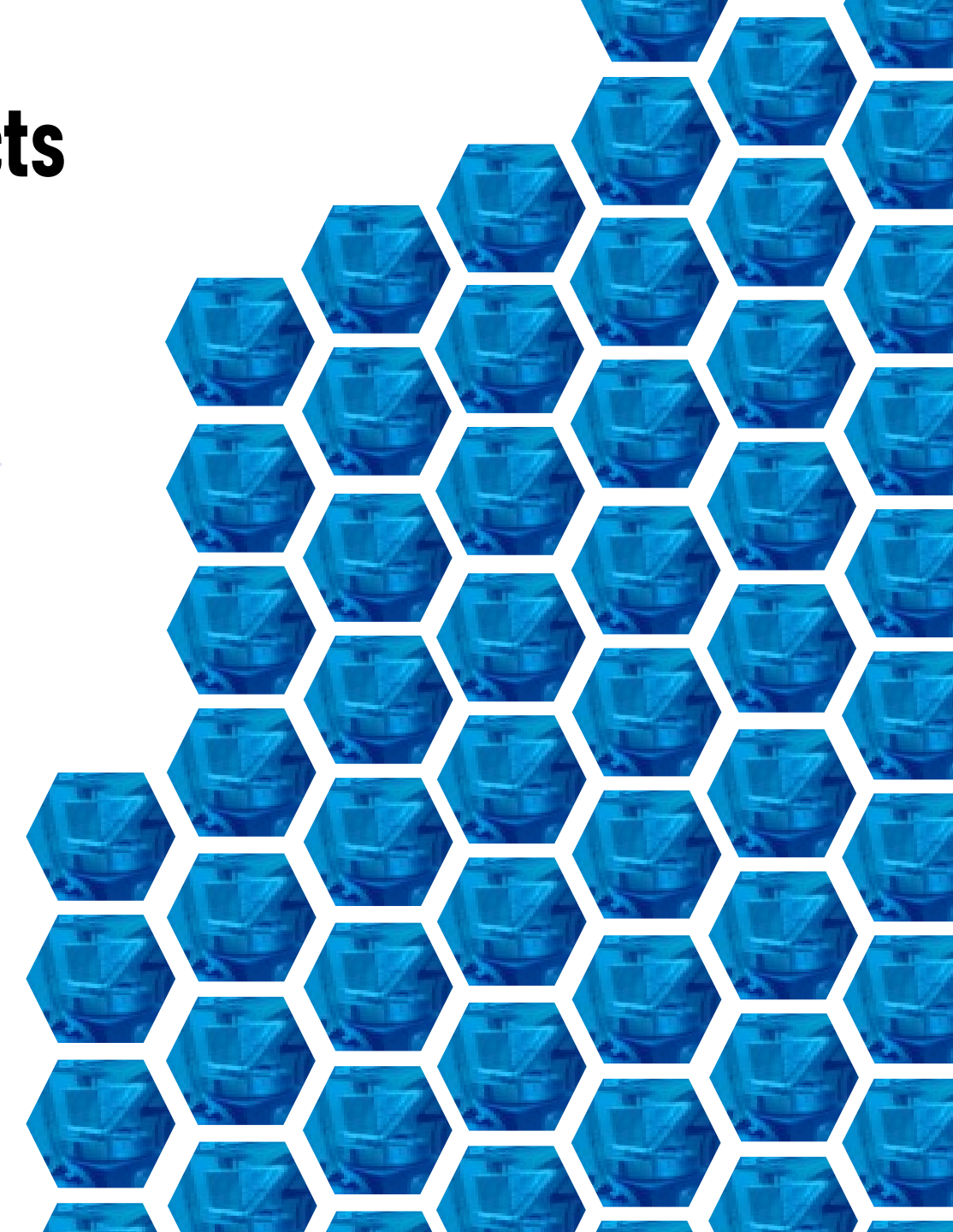
On the formation of structural defects during fire retarded polyethylene rotomolding

Mateusz Barczewski[1], Joanna Aniśko-Michalak[1], Aleksander Hejna[1], Mateusz Maniak[1], Patryk Mietliński[1], Bartosz Gapiński[1], Marek Insbrandt[2], Joanna Paciorek-Sadowska[2], Mariusz Marć[3], Marcin Borowicz[2], Marek Szostak[1]

mateusz.barczewski@put.poznan.pl

[1] Poznan University of Technology, Poland
[2] Kazimierz Wielki University in Bydgoszcz, Poland
[3] Gdańsk University of Technology, Poland



Materials and samples preparation

Polymer

Petrochemical high-density polyethylene (HDPE) GC 7260 (Basell Orlen Polyolefins, USA); melt flow rate (MFR) 8.0 g/10 min (190°C/2.16 kg), density 0.960 g/cm^3.

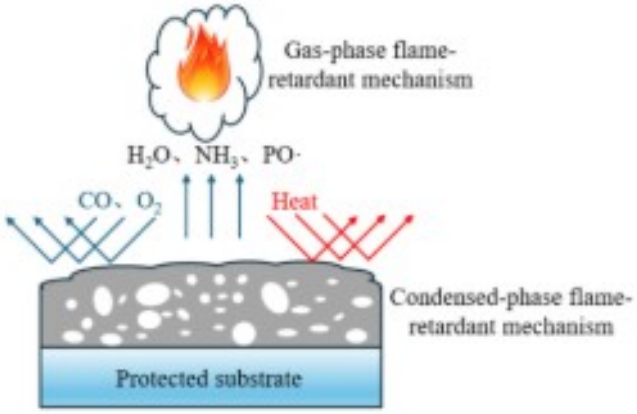
Additives

Ammonium polyphosphate (APP)

Addforce. FR APP 201 (WTH GmbH); density 1.9 g/cm^3.

Pentaerythritol (PEN)

Addforce FR Penta M40 (WTH GmbH), density 1.03 g/cm^3



Flame-retardant mechanism of polymers containing intumescent flame-retardant system (FRS).*

Sample containing IFRs during the cone calorimeter test.

*G. Tang, C. Shang, Y. Qin, J. Lai, Coatings, 15, 1, 99, 2025.

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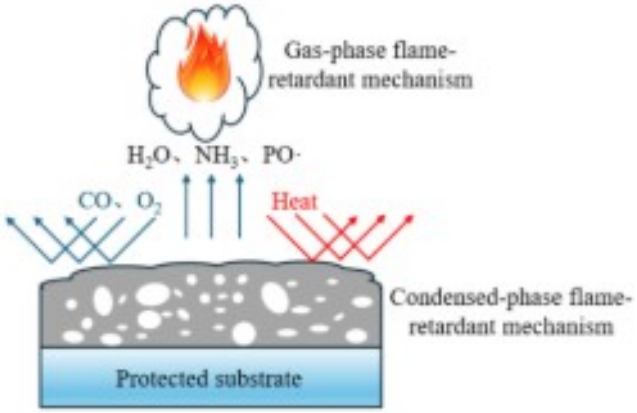

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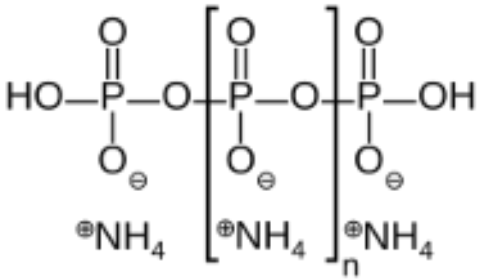
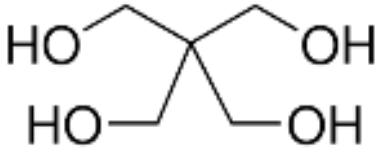


Ammonium polyphosphatre (APP)
Addforce. FR APP 201 (WTH GmbH)

halogen-free acidic source and blowing agent



Pentaerythritol (PEN)
Addforce FR Penta M40 (WTH GmbH)

carbonific agent

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HDPE + 20% FRS (70:30 APP:PEN)

↓

Co-rotating twin-screw extrusion

170°C 170°C 170°C 165°C 165°C 160°C 160°C 155°C 150°C 50°C / **100 rpm**

→

Rotational molding

A prototype RotoLab-X rotational molding machine built for the project

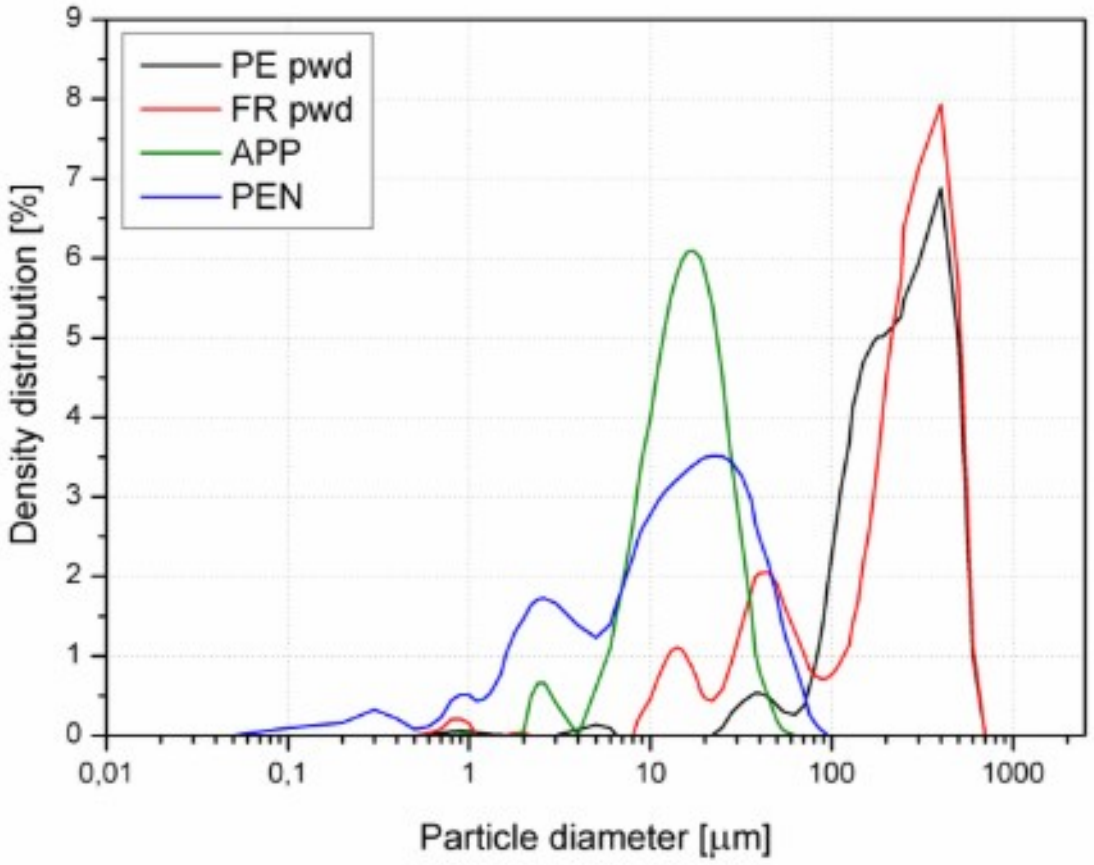
Particle size distribution

Apparatus: **Anton Paar PSA 1190**

Measuring range: **0.01-2500 µm**
Measuring mode: **dry**
Recalculation model: **Mia**

Material	D10	D50	D90
	[%]		
PE pwd	98.35	232.45	428.23
FR pwd	29.52	240.09	429.80
APP	6.91	14.72	27.11
PEN	1.62	12.38	37.82

Diameter at which 10%, 50% and 90% of the sample's volume is composed of particles smaller than that size.



Particle size distribution of polymeric powders and additives.

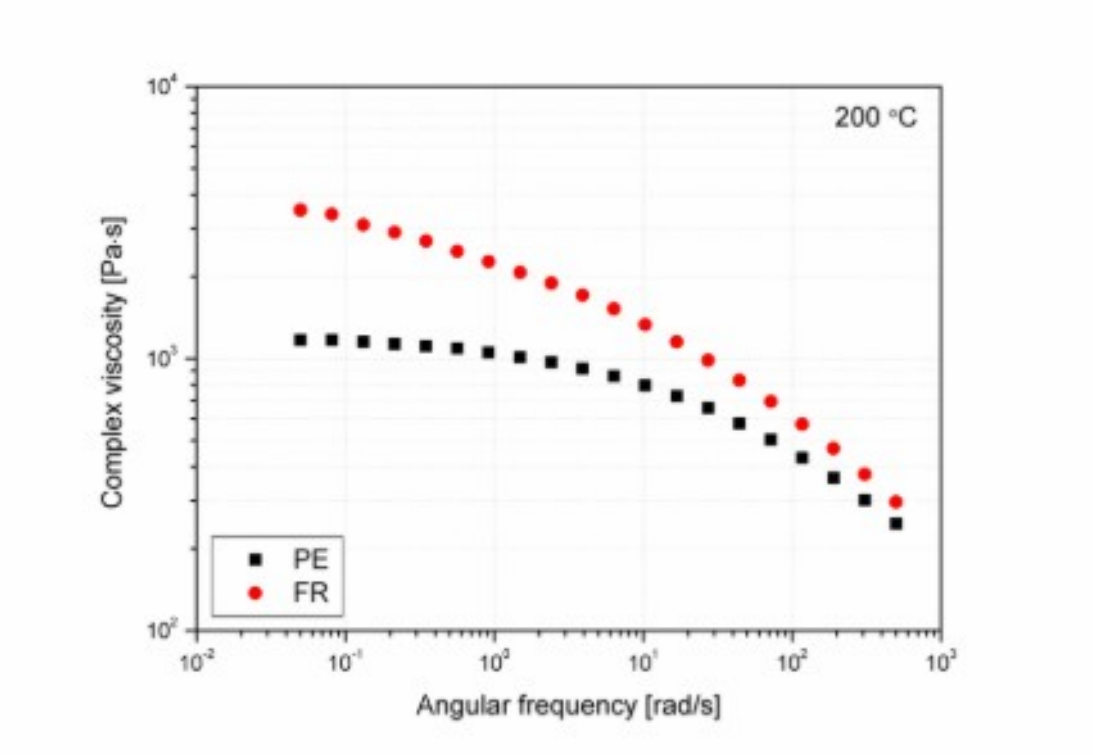
Rheological properties

Apparatus: **Anton Paar MCR 301**

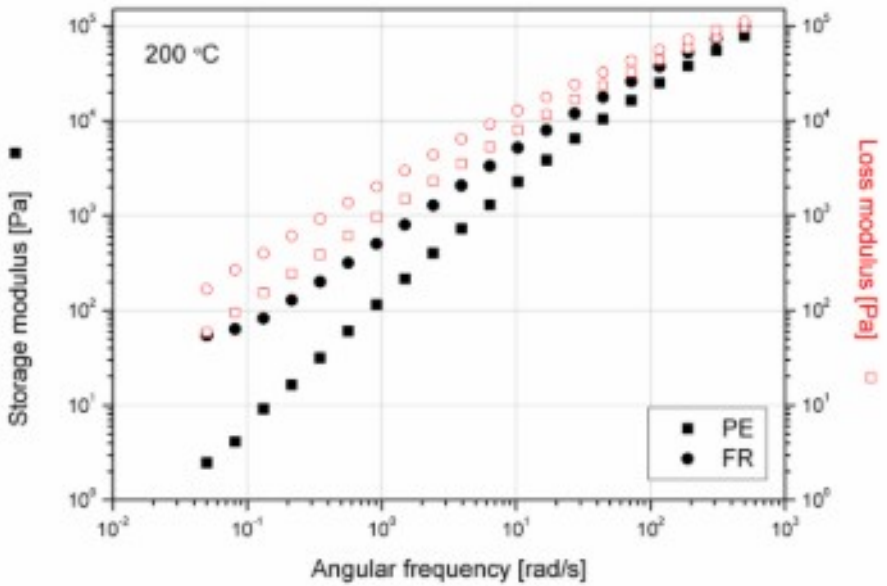
Temperature: **200 °C**

Strain; angular frequency range: **0.5%; 0.05-500 rad/s**

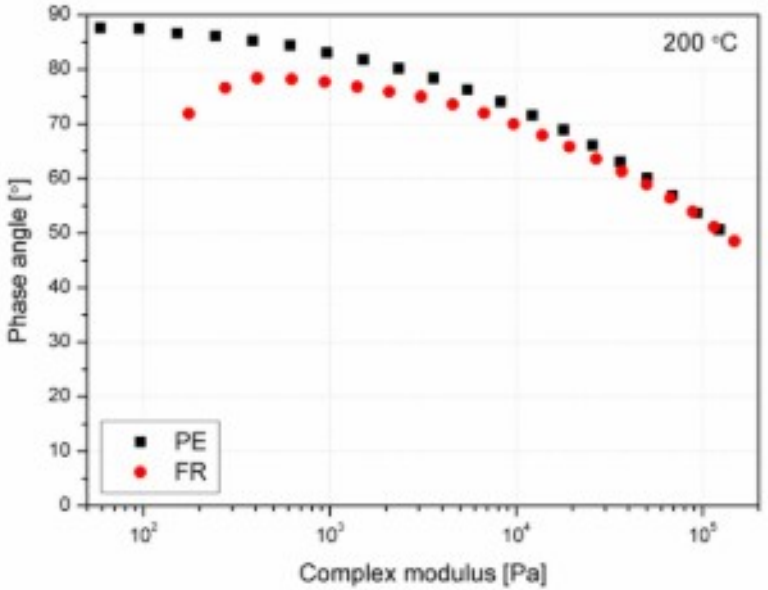
Measuring system: **25 mm plate-plate; 0.5 mm gap**



Complex modulus curve of PE- and FR-series in the form of powder before processing.



Storage and loss moduli vs. angular frequency curves of PE- and FR-series in the form of powder before processing.



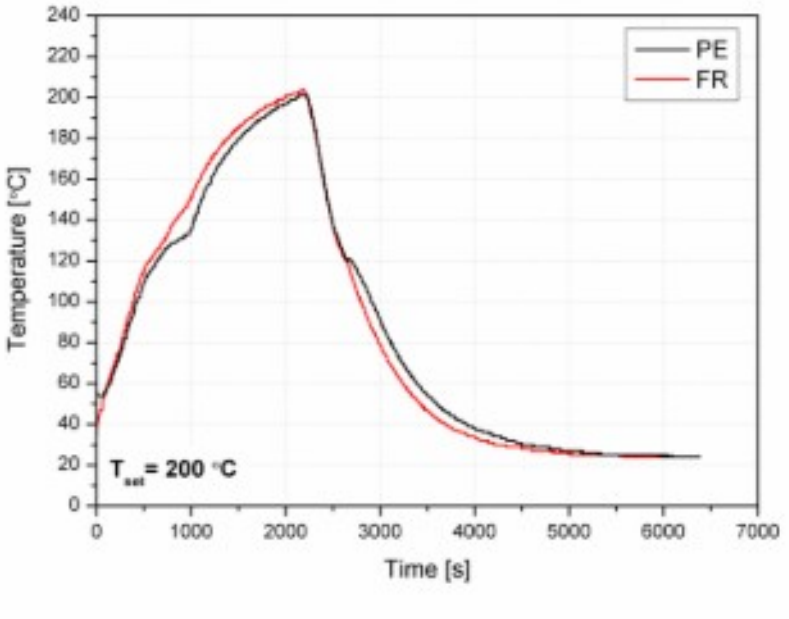
van Gurp-Palmen plots of PE- and FR-series in the form of powder before processing.

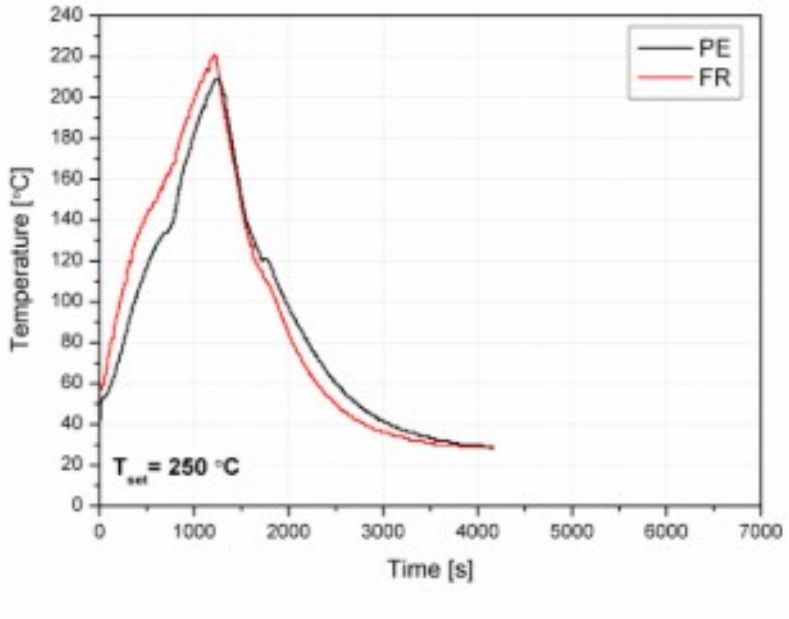
Internal air temperature analysis

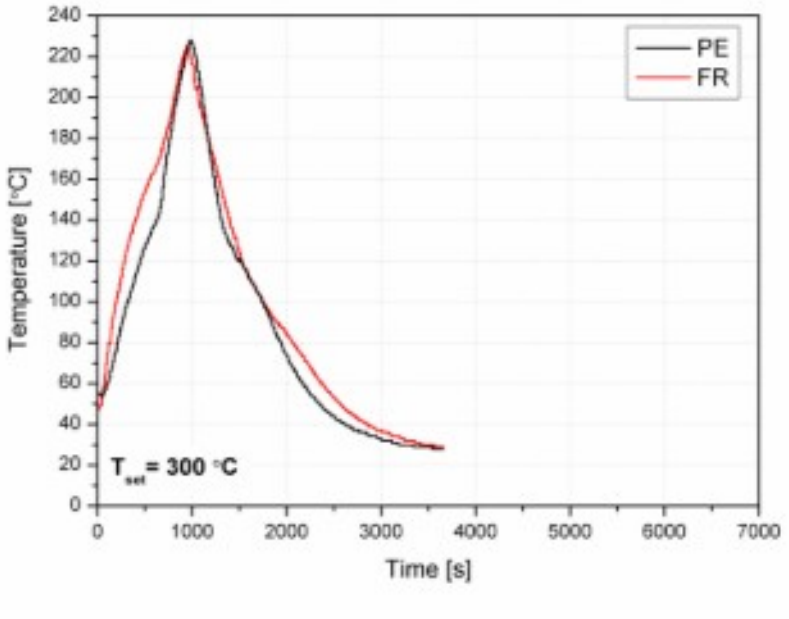
Machine: **Łukasiewicz RotoLab-X (PL)**

Heating chamber temperature set: **200, 250, 300 °C**
Rotational speed: **8 rpm, 10 rpm**
Control temperature/time: **200 °C / 3 min**
Temperature sensor: **PT100**

	Peak internal air temperature [°C; min]		
Temperature set	200 °C	250 °C	300 °C
PE	201; 36.5	209; 20.7	228; 16.4
FR	204; 36.3	221; 20.3	225; 15.9







Internal air temperature as a function of time during processing of PE and FR at different heating chamber temperatures of 200, 250, and 300 °C.

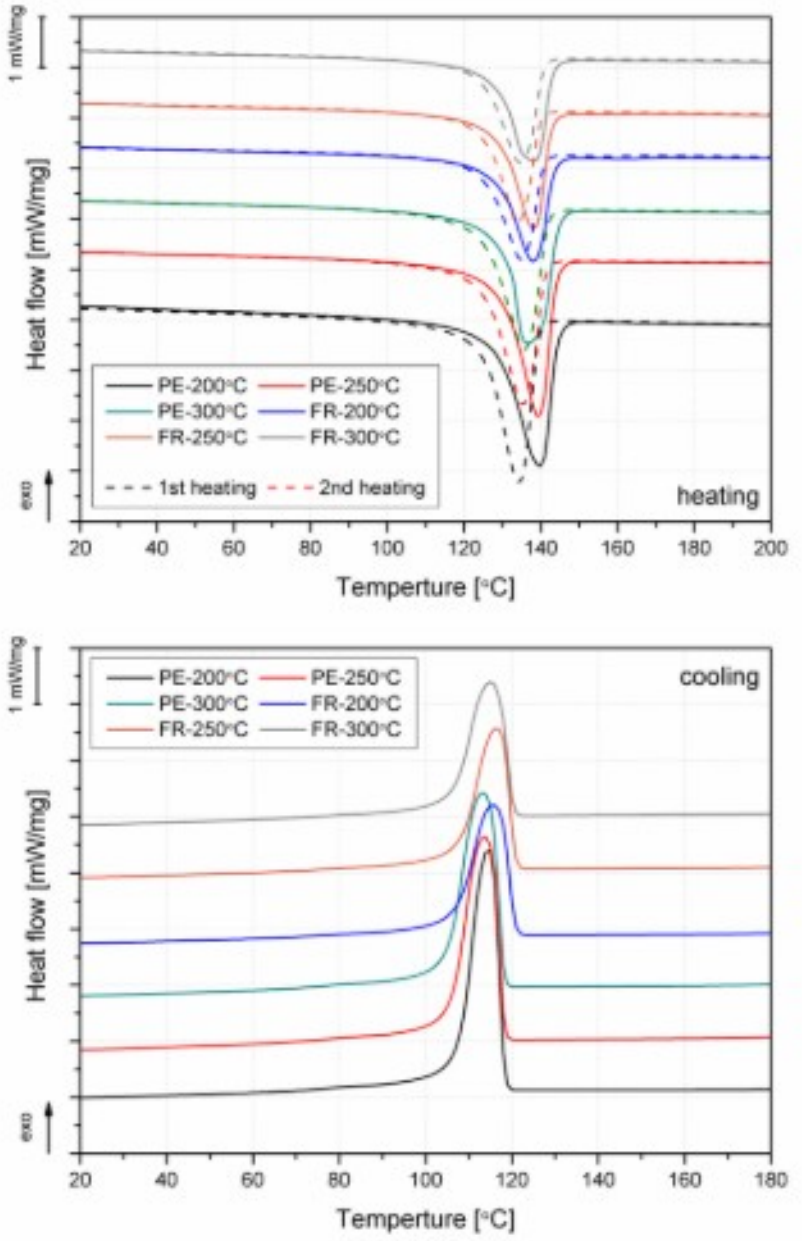
Differential scanning calorimetry (DSC)

Apparatus: **Netzsch 204 F1 Phoenix**

Heating/cooling rate: **10 °C/min**
Temperature range: **-50-200 °C**
Gas: **nitrogen**

Material	T_{M1}	T_C	T_{M2}	X_{C1}	X_{C2}
	[°C]			[%]	
PE-200°C	139.7	114.5	134.3	74.5	73.8
PE-250°C	139.3	113.7	135.5	73.2	72.7
PE-300°C	136.5	113.3	135.9	72.6	73.4
FR-200°C	138.0	115.5	134.9	73.0	72.6
FR-250°C	138.1	116.4	133.9	76.2	75.3
FR-300°C	138.2	115.1	138.2	77.4	76.8

Thermal properties of PE and FR rotomolded parts obtained from DSC measurements.



DSC curves obtained during the first and second heating of rotomolded samples.

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PE-300°C	136.5	113.3	135.9	72.6	73.4
FR-200°C	138.0	115.5	134.9	73.0	72.6
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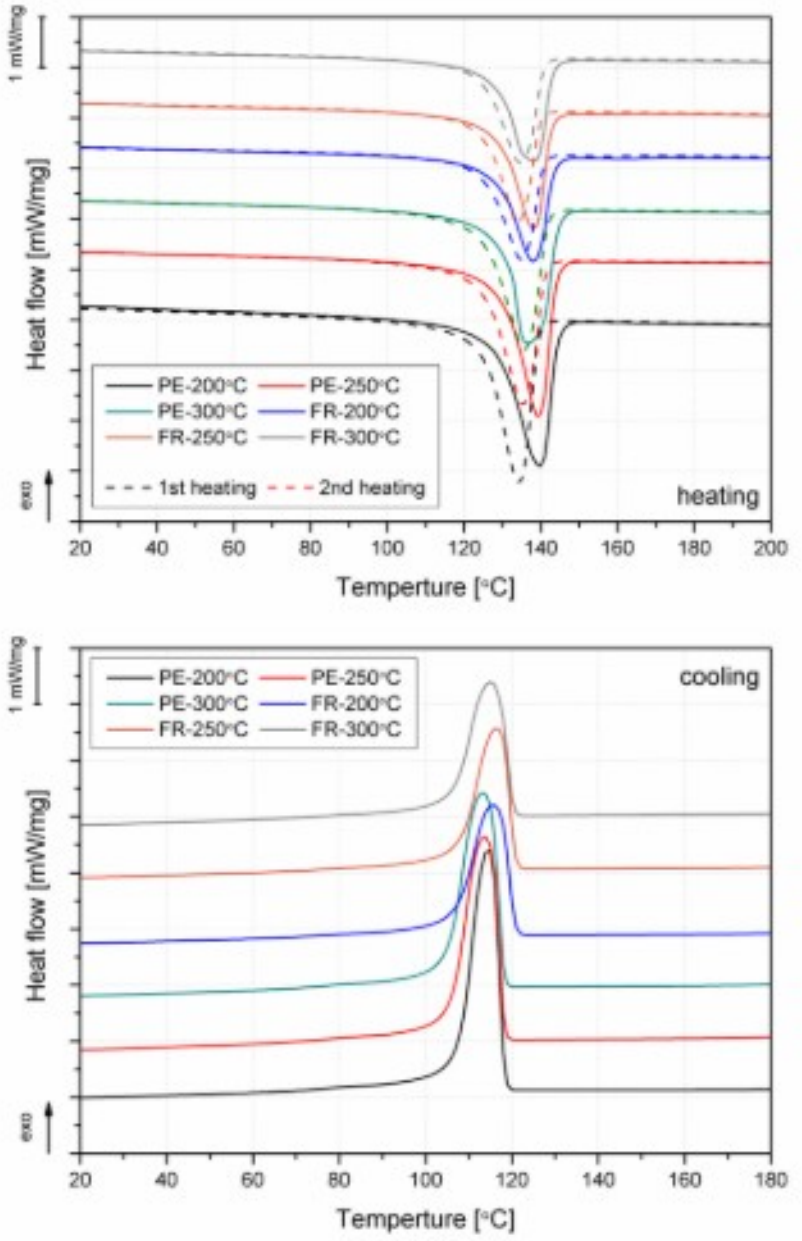
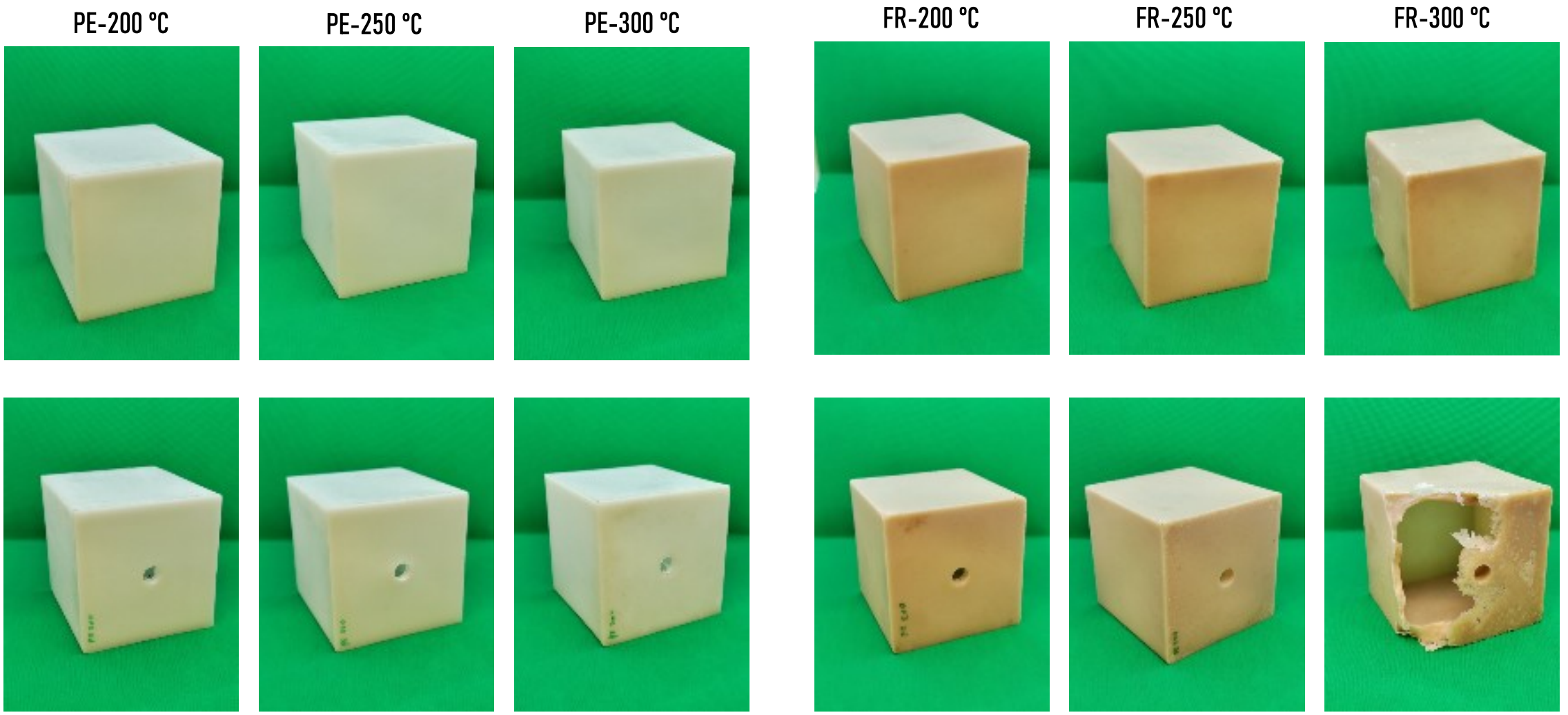


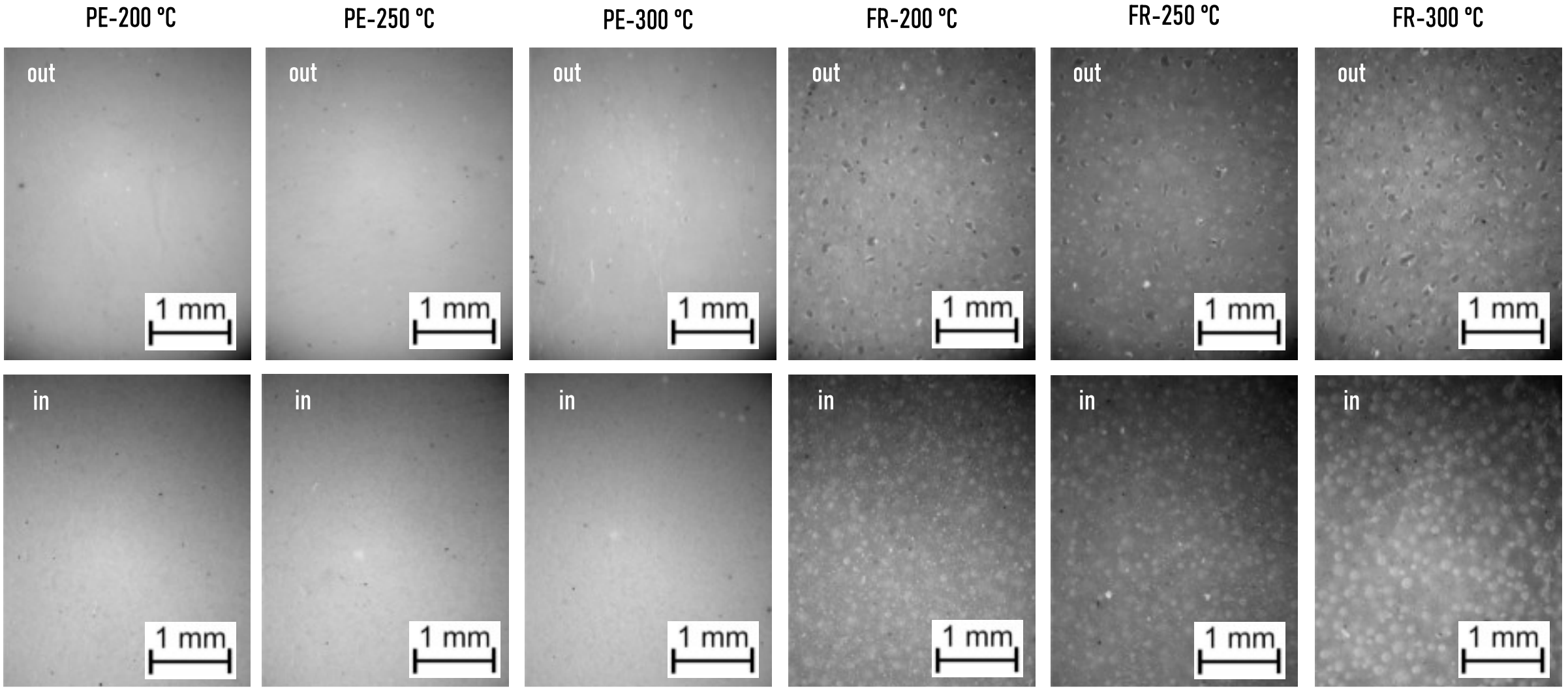
DSC curves obtained during the first and second heating of rotomolded samples.

Rotomolded parts structure analysis



Photos of rotomolded parts from PE and FR series processed at 200, 250 and 300 °C.

Rotomolded parts surface analysis



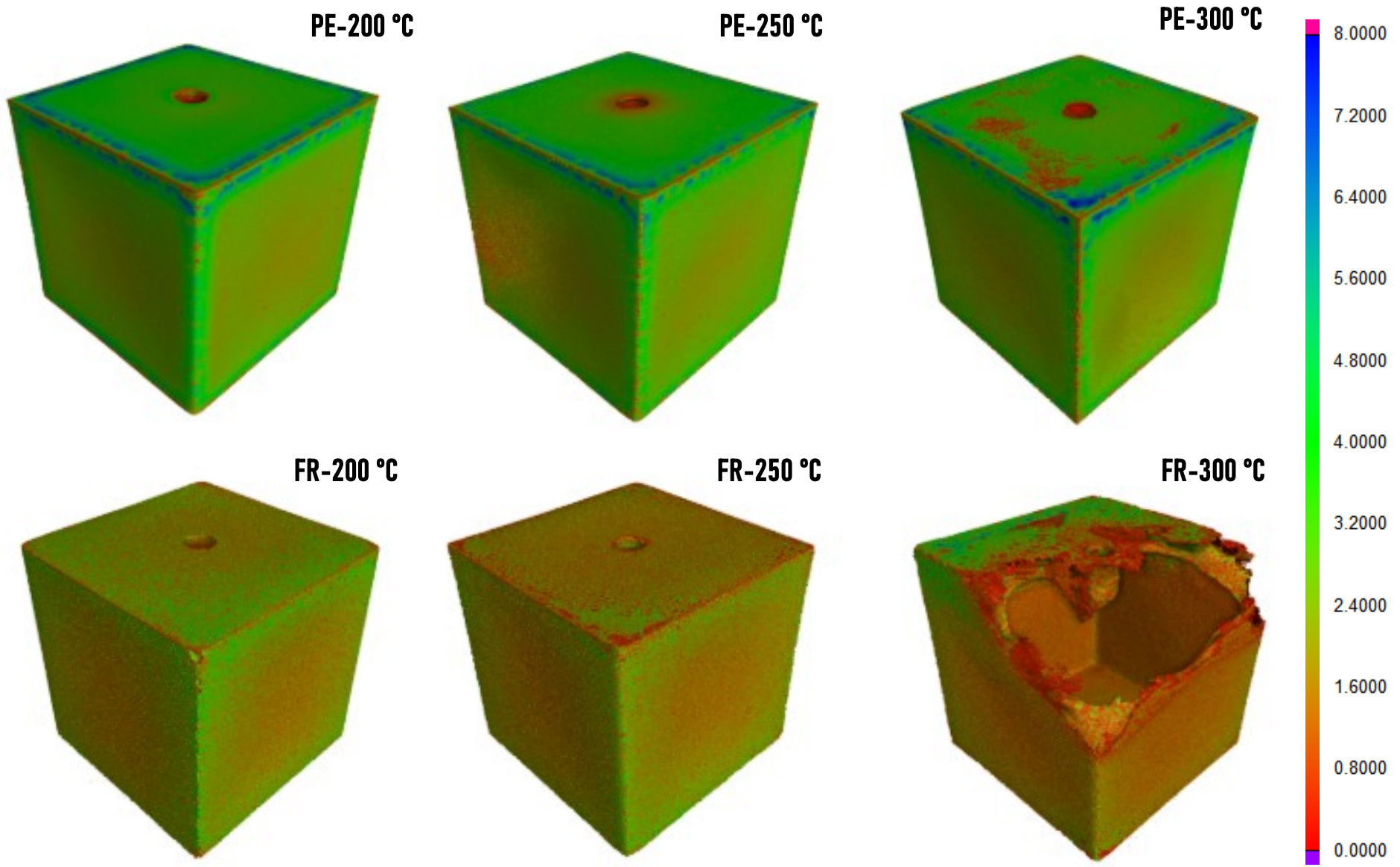
Microscopic photos of the outer (out) and inner (in) surfaces of rotomolded parts made of PE and FR-series at 200, 250, and 300 °C

Rotomolded parts structure analysis – 3D computed tomography

Apparatus : **General Electric v|tome|xswith**

VGStudioMAX 2.2 software

Voxel size: **60 µm**
Voltage: **170 kV**
Exposure time: **350 ms**
Number of photos: **1000**

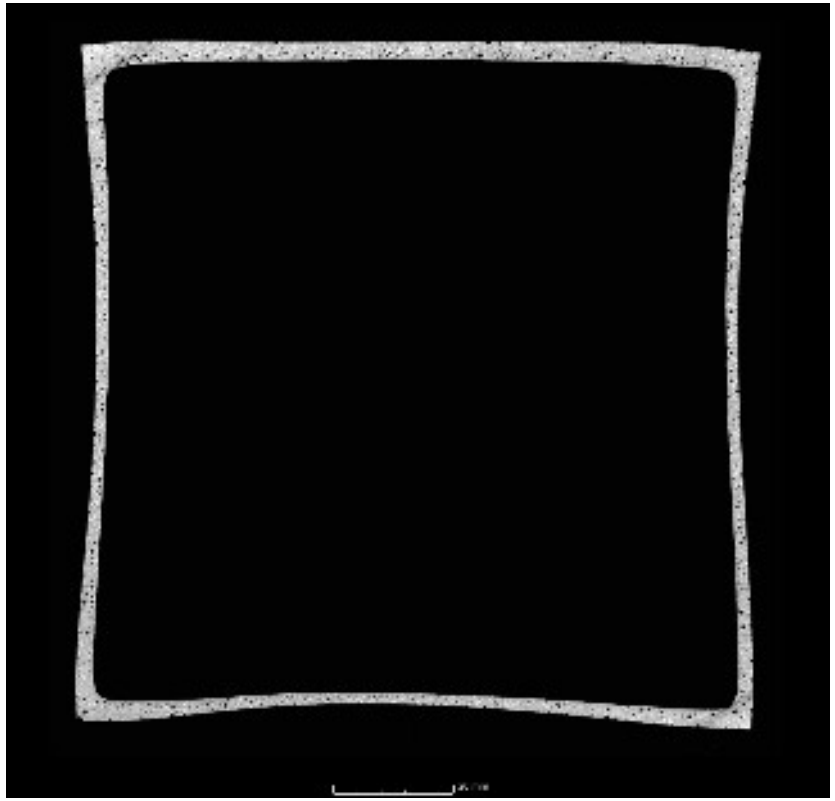


3D CT images of rotomolded parts from PE and FR series processed at 200, 250 and 300 °C.

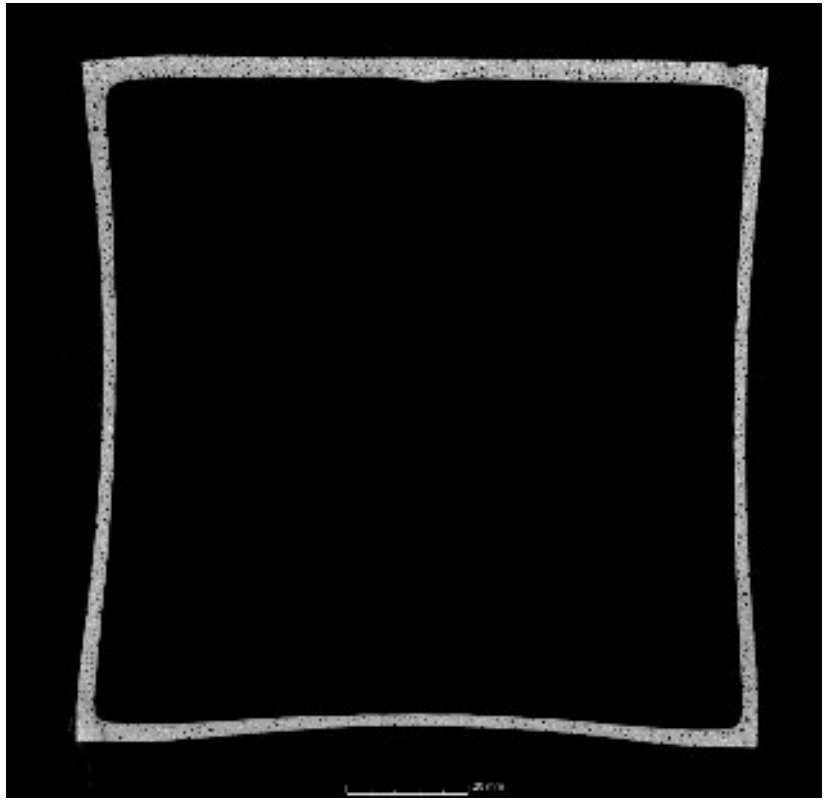
Rotomolded parts structure analysis – computed tomography 3D-CT

Apparatus : **General Electric v|tome|xswith**
VGStudioMAX 2.2 software

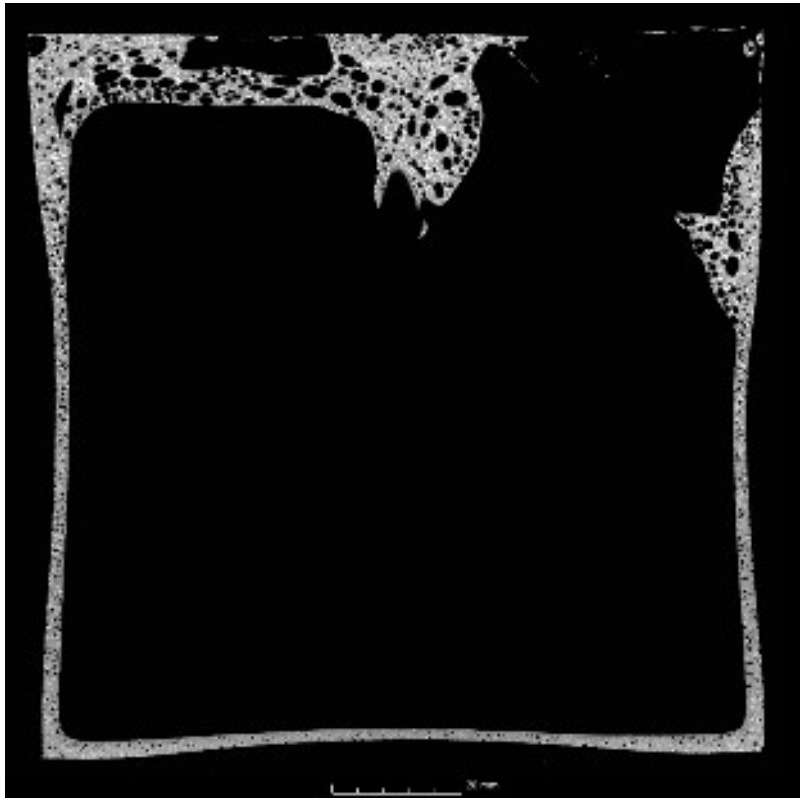
FR-200 °C



FR-250 °C



FR-300 °C



3D CT images of rotomolded parts from FR series processed at 200, 250 and 300 °C.

Colorimetric analysis (CIE L*a*b*)

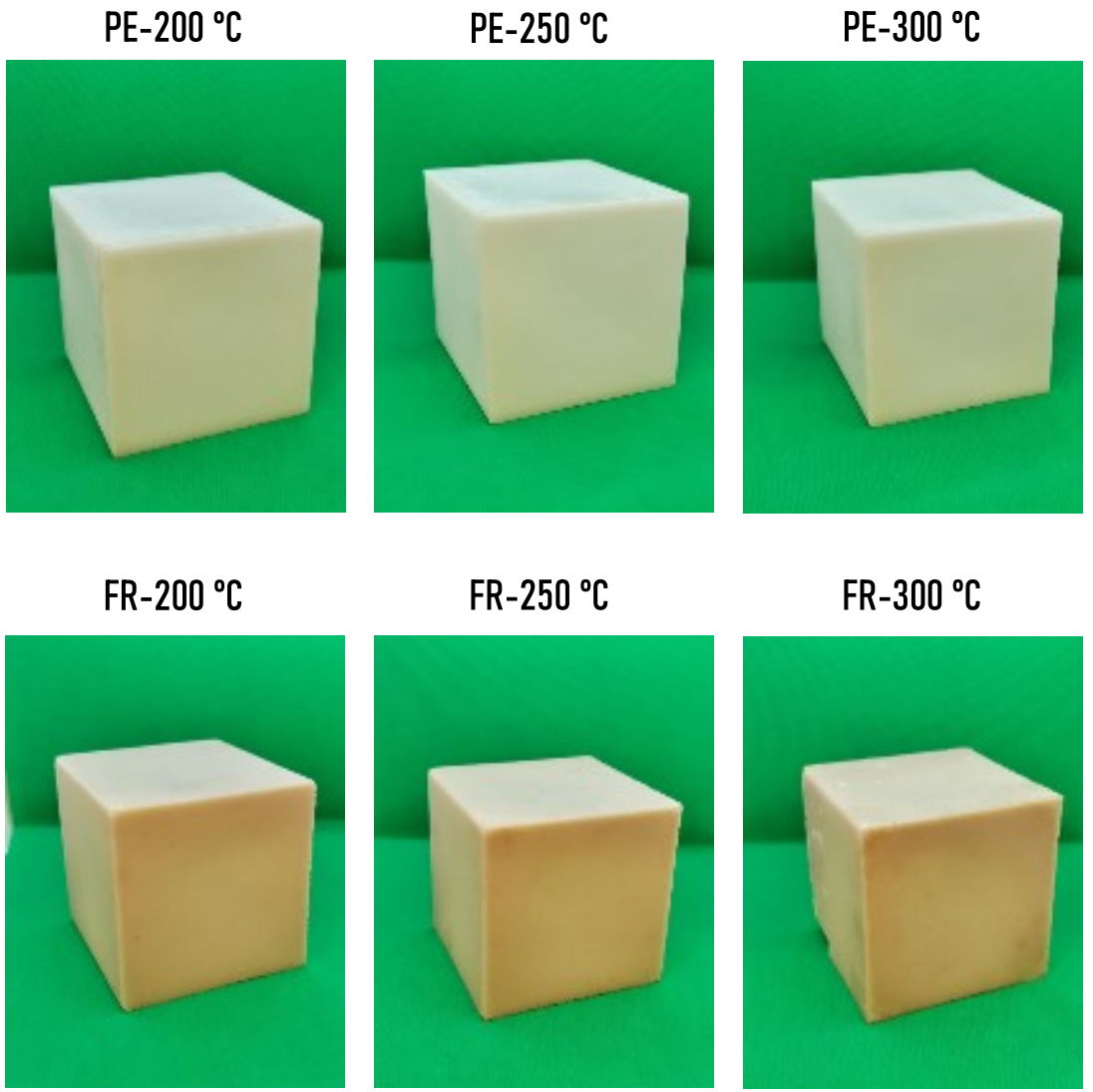
Apparatus: **Portable spectrophotometer - NR145 Precision Colorimeter 3nh**

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}$$

- 0< ΔE <1: no visible color change
- 1< ΔE <2: slight color change, noticeable only by an experienced observer
- 2< ΔE <3.5: medium color change, noticeable by an inexperienced observer
- 3.5 < ΔE < 5 significant color change,- ΔE >5 very pronounced color change

Material	L*	a*	b*	ΔE_{Ref-RM}
PEp	95.15±0.79	0.01±0.122	1.30±0.20	-
PE-200 °C	58.20±1.18	-2.40±0.09	-1.95±0.24	-
PE-250 °C	58.799±0.71	-2.52±0.07	-1.97±0.25	0.39
PE-300 °C	58.47±0.48	-2.35±0.07	-1.87±0.14	0.15
FRp	94.26±0.81	1.15±0.14	4.72±0.63	-
FR-200 °C	59.62±1.00	1.13±0.15	8.48±0.23	-
FR-250 °C	58.44±0.88	1.37±0.14	8.82±0.24	1.77
FR-300 °C	57.60±0.62	1.89±0.29	9.77±0.62	5.92

Color parameters of PE and FR powders and rotomolded parts by CIEL*a*b* and total color difference (ΔE).



Photos of rotomolded parts from PE and FR series processed at 200, 250 and 300 °C.

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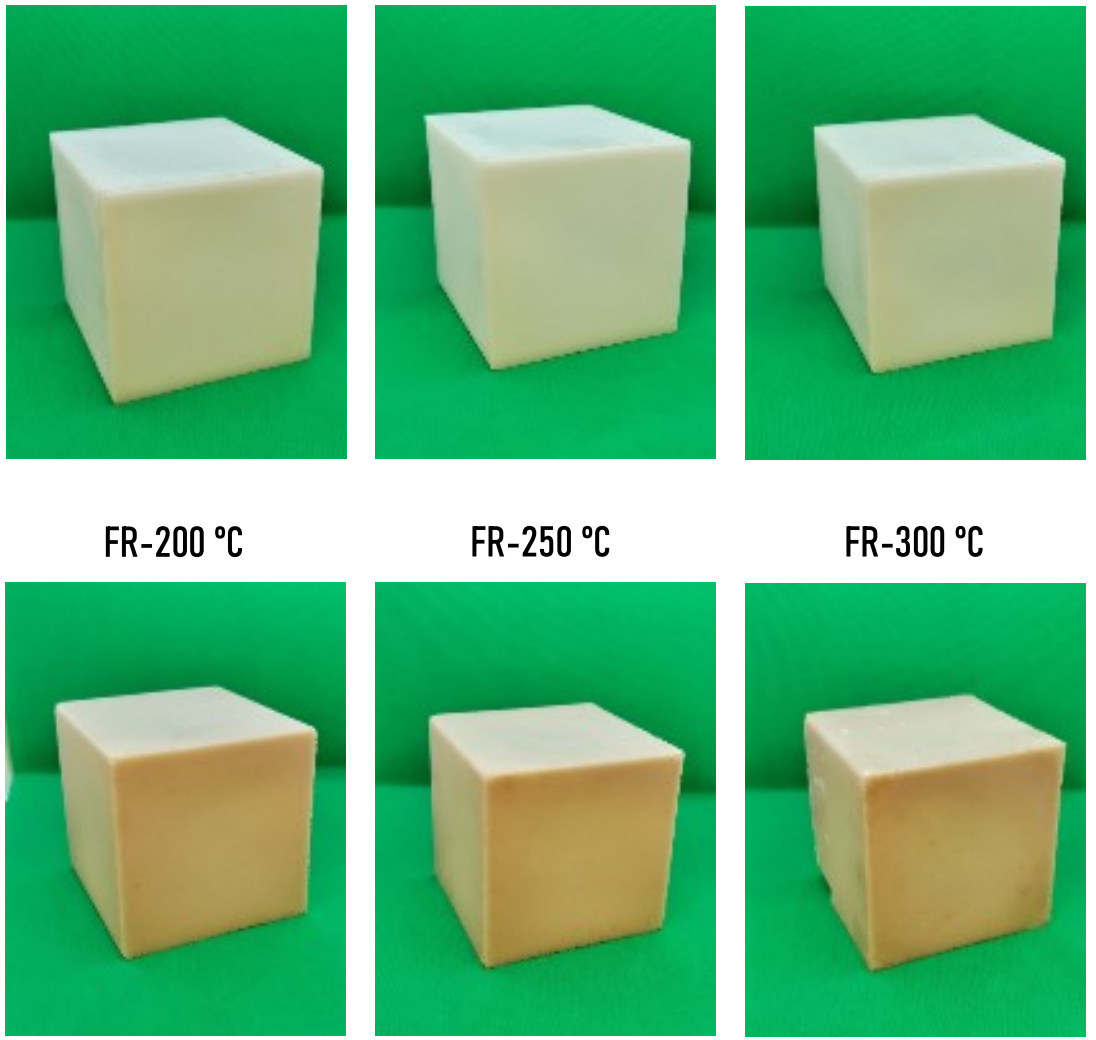


Photos of rotomolded parts from PE and FR series processed at 200, 250 and 300 °C.

Thermogravimetry (TGA) / components and powders

Apparatus: **Netzsch 209 F1 Libra**

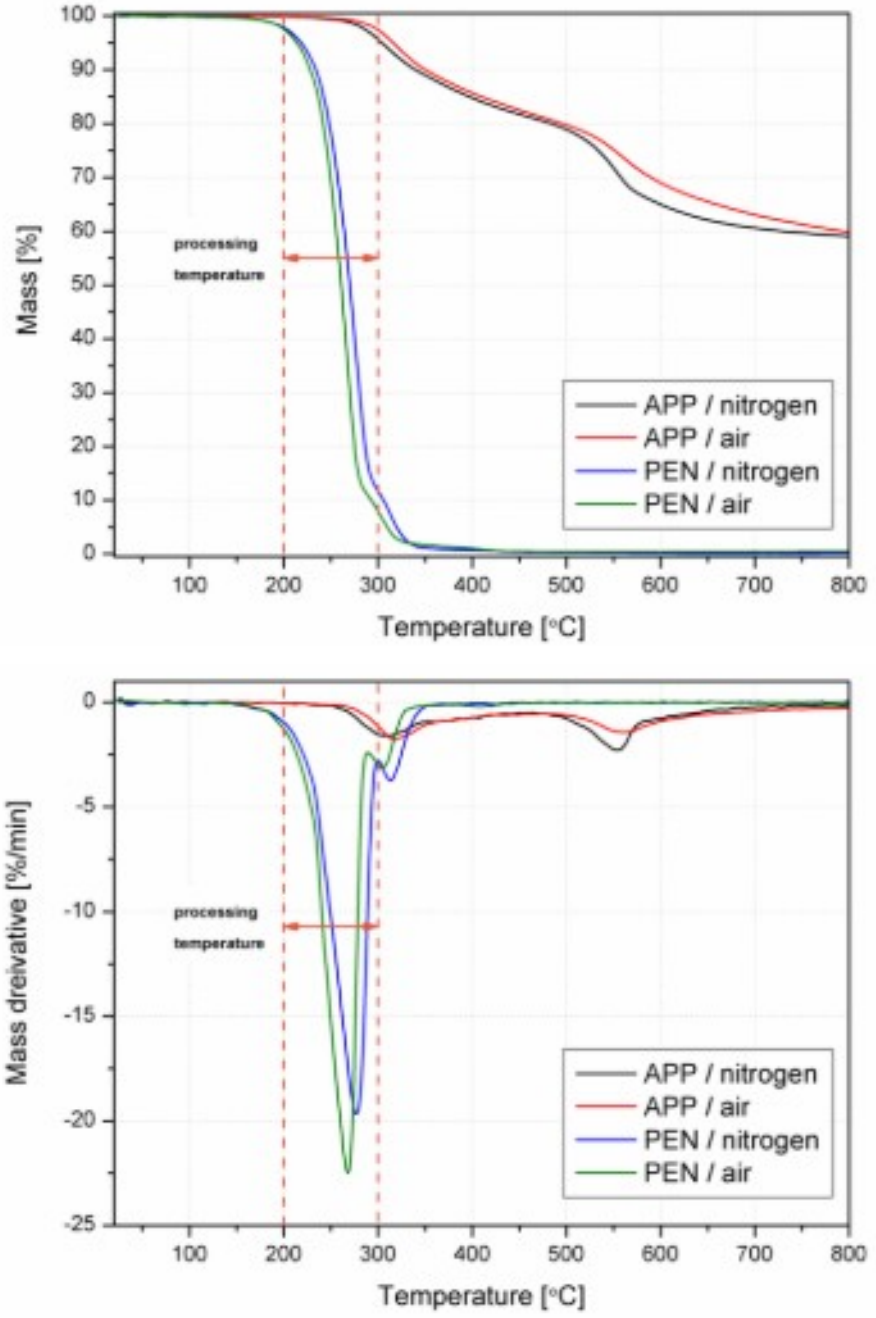
Heating rate: **10 °C/min**

Temperature range: **25-900 °C**

Gas: **nitrogen, air**

Material		$T_{5\%}$	$T_{10\%}$	$T_{50\%}$	Residue	DTG
		[°C]			[%]	[°C]
Nitrogen	PE pwd	445.3	454.5	477.0	0.00	480.7
	FR pwd	310.8	416.3	481.5	15.69	243.9; 337.5; 485.2
	APP	304.6	340.1	-	59.09	309.8; 553.8
	PEN	218.6	234.2	270.1	0.15	277.1; 313.4
Air	PE pwd	312.0	348.9	401.8	0.15	279.8; 352.7; 392.5; 403.5; 425.5; 446.0; 524.7
	FR pwd	278.2	348.9	461.4	13.60	243.6; 263.0; 339.8; 422.6; 437.9; 448.4; 481.5; 565.6
	APP	316.3	350.6	-	57.18	317.7; 561.5
	PEN	214.1	228.2	261.0	0.62	268.1; 304.7

Thermal properties of PE and FR rotomolded parts obtained from DSC measurements.



TG and DTG curves of PE, APP, PEN, and extruded material prior to rotomolding.

Thermogravimetry (TGA) / rotomolded parts

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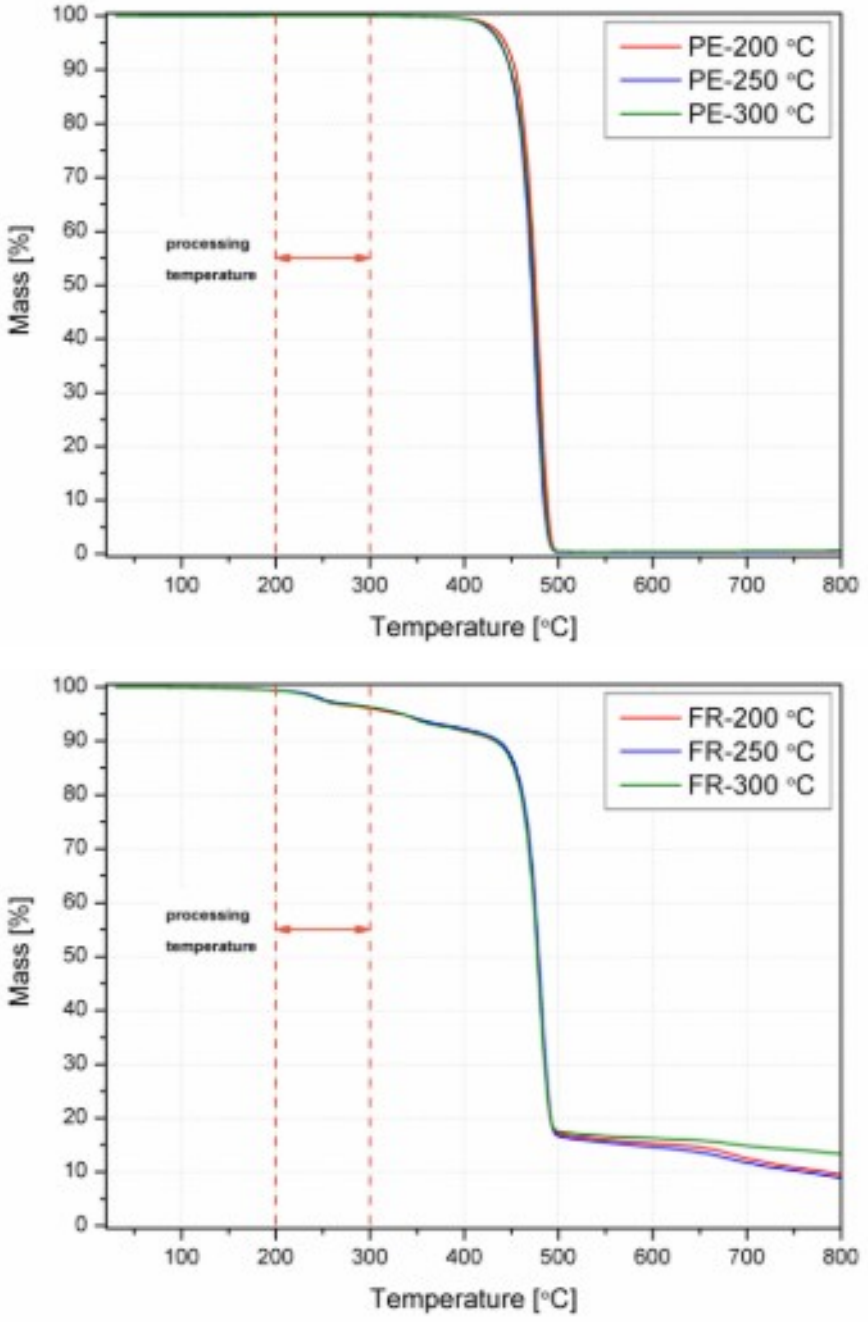
Temperature range: **25-900 °C**

Gas: **nitrogen**

Material	$T_{5\%}$	$T_{10\%}$	$T_{50\%}$	Residue	DTG
	[°C]			[%]	[°C]
PE-200 °C	443.8	454.1	475.4	0.50	480.4
PE-250 °C	437.9	449.0	471.8	0.54	473.8
PE-300 °C	439.0	449.7	473.4	0.63	475.1
FR-200 °C	332.2	432.9	478.0	6.50	246.5; 361.9; 481.0; 691.4
FR-250 °C	334.7	436.7	479.0	5.86	246.5; 348.0; 482.3; 683.9
FR-300 °C	333.6	433.4	477.8	11.30	243.3; 345.3; 477.7; 675.5

Thermal properties of PE and FR rotomolded parts obtained from DSC measurements.



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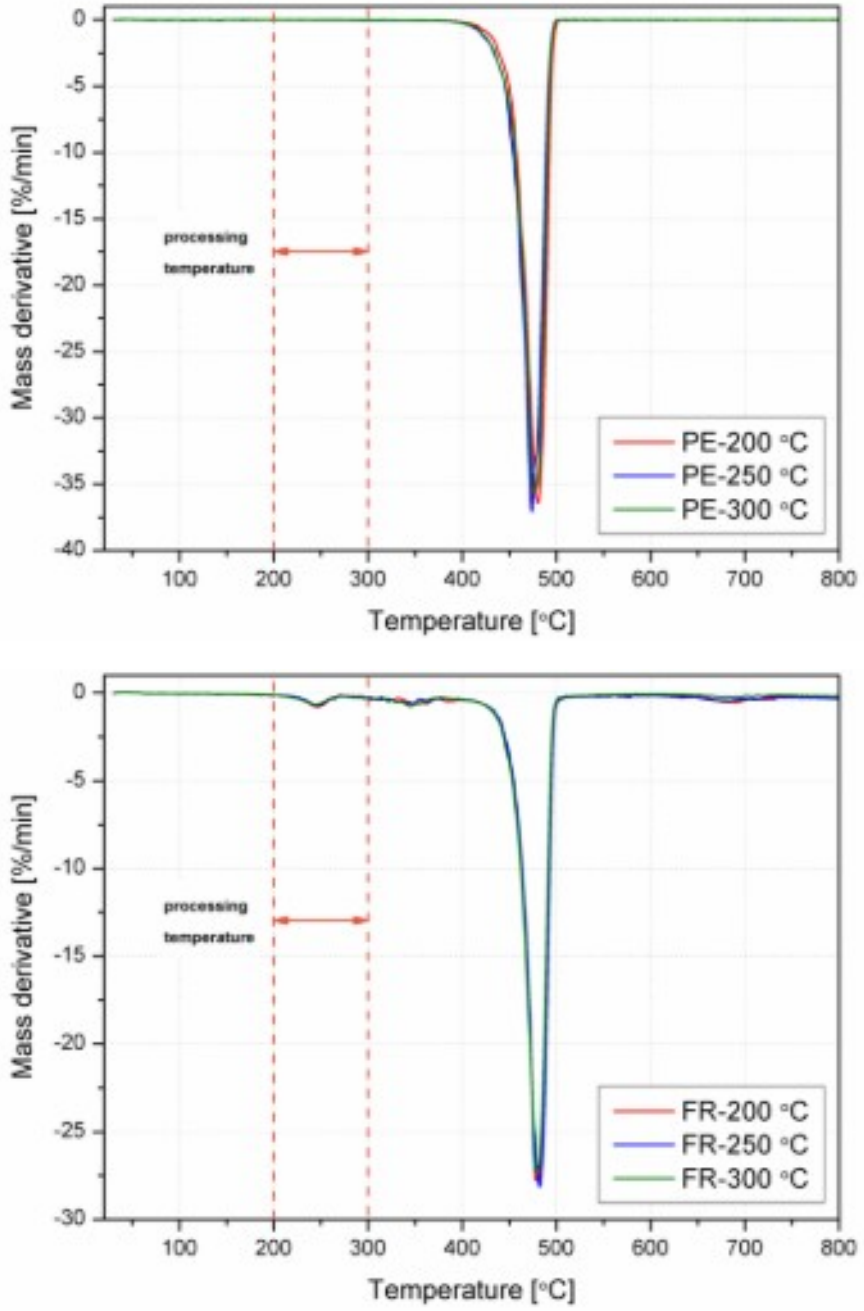


TG and DTG curves of PE, APP, PEN, and extruded material prior to rotomolding.

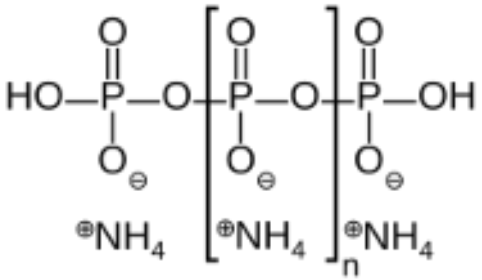
Fourier transform infrared spectroscopy (FTIR)

Apparatus: **Jasco FT/IR-4600**

Waveumber range: **4000-400 cm^{-1}**

Resolution: **4 cm^{-1}**

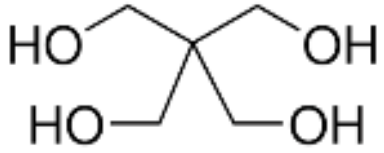
Measurement mode: **attenuated total reflectance (ATR)**



halogen-free acidic source and blowing agent

Ammonium polyphosphatre (APP)

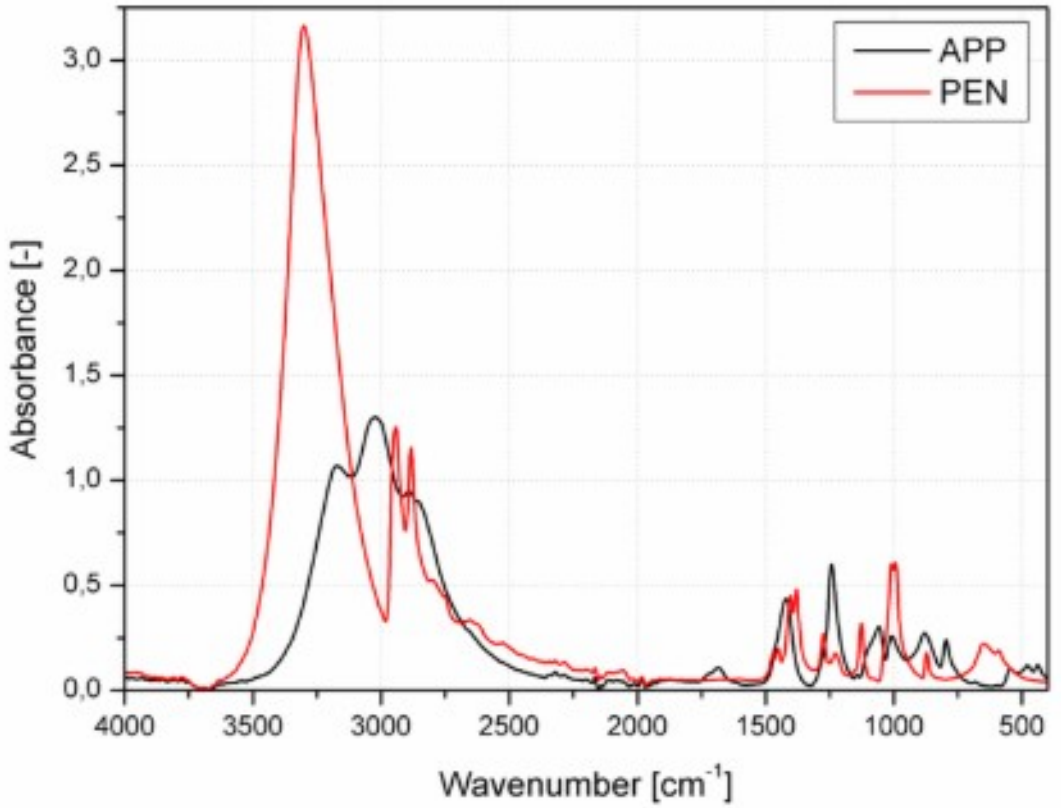
Addforce. FR APP 201 (WTH GmbH)



carbonific agent

Pentaerythritol (PEN)

Addforce FR Penta M40 (WTH GmbH)



FTIR spectra obtained in ATR mode for components of FR system.

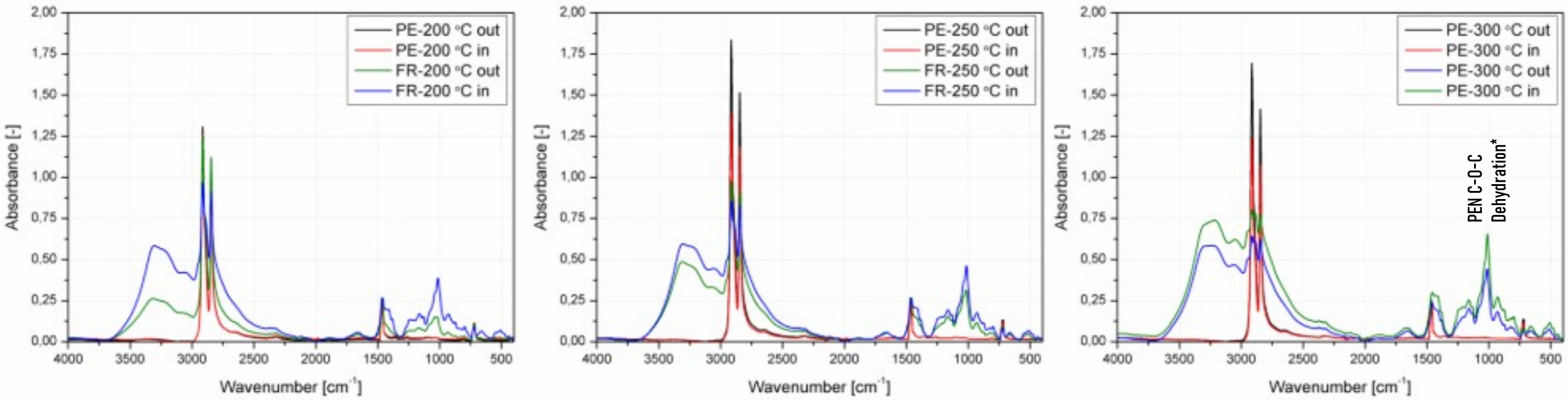
Fourier transform infrared spectroscopy (FTIR)

Apparatus: **Jasco FT/IR-4600**

Waveumber range: **4000-400 cm^{-1}**

Resolution: **4 cm^{-1}**

Measurement mode: **attenuated total reflectance (ATR)**



FTIR spectra obtained in ATR mode for rotomolded products from external (**out**) and internal (**in**) surfaces.

*Z. Wang, P. Lv, Y. Hu, K. Hu, Journal of Analytical and Applied Pyrolysis, 86, 1, 207-214, 2009.

Mechanical properties – static tensile test

Apparatus: **Zwick/Roell Z010**

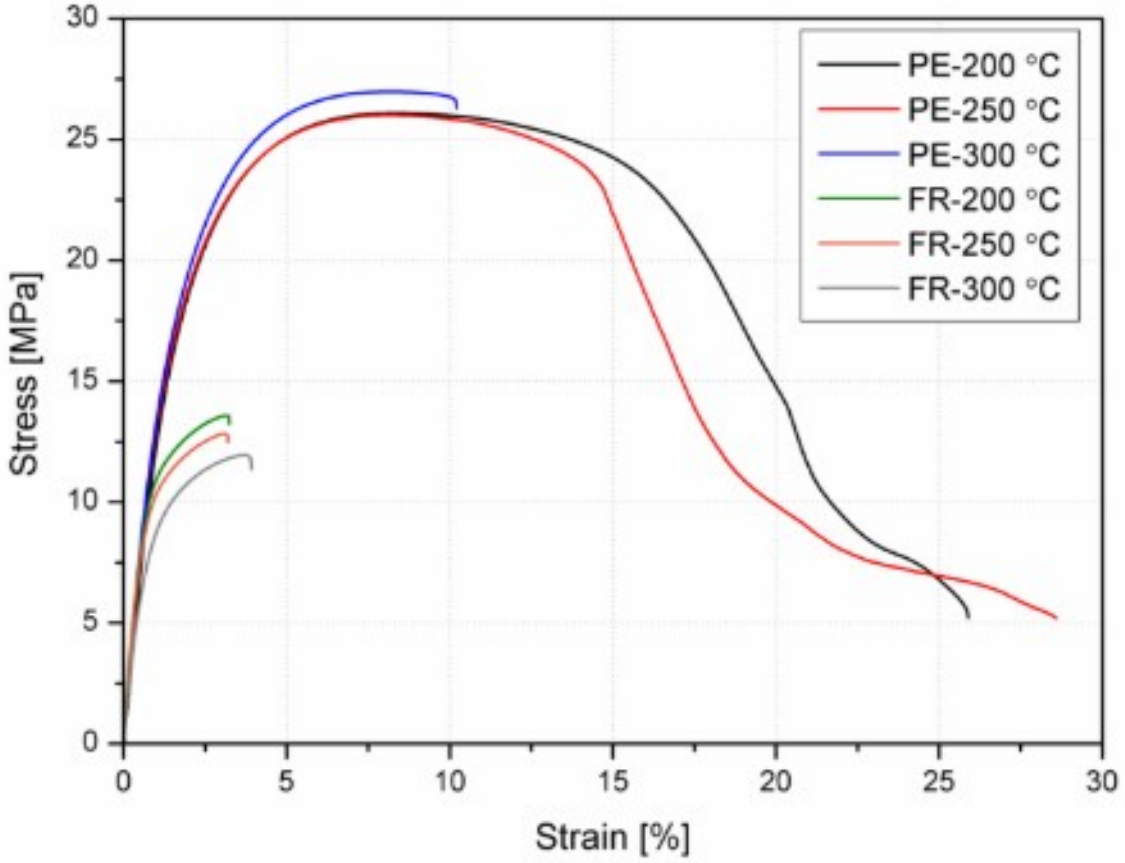
Standard: **ASTM D 638**

Equipment: **automatic mechanical extensometer**

Tensile test speed: **10 mm/min**

Material	Elastic modulus [MPa]	Tensile strength [MPa]	Elongation at break [%]
PE-200 °C	1512±186	25.5±0.5	20.0±9.7
PE-250 °C	1680±77	26.1±0.8	22.5±6.5
PE-300 °C	1756±66	26.4±0.9	15.2±4.8
FR-200 °C	1700±85	13.5±0.6	2.9±0.2
FR-250 °C	1673±70	13.0±0.8	2.8±0.2
FR-300 °C	1346±56	12.1±0.5	3.4±0.7

Mechanical parameters obtained in static tensile test for rotomolded parts made of PE and FR formed at temperatures of 200, 250, and 300 °C.



Stress-strain curves of selected PE and RS samples formed at oven temperatures of 200, 250, and 300 °C.

Thermomechanical properties – static and dynamic tests

VST

Apparatus: **Testlab RV300C**

Standard: **ISO 306**

Heating rate: **120 °C/h**

Load: **50 N**

DMTA

Apparatus: **Anton Paar MCR301**

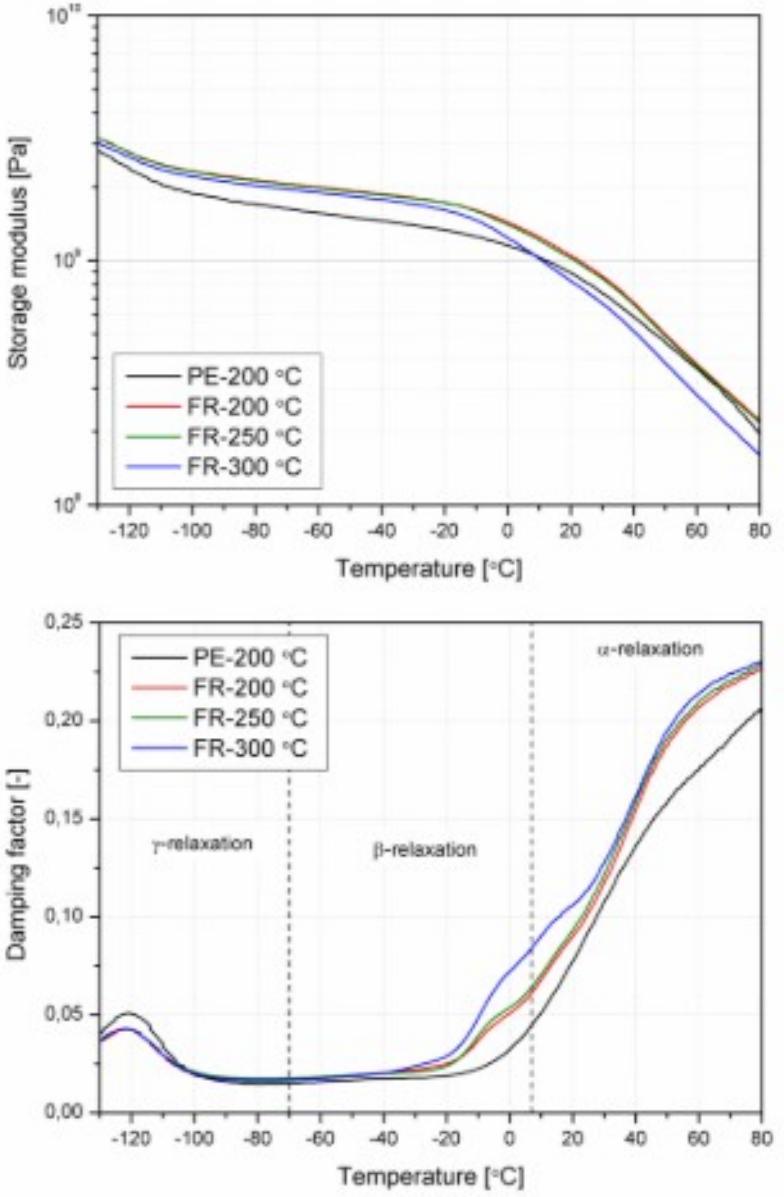
Geometry: **torsion**

Heating rate: **2 °C/min**

Strain; frequency: **0.01%; 1 Hz**

Material	VST [°C]	$G'_{-40°C}$ [Pa]	$G'_{25°C}$ [Pa]	$G'_{80°C}$ [Pa]	T_G [°C]
PE-200 °C	81.4±0.2	$1.45 \cdot 10^9$	$8.22 \cdot 10^8$	$1.96 \cdot 10^8$	-120
PE-250 °C	81.6±1.6	$1.48 \cdot 10^9$	$8.29 \cdot 10^8$	$2.03 \cdot 10^8$	-121
PE-300 °C	81.1±2.7	$1.49 \cdot 10^9$	$8.32 \cdot 10^8$	$2.01 \cdot 10^8$	-121
FR-200 °C	66.1±2.1	$1.87 \cdot 10^9$	$9.56 \cdot 10^8$	$2.18 \cdot 10^8$	-122
FR-250 °C	64.8±1.6	$1.85 \cdot 10^9$	$9.33 \cdot 10^8$	$2.14 \cdot 10^8$	-122
FR-300 °C	61.1±0.8	$1.77 \cdot 10^9$	$7.46 \cdot 10^8$	$1.57 \cdot 10^8$	-122

Mechanical parameters obtained in static tensile test for rotomolded parts made of PE and FR formed at temperatures of 200, 250, and 300 °C.



Storage modulus and damping factor vs. temperature curves of samples taken from rotomolded parts made of PA and FR formed at 200, 250, and 300 °C.

Flammability test – cone calorimetry

Apparatus: **Fire Testing Technology Cone Calorimeter**
Standard: **ISO 5660**
Heat flux: **50 kW/m²**
Optical system: **photodiode and helium-neon laser**

Sample	TTI	TTF	HRR	pHRR	MARHE	THR	EHC	TSR	SEA
	[s]		[kW/m²]			MJ/m²	MJ/kg	m²/m²	m²/kg
PE-200 °C									
PE-250 °C									
PE-300 °C									
FR-200 °C									
FR-250 °C									
FR-300 °C									

TTI – Time to Ignition; TTF – Time to Flameout
HRR - Heat release rate; pHRR – peak Heat release rate
MARHE - Maximum Average Rate of Heat Emission: parameter used to assess fire safety by measuring the peak value of the cumulative heat release rate divided by time, representing a material's propensity for fire development.
THR – Total Heat Release: cumulative heat energy released per unit area the entire duration of combustion.
EHC- Effective Heat of Combustion: quantifies the actual amount of heat released per unit mass of material lost during combustion
TSR - Total smoke release: overall amount of smoke generated by a material during its entire combustion process, normalized by the exposed surface area.
SEA - Specific Extinction Area: measures the optical density of smoke produced per unit mass of material lost during combustion.

Flammability characteristics and data obtained from the cone calorimetry test for rotomolded parts made of PE and FR formed at temperatures of 200, 250, and 300 °C.

Flammability test – cone calorimetry

Apparatus: **Fire Testing Technology Cone Calorimeter**
Standard: **ISO 5660**
Heat flux: **50 kW/m²**
Optical system: **photodiode and helium-neon laser**

Sample	TTI	TTF	HRR	pHRR	MARHE	THR	EHC	TSR	SEA
	[s]		[kW/m²]			MJ/m²	MJ/kg	m²/m²	m²/kg
PE-200 °C	44.5±0.5	153.7±4.5	977.1±39.0	1829±130	760.0±23.3	107.37±4.2	43.9±0.5	622.1±43.4	254.0±8.7
PE-250 °C	41.0±4.2	151.0±2.0	606.8±220.5	1950±286	733.9±92.7	106.7±7.3	44.9±0.9	674.3±68.9	287.2±47.3
PE-300 °C	48.0±1.0	159.5±6.5	539.2±197.1	1650±102	622.9±129.6	108.0±7.8	43.5±0.8	717.5±94.8	321.0±60.9
FR-200 °C	23.3±0.5	243.7±31.5	245.5±18.7	689±31	361.5±17.5	70.7±3.1	37.8±4.7	1010.6±45.2	473.9±113.4
FR-250 °C	24.3±1.9	296.7±31.9	251.2±11.2	554±70	313.4±28.8	71.0±1.7	14.4±4.1	1062.2±55.5	337.2±52.5
FR-300 °C	15.5±0.5	296.5±58.5	283.0±4.0	537±124	298.0±31.7	78.8±0.9	9.6±3.9	1104.1±88.8	141.5±55.1

Flammability characteristics and data obtained from the cone calorimetry test for rotomolded parts made of PE and FR formed at temperatures of 200, 250, and 300 °C.

Flammability test – cone calorimetry

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Standard: **ISO 5660**
Heat flux: **50 kW/m²**
Optical system: **photodiode and helium-neon laser**

Sample	TTI	TTF	HRR	pHRR	MARHE	THR	EHC	TSR	SEA
	[s]		[kW/m²]			MJ/m²	MJ/kg	m²/m²	m²/kg
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Flammability characteristics and data obtained from the cone calorimetry test for rotomolded parts made of PE and FR formed at temperatures of 200, 250, and 300 °C.

Conclusions

- Decomposition of the FRS component acting as a foaming agent plays a major role in the formation of macroscopic structural defects and structural discontinuities.

- Despite partial decomposition of both FRS components, even products rotomolded processed at the highest temperature set showed significant reductions in flammability compared to pure HDPE.

- Decomposition of pentaerythritol resulted in a change in the technological process and led to a deterioration of the thermomechanical stability of FR products, regardless of the processing temperature.

- It is necessary to use a carbonific agent with increased thermal stability to obtain a lower oxygen permeability of a char and reduce smoke emissions during exposure to fire..

Research on the influence of the polymer composites processing conditions on the stabilizing effect of functional plant-derived fillers

SONATA-17 2021/43/D/ST8/01491

Principal Investigator: **Mateusz Barczewski, PhD**

Implementation period : **11.07.2022 – 10.07.2025**

Uniwersytet Kazimierza Wielkiego w Bydgoszczy

POLITECHNIKA GDAŃSKA

Thank you!