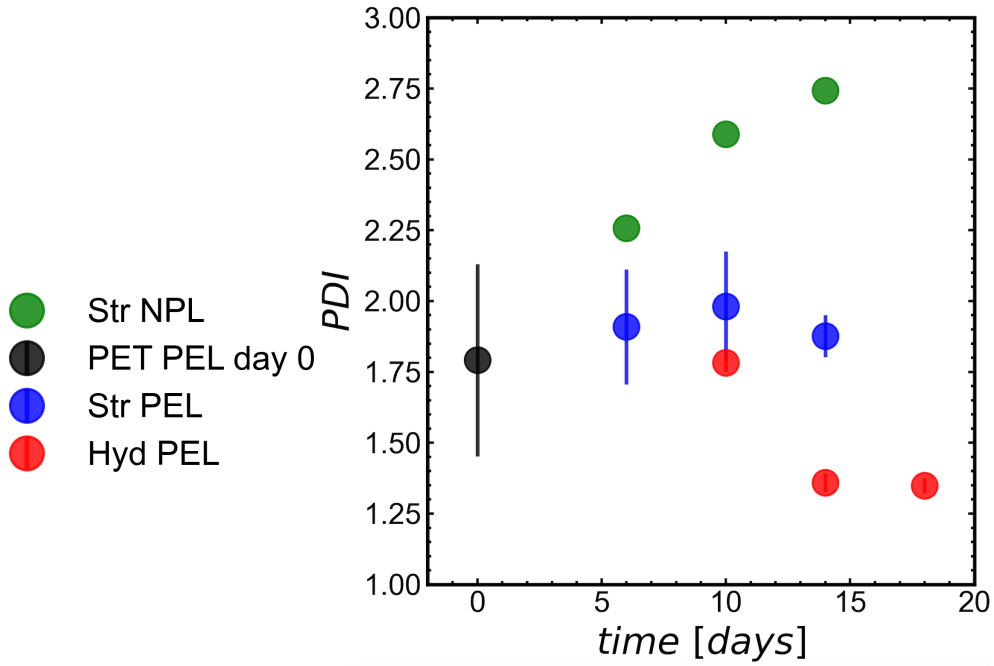






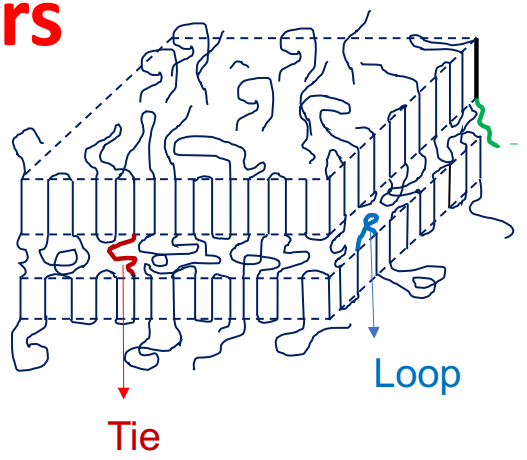
NPL creation under shear





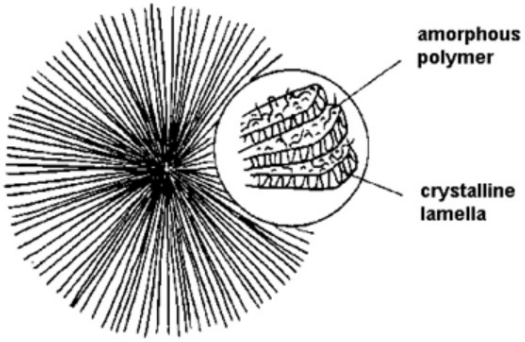
Very few chain breaks under shear
Mechanism is very different

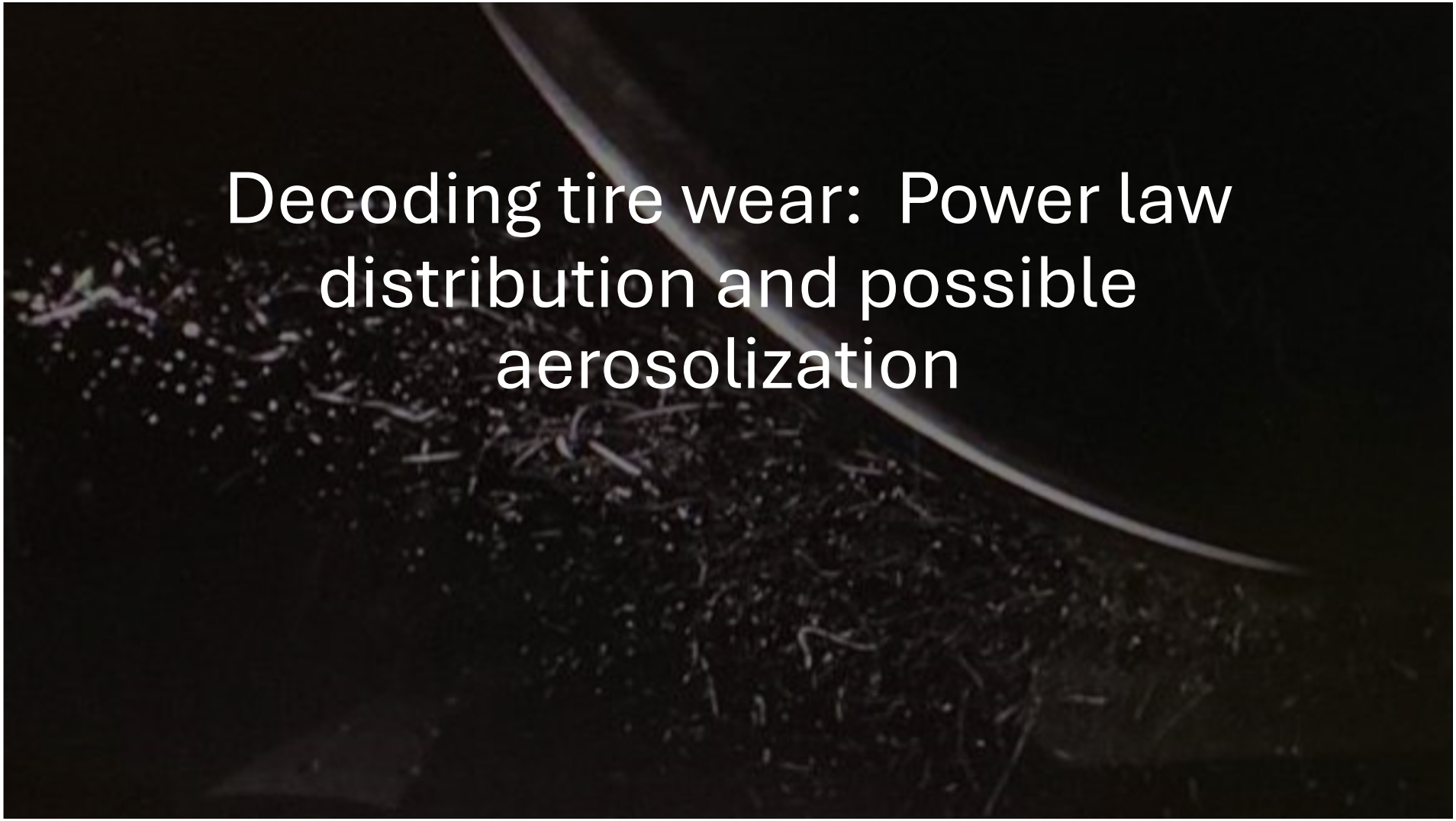
Fate of All Semicrystalline Polymers

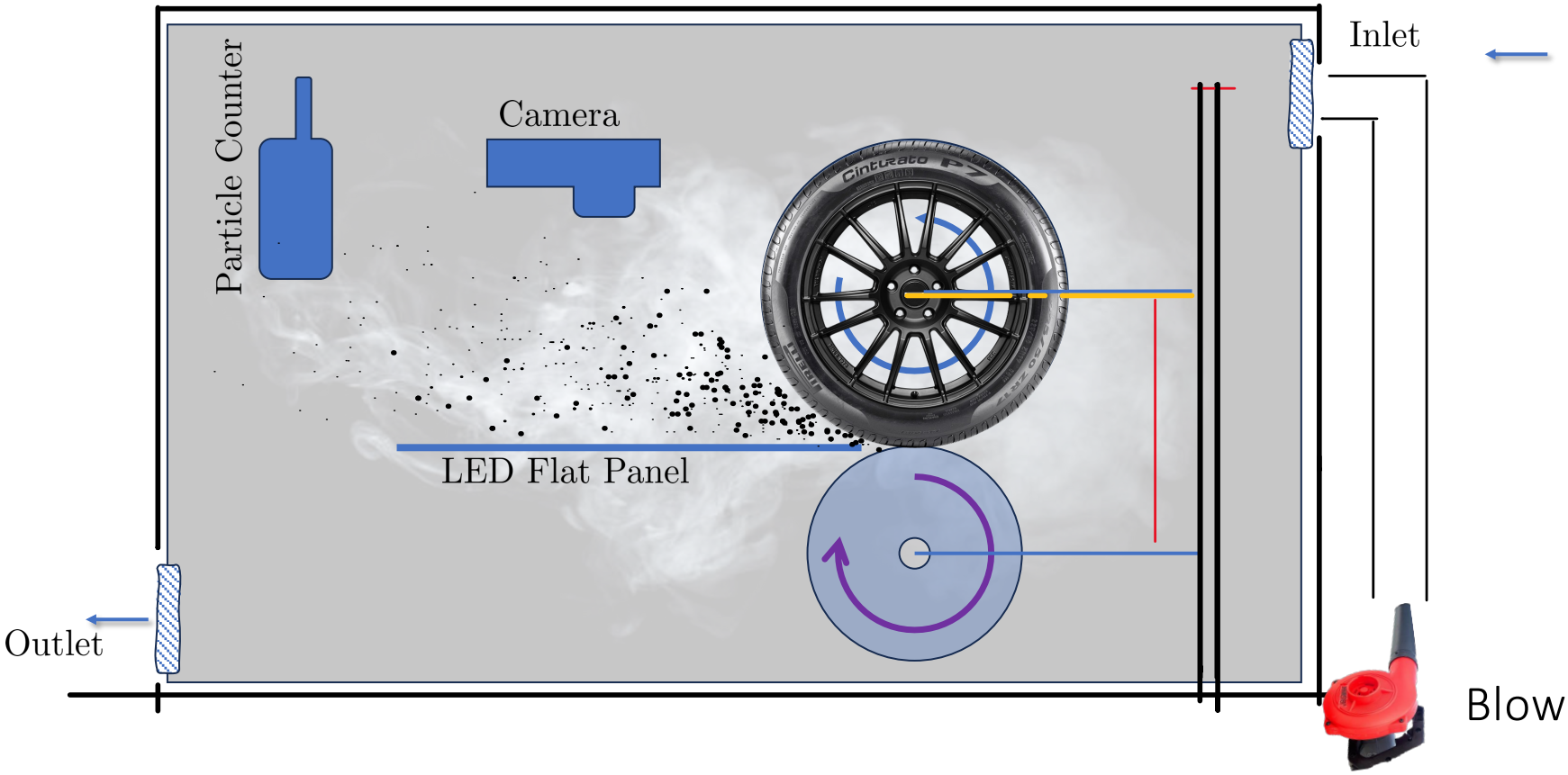


MNPL Formation
successive fragmentation
(Quiescent vs Shear)

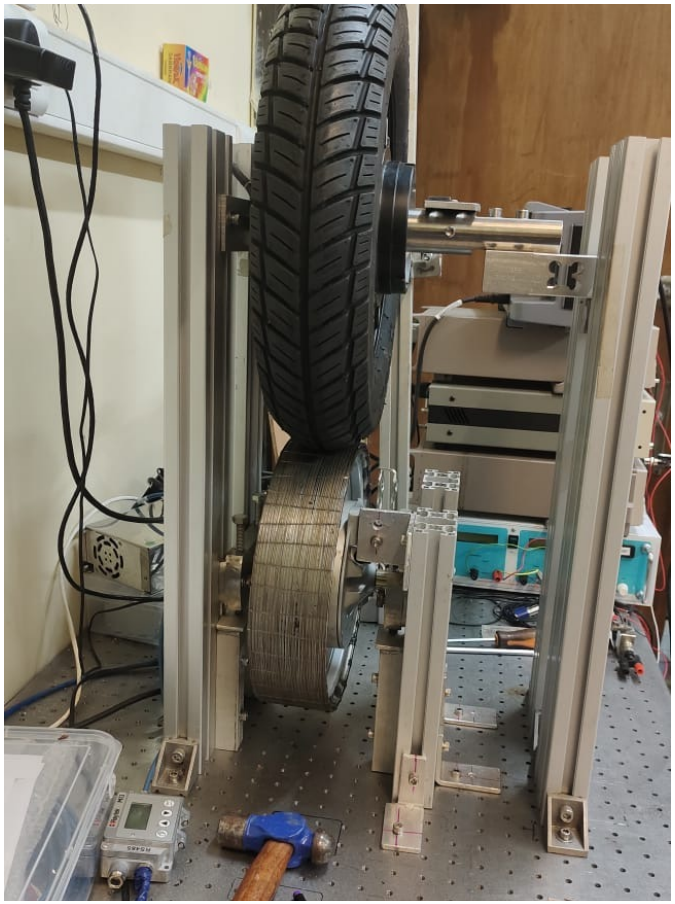
Crystals persist in nature




Decoding tire wear: Power law distribution and possible aerosolization



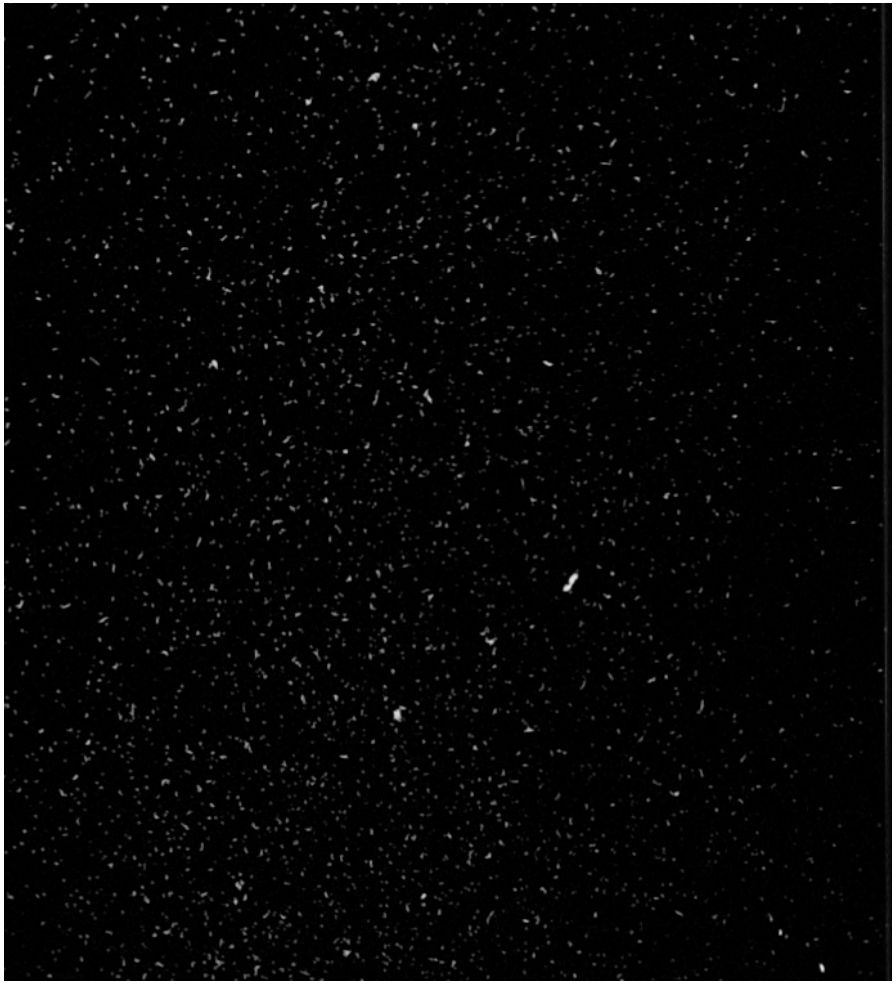
Blower with Hepa filter ,15 litre, 1400watt 16 KPa



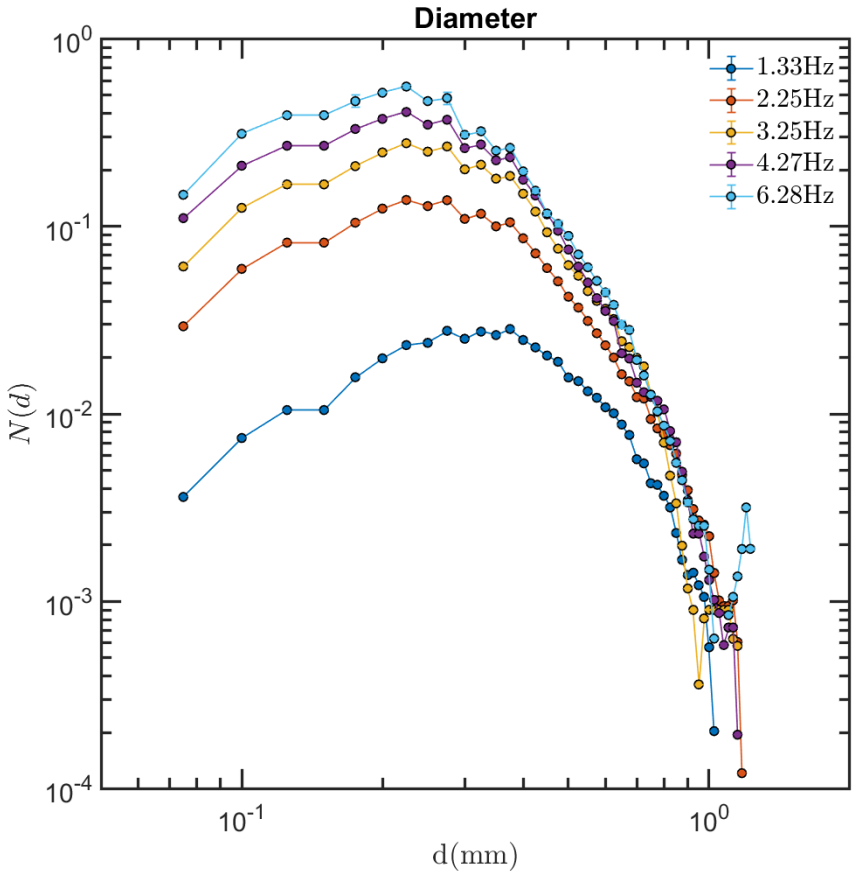
Camera-based particle size measurement.

Before

After

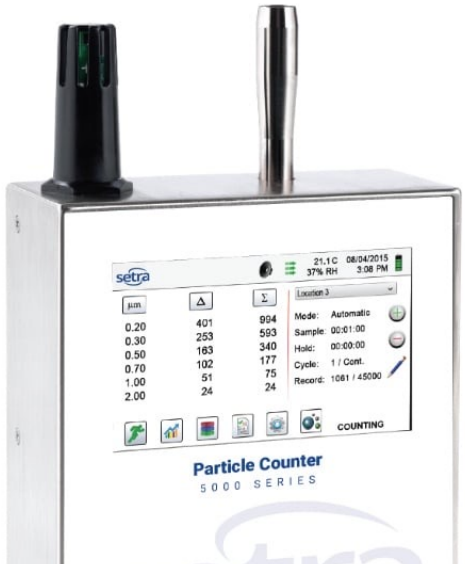


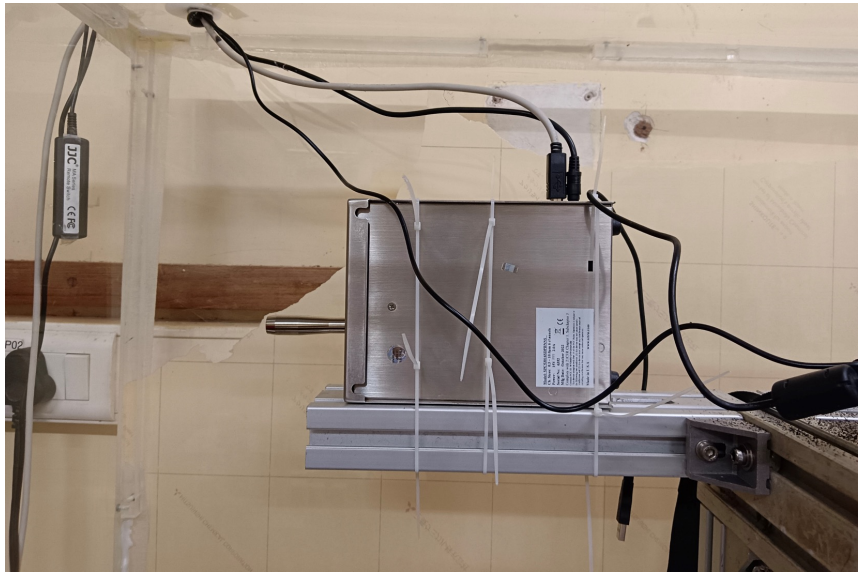
Subtract


Diameter
1.33Hz
2.25Hz
3.25Hz
4.27Hz
6.28Hz
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
$N(d)$
10^{-1}
10^0
d(mm)

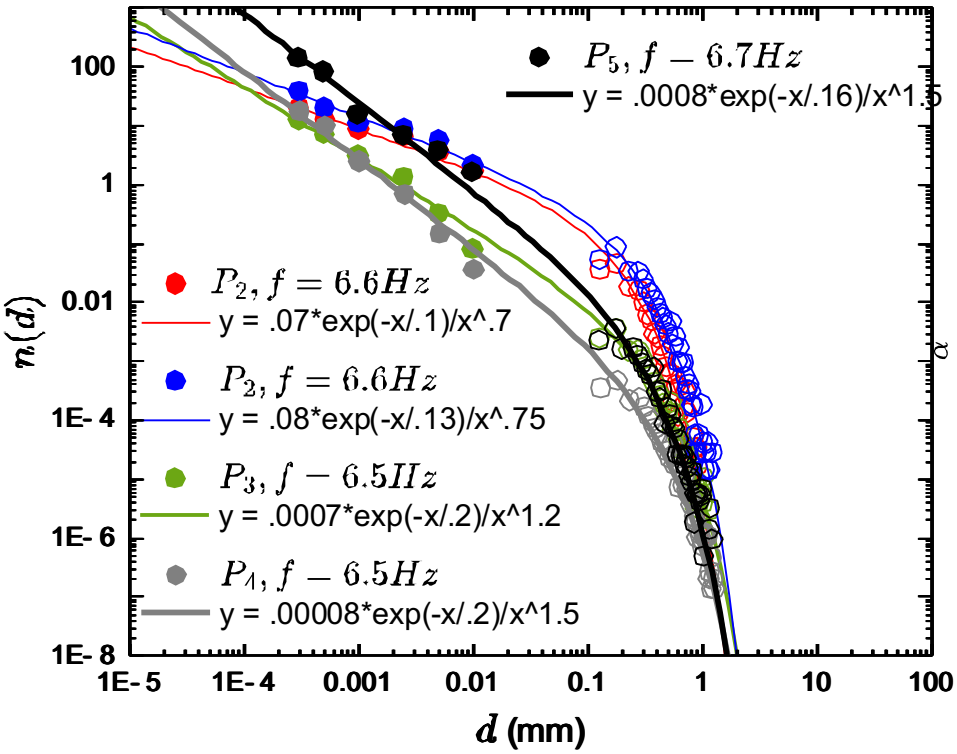
Particle counter

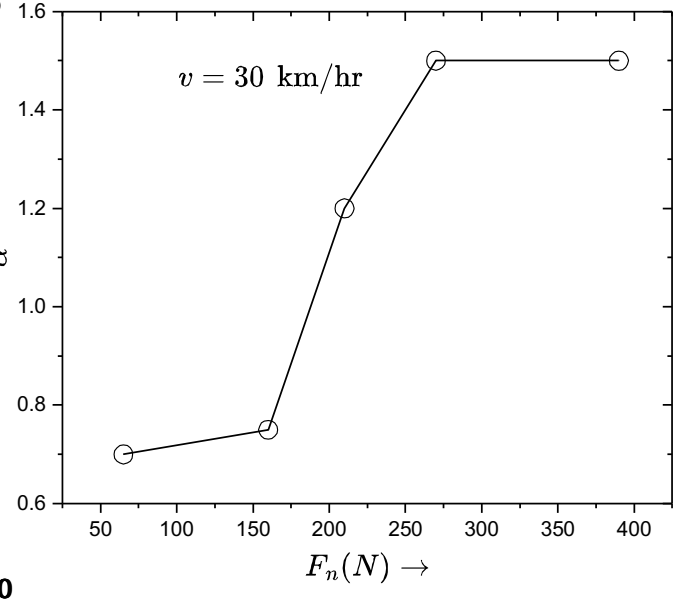
- Size channels: 0.3, 0.5, 1.0, 2.5, 5.0, 10.0 µm
- Flow rate of 2.8 L/min



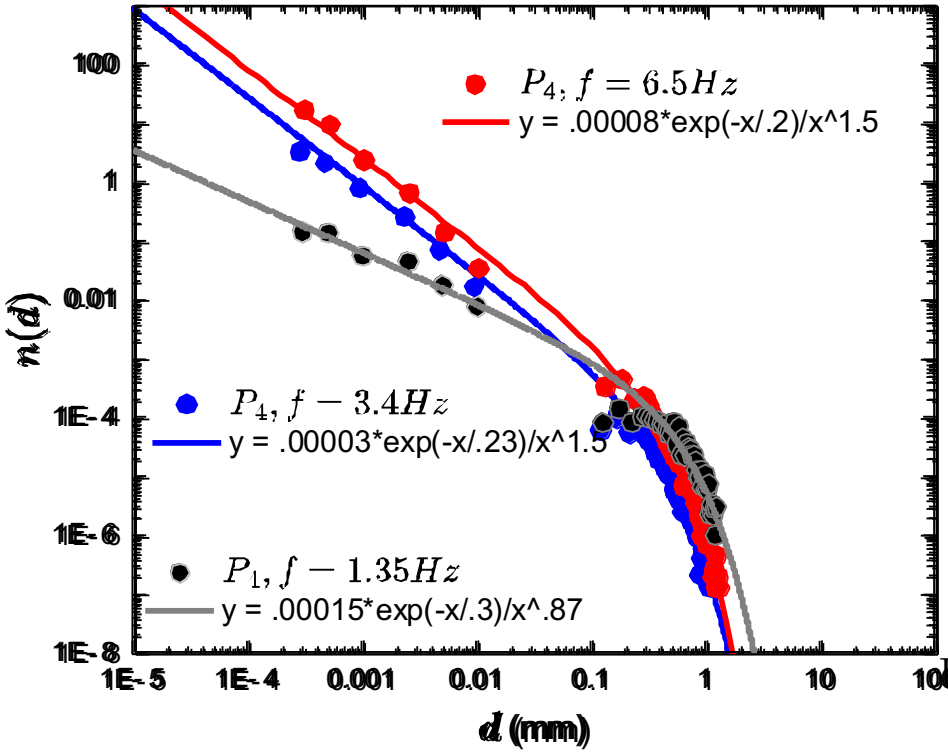


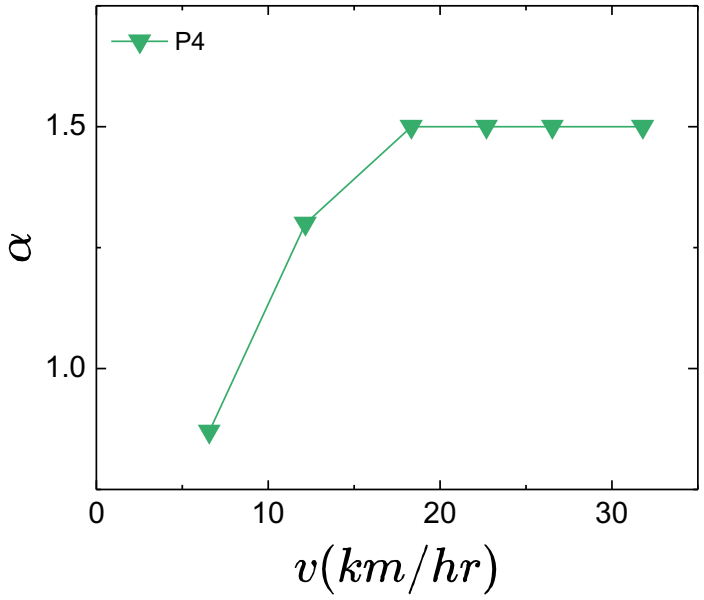
$$n(d|v) \sim \frac{e^{-d/d_0}}{d^{\alpha}}$$





$$n(d|v) \sim \frac{e^{-d/d_0}}{d^{\alpha}}$$



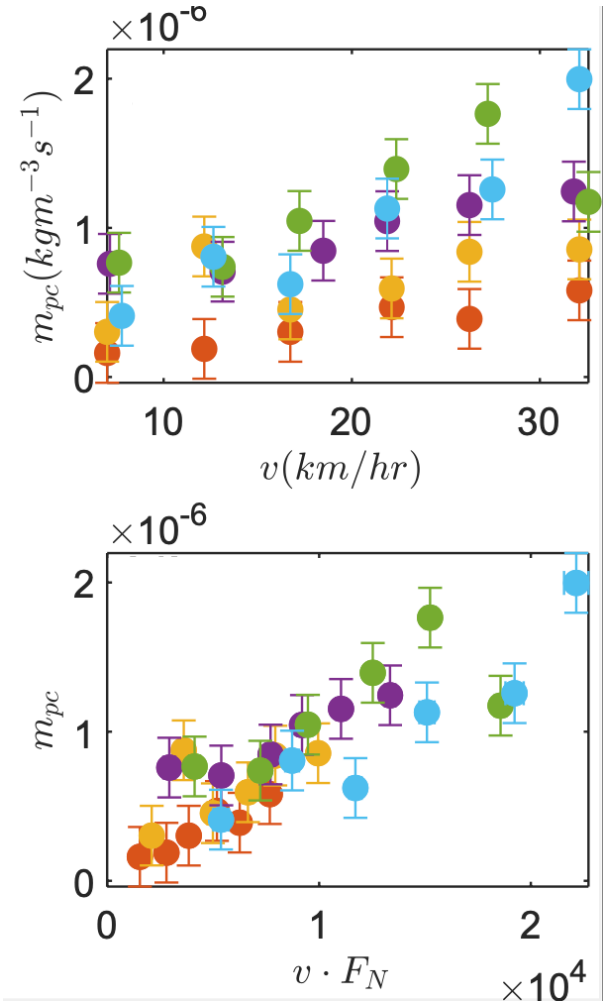


For constant F_N, increase in v increases α

Mass of Aerosolized Fraction

The **Archard wear equation** is a simple model used to describe sliding wear and is based on the theory of asperity contact. The Archard equation was developed much later than **Reye's hypothesis** [it] (sometimes also known as **energy dissipative hypothesis**), though both came to the same physical conclusions, that the volume of the removed debris due to wear is proportional to the work done by friction forces. Theodor Reye's model[1][2] became popular in Europe and it is still taught in university courses of

$$Q = \frac{KWL}{H}$$

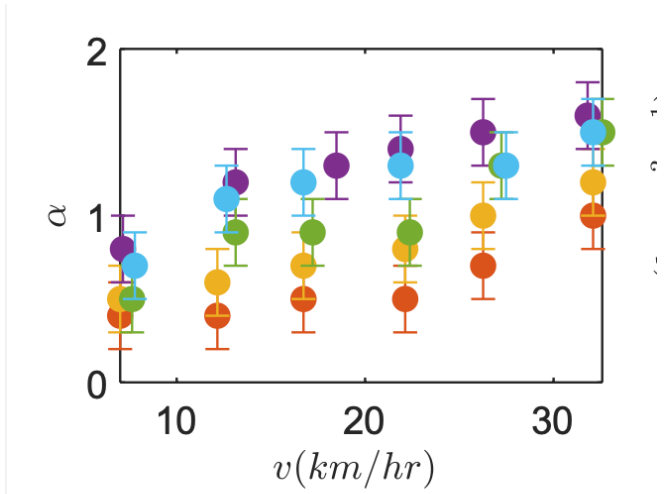


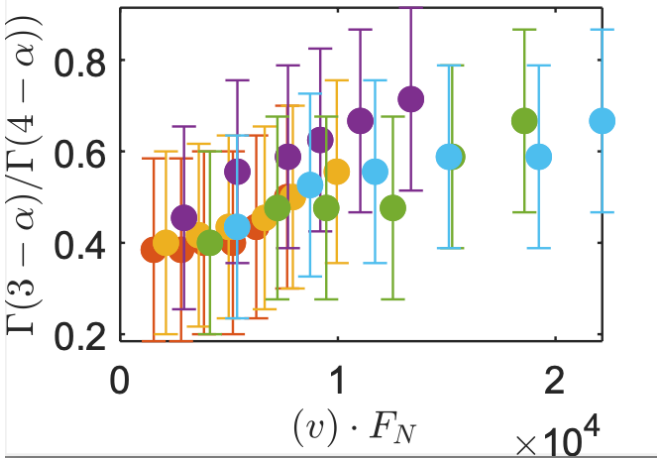
Power Law of Aerosolized Fraction

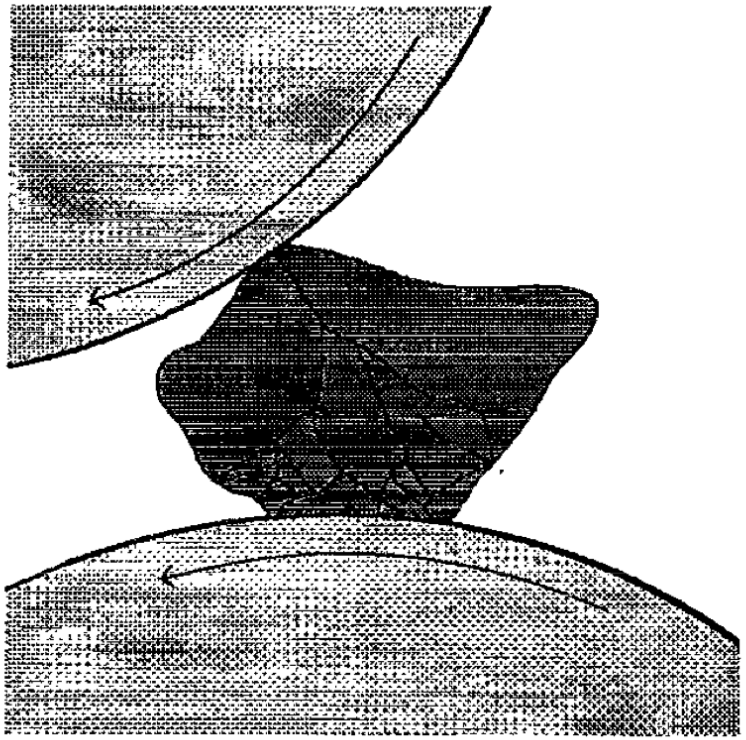
Griffith

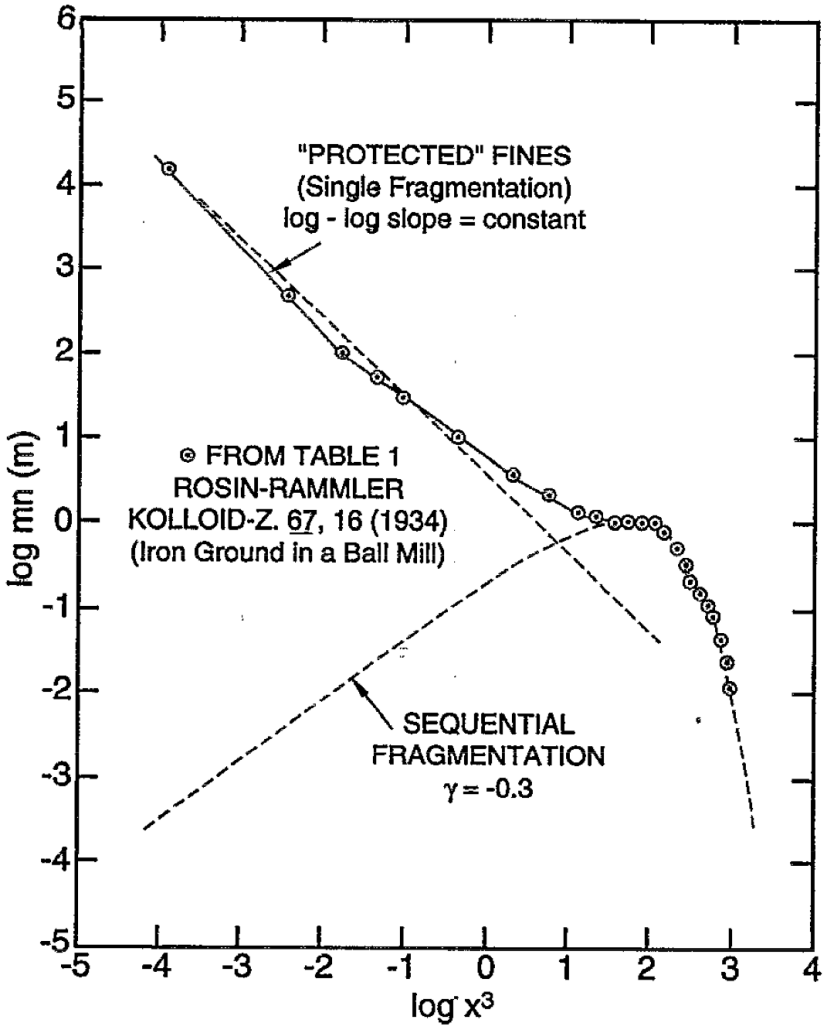
Energy Input creates surfaces
and breaks bonds

$$\frac{\Gamma(3-\alpha)}{\Gamma(4-\alpha)} \text{ is constant}$$








"PROTECTED" FINES
(Single Fragmentation)
log - log slope = constant
⊙ FROM TABLE 1
ROSIN-RAMMLER
KOLLOID-Z. 67, 16 (1934)
(Iron Ground in a Ball Mill)
SEQUENTIAL
FRAGMENTATION
γ = -0.3
log mn (m)
log x3
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
-5
-4
-3
-2
-1
0
1
2
3
4

Conclusion

- Plastics generated at small scales: advected by air.

- Both single and successive fragmentation occurs