Valorization of biopolymers waste through chemical recycling

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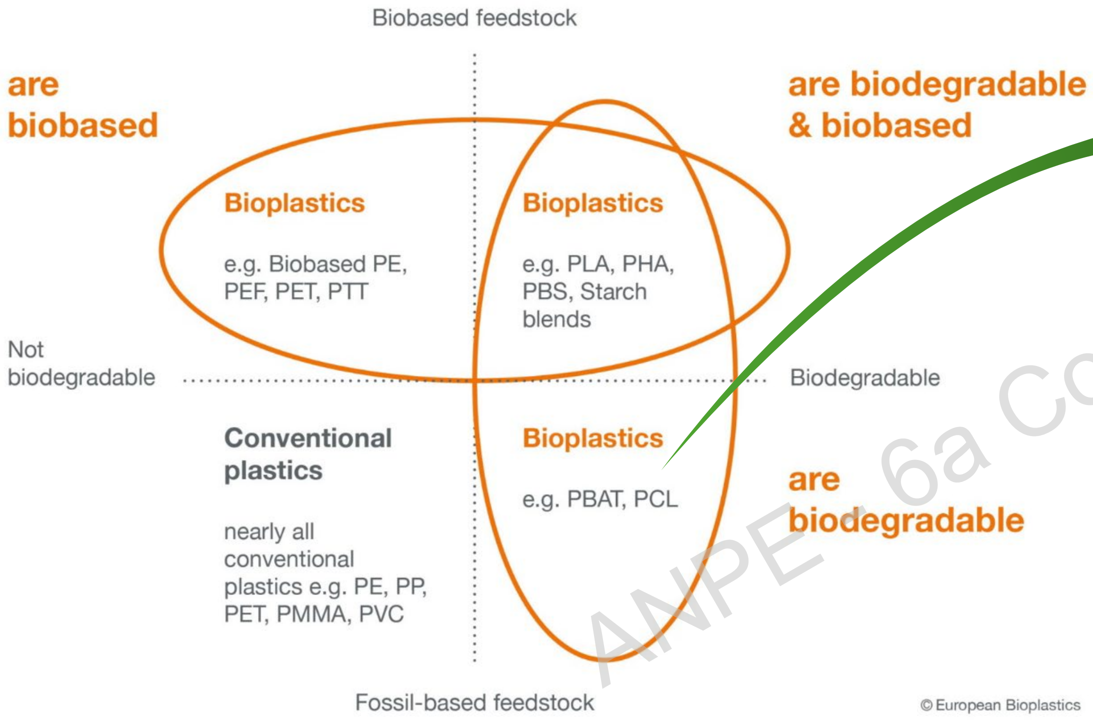
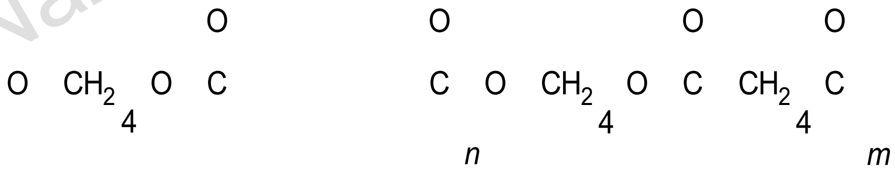
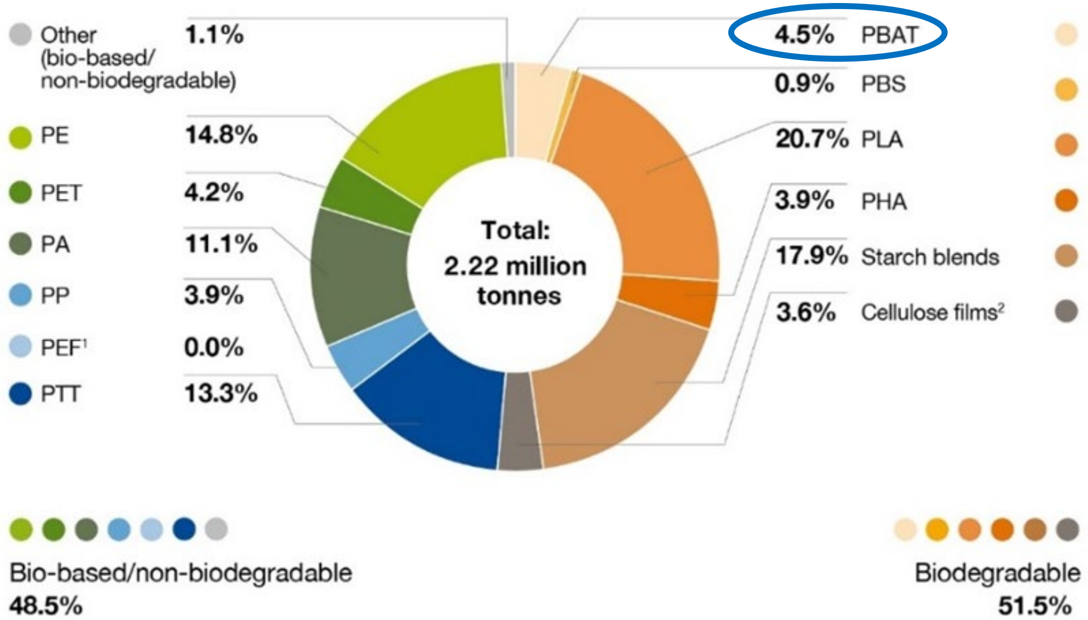
6° Conferenza Nazionale Poliuretano Espanso rigido

Introduction to Biopolymers



Poly(butylene adipate terephthalate) (PBAT)





Introduction to End-of-Life Scenarios

Biodegradation as EoL scenario?

High times required

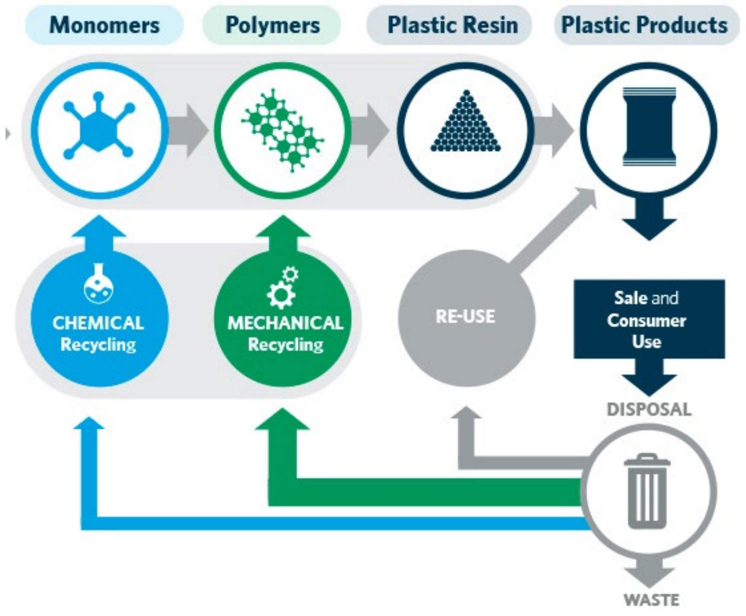
No recovering

This thesis

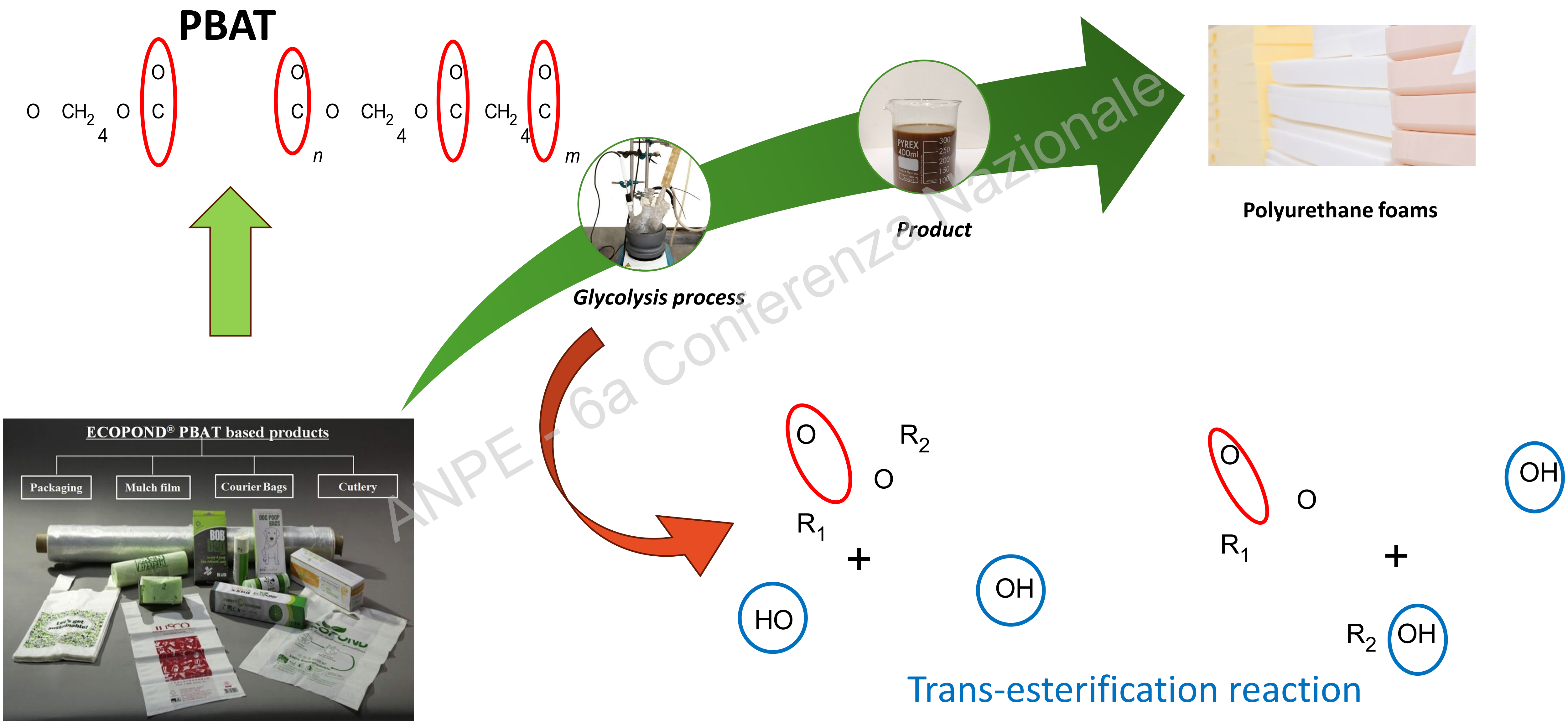
Mechanical recycling → Recovers polymer ✅

Chemical recycling → Recovers monomer ✅

Thermo Recycling → Recovers energy ✅



Glycolysis process



Objective of the thesis

Operative variables

Type of glycol

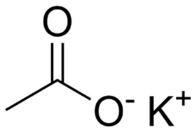
- **Glycol A**
- **Glycol B**

Weight ratio

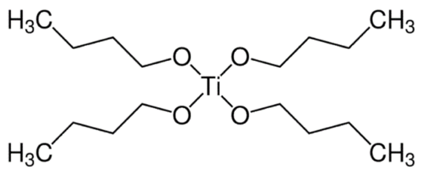
$$\frac{mass\ of\ waste\ [g]}{mass\ of\ glycol[g]}$$

Catalysts

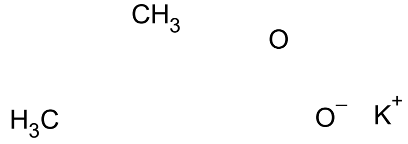
- **Potassium acetate**



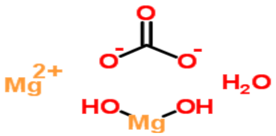
- **Titanium tetrabutoxide**



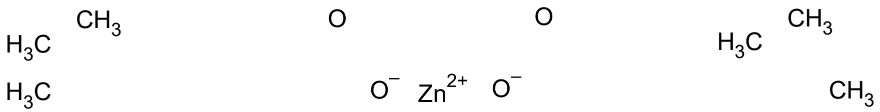
- **Potassium 2-ethylhexanoate**



- **Magnesium carbonate hydroxide**



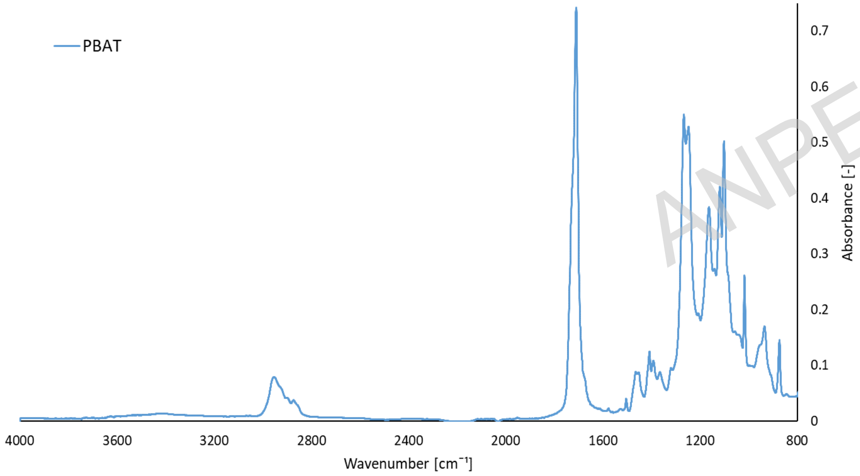
- **Zinc neodecanoate**



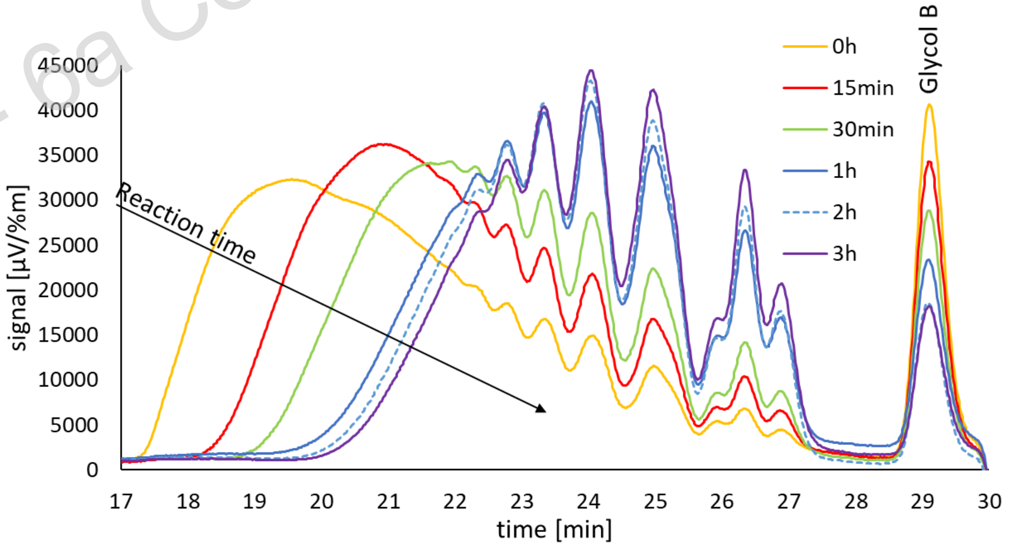
- **Viscosity**
- **Hydroxyl value**
- **Acid value**

Characterization

Fourier-transform Infrared Spectroscopy (FTIR)



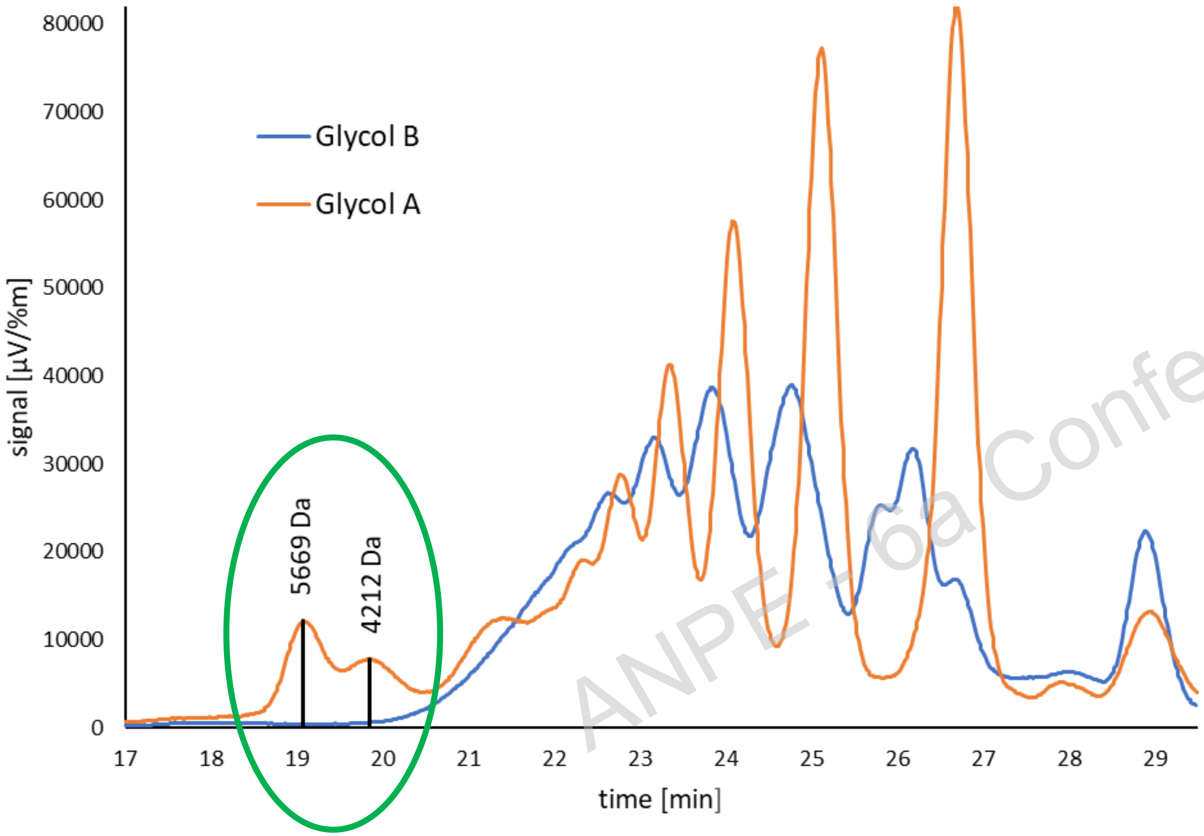
Gel Permeation chromatography (GPC)



Dynamic viscosity

Titrator for hydroxyl and acid values

Glycol A vs Glycol B



Fixed parameters
- ✓ Temperature
- ✓ Weight ratio
- ✓ Reaction time
- ✓ Catalyst
- ✓ Catalyst concentration

Glycol B is more reactive than Glycol A

Tests with Glycol A

Fixed parameters
- ✓ Weight ratio
- ✓ Reaction time

All between 200 and 500 mg_{KOH}/g

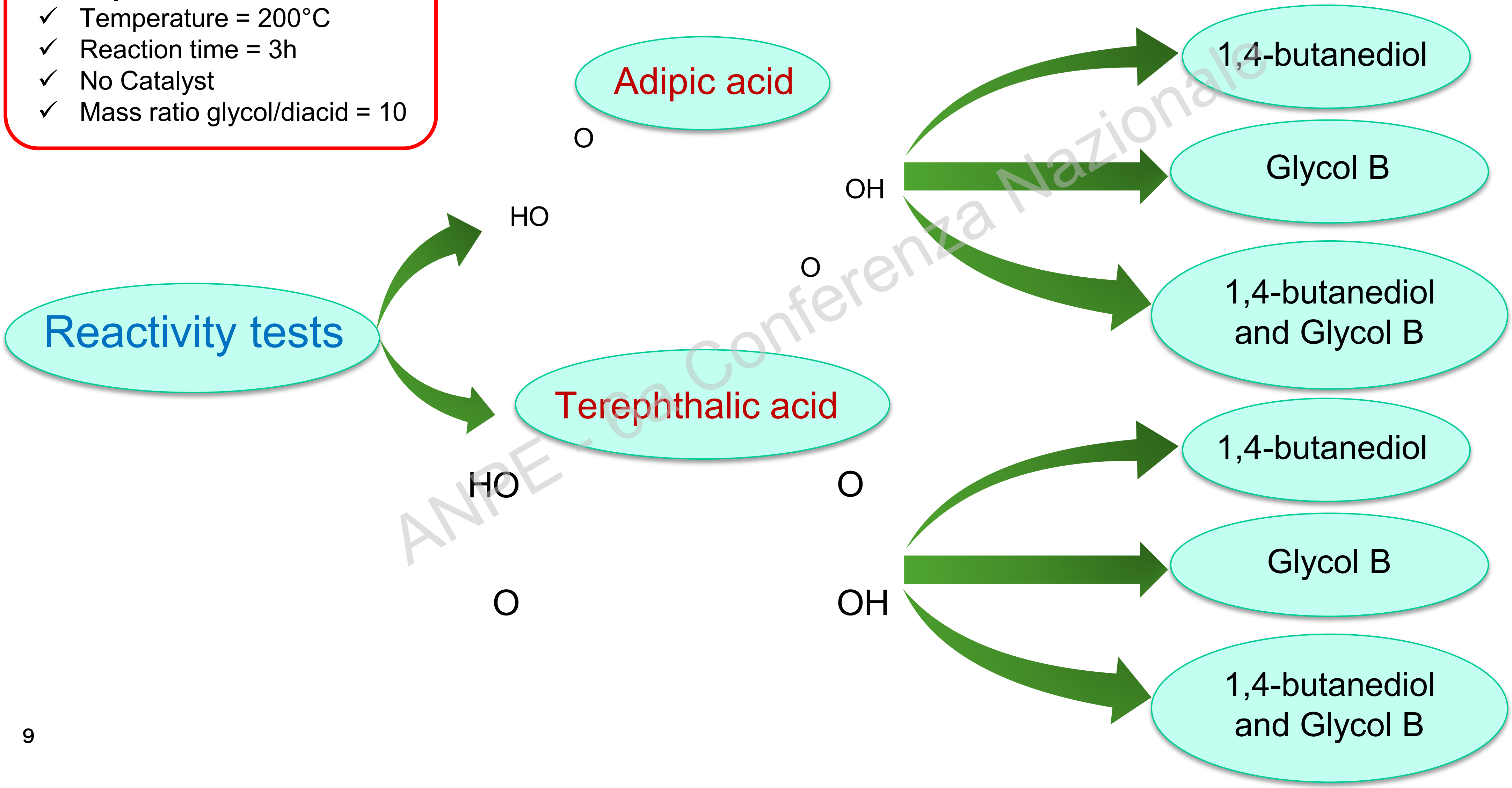
ID test	Viscosity [mPa·s]	HV [mg_{KOH}/g]	AV [mg_{KOH}/g]
TEST_1	3300	308	2.9
TEST_2	5750	257	8.3
TEST_3	3200	273	12
TEST_4	3200	296	20
TEST_5	5750	261	15

All below 8000 *mPa·s*

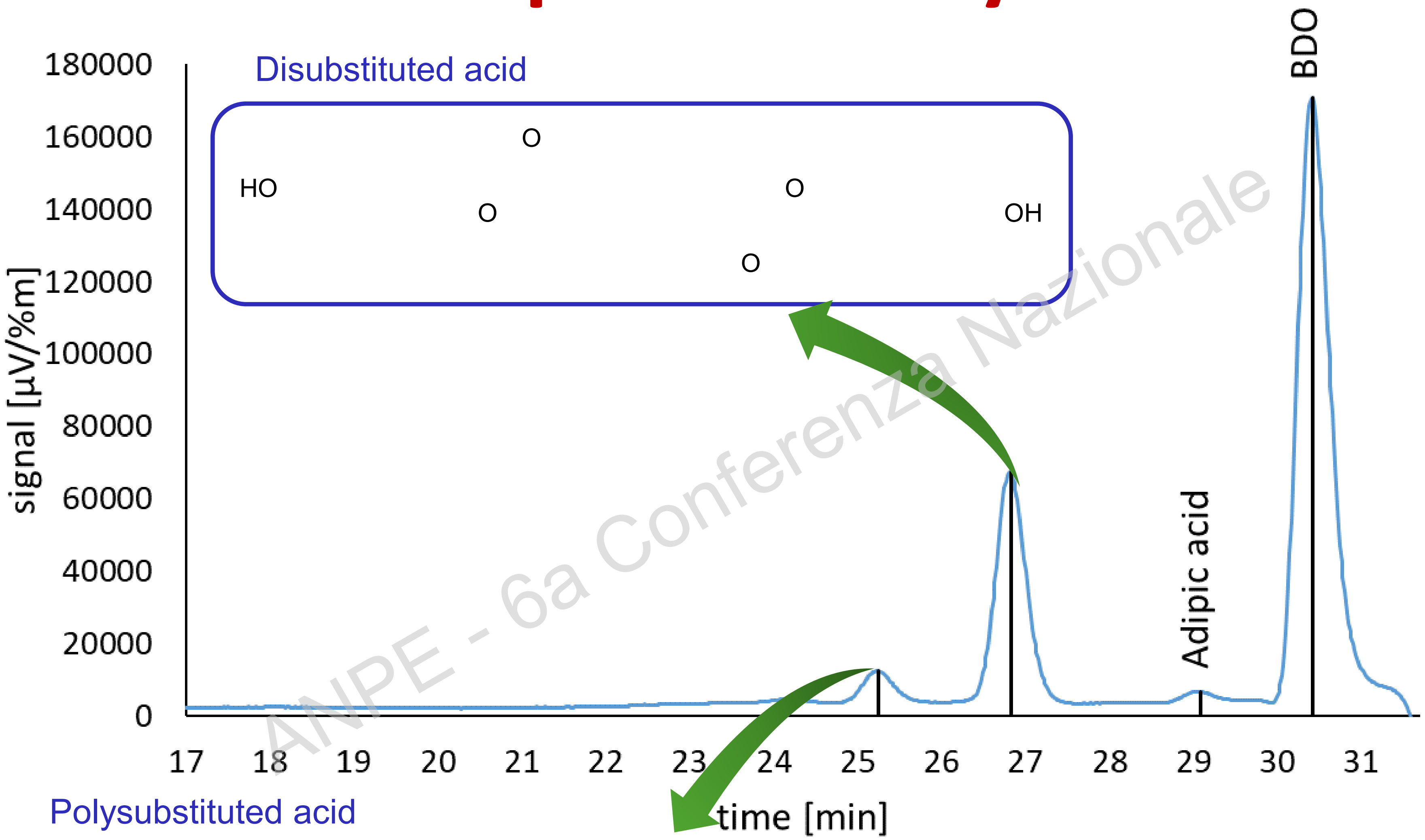
Lowest acid number

Reactivity tests

Fixed parameters
- ✓ Temperature = 200°C
- ✓ Reaction time = 3h
- ✓ No Catalyst
- ✓ Mass ratio glycol/diacid = 10



Gpc reactivity tests



Polysubstituted acid

Kinetic of the tests with adipic acid

$$v = \frac{d[COOR]}{dt} = k[COOH][OH][H^+]$$

Rate of polycondensation without an external catalyst

$$[OH] \sim constant$$

$$[H^+] = K_a^{\frac{1}{2}}[COOH]^{\frac{1}{2}}$$

Weak acid equilibrium

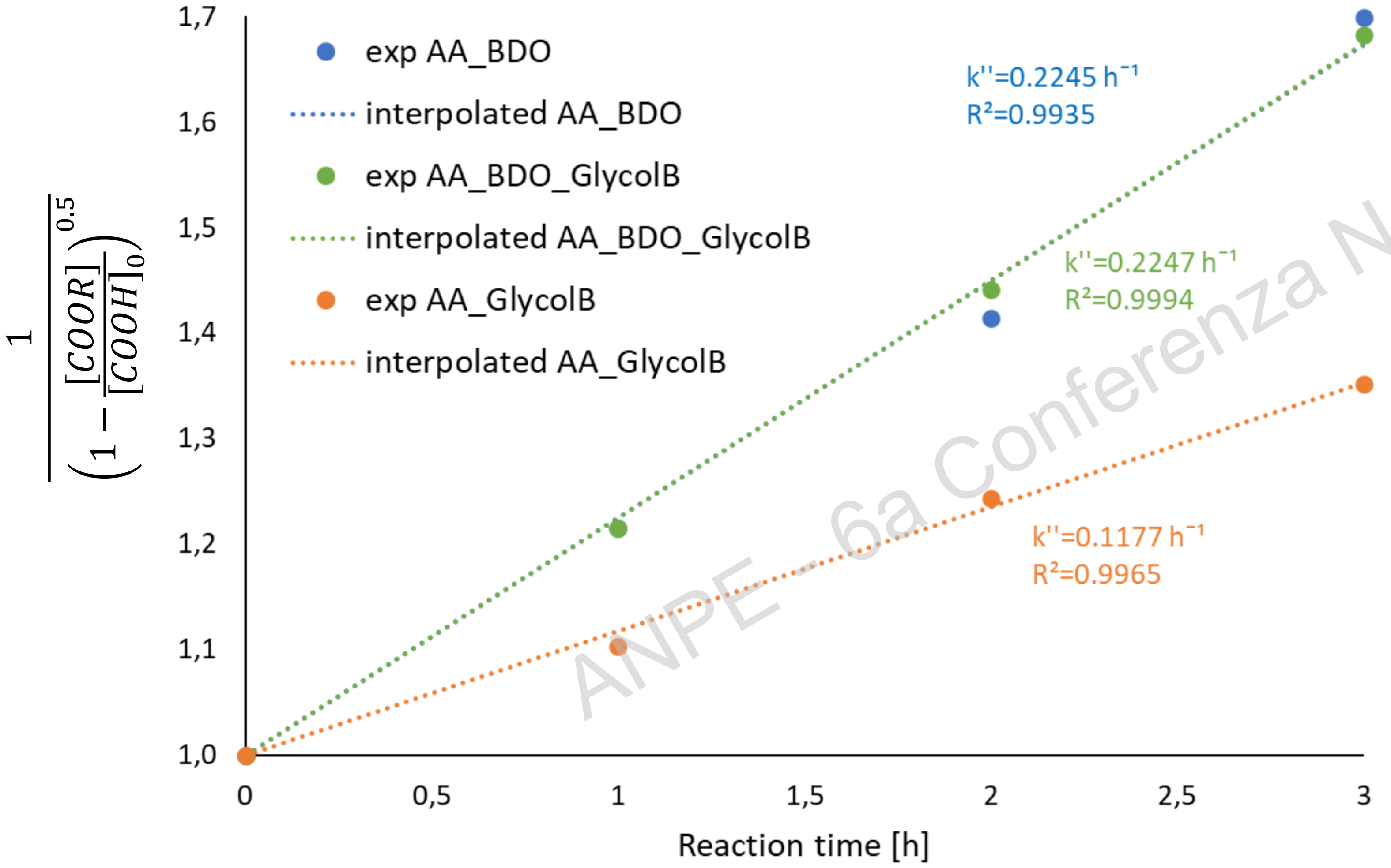
$$[COOH] = [COOH]_0 - [COOR]$$

$$v = \frac{d[COOR]}{dt} = k'([COOH]_0 - [COOR])^{\frac{3}{2}}$$

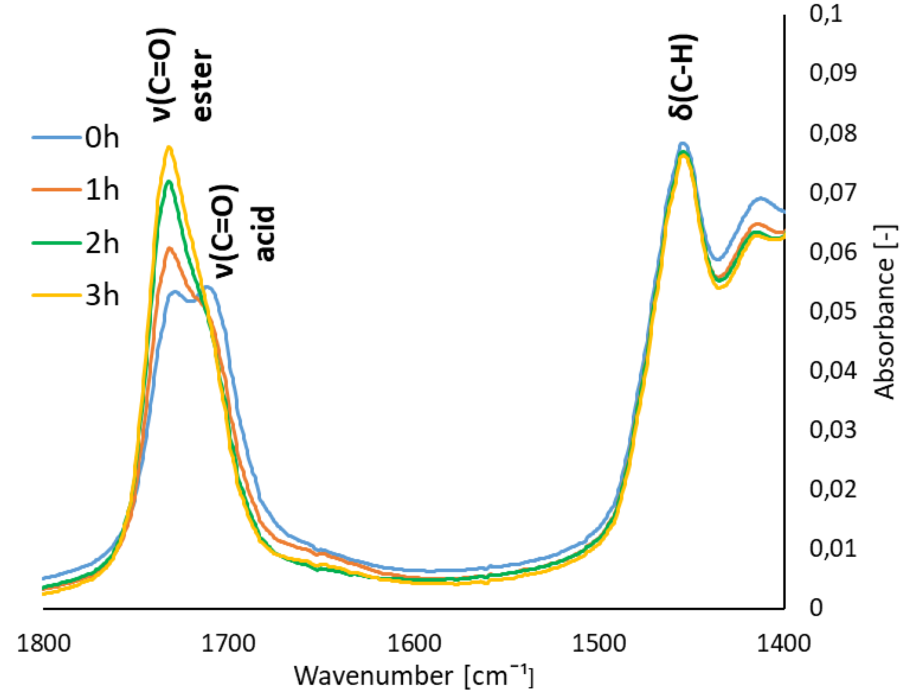
$$\frac{1}{\left(1 - \frac{[COOR]}{[COOH]_0}\right)^{\frac{1}{2}}} = k''t + 1$$

Final expression after integration

Kinetic of the tests with adipic acid

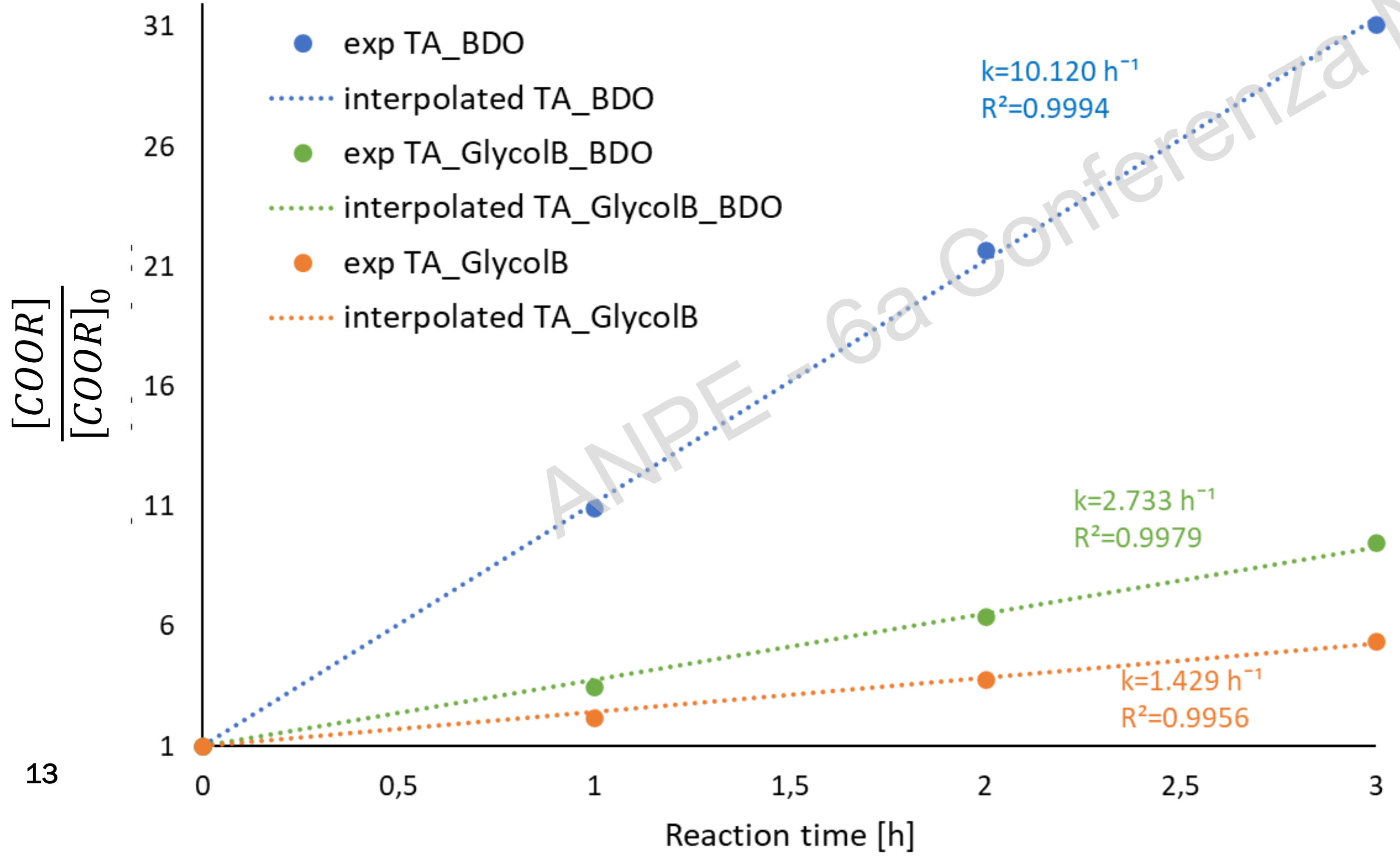


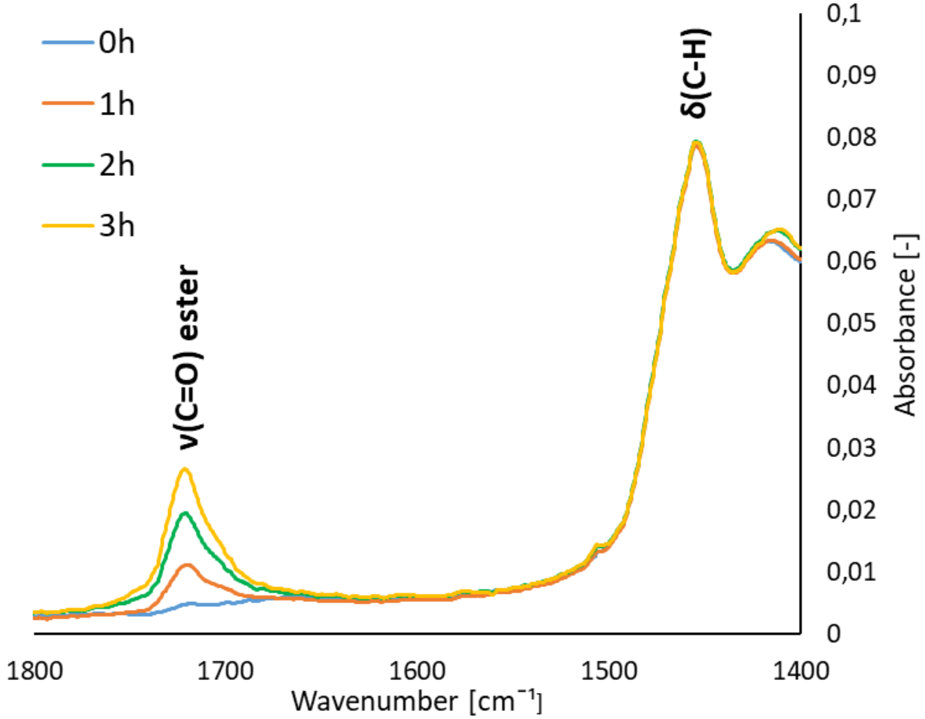
$$\frac{1}{\left(1-\frac{[COOR]}{[COOH]_0}\right)^{\frac{1}{2}}} = k''t + 1$$



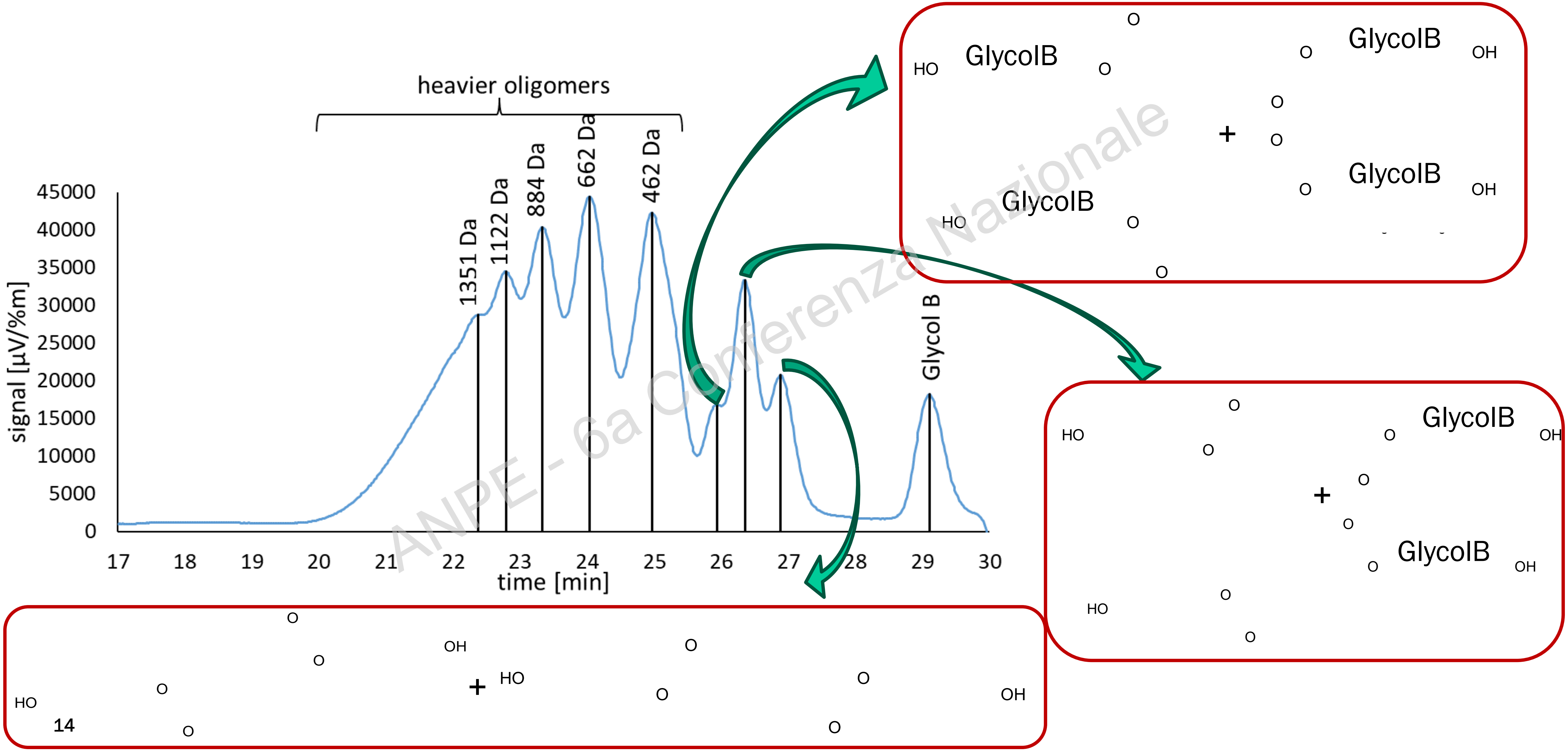
Kinetic of the tests with terephthalic acid

Low solubility of the acid → Mass transfer from solid to liquid is the controlling step → $\frac{[COOR]}{[COOR]_0} = k \cdot t + 1$





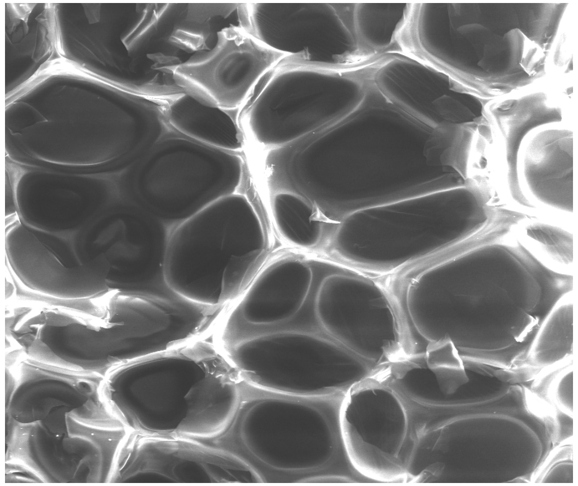
Gpc glycolyzate used for foams



Foam formulation

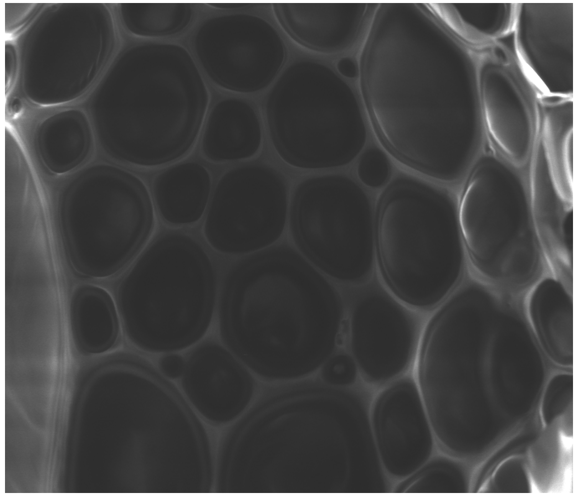
	Component	REF	25% RP	50% RP	75% RP	100% RP
Industrial polyols	**Pol 1 [g]**	50	25	-	-	-
	Pol 2 [g]	50	50	50	25	-
Glycolyzate	**RP [g]**	-	25	50	75	100
Catalysts	**Cat 1 [g]**	0.86	1	1.2	1.2	1.3
	Cat 2 [g]	3	3	3	2.7	3
Silicone	**B8443 [g]**	2	2	2	2	2
Blowing agents	**H_2O [g]**	1	1	1	1	1
	C_5 [g]	10.2	11.6	11.2	10.8	11.3
Isocyanate	**MDI [g]**	217	210	203	213	223
Characteristic times	**Cream [s]**	29	27	16	20	27
	Gel [s]	48	56	43	56	69
	Tack-free [s]	59	80	70	85	112

Pur/pir Foams

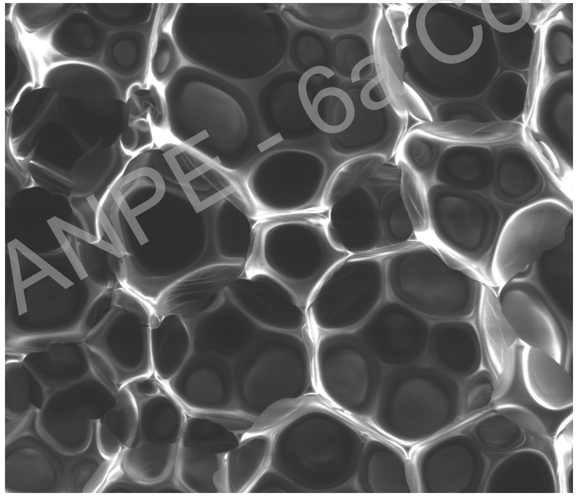


REF

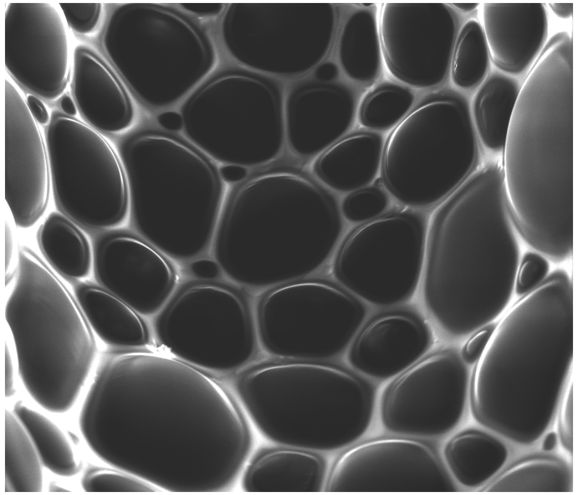
	ρ [kg/m³]	$\sigma_{//,norm}$ [kPa]	$\sigma_{\perp,norm}$ [kPa]	Aniso ratio [-]	λ [mW/(m·K)]	d [µm]
REF	40.4	318±5	141±4	2.25	25.0±0.2	136±23
25% RP	42.9	349±23	160±11	2.18	25.2±0.2	114±18
50% PBAT	42.3	360±26	179±10	2.01	24.2±0.2	103±19
75% PBAT	42.8	353±7	165±13	2.14	23.7±0.2	98±20
100% PBAT	43.6	305±6	167±14	1.83	24.6±0.2	167±31



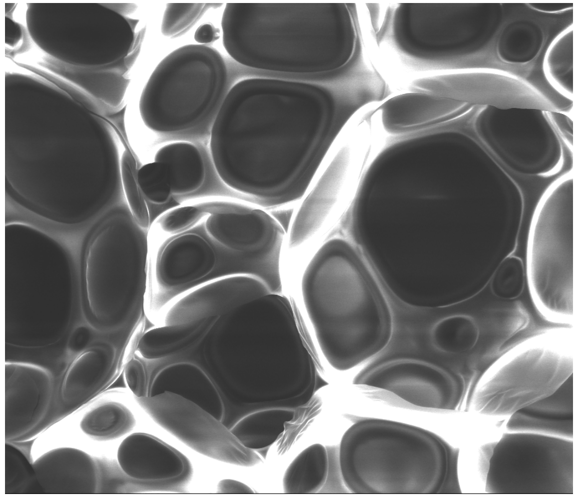
25% PBAT



50% PBAT



75% PBAT



100% PBAT

Conclusions and further studies

- **Glycolysis** is a **promising** method for recycling PBAT;
- PUR/PIR foams can be produced with up to **100% of glycolyzate** with **comparable performances** with respect to reference foam;
- Since **PBAT** is mainly utilized in **blends** with other polymers, additional research will be done.

Thank you for your attention

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