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# Characterization and biodegradation of two technical mixtures of side-chain fluorinated acryl copolymers

Christian Eschauzier<sup>1,2,3</sup>, Xenia Trier<sup>4</sup>, Linda Bengtström<sup>4</sup>, Tobias Frömel<sup>3</sup>, Pim de Voogt<sup>2,1</sup>, Thomas P. Knepper<sup>3</sup>

<sup>1</sup> KWR Watercycle Research Institute, P.O.Box 1072, 3430 BB Nieuwegein, Netherlands

<sup>2</sup> Earth Surface Sciences, Institute for Biodiversity and Ecosystem Dynamics, Universiteit van Amsterdam, POBox 94248, 1090GE Amsterdam, Netherlands

<sup>3</sup> Hochschule Fresenius, Limburger Straße 2, 65510 Idstein, Germany

<sup>4</sup> National food institute, Technical University of Denmark, Mørkøvej Bygade 19, 2860 Søborg, Denmark

christian.eschauzier@kwrwater.nl, xtr@food.dtu.dk



## Introduction

- PFAA sources to the environment: direct & indirect.
- Biodegradation of side-chain fluorinated acryl copolymers (fluorotelomer alcohols (FTOH) based), leaching of residual perfluoroalkylacids (PFAA) and biodegradation of residual monomers/oligomers as sources of PFAA?
- Large uncertainty of the indirect sources for fluorotelomer based products 6-160 t (Prevedouras, 2006) vs. amount of produced FTOH based side-chain fluorinated copolymer (4000 to 5200 t/year for 1995-2004)
- Both side-chain fluorinated acryl copolymers are used for coating of food paper and board packaging

- Aim of the study: Characterize two fluorinated acryl copolymers and their PFAA precursor potential



Figure 1: 10% polymer solutions before centrifugation

## Materials & Methods

- Two technical mixtures of side-chain fluorinated acryl copolymers were obtained:
  - Copolymer 1: cationic, solvated in methanol
  - Copolymer 2: non-ionic, solvated in water
- 10% solutions ultracentrifuged: 3 kDa mass cutoff analyzed
- Biodegradation experiments at 100 mg/L
  - Innoculum: wastewater treatment plant effluent
- Instrumentation:
  - UHPLC-ESI-QqQ (Waters Quatro Ultima)
  - UHPLC-ESI+-QTOF (Bruker, MicroTOF)
  - <sup>19</sup>F-NMR (500 MHz Varian Unity Inova)

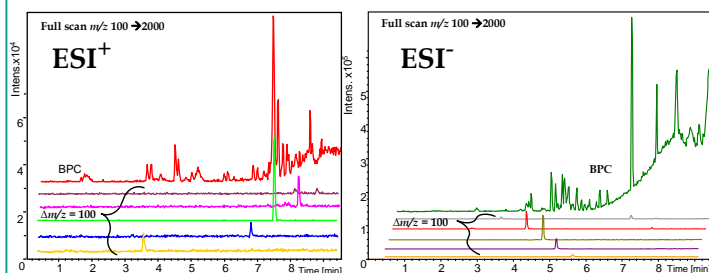


Figure 2: Biodegradation setup

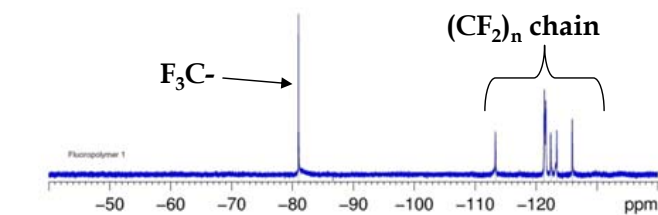
## Results & Discussion

### Side-chain fluorinated acryl copolymer 1

- Large amount of residuals FTOH and PFAA present in fluoropolymer mixture. FTOH: C6 (2%), C8 (45%), C10 (40%) and C12 (13%).
- UHPLC-ESI+ microQTOF scan shows homologues series separated by  $\Delta m/z = 100$  ( $CF_2CF_2$ ), probably from fluorotelomer acrylates (FTAC)



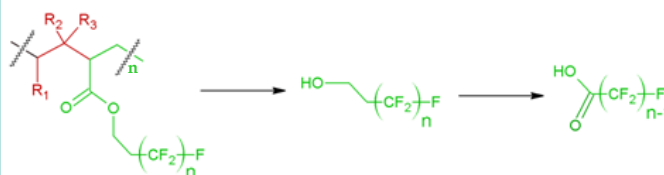
- <sup>19</sup>F-NMR spectrum:



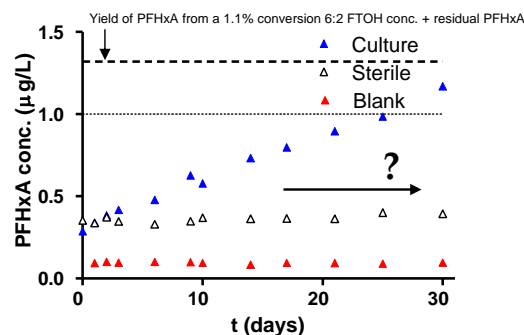
H/F nanoprobe spinning at  $\approx 2000$  Hz

### Side-chain fluorinated acryl copolymer 2

- 1‰ of residual FTOH and minor amounts of PFAA present in fluoropolymer mixture: FTOH: C6 (90%), C8 (5%) and C10 (5%).
- Degradation of a fluorinated acryl copolymer



- First results on biodegradation experiment of residual 6:2 FTOH or C6 based side-chain fluorinated acryl copolymer technical mixture



## Conclusions

- FTOH and PFAA residuals were present in both mixtures.
- Homologues series of "unknown" fluorinated compounds were found in fluorinated copolymer 1 by accurate MS (LC-QTOF MS)
- Perfluorinated side chains were observed in copolymer 1 by <sup>19</sup>F NMR
- Side-chain fluorinated acryl copolymer 2 had broad peaks in the <sup>19</sup>F NMR spectrum, possibly due to micellization.
- Degradation of FTOH residuals or side-chain fluorinated acryl copolymers are sources of PFAA in food packaging and in the environment
- More knowledge on production volumes of side chain fluoropolymers and individual brands is required for a thorough assessment of the precursor potential of side-chain fluorinated acryl copolymers

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