HIGH PERFORMANCE BIO-BASED POLYMERS

STATE OF THE ART AND CHALLENGES IN ENDING PLASTIC WASTE

24 SEPTEMBER 2024

FURIOUS

THERMO FIRE

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UNIVERSITÀ DI BOLOGNA

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Circular Bio-based Europe Joint Undertaking

Bio-based Industries Consortium

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FURIOUS - Beyond State of Art

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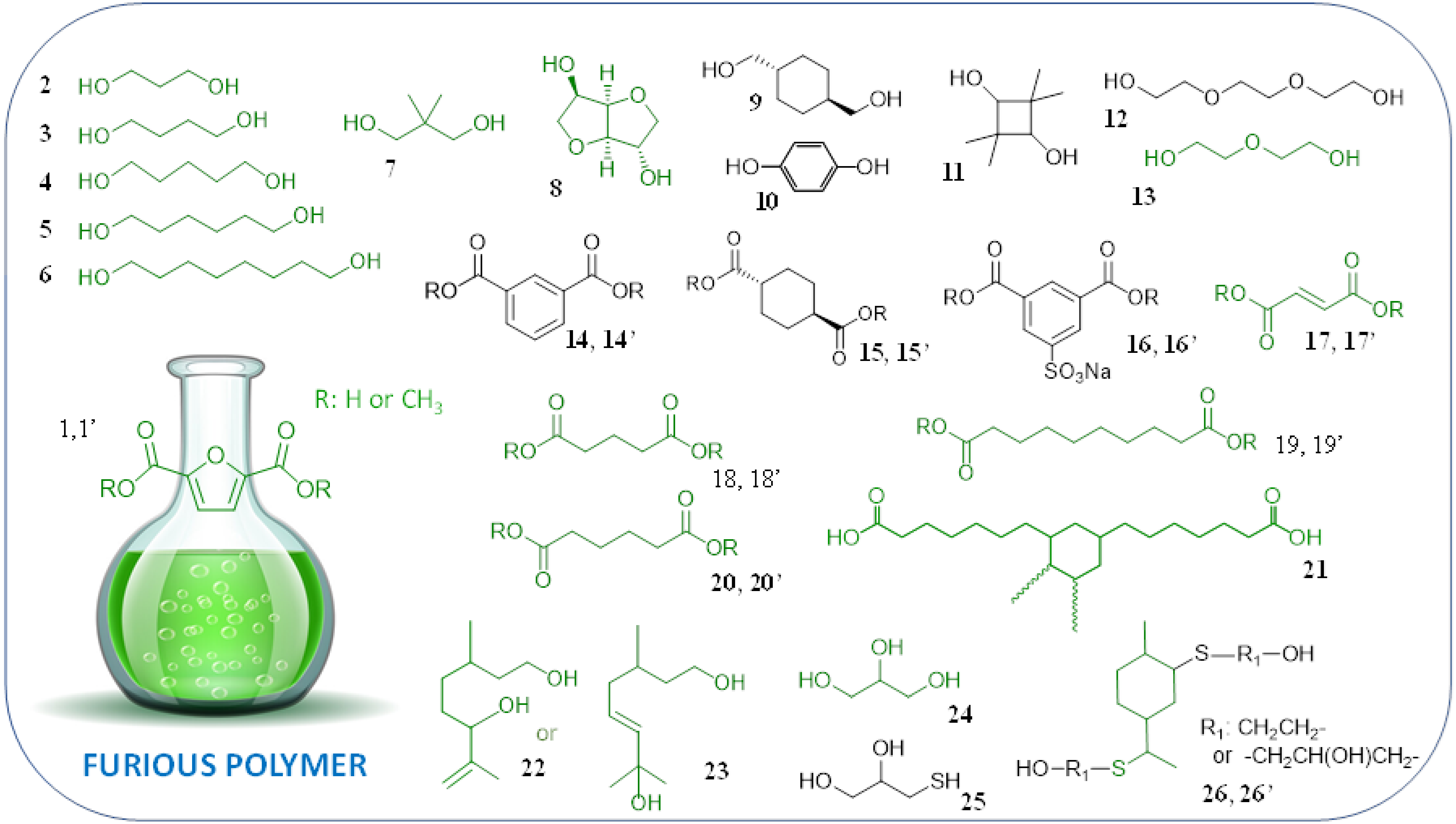

FDCA combination with different glycols, diacids (or corresponding dimethylester) (biobased- ***green*** *and petroleum-****black*** *source)*

Strategic objectives → Results

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SO1: Development of 2,5-FDCA monomer at high purity

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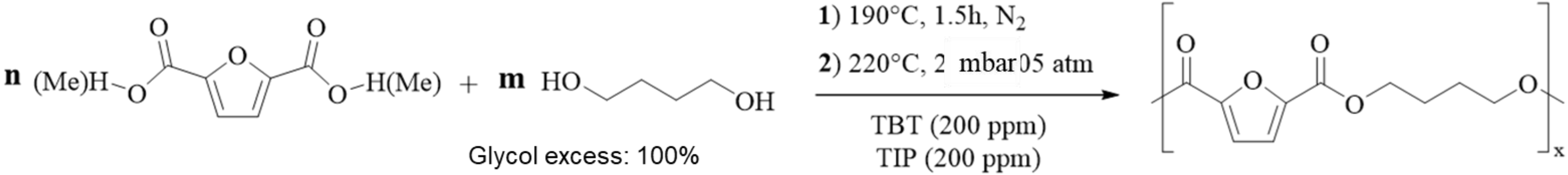
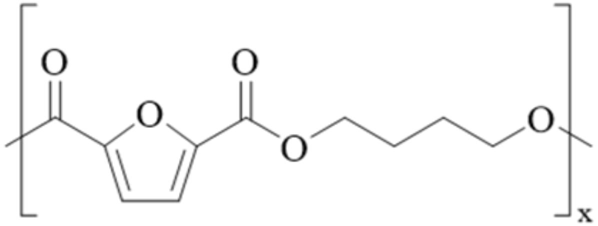
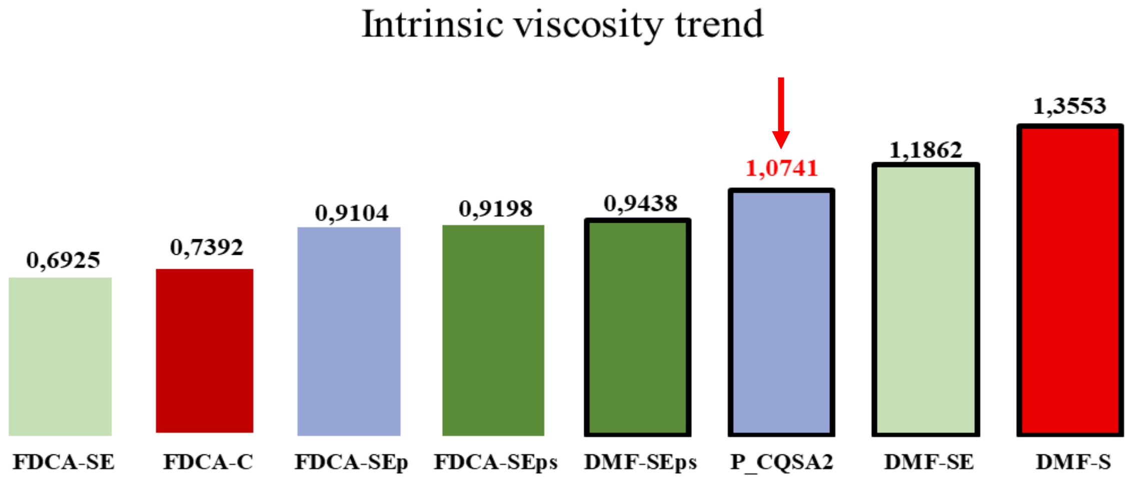
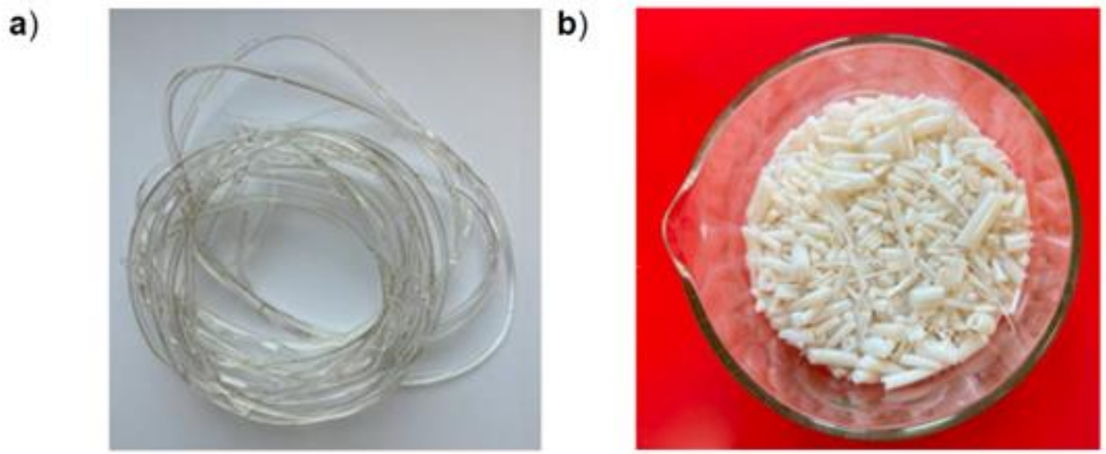
- **high purity** (> **99.8** %) - tested with a **reference polymer (PBF)**
- **Derivatizing procedures** of 2,5-FDCA into the corresponding ester (**acid catalysed esterification**) optimized to make the process cost effective for high-volume, mass production

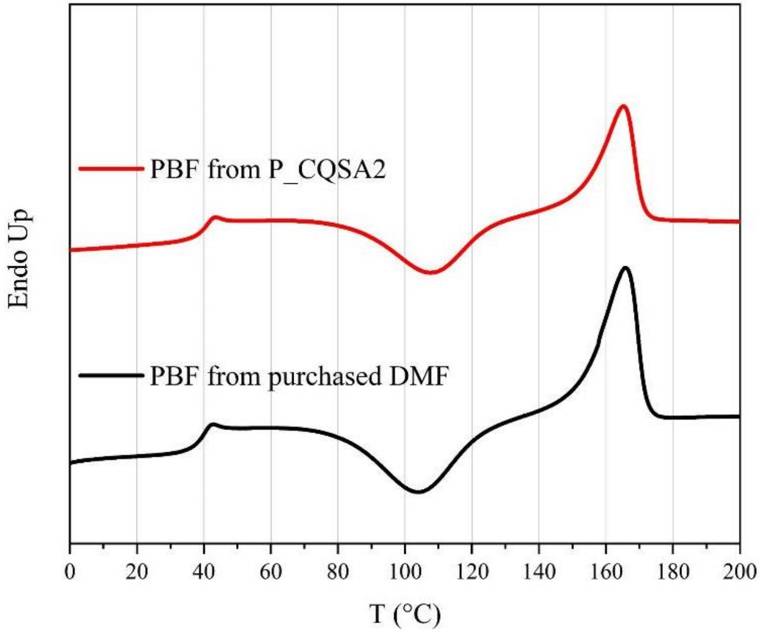



Poly(butylene 2,5-furanoate) **PBF**





Picture of PBF extruded from reactor as a wire (**a**) and PBF granules (**b**) after drying at 50 °C under vacuum before further processing.



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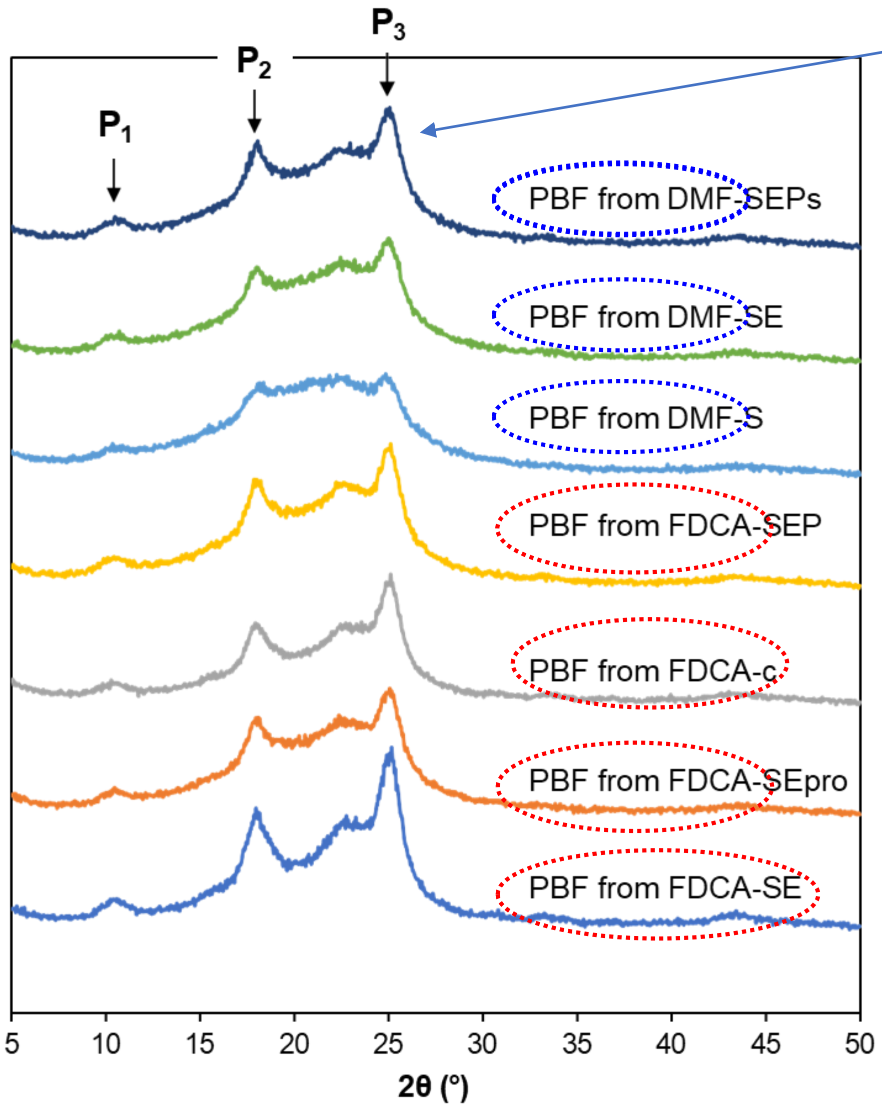
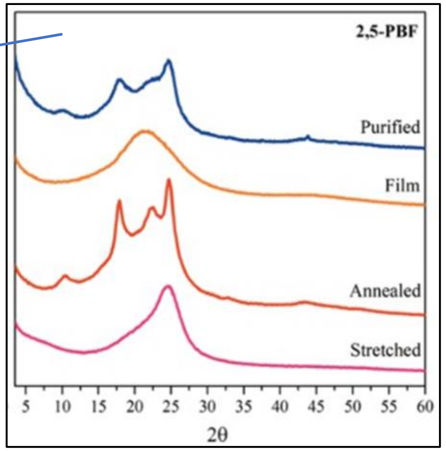
West Pomeranian University of Technology Szczecin

- ✓ **Monomer purity affects color and molecular weight of PBF polyester.**
- ✓ The **esterification of FDCA** revealed to be **effective** when applied to low purity FDCA monomer
- ✓ Objective: minimize impurities and improve colour of the product.





Bianchi et al. (2021) ACS Sustainable Chemistry & Engineering, 9, 35, 11937-11949

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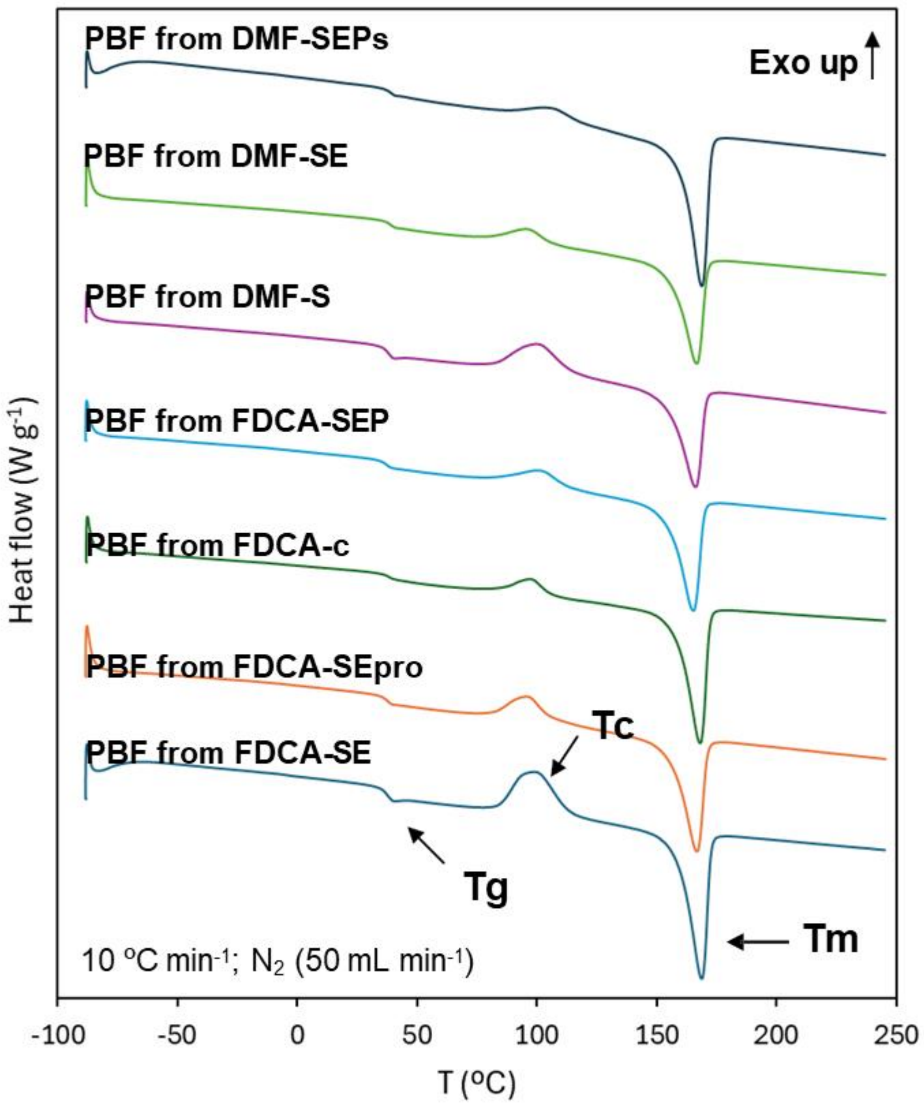
2nd heating



PBF cast film extrusion - lab scale

Experimental conditions:

Extruder Zone	Feeding (°C)	Compressing (°C)	Metering (°C)	Die (°C)
Temperature profile	220	225	230	210

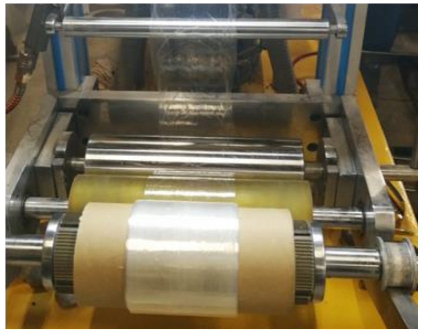
Compounding	Screw set	Time (s)	Speed (rpm)	Force (N)
Parameters	Co-rot	120	60	2700

Die casting film parameters	Force (N)	Speed (mm/min)	Torque (N-mm)	Cooling flow (l/min)
Set values	650	250	30	28

- Regardless the thermochemical performance, processing of PBF was easily *moved from compression molding to cast film*
- PBF can represent a relatively simple option for placing furanoates in the market for ***flexible*** packaging
- Up to now, only *rigid PEF* demonstrated to reach the market size

PBF extrusion- blow extrusion scaled production and processing

bio-mi SUSTAINABLE SOLUTIONS

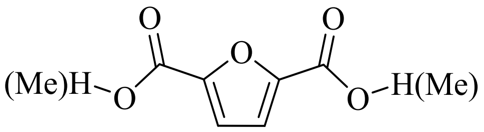


Zachodniopomorski Uniwersytet Technologiczny w Szczecinie

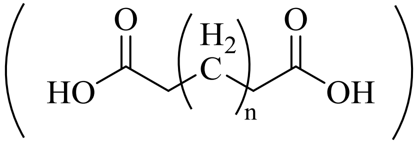
Parameter	PBF	PLA LX175	Bio-PE
Tensile (yield), MPa	26.6 ± 8.8	45.2 ± 2.5	15.3 ± 0.9
Elongation (yield), %	4.6 ± 0.9	1.7 ± 0	598.2 ± 33.7
Tensile strength, MPa	**48.0 ± 5.9**	47.0 ± 2.6	34.0 ± 2.0
Elastic modulus, MPa	**941.0 ± 100.7**	3289.5 ± 111.7	174.5 ± 17.4
Elongation (break), %	**398.8 ± 24.7**	**49.5 ± 19.5**	930.3 ± 62.4
Thickness, µm	105	54	70
Width, cm	9.6	9.7	8.9
Transmittance, %	92.5	93.8	90.4
Haze, %	4.9	0.6	28.1

Mechanical performance comparable (and even better) than PLA

Flexibility



FDCA (DMF)



Partial replacement of FDCA with other long linear aliphatic or heteroatom containing diacids

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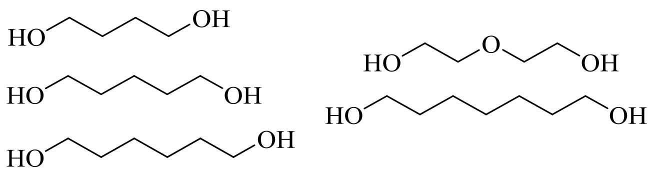
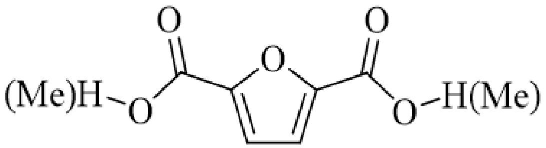


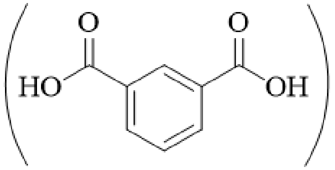
Long linear aliphatic or heteroatom containing glycols

Flexible behavior can be obtained by **reducing the T_g and by preferring co-units having an odd number of methylene groups** (decrease the crystallinity of the final polymer)

Stiffness



FDCA (DMF)



Partial replacement of FDCA with other aromatic diacids

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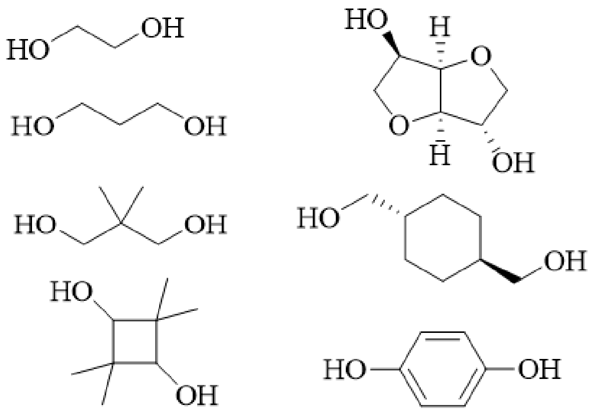

Stiff materials can by achieved by combining **short aliphatic glycols, diols containing short side branches or cyclic glycols**

SO2: Development of FLEXIBLE and rigid 2,5-FDCA based polyesters

FLEXIBLE PACKAGING

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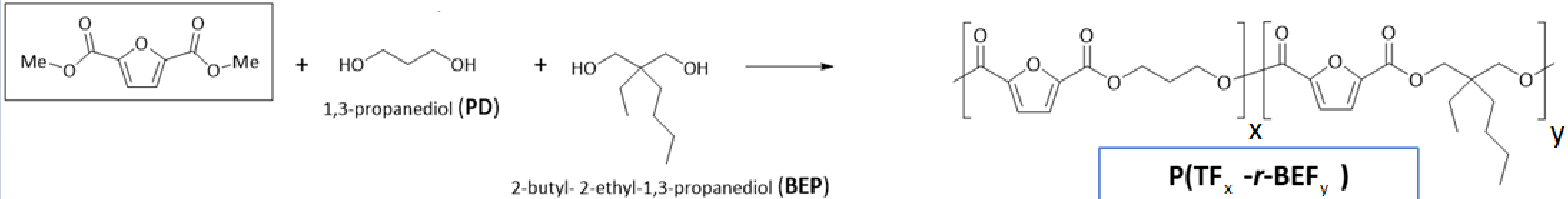
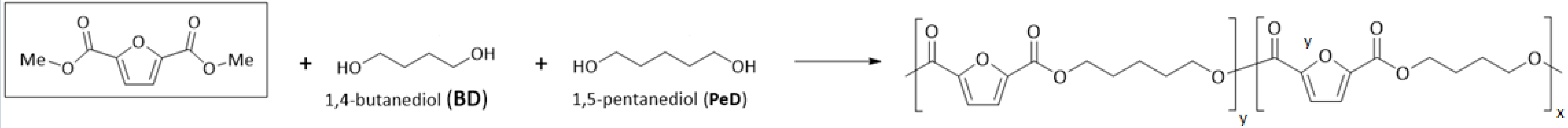
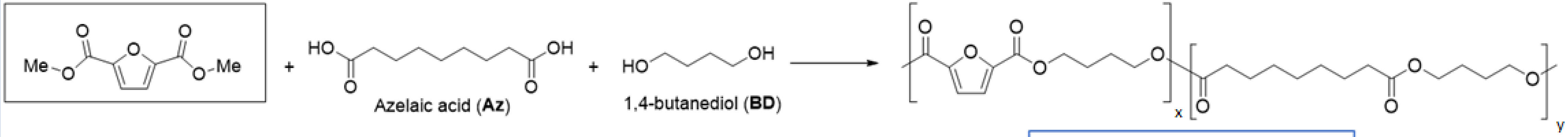


P(TF$_x$ -*r*-BEF$_y$)
random copolymer



P(BF$_x$ -*r*-PeF$_y$)
random copolymer



P(BF$_x$ -*r*-BAz$_y$)
random copolymer

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S02: Development of FLEXIBLE and rigid 2,5-FDCA based polyesters

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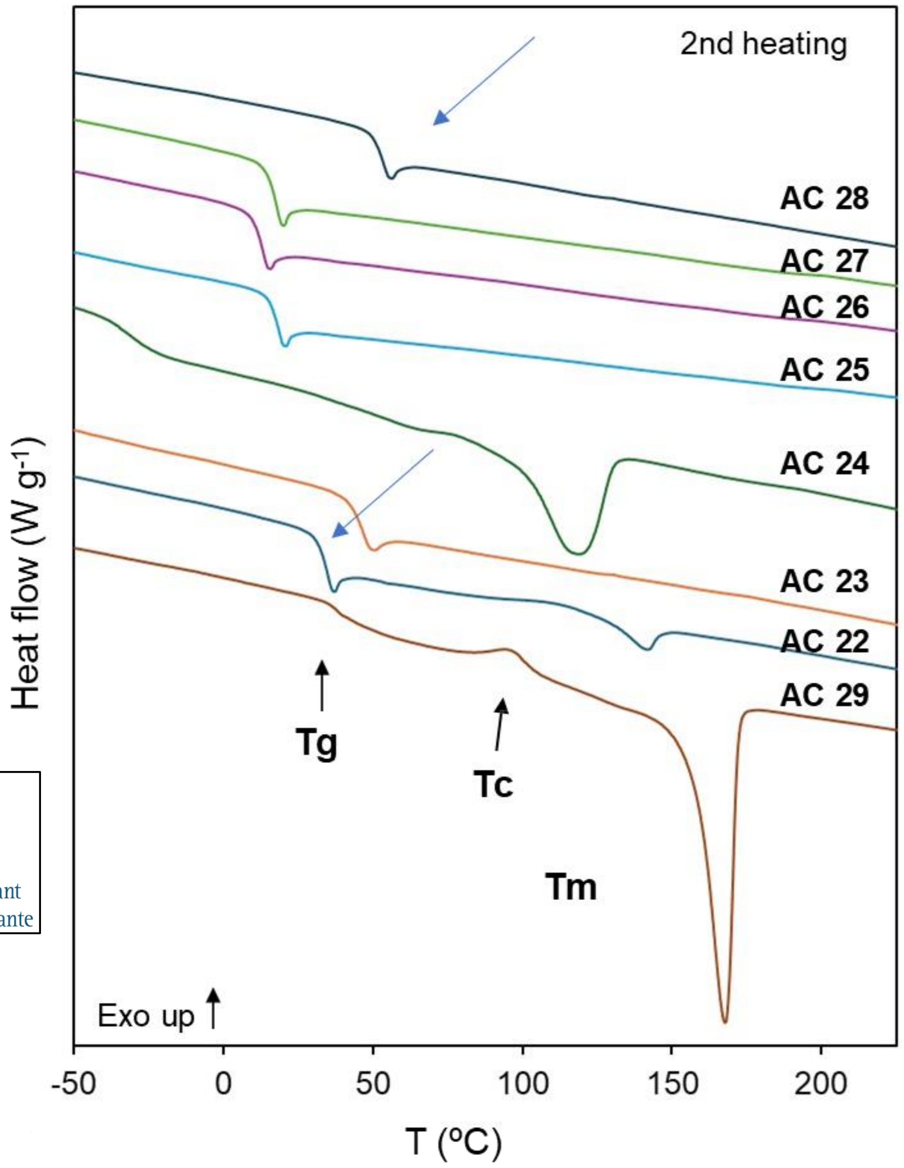
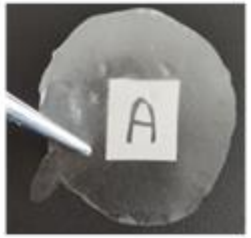


WCA (30")

AC 28
P(TF$_x$ -*r*-BEF$_y$)
random copolymer

97.7 ± 3.04°

AC 22
P(BF$_x$ -*r*-PeF$_y$)
random copolymer



83.6 ± 1.13°

P(BF$_x$ -*r*-BAz$_y$)
random copolymer

91.3 ± 3.47°

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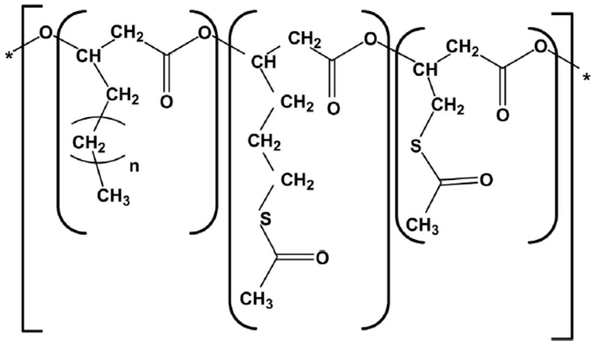
Antibacterial properties

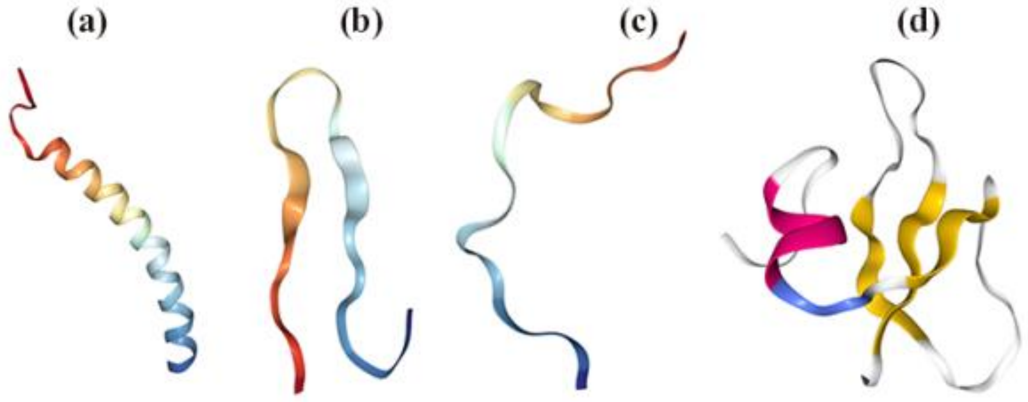
→ *Addition of bio-based additives with antioxidant and antibacterial properties to the final material*

→ *Antimicrobial activity can be imparted by* ***inserting long aliphatic side chains containing sulfur atoms on the main polymer macromolecule***



Is it feasible to have antibacterial activity by **adding sulfur atoms to the main chain**

ANTIMICROBIC POLYMERS: mimics' mechanisms of systems already present in nature → **AMPs** (AntiMicrobial Peptides), they are small glycoproteins presents in almost all innate immune systems



One portion with high content of amino acids with cationic lateral chains. These charges can interact with the negative charges present in the bacterial membranes.

The second area is composed of **amino acids with hydrophobic lateral chains**. The chains can interact with the hydrophobic bilayer of bacterial membrane.

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S03: Development of injection mouldable and ELECTROSPINNABLE 2,5-FDCA-based polyesters

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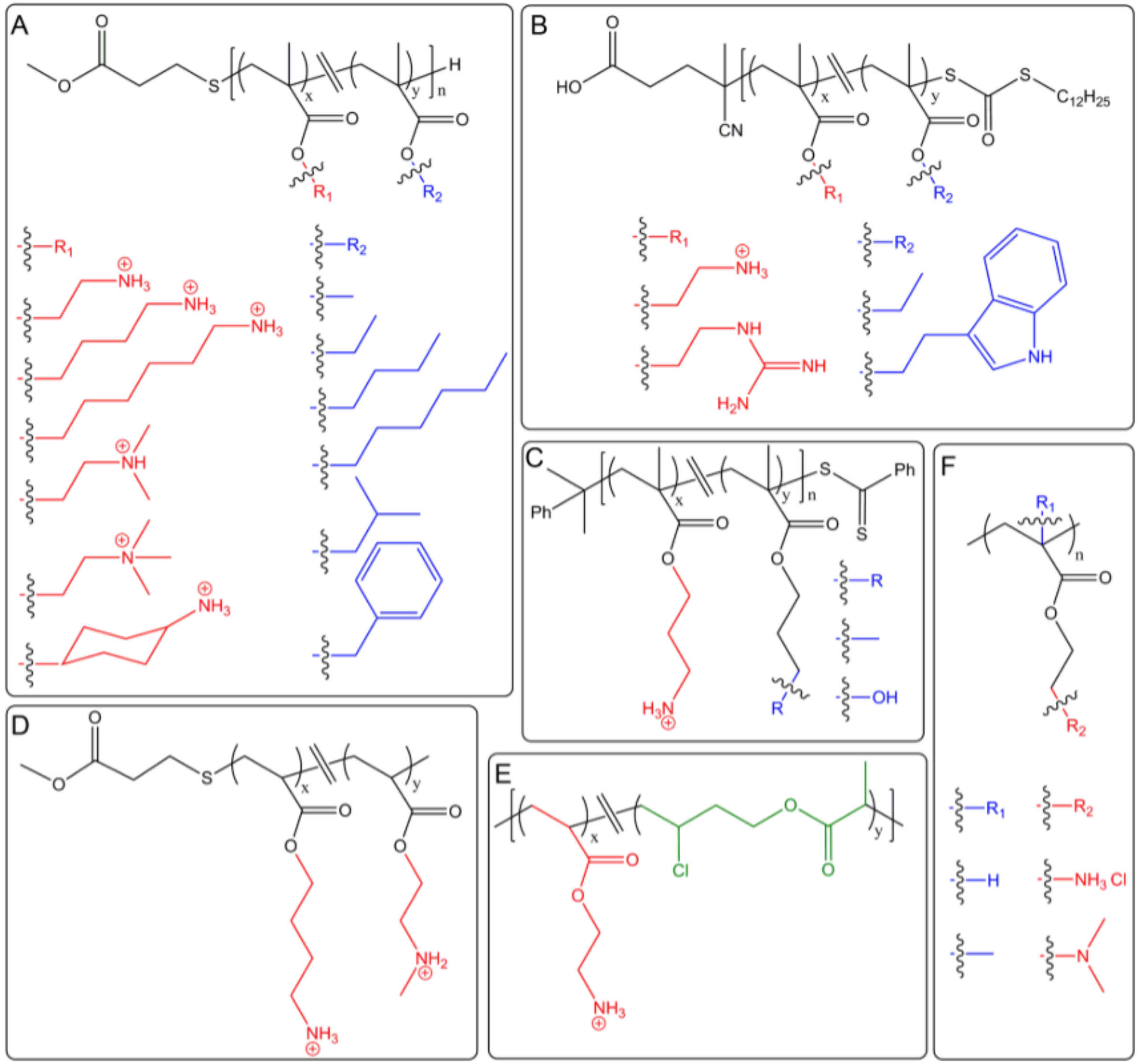
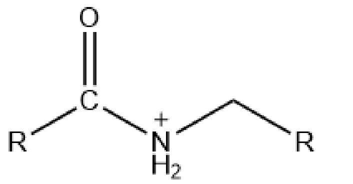
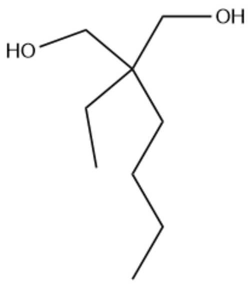
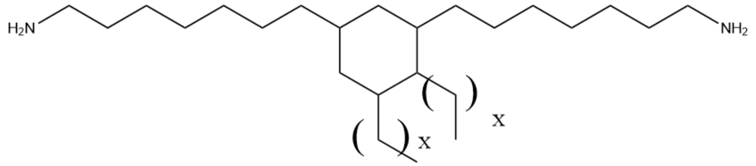


- The **insertion of positive charges** in the polymer



- The insertion of **hydrophobic chains**





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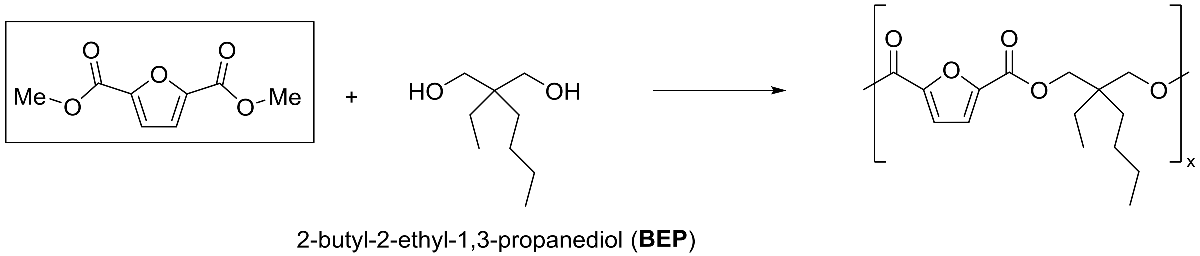
Konai, M. M., Bhattacharjee, B., Ghosh, S., & Haldar, J. (2018). Recent Progress in Polymer Research to Tackle Infections and Antimicrobial Resistance. In Biomacromolecules (Vol. 19, Issue 6, pp. 1888–1917). American Chemical Society.

S03: Development of injection mouldable and ELECTROSPINNABLE 2,5-FDCA-based polyesters



PBEF
homopolymer

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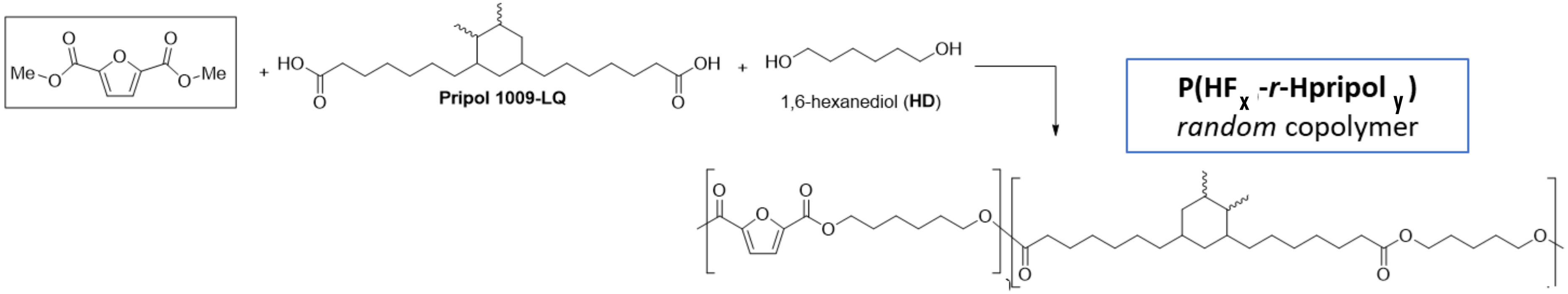
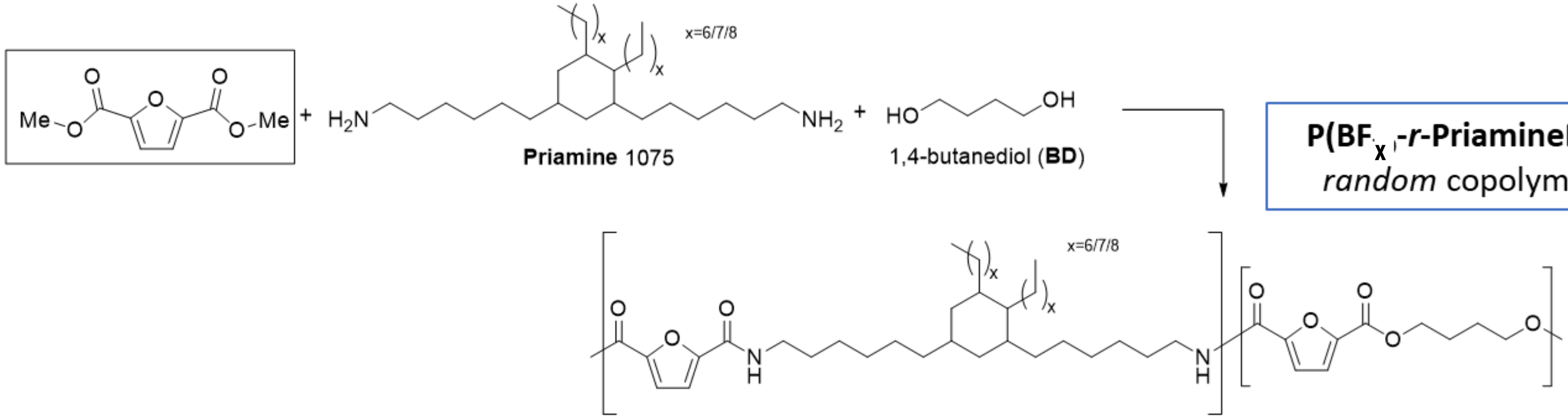
PBEF



P(HF$_x$-*r*-Hpripol$_y$)
random copolymer

P(HF$_x$-*r*-Hpripol$_y$)
random copolymer



P(BF$_x$-*r*-PriamineF$_y$)
random copolymer

P(PriamineF$_x$-*r*-BF$_y$)
random copolymer

S03: Development of injection mouldable and ELECTROSPINNABLE 2,5-FDCA-based polyesters

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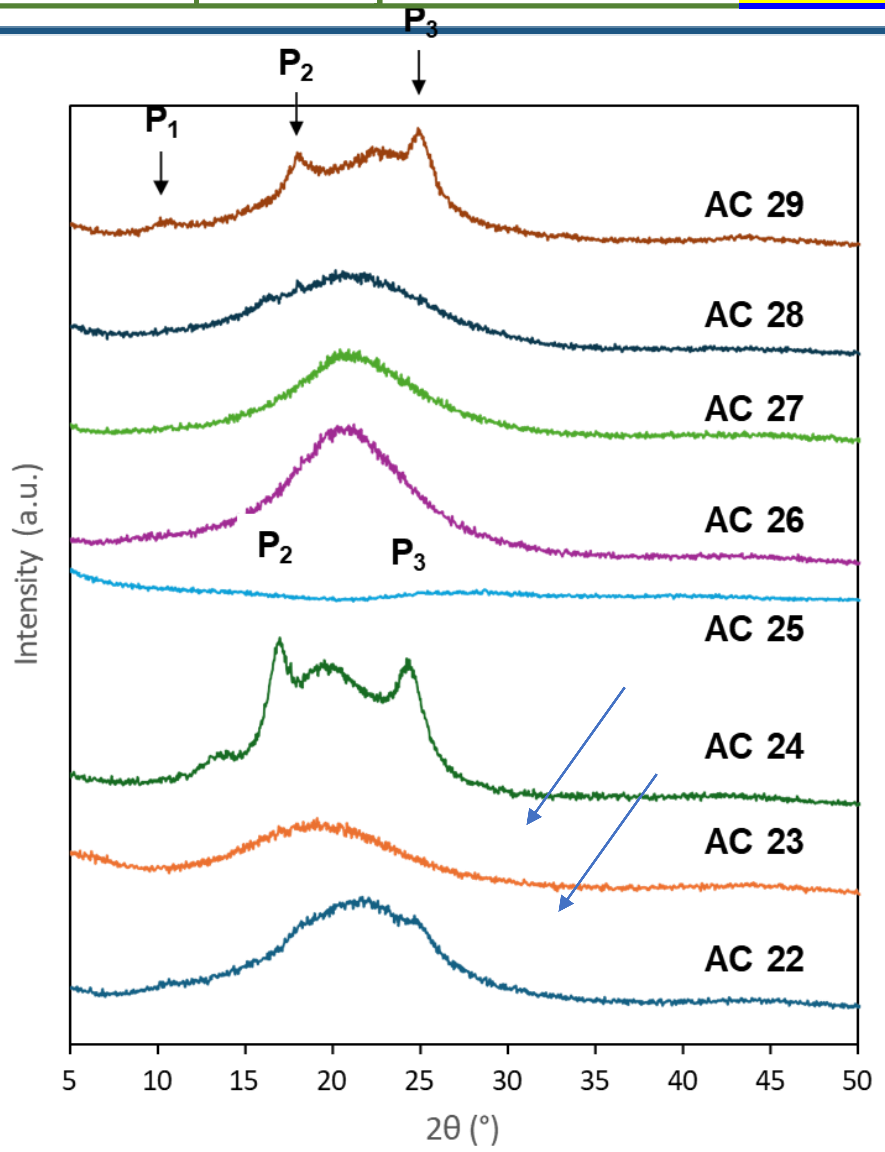

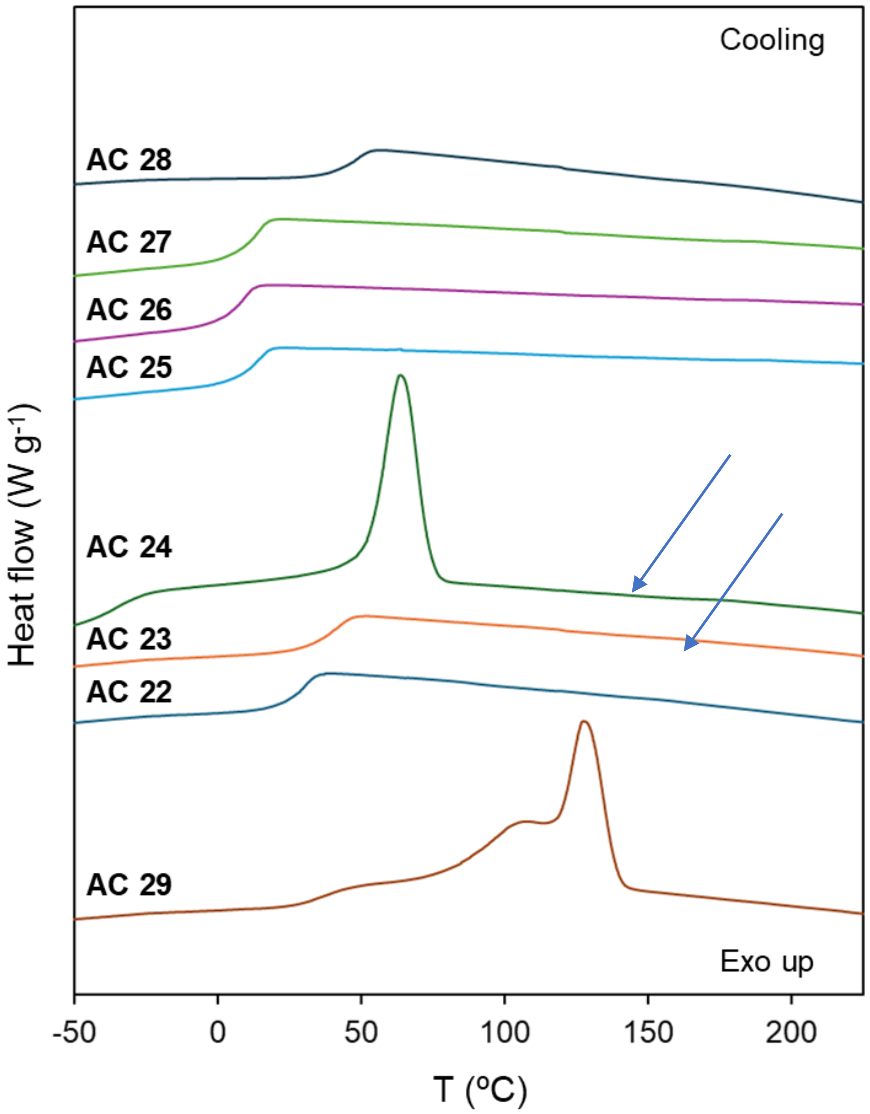

AC 23

PBEF
homopolymer

AC 24

P(HF$_x$-*r*-Hpripol$_y$)
random copolymer

P(PriamineF$_x$-*r*-BF$_y$)
random copolymer

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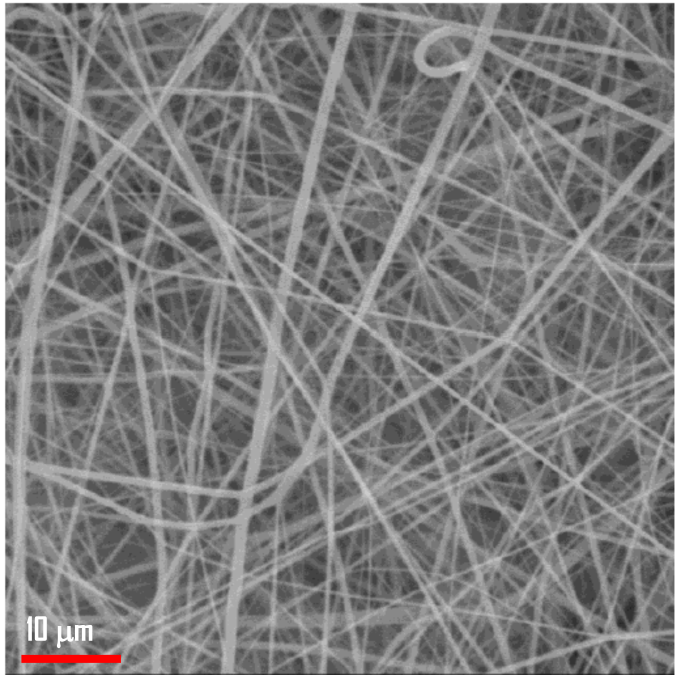
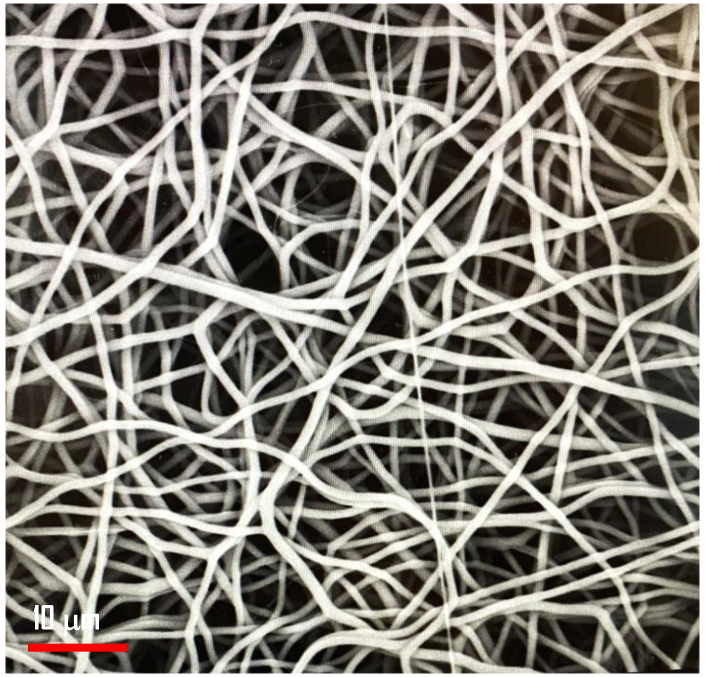
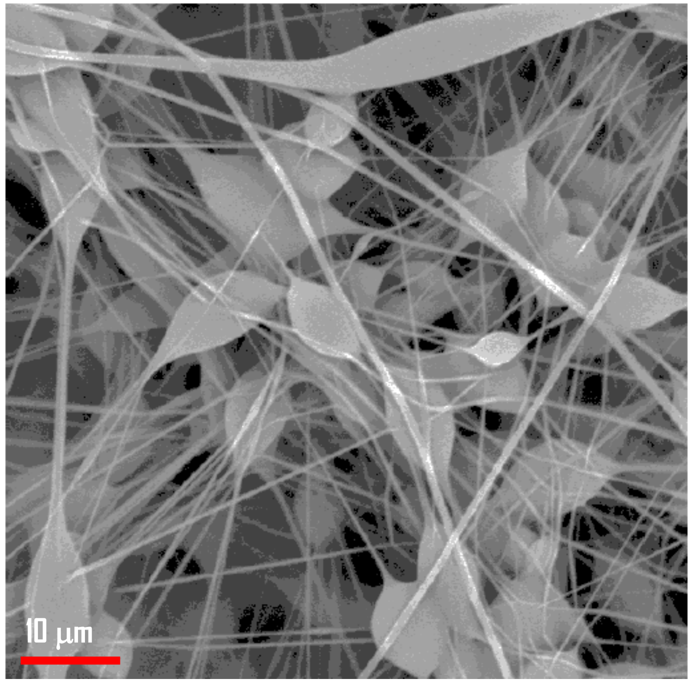
PBF (1), PBF copolymer (2) and PBEF (3)



PBF homopolymer



P(HF$_x$-*r*-Hpripol$_y$)
random copolymer



PBEF homopolymer

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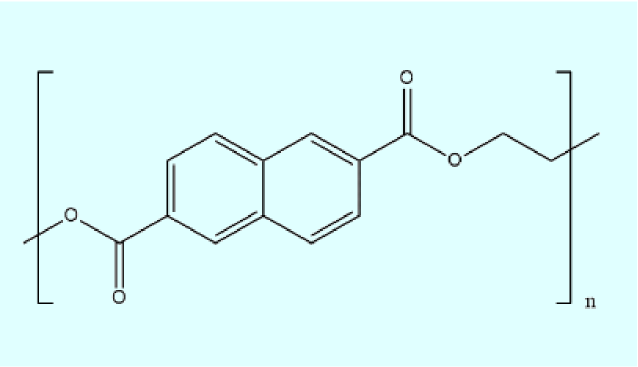
IN SUPREMÆ DIGNITATIS 1343

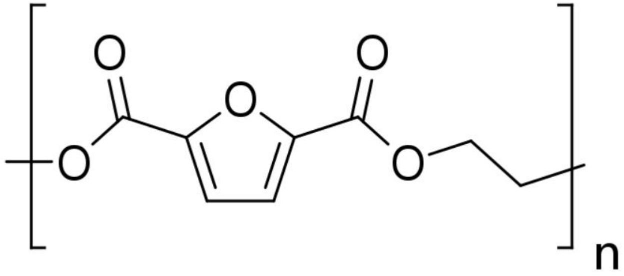
S03: Development of INJECTION MOULDABLE and electrospinnable 2,5-FDCA-based polyesters

Poly(ethylene naphthalate) (PEN)

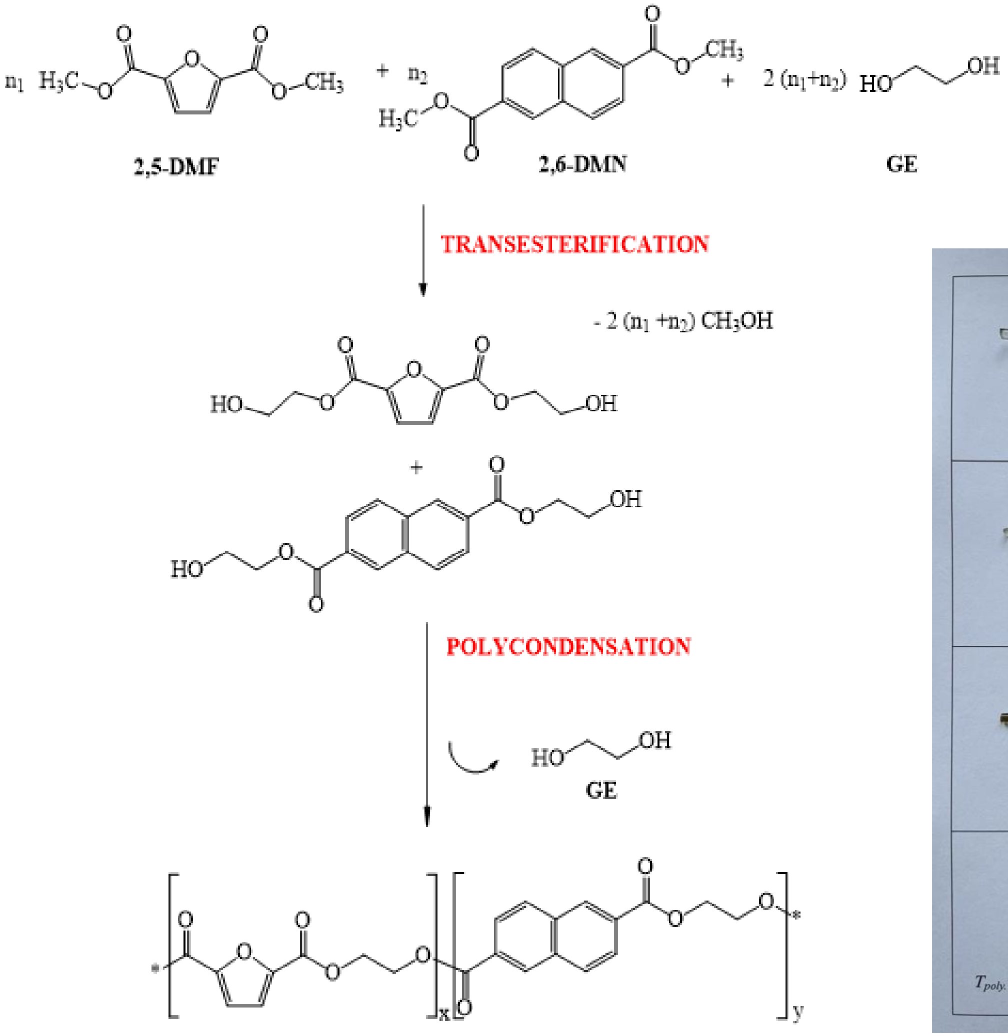


T_g = 120 °C , T_m = 262-275 °C

Poly(ethylene-2,5-furandicarboxylate) (PEF)

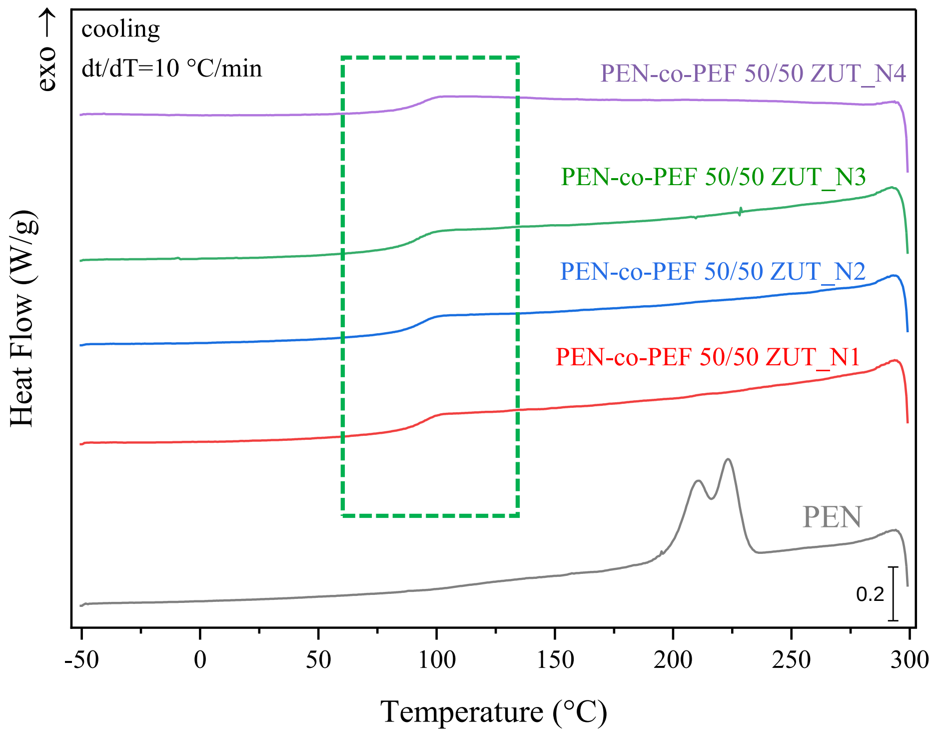


T_g = 85 °C, T_m = 195 °C

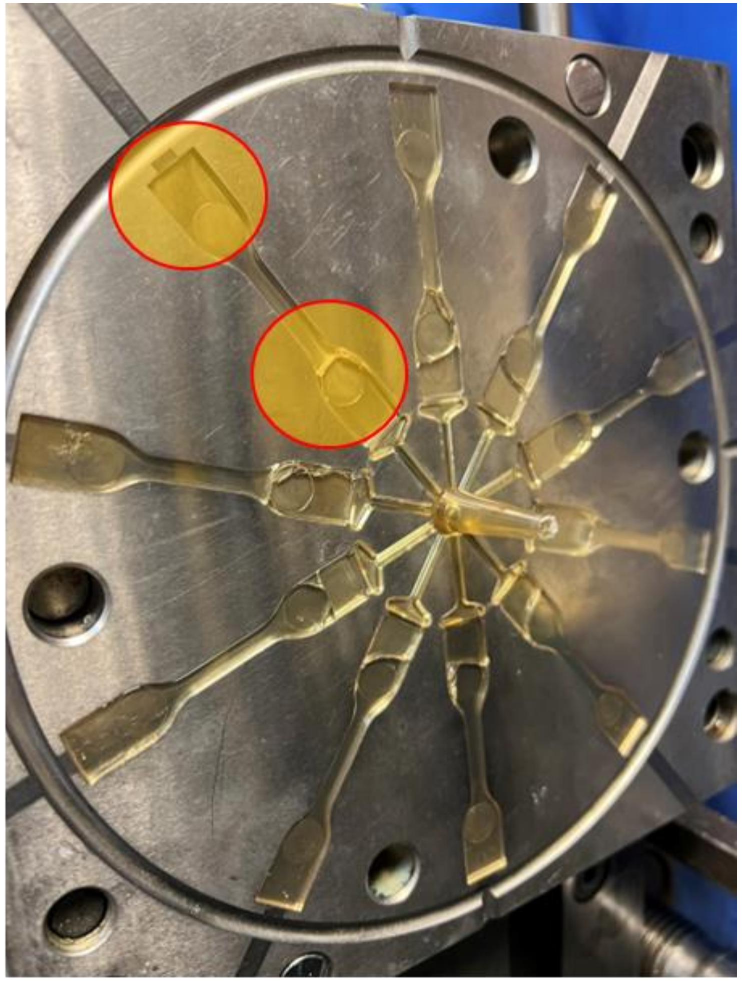


random copolymer PEF-*co*-PEN

S03: Development of INJECTION MOULDABLE and electrospinnable 2,5-FDCA-based polyesters

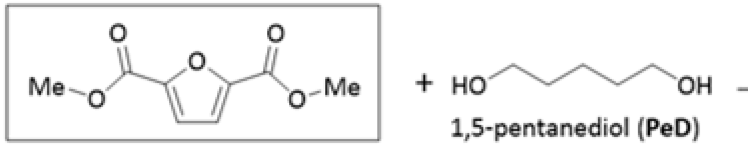


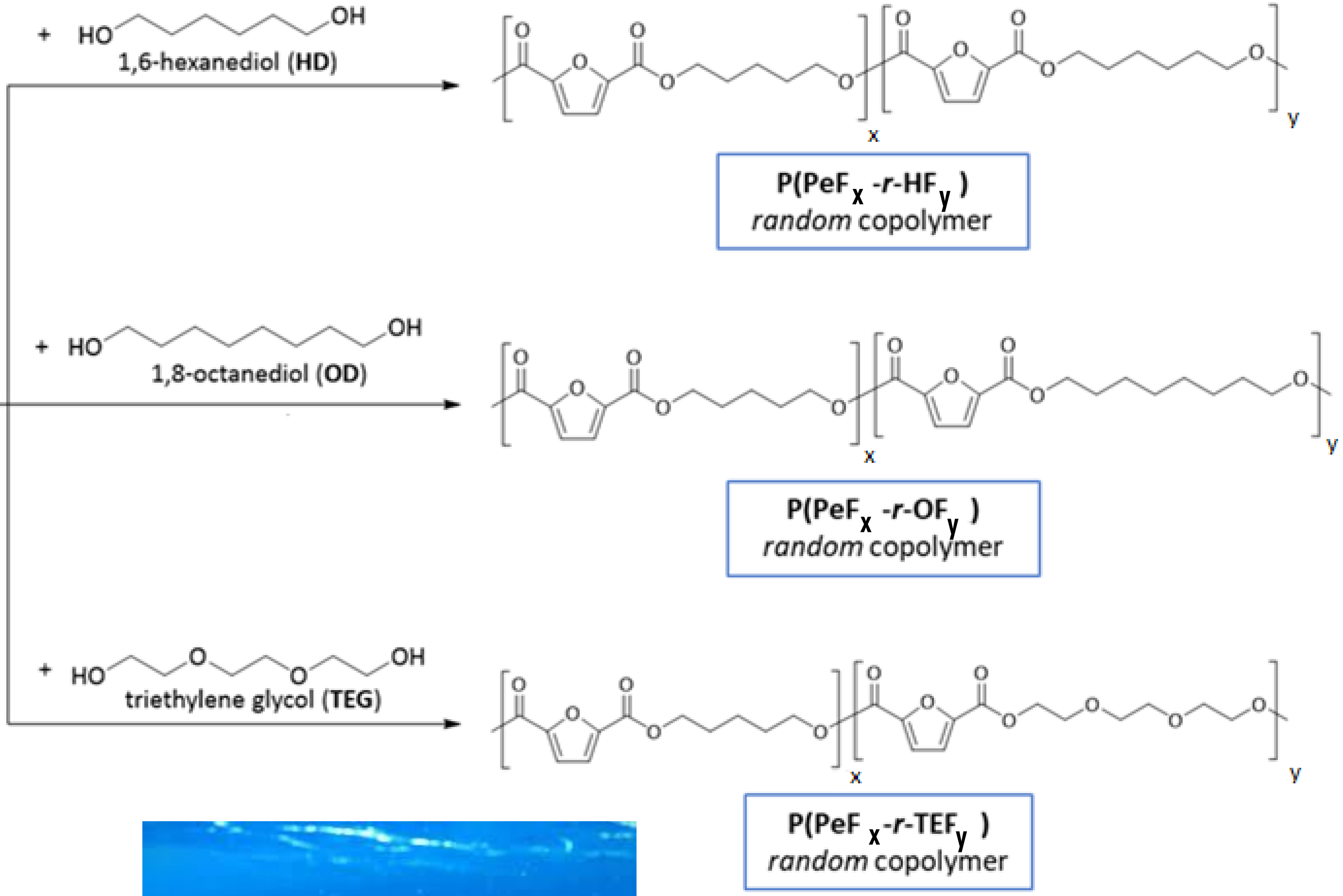
Sample	Glass transition		Crystallization		Melting	
	T_g [°C]	Δc_p [J/g °C]	T_c [°C]	ΔH_c [J/g]	T_m [°C]	ΔH_m [J/g]
PEN	118	0.11	223	47.65	264	47.92
PEN-co-PEF 50/50 20.04.2024 (ZUT_N1)	98	0.29	-	-	-	-
PEN-co-PEF 50/50 24.04.2024 (ZUT_N2)	95	0.31	-	-	-	-
PEN-co-PEF 50/50 30.04.2024 (ZUT_N3)	95	0.32	-	-	-	-
PEN-co-PEF 50/50 30.04.2024 (ZUT_N4)	95	0.32	-	-	-	-

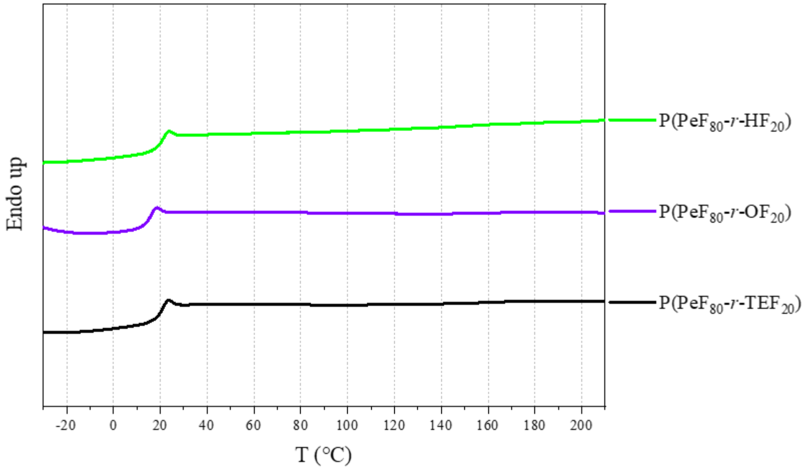


Fully filled mold cavity

Development of FLEXIBLE and transparent furanic polyesters for underwater applications

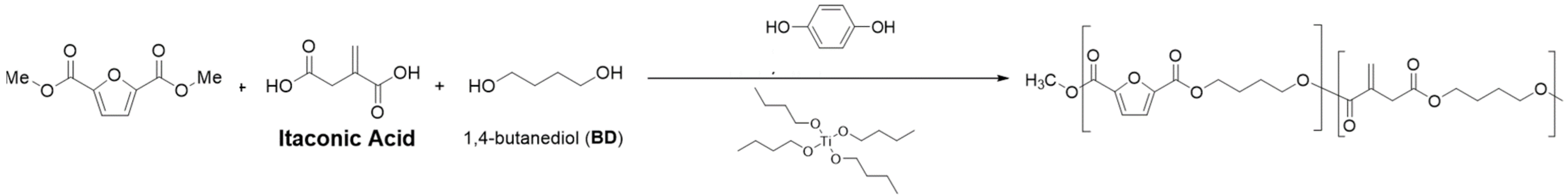


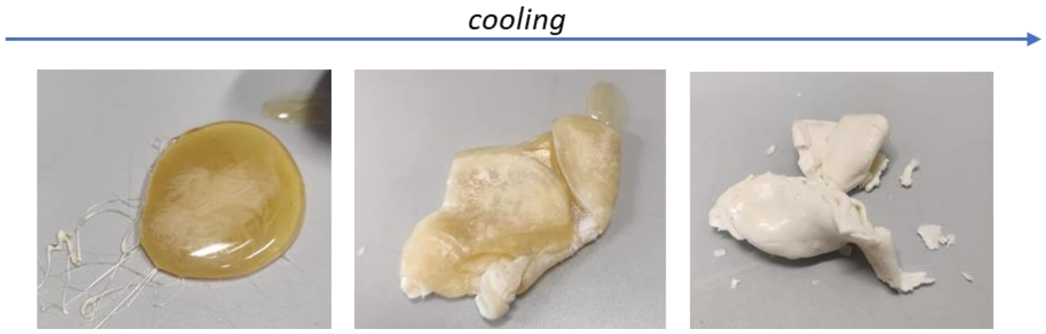


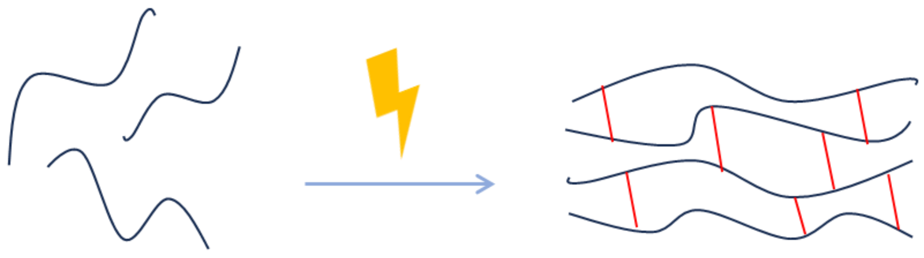


Development of 3D-printable and UV crosslinkable 2,5-FDCA-based polyesters

1)



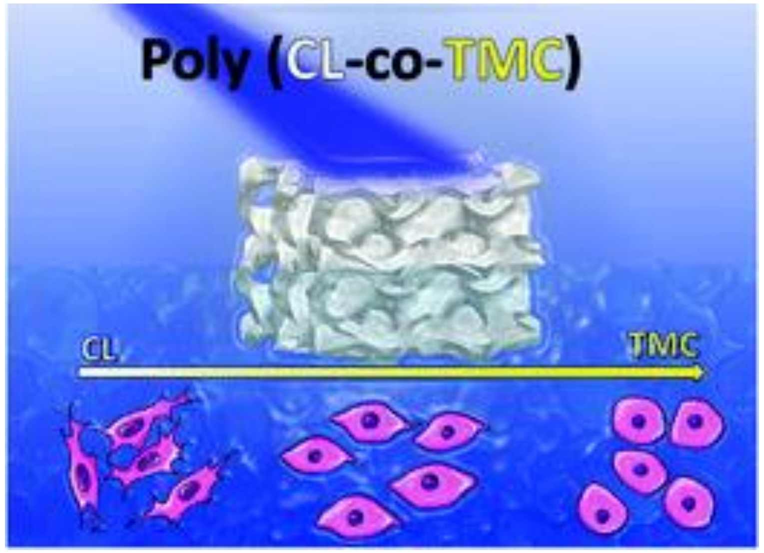




Crosslinkable oligoesters

Crosslinked polymer

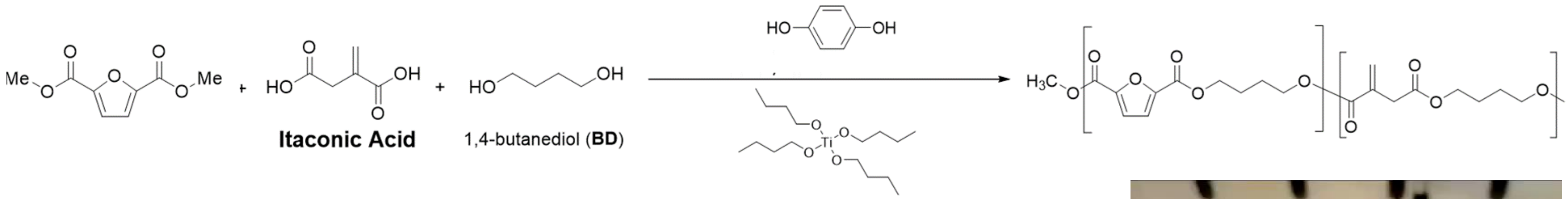
2)



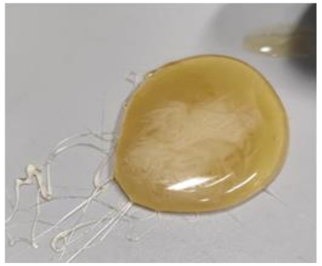
Poly(caprolactone-co-trimethylenecarbonate) urethane acrylate resins for digital light processing of bioresorbable tissue engineering implants

Development of 3D-printable and UV crosslinkable 2,5-FDCA-based polyesters

1)



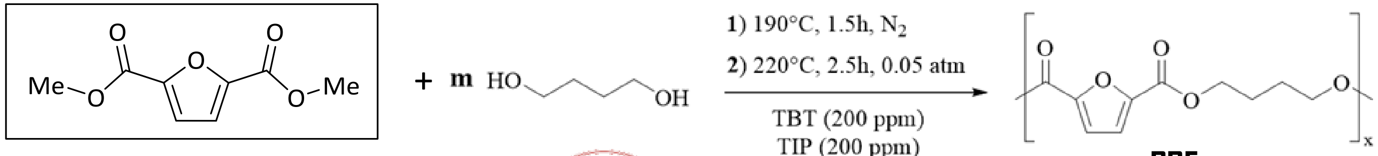
We introduced different protocols for increase the molecular weight and number of double bond, obtained different products:



Optimization of the synthesis protocol

Last result

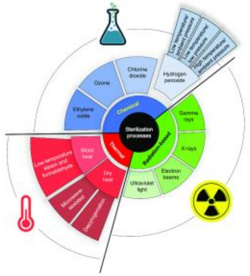
Validation of high gas and water barrier, gamma ray resistant films for biomedical and electronic packaging applications



PBF

Film formation

γ-rays treatment



GAMMA rays samples treatment

- PBF film about 50 μm thick, 2 strips of 0.5x5 cm for each absorbed dose

- Irradiation treatment: in air by ^{60}Co sources at GAMMA facilities

- total absorbed doses: 25, 50, 75 and 100 kGy;
hot point in the 25 kGy cycle

untreated

25 kGy - C

25 kGy - H

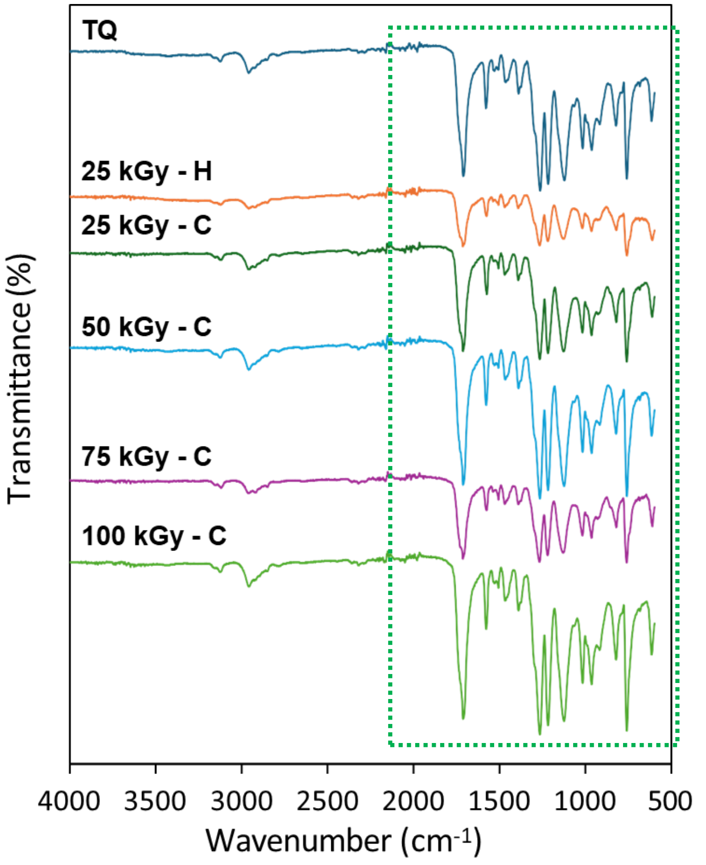
50 kGy - C

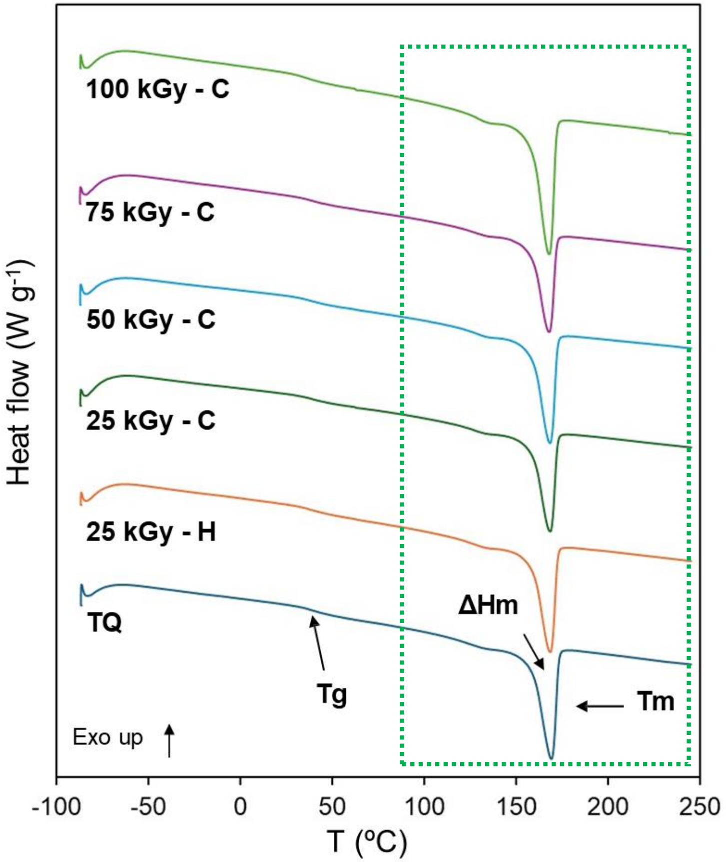
75 kGy - C

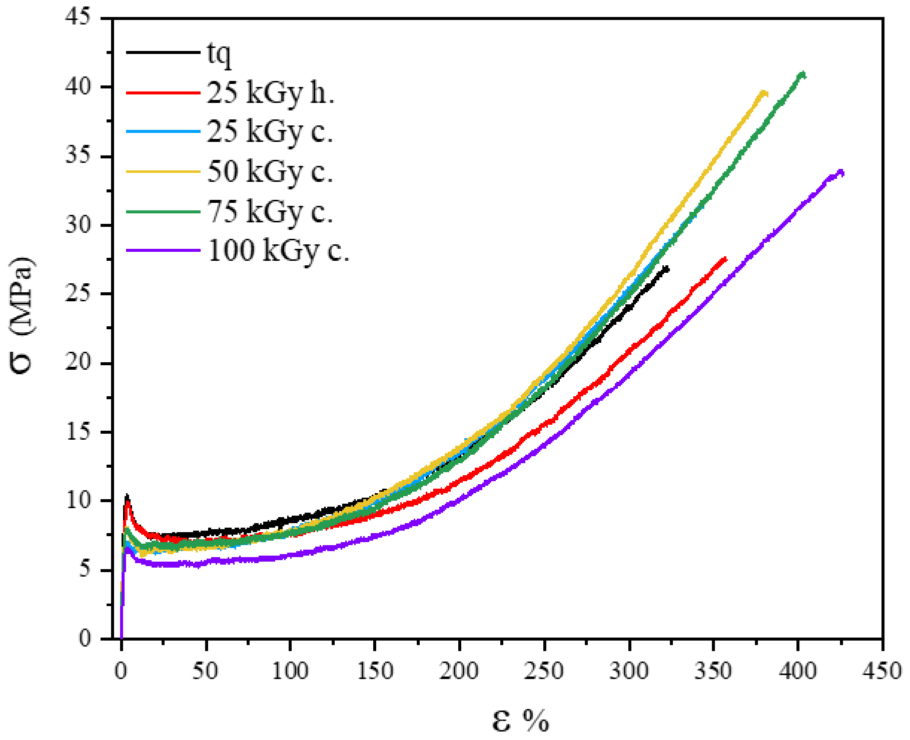
100 kGy - C

Validation of high gas and water barrier, gamma ray resistant films for biomedical and electronic packaging applications

PBF irradiated samples - Effect of radiation on mechanical performance and wettability







Validation of high gas and water barrier, gamma ray resistant films for biomedical and electronic packaging applications

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ALMA MATER STUDIORUM UNIVERSITÀ DI BOLOGNA

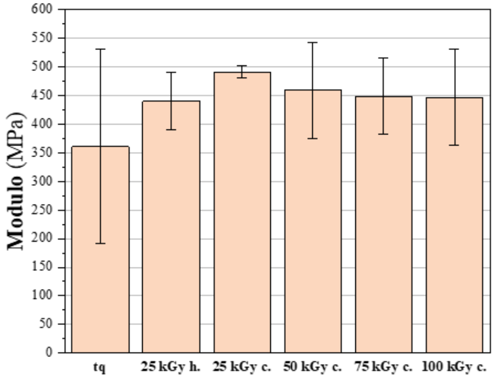
POLIMI RAD CHEM LAB RESEARCH AND EDUCATION

gammatom

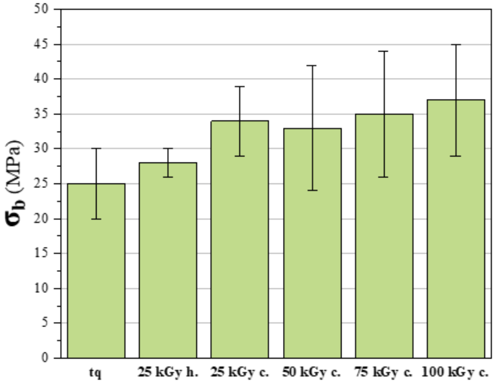
PBF irradiated samples - Effect of Radiation on mechanical performance and wettability

- ✓ Radiation treatment, particularly at doses of *50 kGy and 100 kGy, reduces the efficiency of enzymatic hydrolysis.*
- ✓ WCA and tensile confirmed that **no significant variation in Water Contact Angle** (sessile drop) and Elastic modulus, Stress at break and Elongation at break were found.
- ✓ possibility of **using both lower and higher dosages to avoid crosslinking and enhance depolymerization**

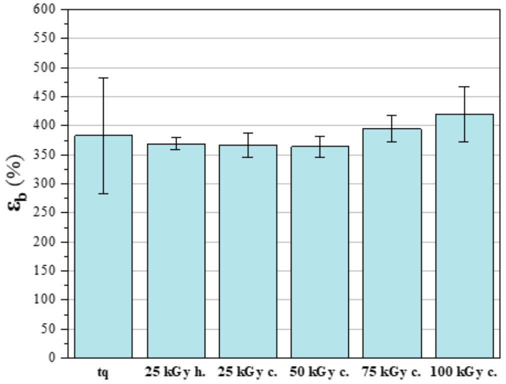
Elastic modulus

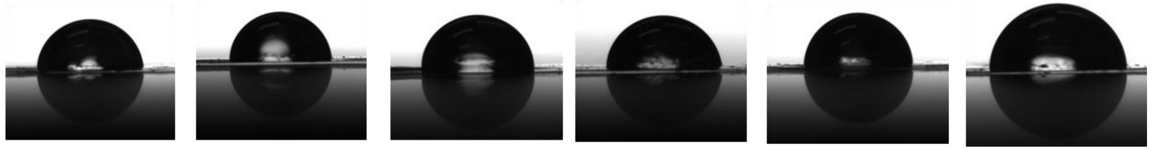


Stress at break



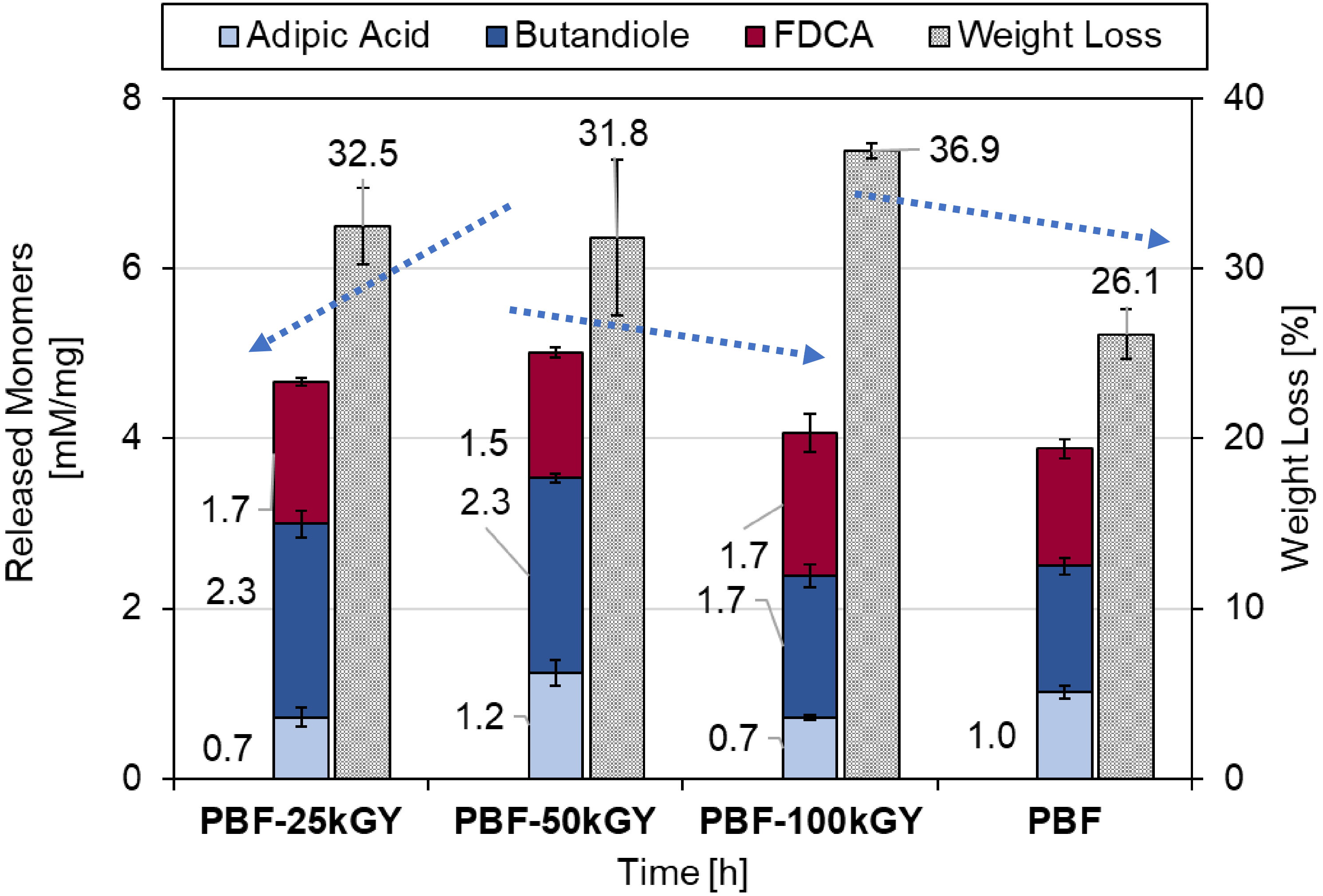
Elongation at break





TQ | 25 kGy (hot spot) | 25 kGy (cold spot) | 50 kGy (cold spot) | 75 kGy (cold spot) | 100 kGy (cold spot)

Results- Weight Loss and HPLC



- a sensitive balance point related to radiation
- High doses could cause crosslinking

- *Short aliphatic chains can be recovered*
- FDCA recovery compete with weak crosslinking

- Lower dosages (< 25 kGy) will be tested only for **hydrolysis purpose**

Verification of **competitive effect (crosslinking vs depolymerization) for gamma rays treated furan-based polymers**