Innovative **Materials**: Safety along the **Life** Cycle

Polymers and their toxicity to algae – lessons learned from a comparative study.

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Introduction

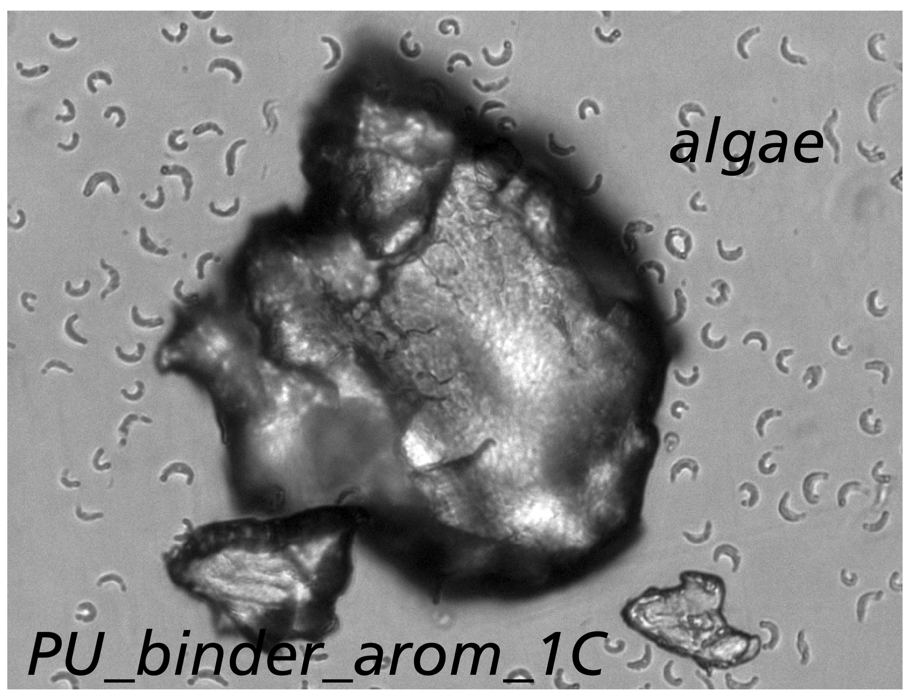
- Polymer particles are used in various applications, but can also be intermediates in advanced manufacturing (e.g. additive manufacturing) → heterogeneous group of chemicals.
- Ecotoxicity of nanomaterials has been intensively investigated, information on toxicity of larger particles including those consisting of solid, insoluble polymers is still limited.

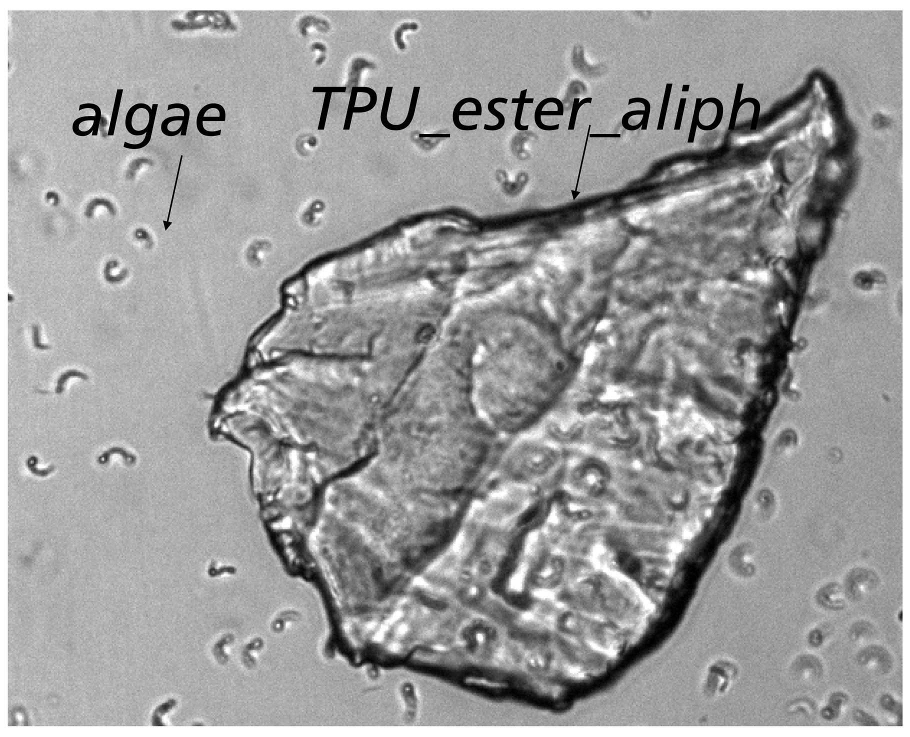
➔ Investigation of eight non-reactive polymers differing in their chemical identity, polymer backbone, aromaticity, crosslinking degree, size (0.3 –270 µm), surface area (0.03 – 15 m^2/g) and dispersibility regarding their ecotoxicity to algae (*Raphidocelis subcapitata*; length: 8 – 14 µm, ∅ 2 – 3 µm) in the growth test (OECD TG 201).

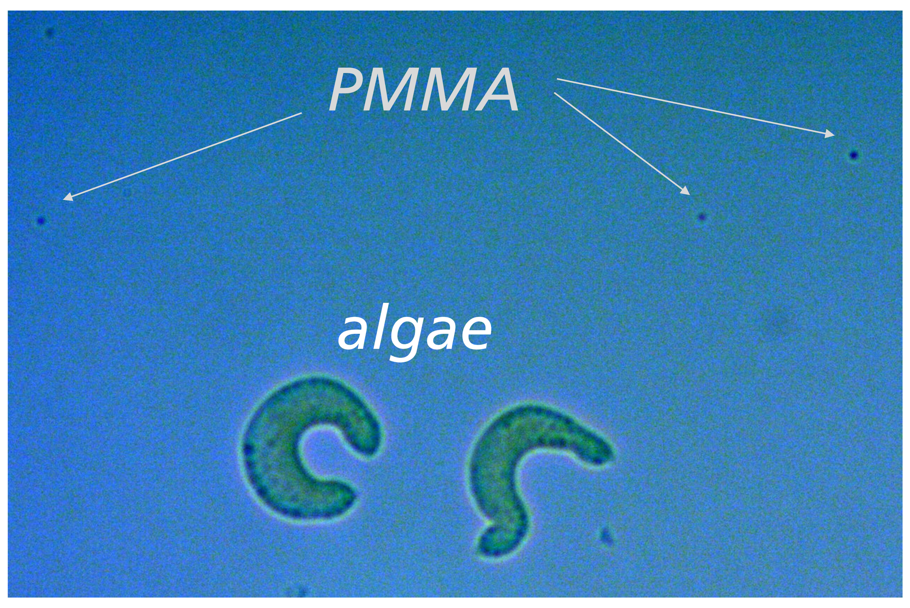
Materials

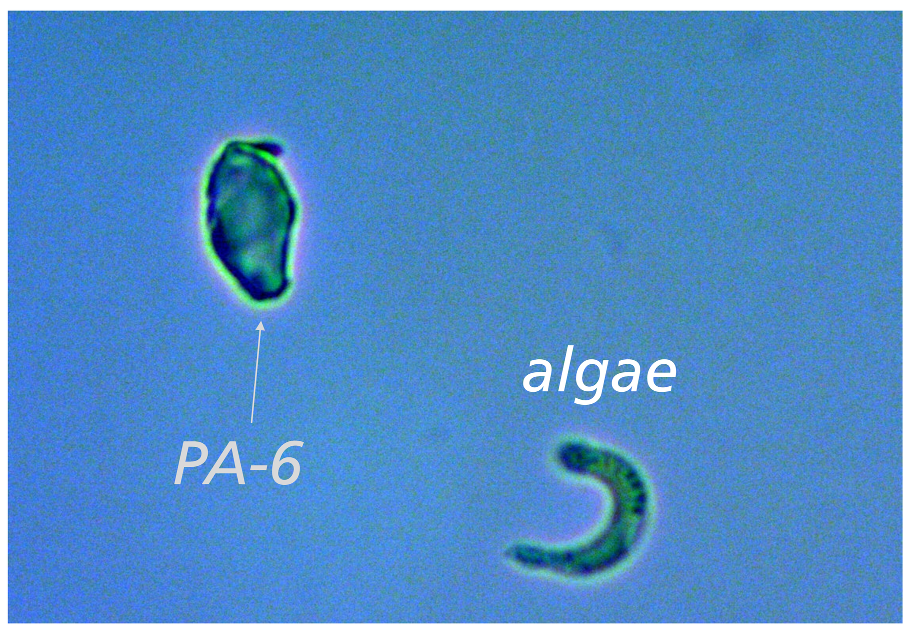
Material short name	Supplier	State of material	Average primary particle size	Surface area (BET) [m^2/g]	Reactivity DMPO [7]
PMMA [1]	Polysciences	Dispersion (2.5 wt%)	∅ 0.3 µm [5]	15.0	n.d. [8]
PA-6 [2]	BASF SE	Powder	∅ 42.2 µm [6]	0.366	1.03
TPU_ester_arom [3]	BASF SE	Powder	∅ 254 µm [6]	0.027	1.02
TPU_ether_arom [3]	BASF SE	Powder	∅ 246 µm [6]	0.030	1.28
TPU_ester_aliph [3]	BASF SE	Powder	∅ 262 µm [6]	0.034	1.37
TPU_ether_aliph [3]	BASF SE	Powder	∅ 267 µm [6]	0.033	n.d. [8]
PU_binder_arom_1C [4]	BASF SE	Powder	∅ 200 µm [6]	0.145	n.d. [8]
PU_binder_arom_2C [4]	BASF SE	Powder	∅ 201 µm [6]	0.159	n.d. [8]

[1] poly(methylmethacrylate); [2] polyamide; [3] ester or ether based thermoplastic polyurethane (TPU) with aromatic or aliphatic hydrocarbons; [4] polyurethane; [5] information by supplier; [6] particle size distribution determined using a Mastersizer 3000 (MV Hydro unit); Dx50 presented; [7] Sample to blank ratio; hydroxyl radical generation measured according to Shi et al. (2003a); [8] not determined.









Preparation of stock dispersion

- PA-6: mixing 100 mg + 50 mL of the OECD test medium and stirring with a magnetic bar.
- PMMA: 2 mL of the dispersion + 498 mL of the OECD test medium and gently stirring.
- TPU, PU: 100 mg + 1000 mL OECD test medium + 25 µL Tween 40:and stirring with a magnetic bar.

Test design

- Growth inhibtion test with algae: OECD TG 201
- Test concentrations: 100, 10, 1, 0.1 mg/L
- Determination of algal biomass with *in-vitro* fluorescence assay
- Test algae: *Raphidocelis subcapitata*
- Microscopic determination of algal-particle interaction in a short-term assay [1]

Results and Discussion

- None of the materials showed toxic effects.
- Despite large variability in size (0.3–270 µm), condition (powder, dispersion), surface area (0.03 – 15 m^2/g) no evidence that a particular size, state of material or surface area causes ecotoxicity.
- TPU, PU polymer particles could only be dispersed with Tween 40.
  Tween 40 coats materials → no contact between algae and material → false negative effect?
  Similar dispersion effect with algal exudates (corresponding to $3*10^6$ cells/mL = cell concentration at test end) → Tween 40 simulates effects which can also occur in the environment!
  Advantage of Tween 40 over algae exsudates: defined chemical composition.
- Nanomaterials: hetero-agglomeration driving factor for ecotoxicity[1]
  Nano/micro-)sized polymer particles: no hetero-agglomeration
  → agrees with lack of toxicity!

Conclusion

If there is no hetero-agglomeration, the probability of polymers being toxic seems to be low, unless they contain bioavailable toxic components.

[1] *Hund-Rinke et.: Attachment efficiency of nanomaterials to algae as an important criterion for ecotoxicity and grouping. Nanomaterials 2020, 10, 1021.*

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BASF We create chemistry

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