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OF TECHNOLOGY AND ECONOMICS
FACULTY OF MECHANICAL ENGINEERING

Flame-retardant coatings for carbon fibre-reinforced polyamide 6 composites

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Introduction

- **Use of composites in the automotive industry**
  - Reduced weight, high strength, high stiffness, good corrosion resistance

- **Disadvantages of thermoset composites:**
  - Long cycle time
  - Difficult to recycle
  - High cost

  } → Use of thermoplastic polymer composites

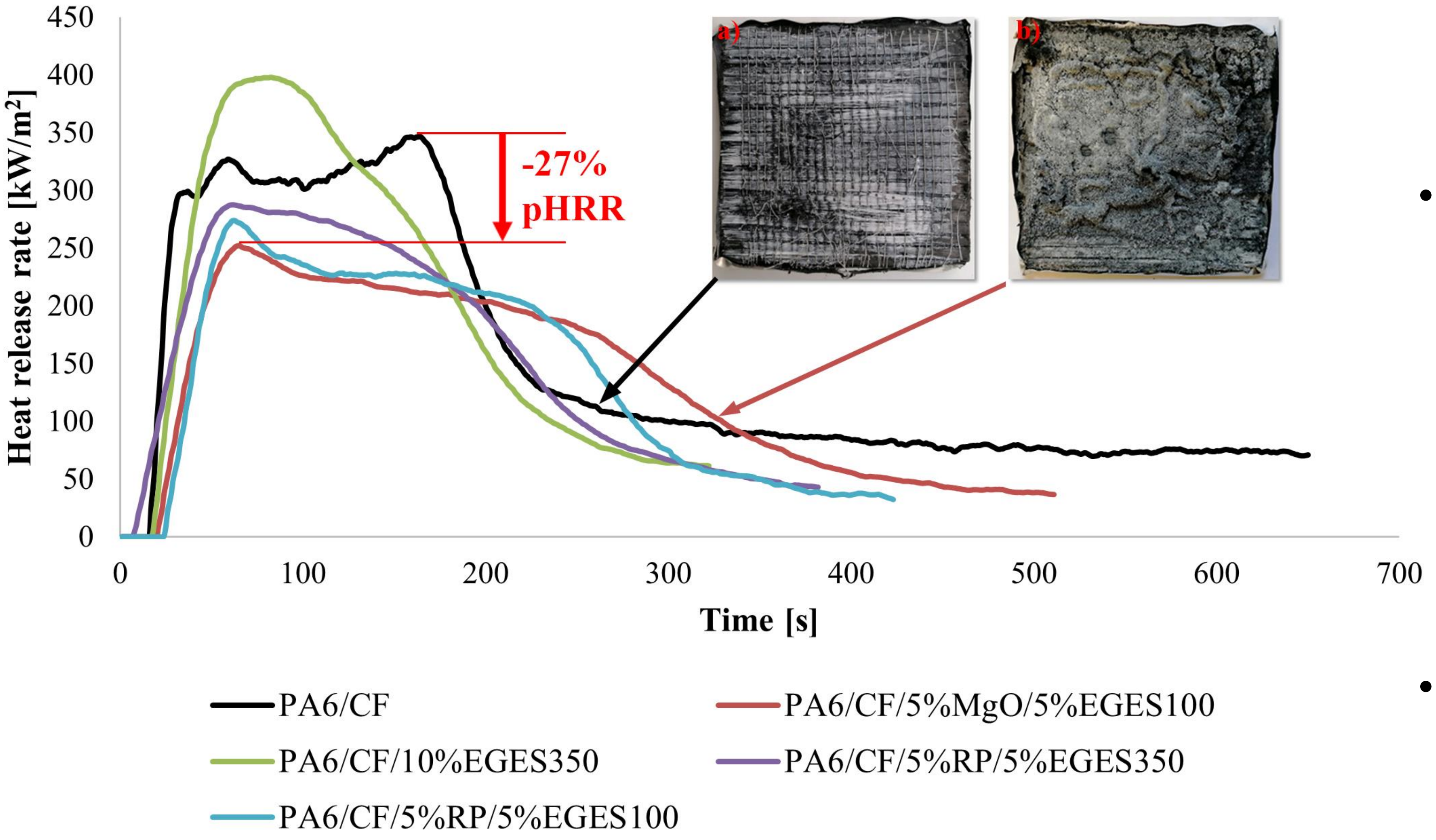
- **Disadvantage of polymers is their flammability**
- **Solution:** flame retardancy

Introduction

- **Flame retardant in matrix:**
  - Large amount of flame retardants can adversely affect the mechanical properties of the composite
  - Solid phase flame retardants can be filtered by reinforcement layers
  - Fibre reinforcement can hinder the formation of a protective charred layer
- **Solution:** flame retardant coating

- **Goals of the research:**
  - Preparation of polyamide 6 composite by anionic ring-opening polymerization of ε-caprolactam
  - Preparation of flame retardant coating by in-mould coating

Antecedents



a) PA6/CF after MLC
b) PA6/CF/5% MgO/5% EG ES100 after MLC

- **Flame retardants (insoluble in ε-caprolactam):**
  - Expandable graphite with small and large particle sizes (EG ES100 and EG ES350)
  - Magnesium oxide (MgO)
  - Red phosphorus (RP)

- **Further investigations with caprolactam-soluble hexaphenoxycyclotriphosphazene (HPCTP)**

Materials

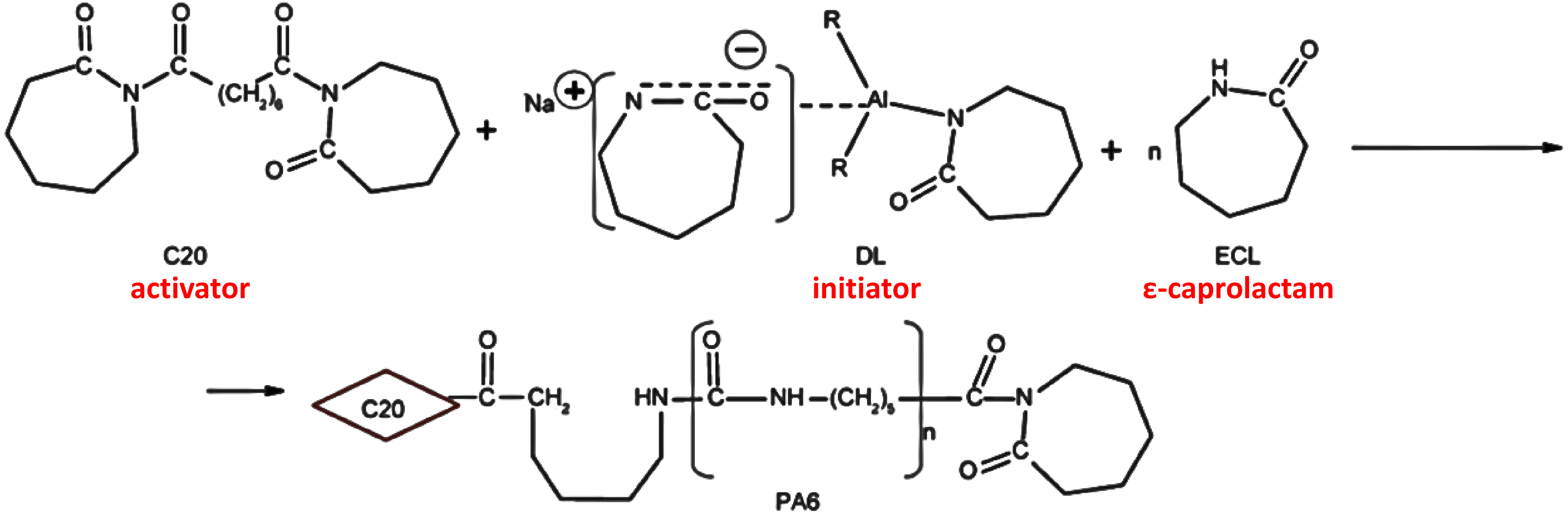
- **Preparation of PA6:**
  - 87 mass% ε-caprolactam (monomer)
  - 3 mass% activator (C20P)
  - 10 mass% initiator (DL)
- **Flame retardants:**
  - Expandable graphite (EG ES100)
  - Hexaphenoxycyclotriphosphazene (HPCTP)
- HPCTP is soluble in ε-caprolactam → concentration series

Flame retardant	Main component	Manufacturer	Brand name	P content (mass%)	Appearance	Soluble in molten ε-caprolactam	Polymerisation not hindered
EG ES100	Expandable graphite	Graphit Kropfmühl	ES 100 C10	-	Black powder	✗	✓
HPCTP	Hexaphenoxycyclotriphosphazene	Fushimi/NRC	Rabitle FP110	13,4	White powder	✓	✓

Preparation of coating materials

- **Preparation of the samples:**
  - The monomer, the activator, and flame retardants were mixed and melted at 120 °C using a heated magnetic stirrer
  - Adding the initiator
- **150 °C aluminium tool**
  - For modelling T-RTM

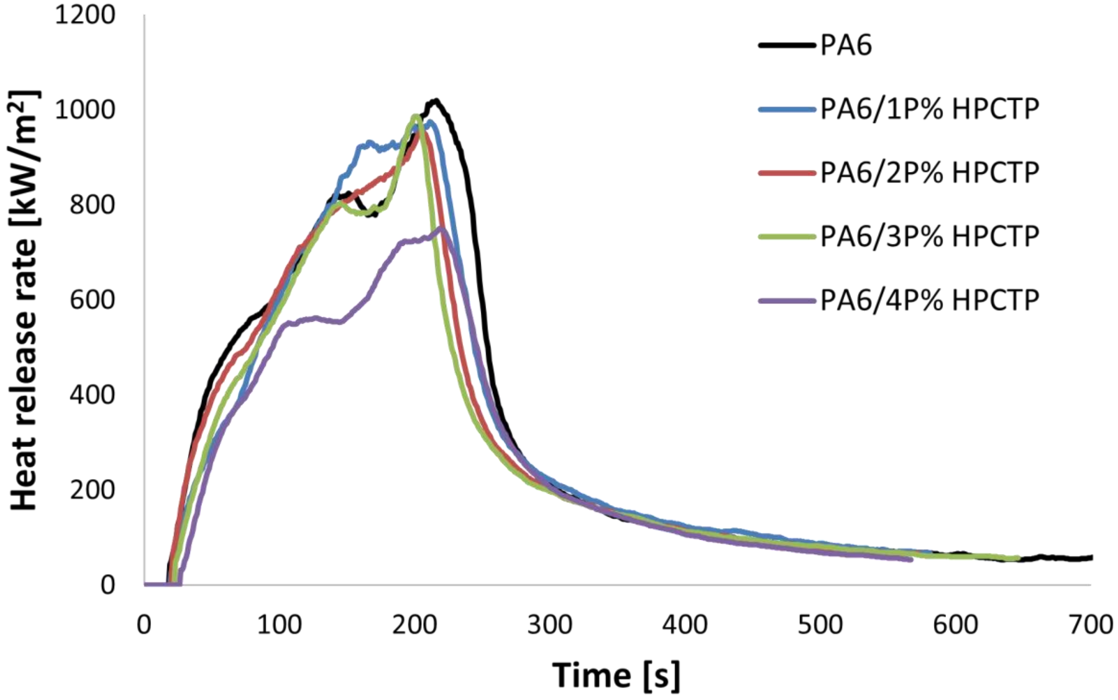
Aluminium tool



Mass loss calorimetry

- **HPCTP containing samples:**
  - Best results: 4P% HPCTP → uneven surface
- Combination of 3P% HPCTP with expandable graphite

Sample	TTI [s]	pHRR [kW/m²]	Time to pHRR [s]	THR [MJ/m²]	Residue [%]
PA6	19	1019	218	213	1,5
PA6/1P% HPCTP	20	975	211	196,9	0
PA6/2P% HPCTP	21	956	205	188,2	0
PA6/3P% HPCTP	23	987	202	181,9	0
PA6/4P% HPCTP	27	750	219	159,6	1,4

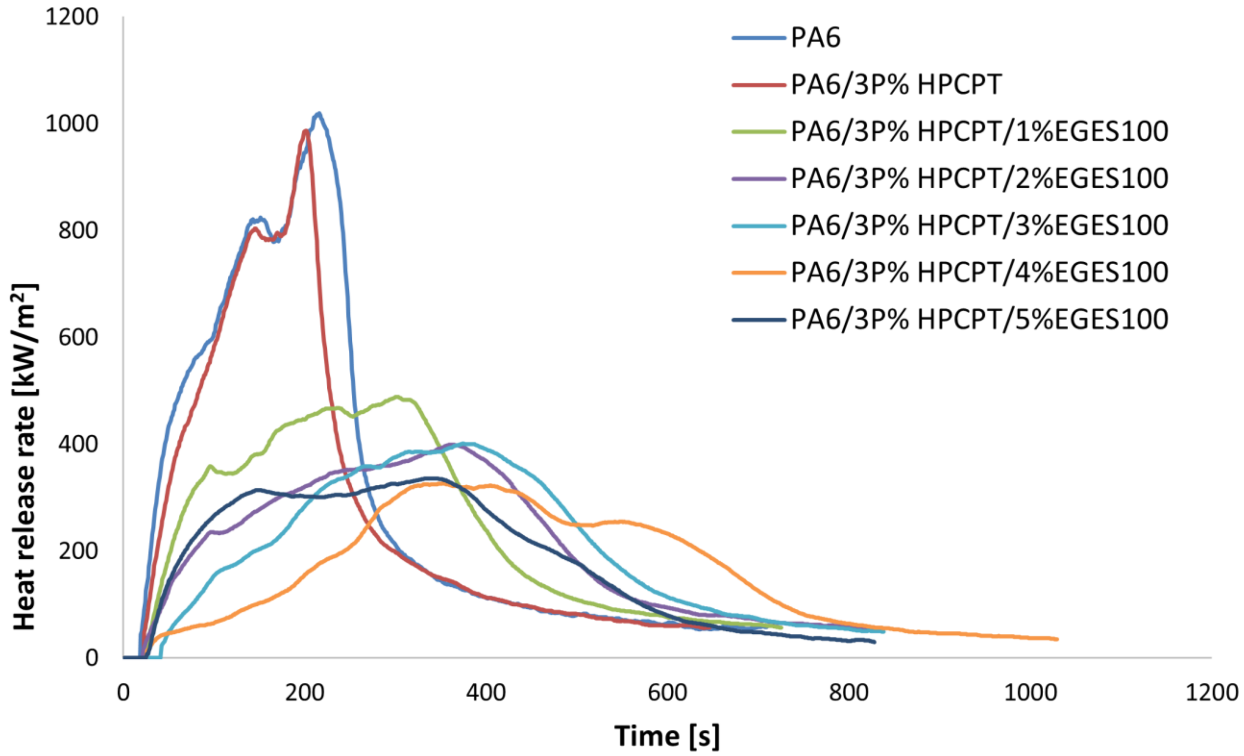


a) b)

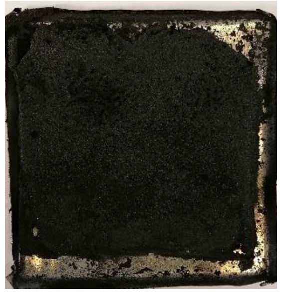
4 %P HPCTP containing sample before (a) and after (b) MLC

Mass loss calorimetry

- As a single additive HPCPT did not show outstanding results → **combination with expandable graphite** is favourable in terms of flame retardancy.
- Combined gas (HPCPT) and solid phase (expandable graphite) mechanism → **synergistic flammability** results



PA6/3P% HPCPT



PA6/3P% HPCPT/ 1%EGES100

PA6/3P% HPCPT/ 4%EGES100

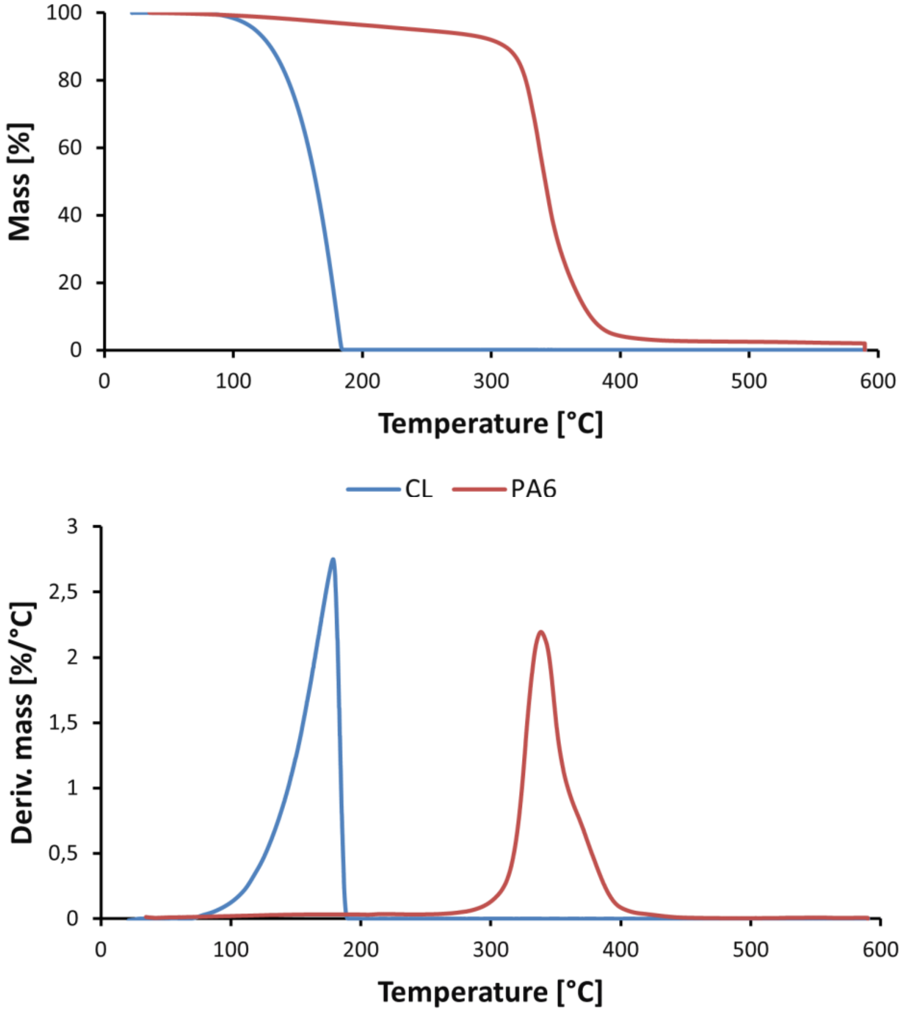
Samples	TTI [s]	pHRR [kW/m²]	Time to pHRR [s]	THR [MJ/m²]	Residue [%]
PA6	19	1019	218	213	1,5
PA6/3P% HPCPT	23	987	202	182	0
PA6/3P% HPCPT/1%EGES100	27	489	302	174	3,3
PA6/3P% HPCPT/2%EGES100	22	399	360	168	5,3
PA6/3P% HPCPT/3%EGES100	42	401	375	166	7,8
PA6/3P% HPCPT/4%EGES100	26	327	353	151	9,8
PA6/3P% HPCPT/5%EGES100	26	336	345	151	7,6

Based on the MLC tests, the selected flame retardant compositions:

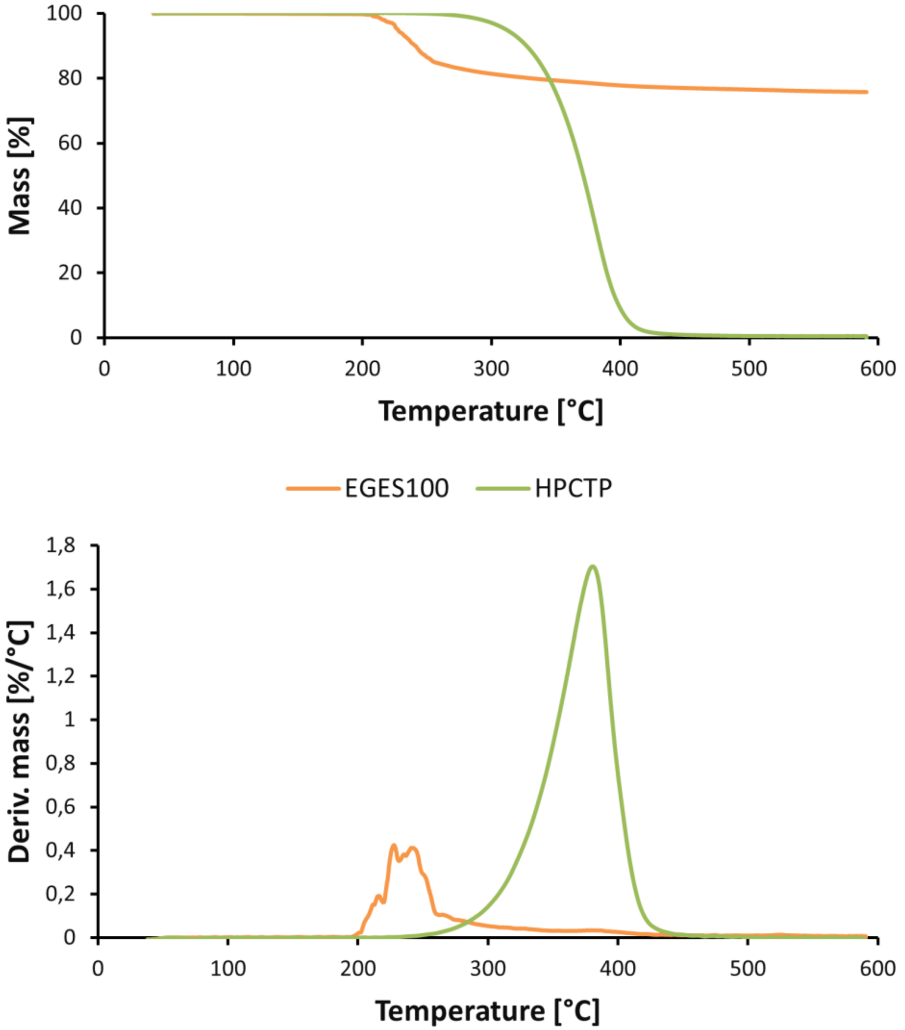
- **PA6/3P% HPCTP/3%EGES100**
- **PA6/3P% HPCTP/4%EGES100**

Monomer conversion

The result of TGA measurements for CL and PA6:

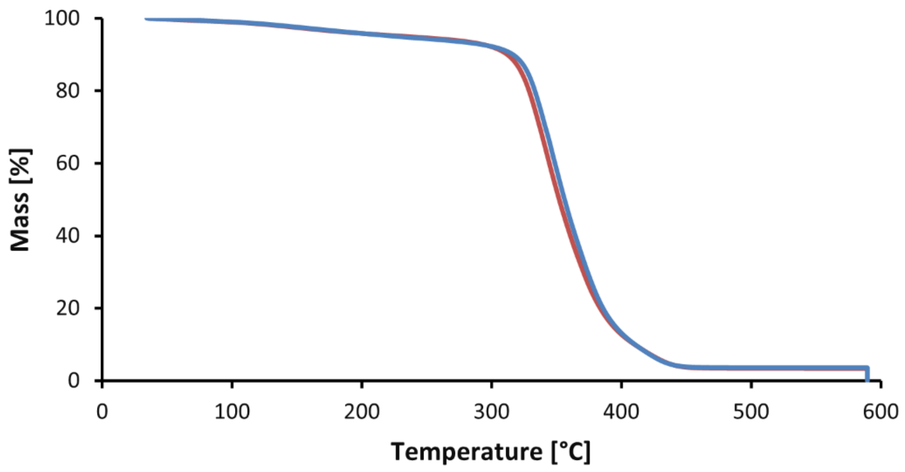


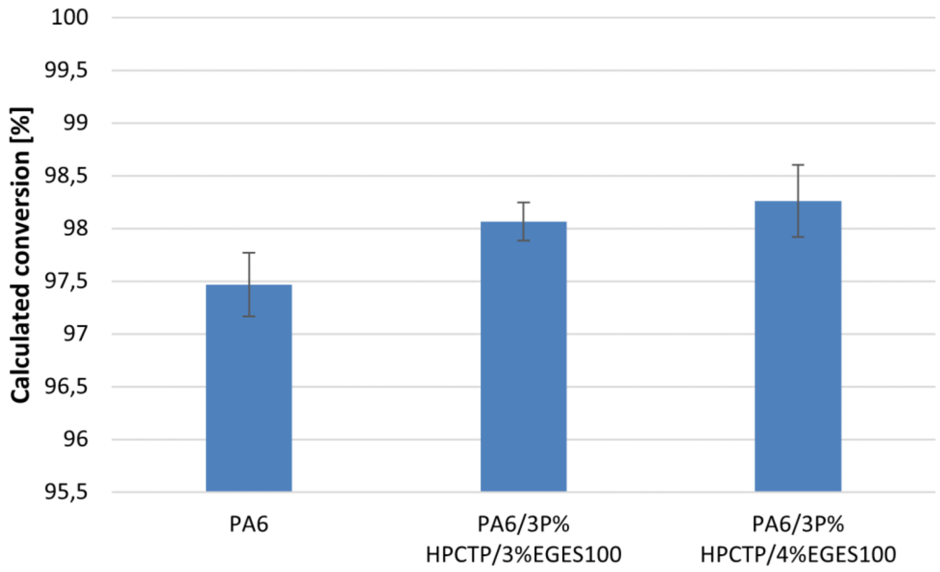
The result of TGA measurements for EGES100 and HPCTP:

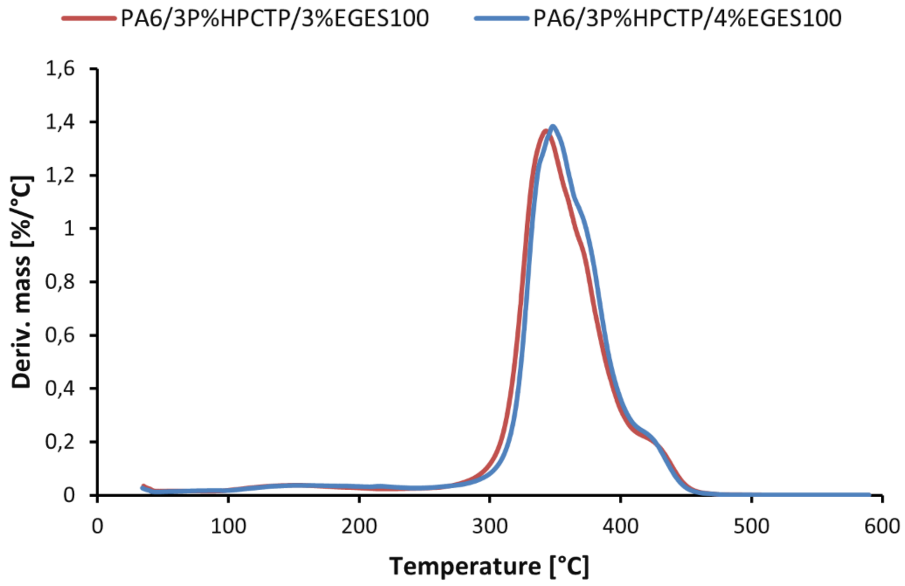


Monomer conversion

- During the first stage of decomposition (up to ~100 °C), the water remaining in the sample is removed
- CL decomposition takes place between 100-190 °C
- Above 200 °C, PA6 depolymerizes and the detectable caprolactam is derived from the decomposition, rather than an unreacted residue
- The residual monomer content of the flame retarded samples was investigated between 100-190 °C
- Monomer conversion of 97-98%

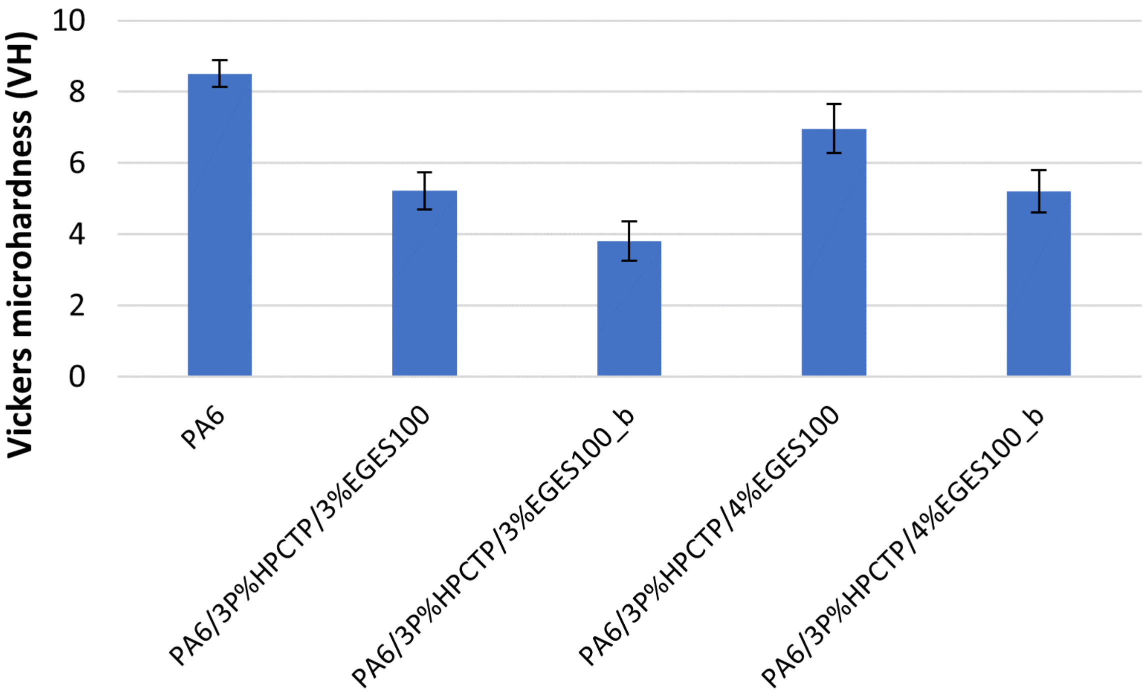






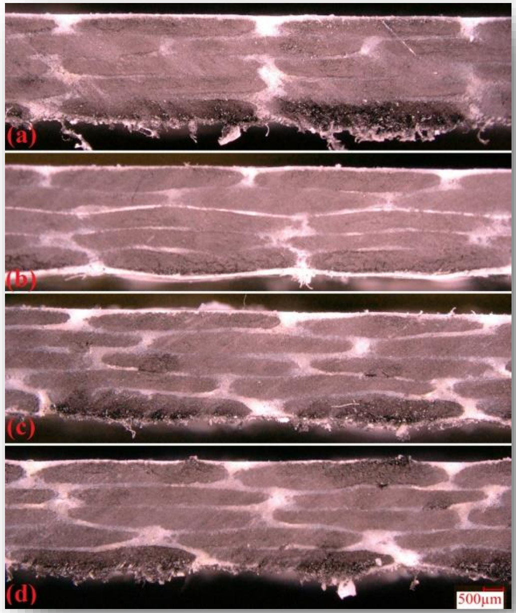
Microhardness testing

- **The microhardness of the reference PA6 was 8.5 HV**
- **HPCTP acts as a plasticizer**
- **Increasing the amount of EGES100 also increased the microhardness**
- **There is a difference in hardness between the two sides of the sample**
  - Sedimentation can be observed



Preparation of PA6 composites

- **Dimensions of the mould: 100 mm x 100 mm x 2 mm**
- **5 layers of unidirectional carbon reinforcement were pre-placed in $[0]_5$ layup**
- **Preheating at 150 °C**
- **Preparation of matrix:**
  - 87% ε-caprolactam
  - 3% activator (C20P)
  - 10% initiator (DL)
  - mixed and melted at 120 °C using a heated magnetic stirrer



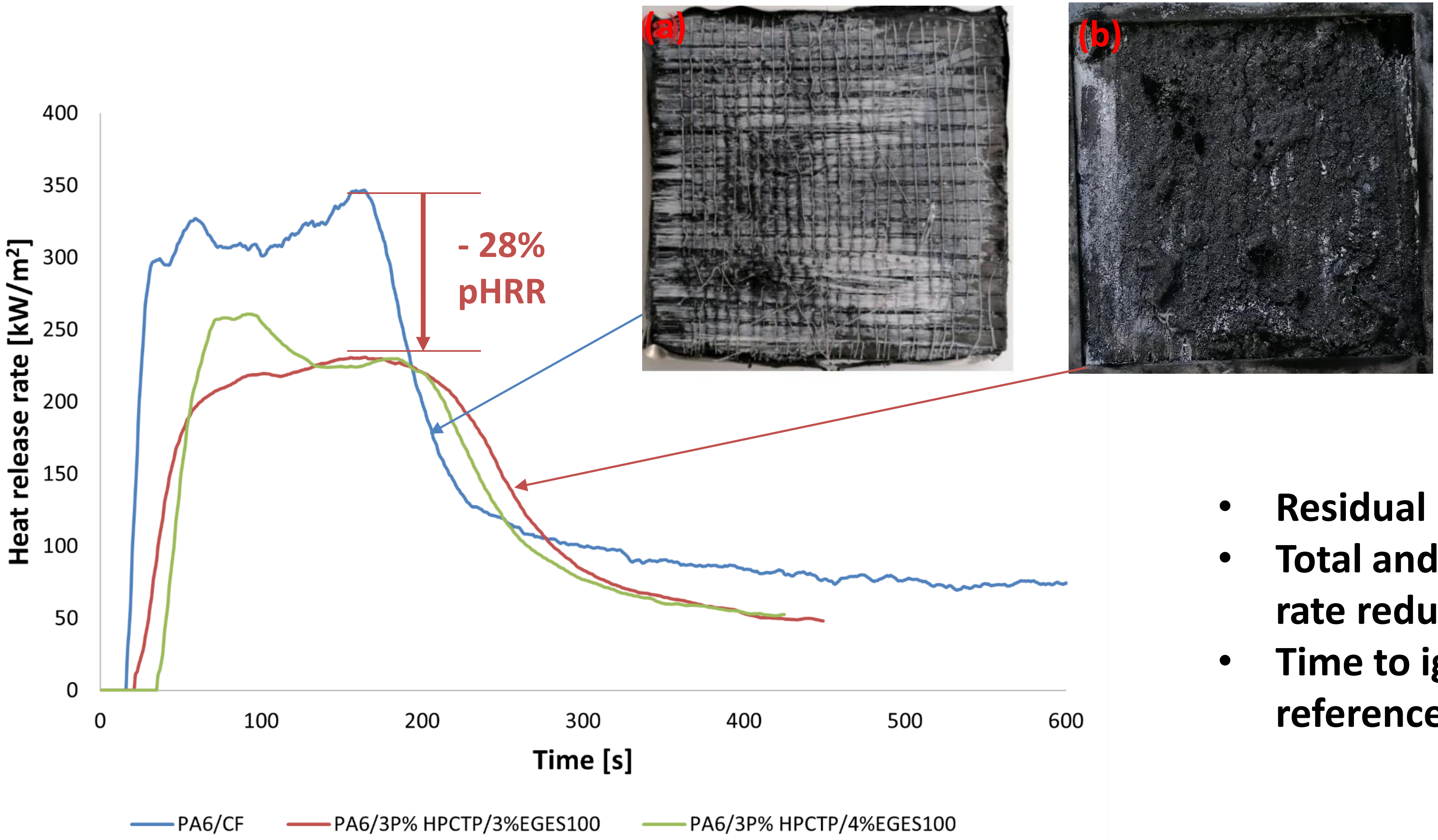
Sample cross-section

a) near injection, sample edge
b) near injection, sample centre
c) away from injection, sample edge
d) away from injection, sample centre

Preparation of composites with coatings

- **Modelling of in-mould coating**
- **Dimensions of the mould: 100 mm x 100 mm x 2,5 mm**
- **Coating thickness: 0,5 mm**
- **Preheating at 150 °C**
- **Preparation of coatings:**
  - ε-caprolactam, activator (C20P) and flame retardants were mixed and melted at 120 °C using a heated magnetic stirrer
  - initiator (DL) was added
- **Injection using a glass syringe**

Mass loss calorimetry



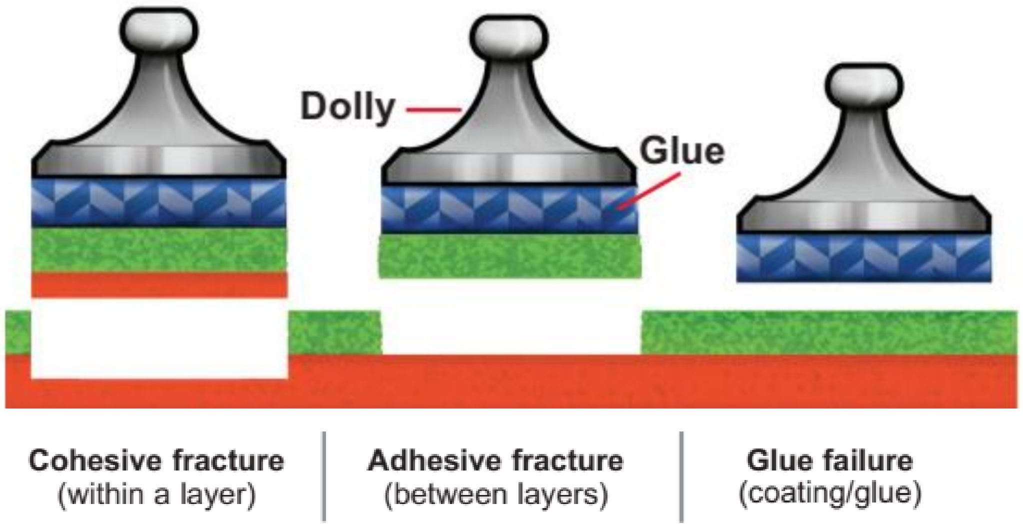
a) PA6/CF after MLC
b) PA6/CF/3P% HPCTP/3%EGES100 after MLC

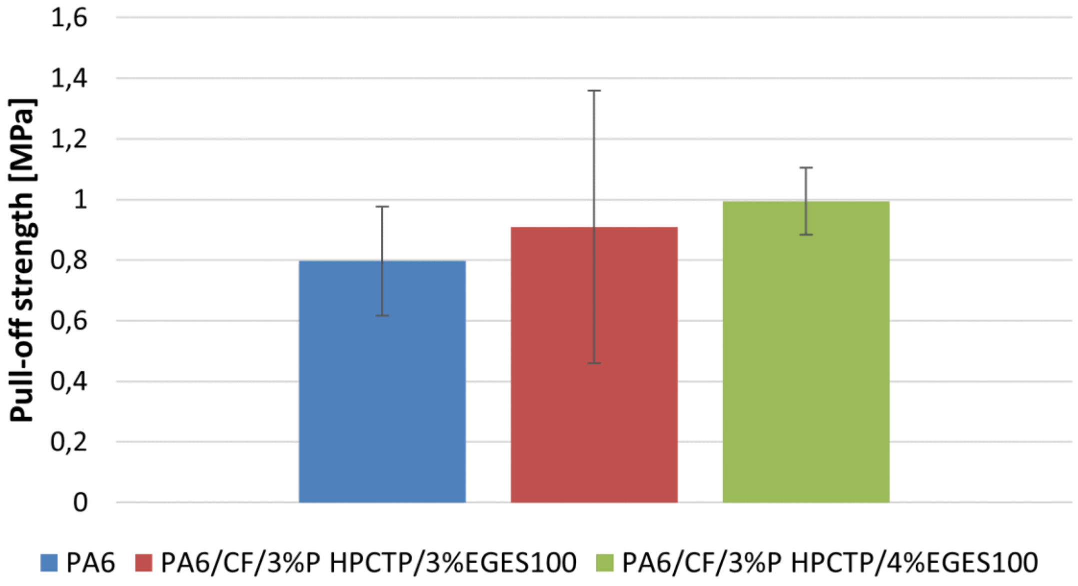
- **Residual mass increased**
- **Total and maximum heat release rate reduced**
- **Time to ignition is longer than the reference**

Pull-off adhesion test

Steps of the test:

1. Dolly and coating preparation (cleaning)
2. Glue and dolly application (minimum 24 hours for cross-linking)
3. Test area separation (The test area of the coating is isolated from the area surrounding)
4. Pull-off test

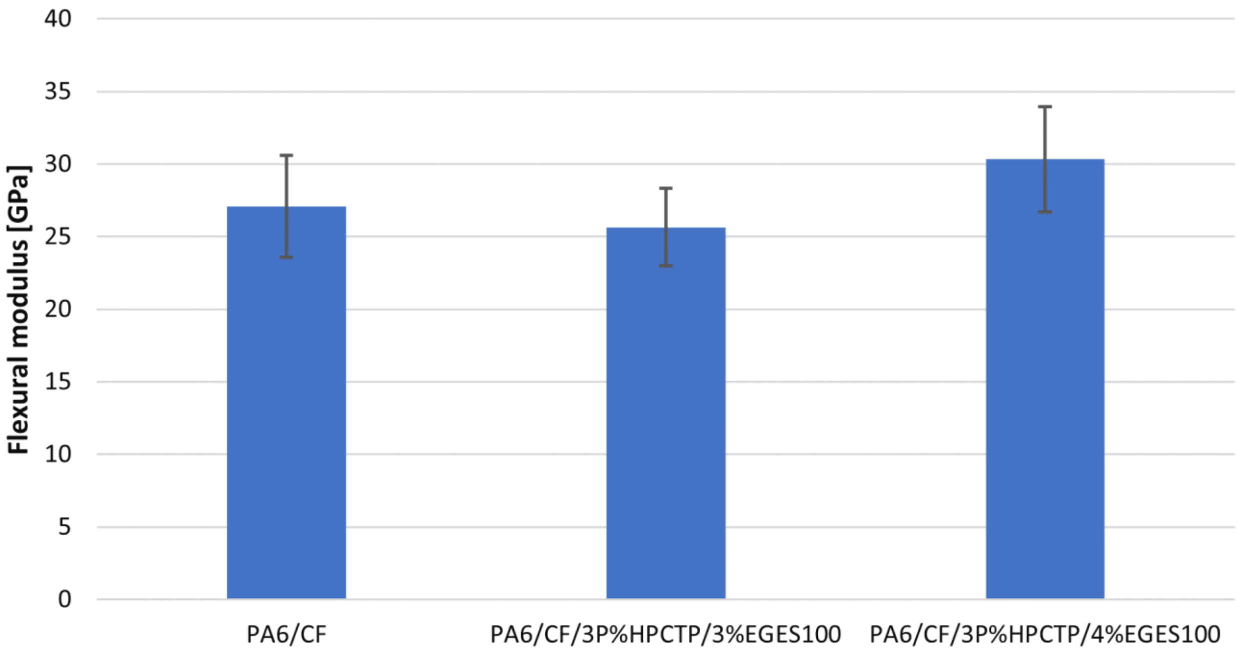


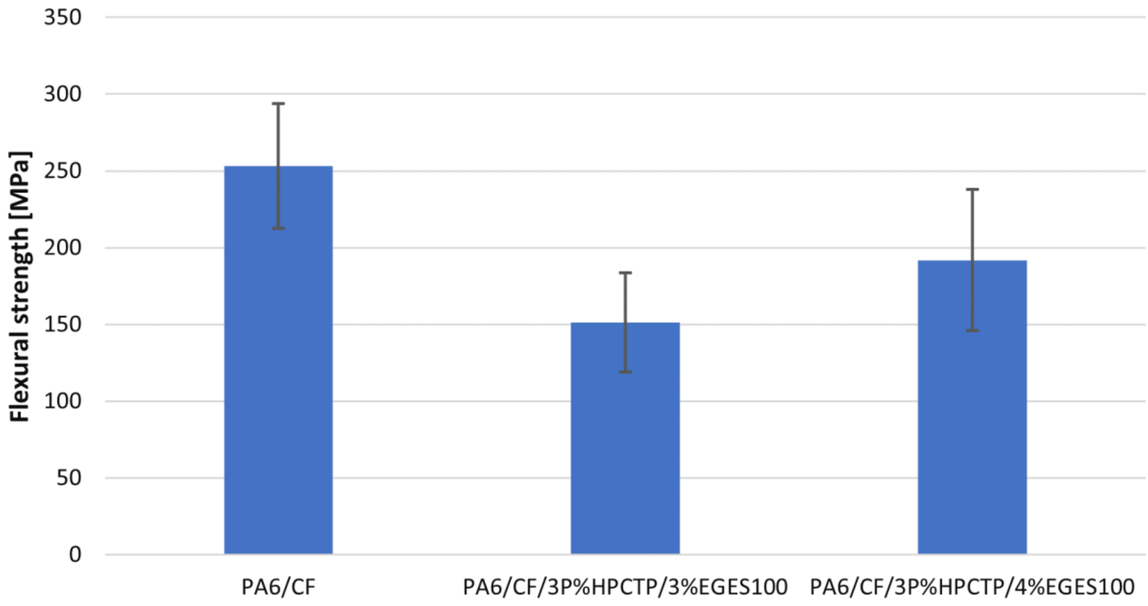


- **Reference:** flame retardant free PA6 coating
- Pull-off strength slightly increased
- Adhesive fracture

Three-point bending test

- The flame retardants have reduced the flexural strength
- HPCTP acts as a plasticizer and weakens intermolecular interactions between polymer chains
- Flexural modulus values remained almost the same





The flame retardant coatings did not break after bending but separated from the composite surface in the pressed area.

PA6/CF/3P%HPCTP/4%EGES100 sample after three-point bending test

Conclusion

- HPCTP and expandable graphite were used as flame retardants
- HPCTP did not show outstanding results when used as sole additive, but the combination with expandable graphite is favourable in terms of flame retardancy
- A synergistic effect is achieved by combining HPCTP and EGES100
- The composite coated with 3P% HPCTP and 3% EGES100 showed the best fire performance (-28% pHRR)
- HPCTP acts as a plasticizer

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Thank you for your attention!

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