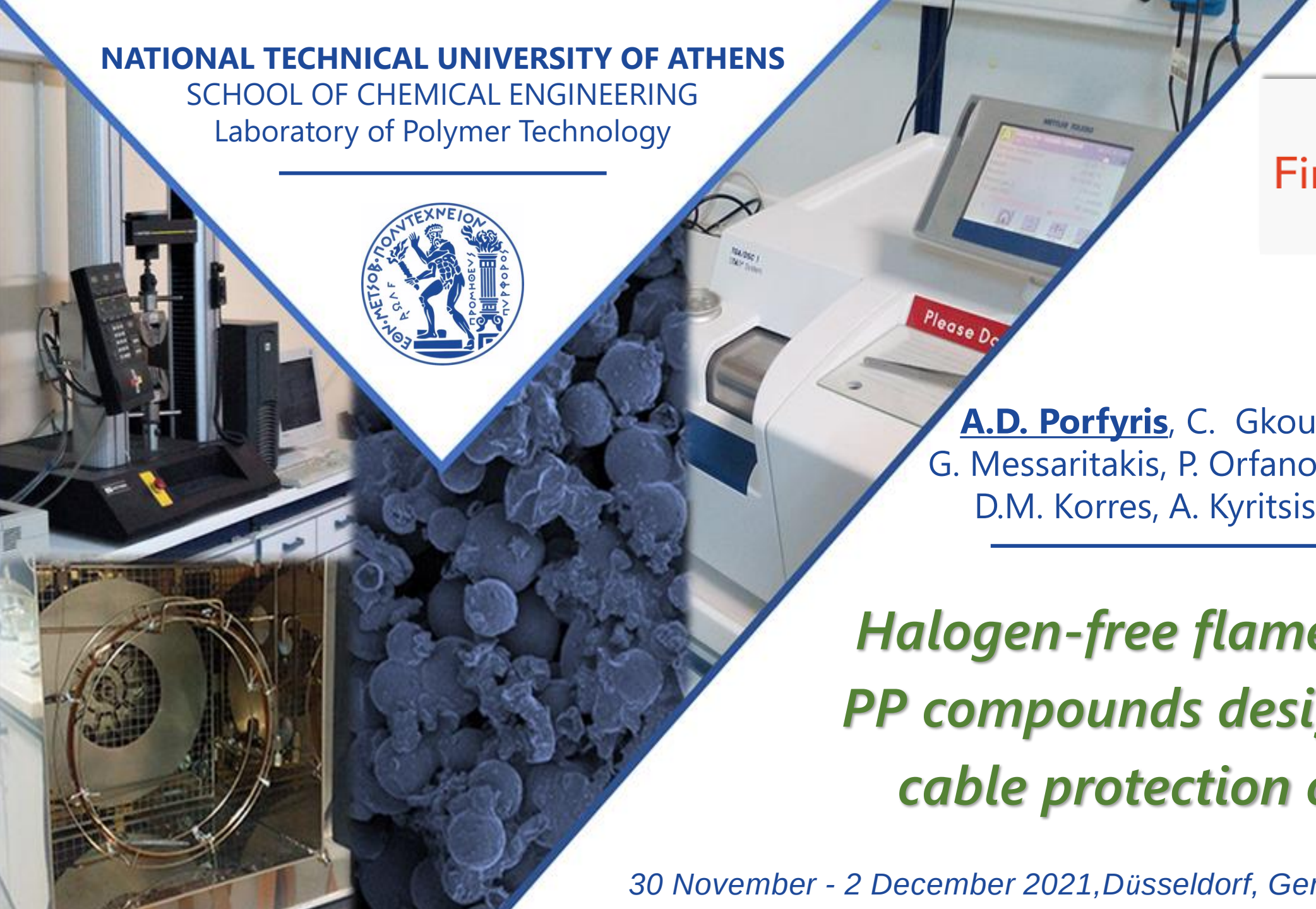
NATIONAL TECHNICAL UNIVERSITY OF ATHENS
SCHOOL OF CHEMICAL ENGINEERING
Laboratory of Polymer Technology



Fire Resistance in Plastics

A.D. Porfyris, C. Gkountela, C. Politidis, G. Messaritakis, P. Orfanoudakis, S. Pavlidou, D.M. Korres, A. Kyritsis, S.N. Vouyiouka

Halogen-free flame retarded PP compounds designated for cable protection conduits

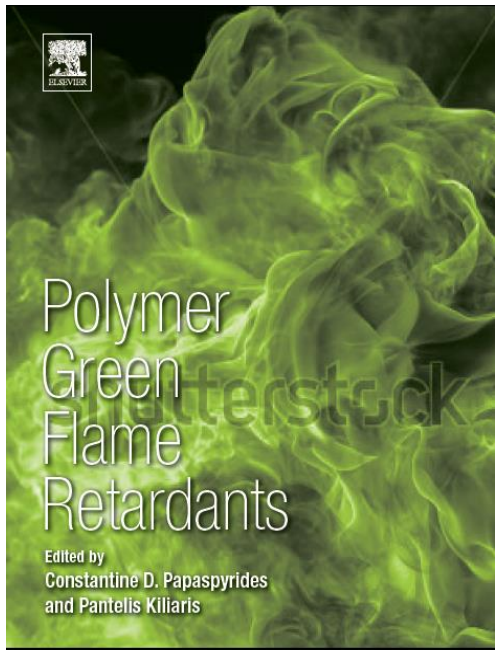
30 November - 2 December 2021,Düsseldorf, Germany - Session 7

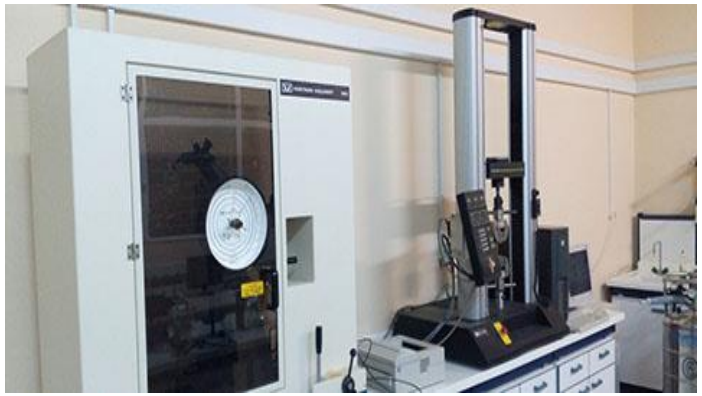
National Technical University of Athens (NTUA)

- **NTUA** (www.ntua.gr) is the oldest and most prestigious educational institution of Greece in the field of technology and has contributed unceasingly to the country's scientific, technical and economic development since its foundation in **1837**.
- **9 Engineering Schools**, 409 faculty members, 3000+ scientists, 1504 PhD students, 21.257 students, 300,000 m^2 of installations.
- According to the international **QS rankings**, **NTUA** is ranked among the top universities in the world for the year **2020**. In the **subject of Engineering & Technology**, NTUA holds the **No. 106 position** worldwide and **No. 29 in Europe**. NTUA is coordinating or participating in several European Projects and received 400 million EUR funding from EC in the last decade.

Laboratory of Polymer Technology (LPT)

- The School of Chemical Engineering comprises **16 teaching and research laboratories**, one of them **is the Laboratory of Polymer Technology (LPT)**. Our research unit, specialized in the area of Polymer Science and Technology, has grown in size and experience **since 1975**.





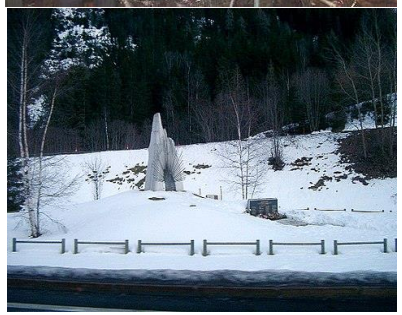
http://polymers.chemeng.ntua.gr/PolymeReEng/research.html

Contents

Building fire protection and security

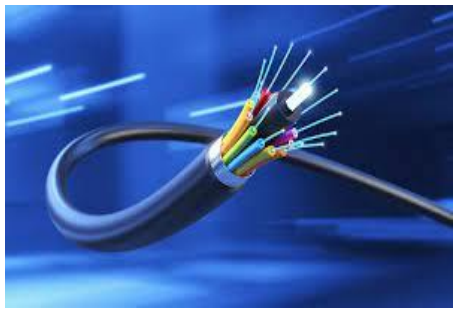
1987, London, Kings Cross Station, UK
Short circuit on the escalator with a death toll of 31

1996, Düsseldorf Airport, Germany
17 dead from toxic gases after cable fire in the false-ceilings of the terminal



1999, Mont Blanc Tunnel, France
39 dead from the release of toxic gases after a truck fire

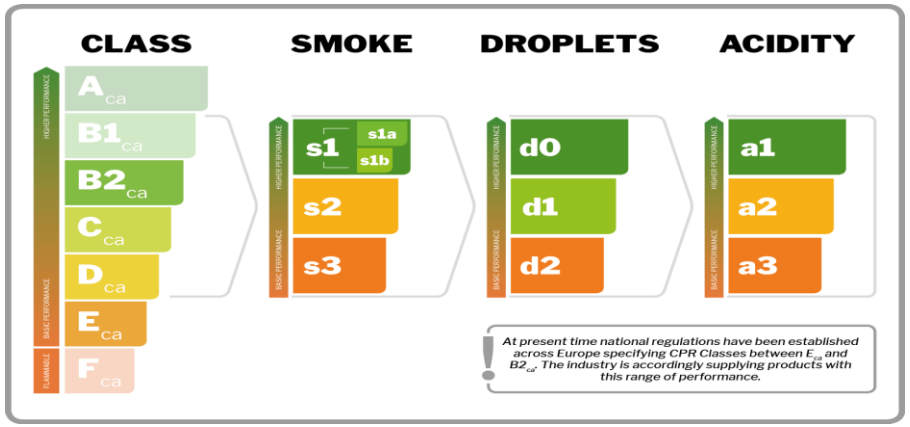
2003, Daegu, South Korea
198 dead and 147 injured in train fire



Strict Regulations for Fire Protection

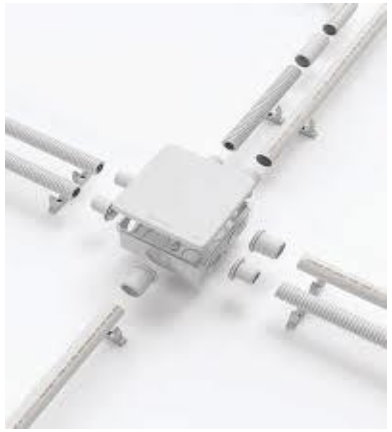
Construction Product Regulation (CPR)

- Cables **included** in CPR
- Use of halogen-free low smoke **(HFLS)** cables in various types of buildings



European standards for the fire hazard of cable conduits

- **Conduits:** Cable protection pipes
- Cable **conduits are** currently **excluded** from **CPR**
- Cable **conduits** are included in **Low Voltage Directive** (LVD) (2014/35/EU)



Nr.	Fire hazard of conduits	Standard
1	**Flame propagation**	**EN 61386-1** Conduit systems for cable management - General requirements
2	**Halogen content**	**EN 50642** Cable management systems Test method for content of halogens
3	**Smoke density**	**EN 61034-2** Measurement of smoke density of cables burning under defined conditions - Part 2: Test procedure and requirements
4	**Corrosiveness**	**EN 60754-2** Test on gases evolved during combustion of materials from cables - Part 2: Determination of acidity (by pH measurement) and conductivity

Need for HFLS conduits in various types of buildings

Need for HFLS PP compounds

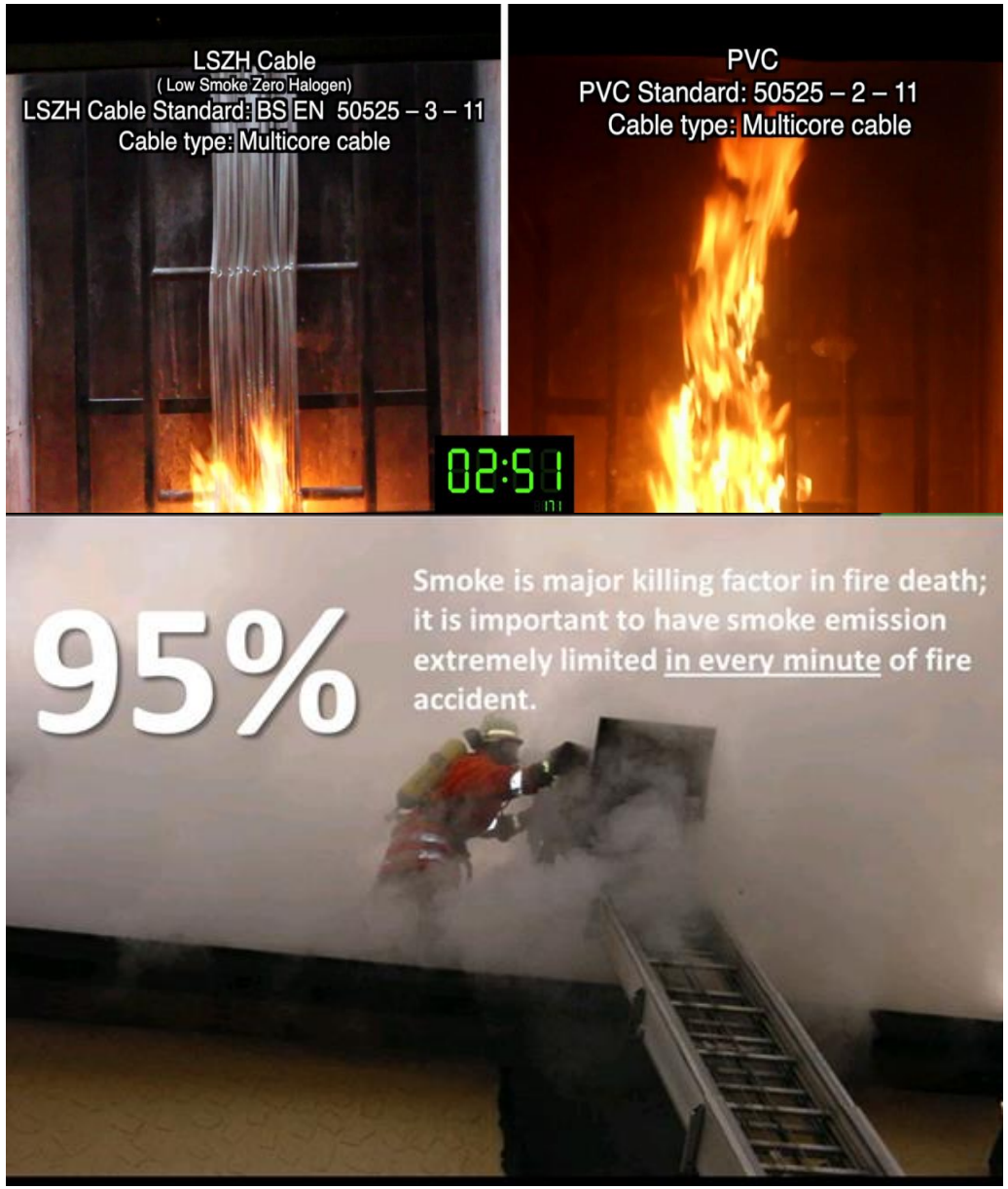
❑ PVC: Traditional Conduit material

☺ Ignition resistant, inherent self-extinguishing material due to Cl
☹ Release of toxic gases and dense smoke upon burning

❑ PP: Alternative commodity polymer

☺ Mechanical durability, chemical resistance, electrical insulation
☹ Highly flammable
☺ Eco-friendly Flame Retardants (FRs) improve FR performance

- **Smoke density and toxicity** critical factors in fire accidents
- **Low Smoke Density → EN61034-2:** visibility and fast access to emergency exits
- **Smoke Toxicity** → no toxic emissions → avoid respiratory infection → **EN50642** (Halogen Free) & **EN60754-2** (corrossiveness)



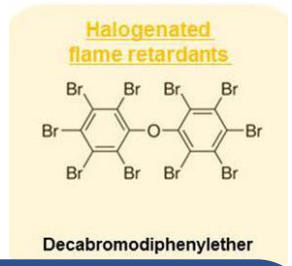
Flame Retardants (FRs)

- FRs comprise the **2nd most common** (ca. 15%) additive category after plasticizers
- Global FR production more than **2 million tons/year**
- Estimation of market cost in 2021 → 7.15 billion $

1. Halogenated (HFRs)

☺ Effective in low loadings (2-15%)

☹ equipment corrosion, toxic gases

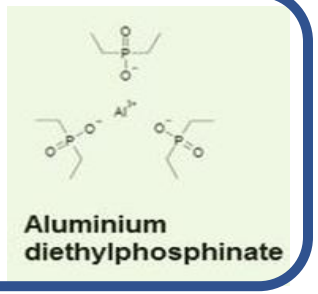


2. Organo-phosphorous FRs

☺ Environmentally friendly

☺ Halogen Free

☺ Effective in intermediate loadings (15-30%)

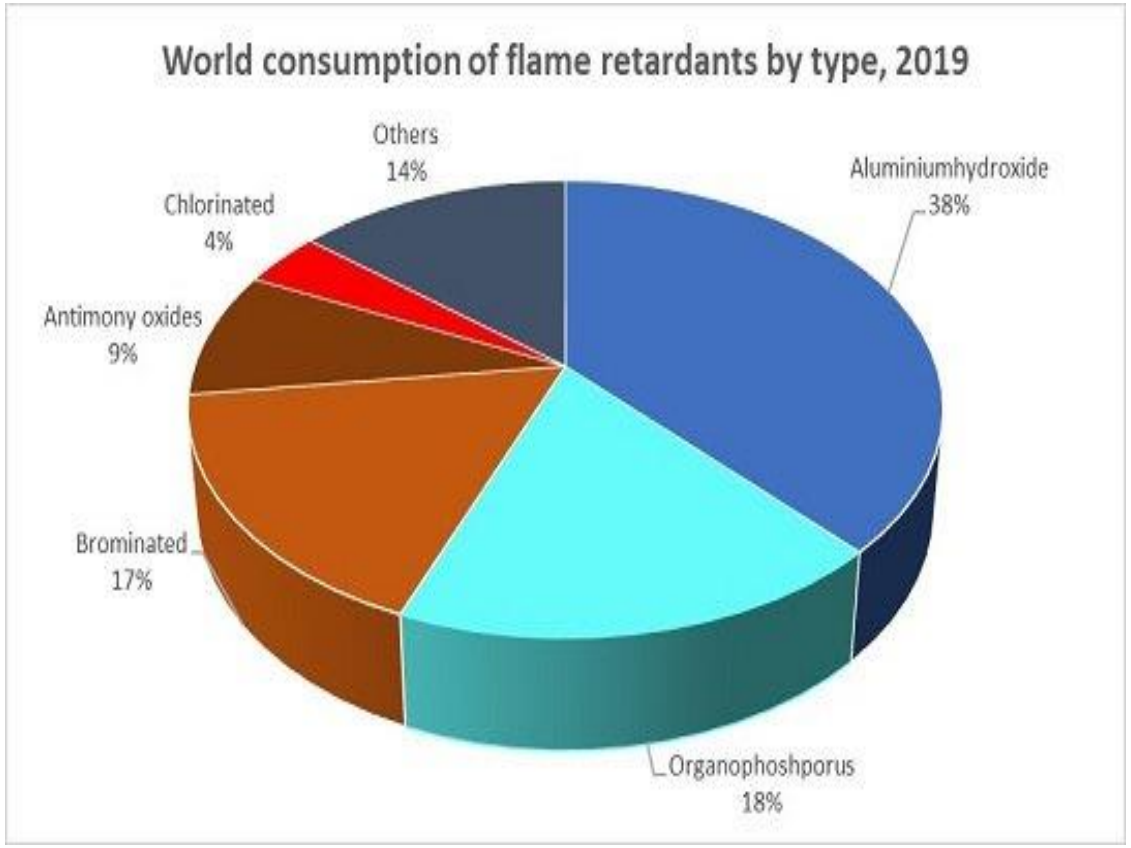


3. Inorganic - Minerals

☺ Environmentally friendly

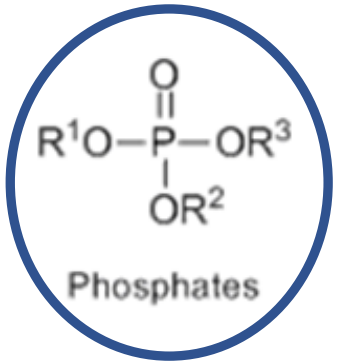
☹ Effective in high loadings (>50%)

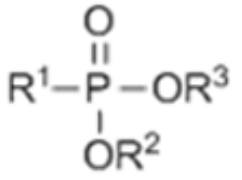
☹ poor mechanical behavior

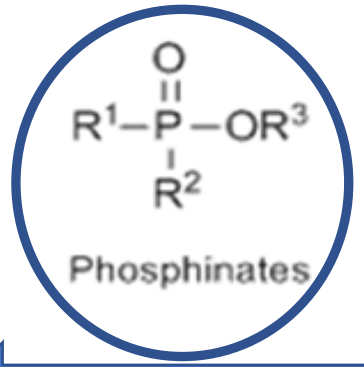


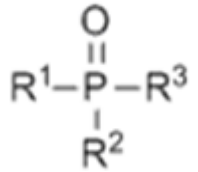
- A. D. Porfyris. Value-added Green Polyolefin Formulations: Halogen-Free Flame retardants. **EPF 2019**, 9-14 June 2019, Crete, Greece.
- R. Pfaendner, Eco-friendly fire prevention. New developments in flame retardants. **Kunststoffe international 8/2014.**

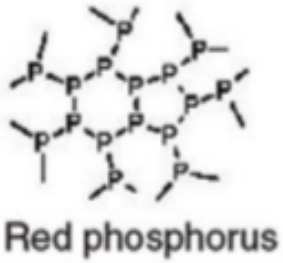
Organo-phosphorous Flame Retardants







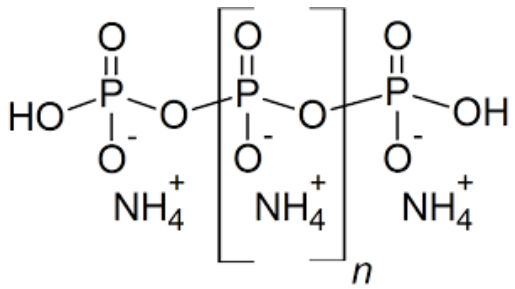




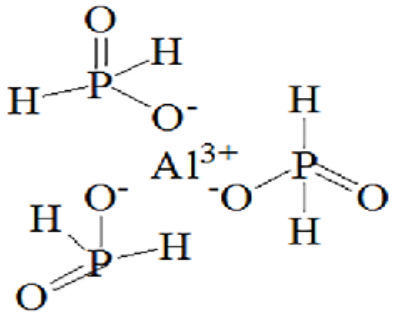
Condensed phase mechanism
Charring – Protective Layer

Oxygenation level ↑

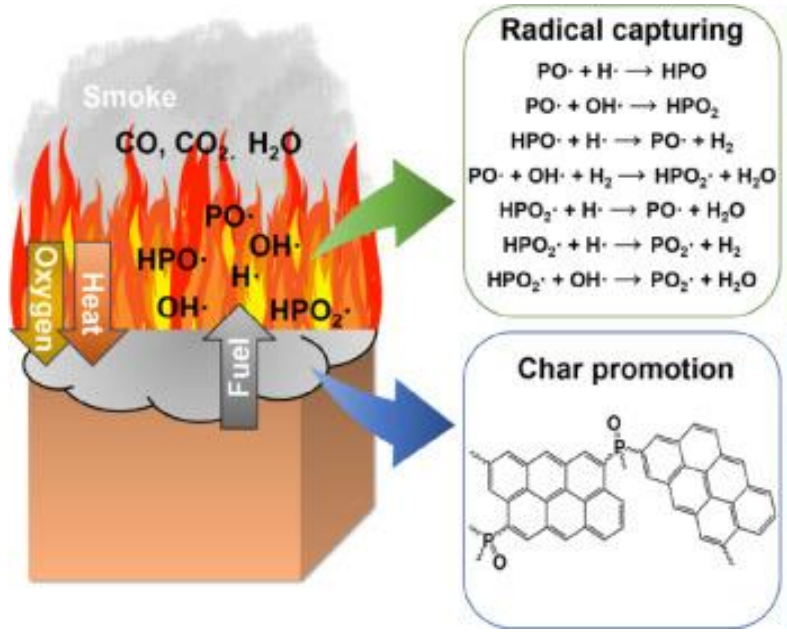
Gas phase mechanism
Radical Quenching



Ammonium Polyphosphate (APP)



Aluminum Hypophosphite (AHP)



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European Union
European Regional Development Fund
EPAnEK 2014-2020 OPERATIONAL PROGRAMME COMPETITIVENESS ENTREPRENEURSHIP INNOVATION
ΕΣΠΑ 2014-2020 Partnership Agreement 2014 - 2020
Co-financed by Greece and the European Union

NATIONAL TECHNICAL UNIVERSITY OF ATHENS
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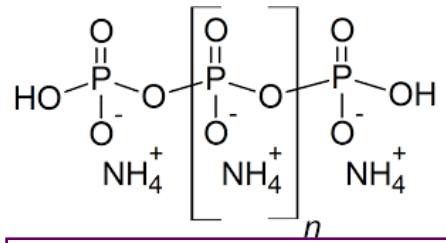
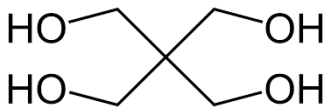
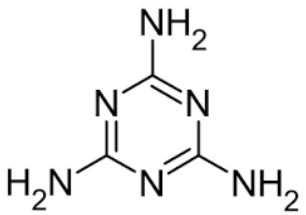
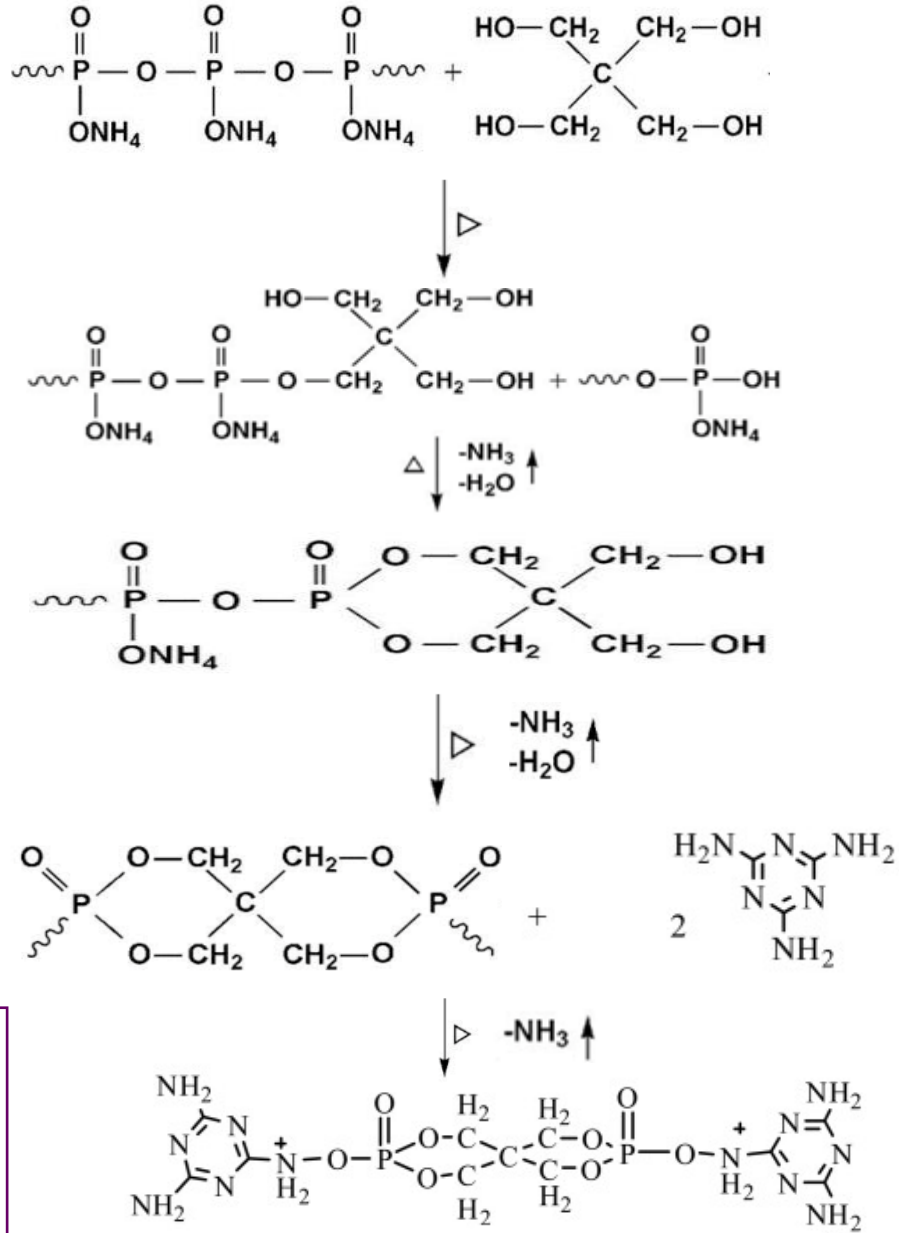
Condensed phase: Intumescence

- **Phosphorus-nitrogen** synergism
- 3 ingredients: **acid source**, **carbon source** *(char forming agent, CFA)* **gas source** *(blowing/spumific agent)*
- **Acid source**: decomposes at low *T* → generates $(H_3PO_4)_n$
- **Carbon source:** esterification with inorganic acid → Protective char layer
- **Gas source:** release of gases (e.g. H_2O, NH_3) → Swelling of char layer
- **Mechanism:** Swollen char on the surface of the polymer → Heat insulator and barrier for O_2 and pyrolysis products
- **Typical System:** APP, PER and MEL









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- M. Ba, B. Liang, Ch. Wang, *Fibers and Polymers* **2017**; 18:907-914
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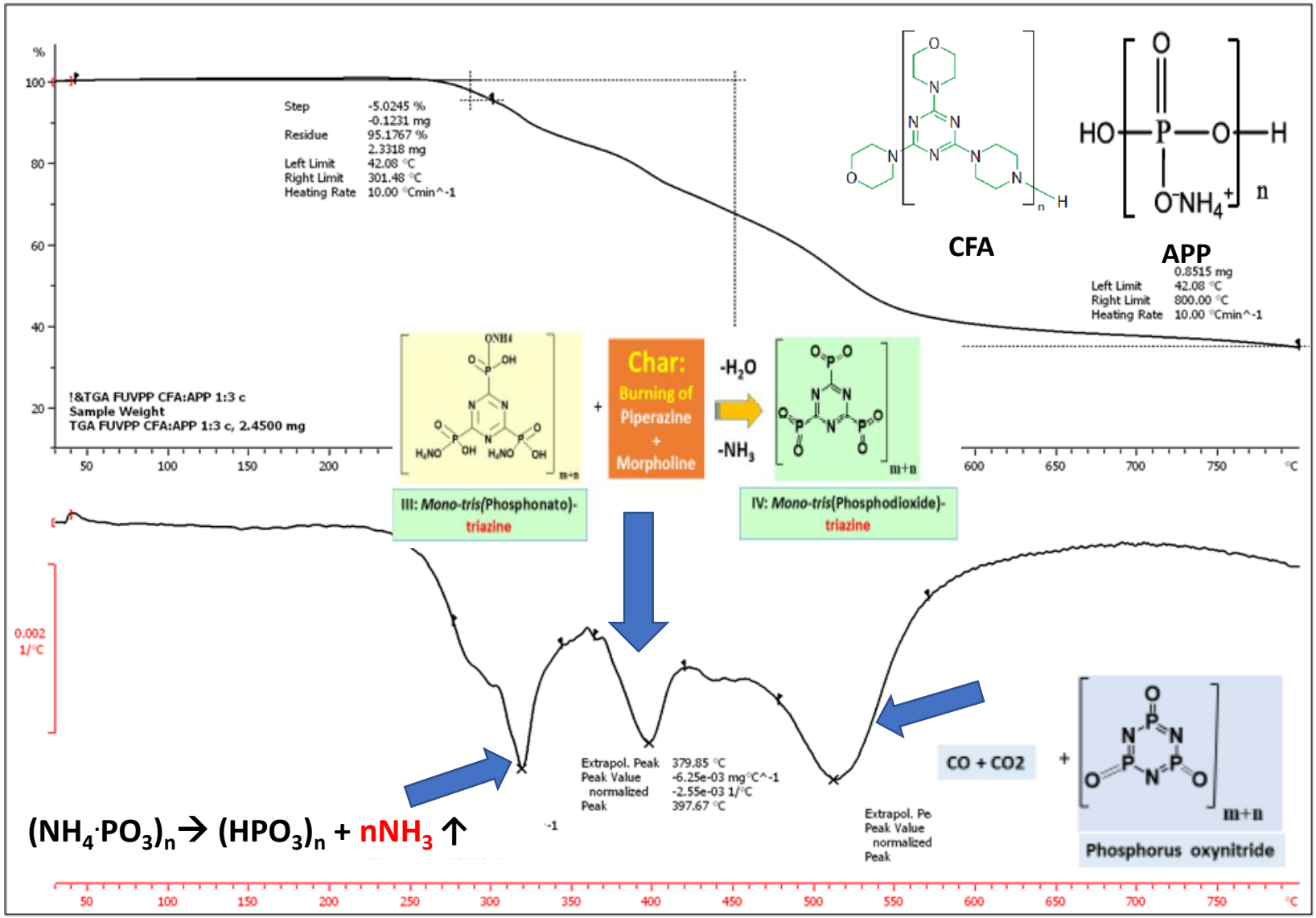
- R. Pfaendner. Flame retardants for polyethylene. Handbook of Industrial Polyethylene and Technology. Spalding M, Chatterjee A, Editors. Wiley **2016**, 921-934

Intumescent System FRs

- **Acid + Gas Source**: APP
- **Char Forming Agent (CFA)**: Poly-(piperazine, morpholinyl, triazine)
- More efficient CFA → more C & N due to morpholine and piperazine
- ~**35%** char at 800 °C
- Formation of phosphorous oxynitride (high temperature resistant)



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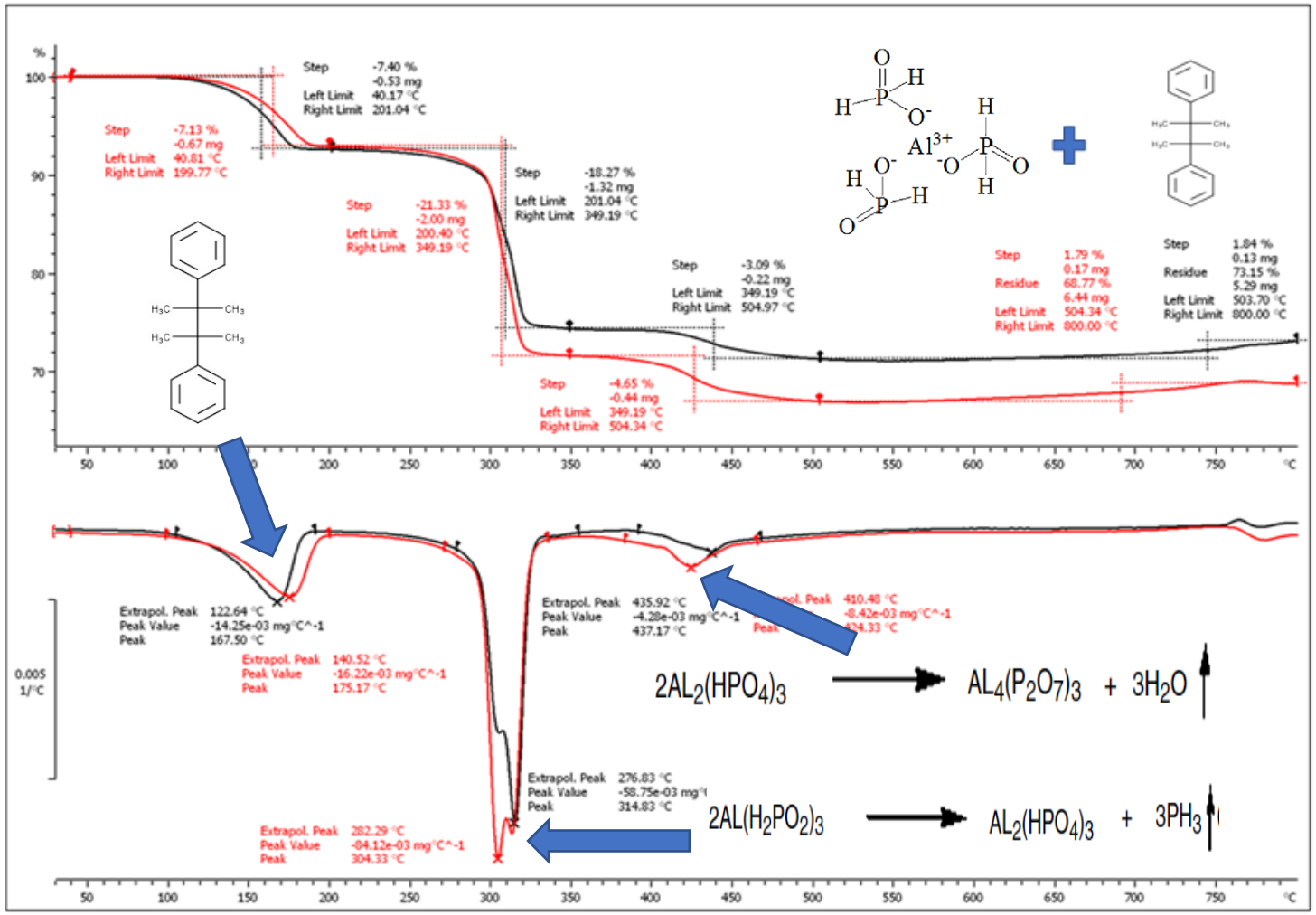
- A. S. Luyt et.al. *Polymers* **2019**;11, 1479.
- H. Xie et al. *Polym. Degrad. Stab.* **2015**;118:167-177.
- D. Enescu et. al. *Polym. Degrad. Stab.* **2013**;98:297-305.

Gas phase: Phosphinate-based FR

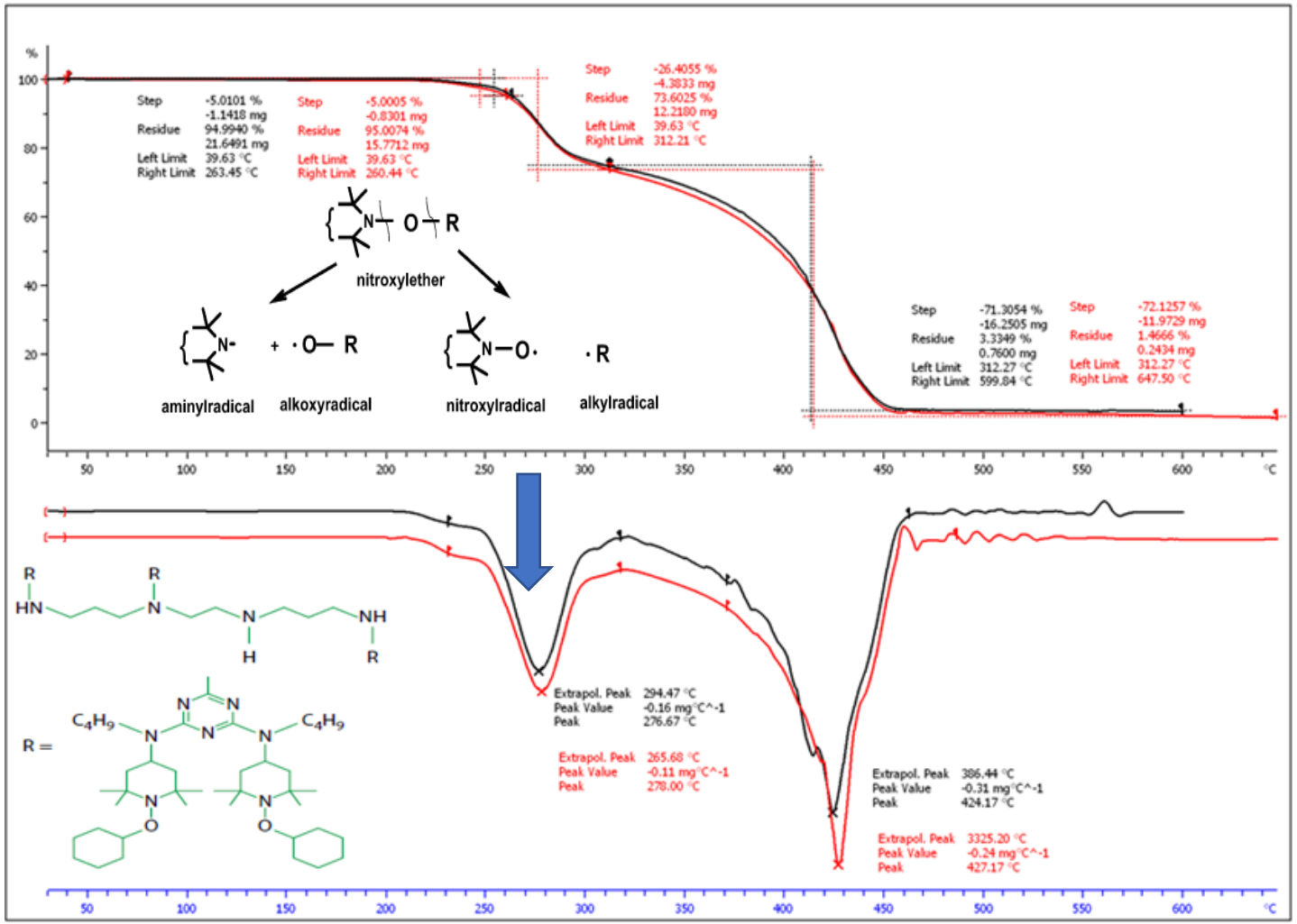
- **Aluminum hypophosphite + Phosphorous/Bromine Salt + dripping meltable synergic**
- Dosage control → Halogen free levels
- Triple Functionality:
  1. **Dripping** → Removal of polymer (fuel) from the flame zone
  2. **Production of PH_3, H_2O** → Dilution and Cooling of the gas phase
  3. **Generation of Br** → Quenching of $H^{\cdot}$, $OH^{\cdot}$, $CH_3^{\cdot}$
- High char (~70%) due to **$Al_4(P_2O_7)_3$**



- U. Zucchelli. Addcon World 2007, Frankfurt, Germany, **2007.**
- L. S. Atabek et al. *Fire and Materials.* **2019**;43:294-302.
- P. Zhao et al. *J. Therm Anal. Calorim.* **2019**;135:3085-3093.
- S. Furtana et al. *J. Therm Anal. Calorim.* **2020**;139:3415-3425.

Gas Phase: Radical Generator

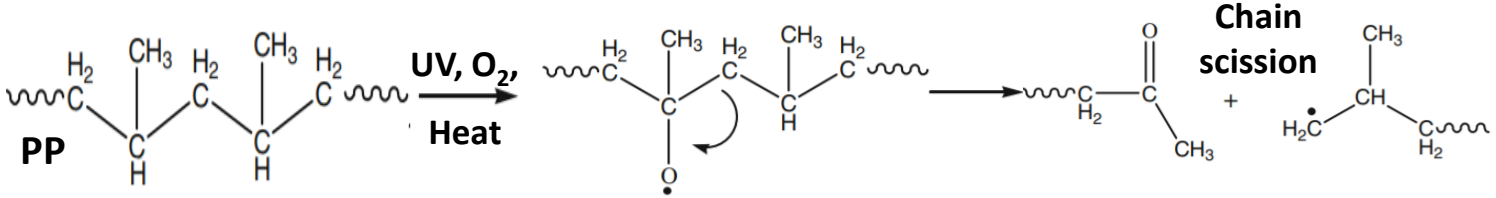
- **Radical Generator:** Nitroxyl-ether
- *T* > 250°C → **Thermolysis** of nitroxyl-ether
  - Aminyl & alkoxy decompose PP → **dripping**
  - Nitroxyl & alkyl → **Quenching of** H·, OH·, CH_3·
- **UL94 V2** classification for polyolefin fibers and films.
- Contributes to **UV and thermal** stabilization.
- **No charring** ability.



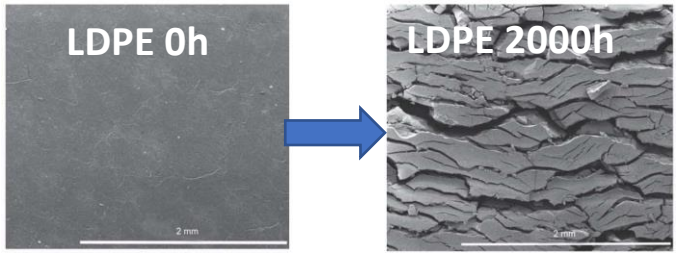
- R. Pfaendner, *C. R. Chimie* **2006**;9:1338–1344.
- A. S. Luyt et.al. *Polymers* **2019**;11, 1479.
- H. Xie et al, *Polym. Degrad. Stab.* **2015**;118:167-177.

Research challenge

Polyolefins susceptible to **weathering**

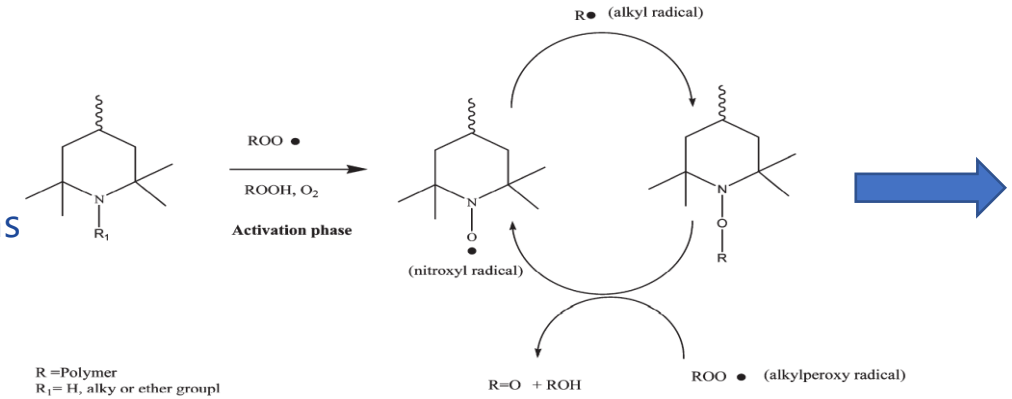


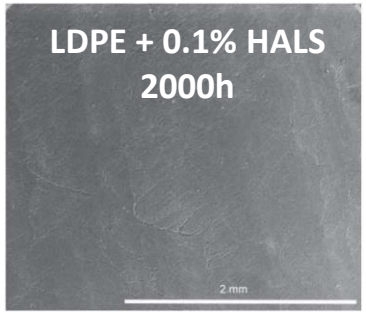
Deterioration of mechanical performance



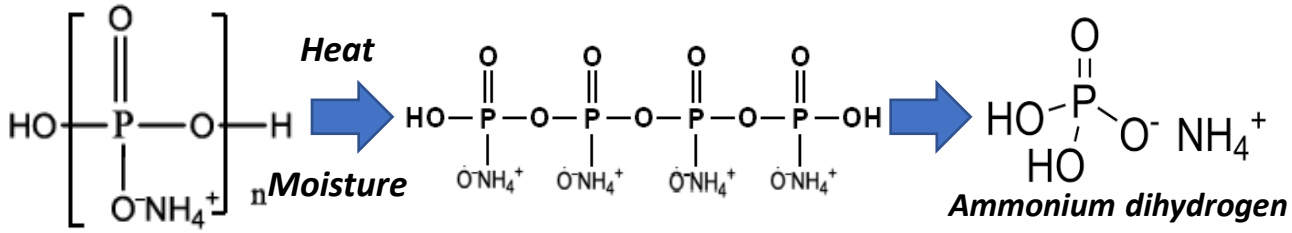
Stabilization with **HALS** additives

- Effective in very low concentrations
- Effective due to regeneration





- **APP** upon ageing → Polyphosphoric acid salts
- **Halogenated FRs** UV instable → release of **X•**
- **Antagonism** between **FRs** and **HALS** additives



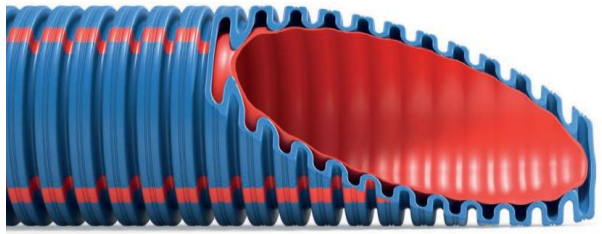
Risk of HALS deactivation in Flame retarded polymers

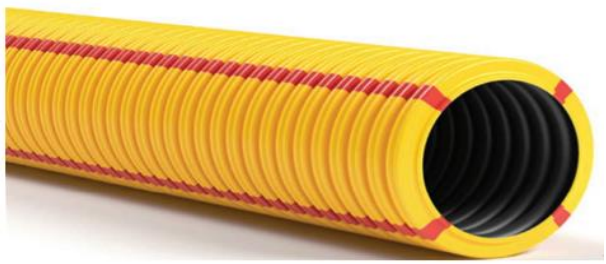
- C.E. Wilen, R. Pfaendner. *J. Appl. Polym. Sci.* **2013**;APP38979.
- A.D. Porfyris et. al. *J. Appl. Polym. Sci.* **2020**;APP50370.
- S. Yhang, Z. Chen. *Procedia Engineering* **2018**;211:906-910.

FUVPP – Fire and UV Protected Polypropylene Pipes

- ❑ Develop **flame retarded PP** of low environmental impact and **high resistance to ageing**
- ❑ New materials will be used in a totally new and patented production process that allows producing **corrugated PP conduits of low external diameters (ø16-ø32 mm)**
- ❑ Produce **novel conduit systems for cable protection** in building installations

- 3 year research project (Started July 2020)
- **NTUA:** Laboratory of Polymer Technology & Dielectrics Group
- **MIRTEC:** Technological Center, Certification Company
- **KOUVIDIS:** biggest Greek plastic pipe manufacturer - conduit manufacturer – cable management and protection systems

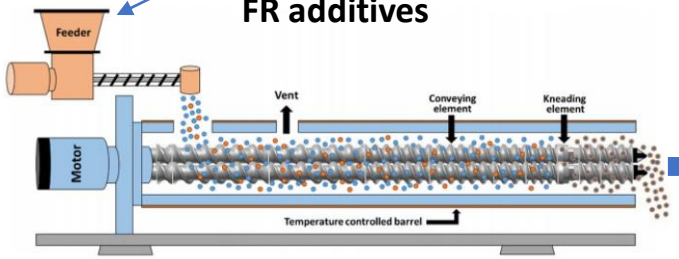




http://fuvpp.chemeng.ntua.gr/project.html

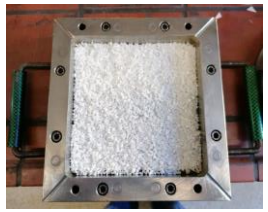
Development of FR/PP formulations

PP heterophasic co-polymer
+
FR additives

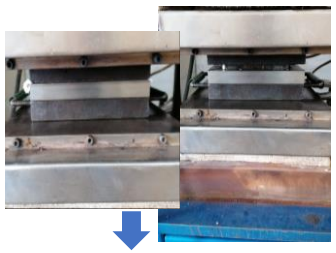


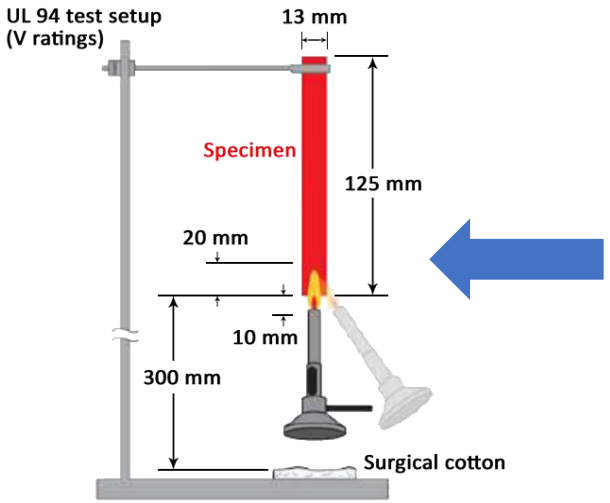
Twin-screw extrusion
(HAAKE Thermo Fischer PTW16, L/D = 25, 190-220 °C, 50 rpm)

FR compounds (FR1-FR10)



Compression molding → UL94 specimens (125x13x1.6mm)
(210 °C, 200 bar, 15 min)



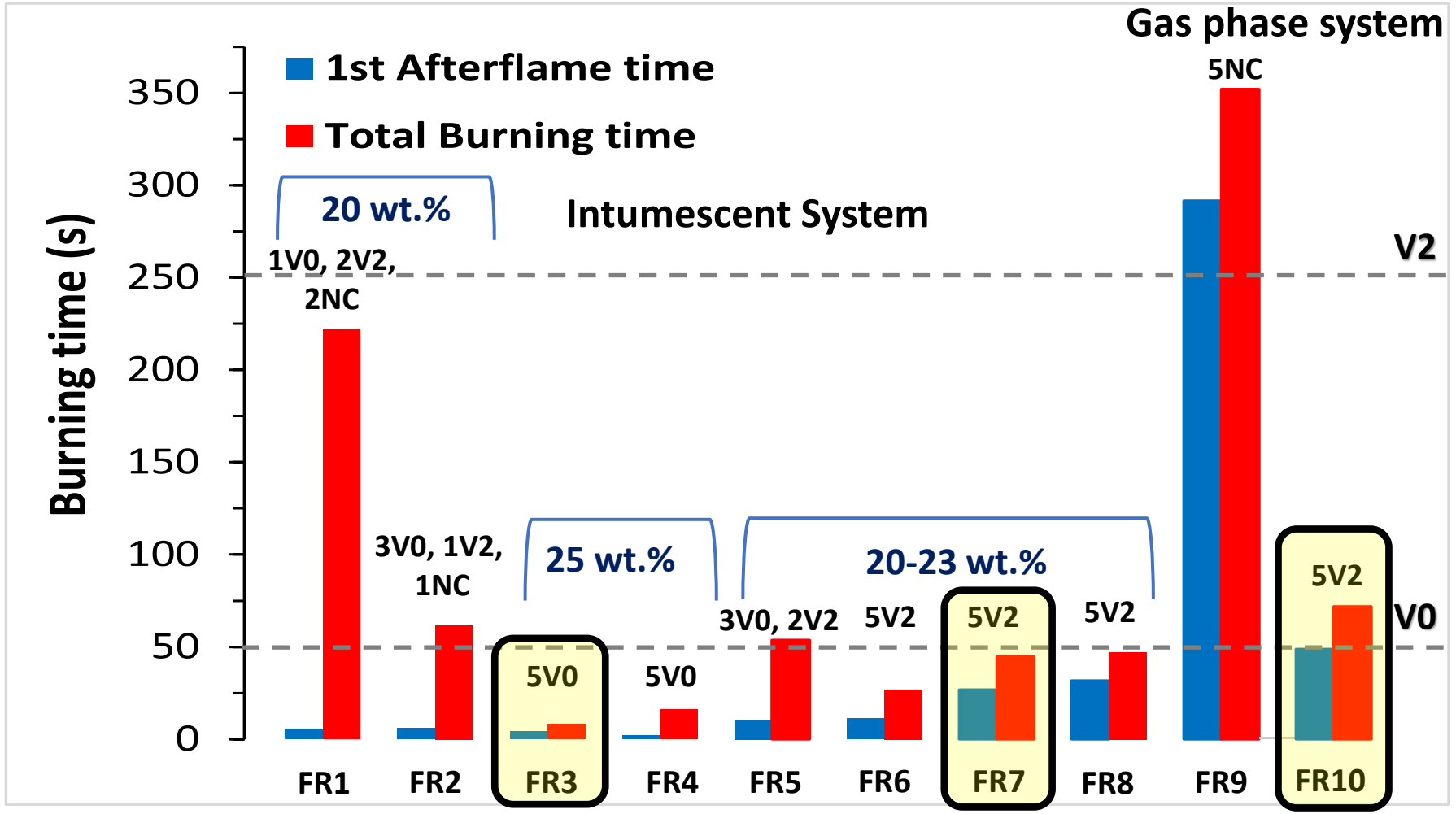


UL94V Test
(ASTM D3801)

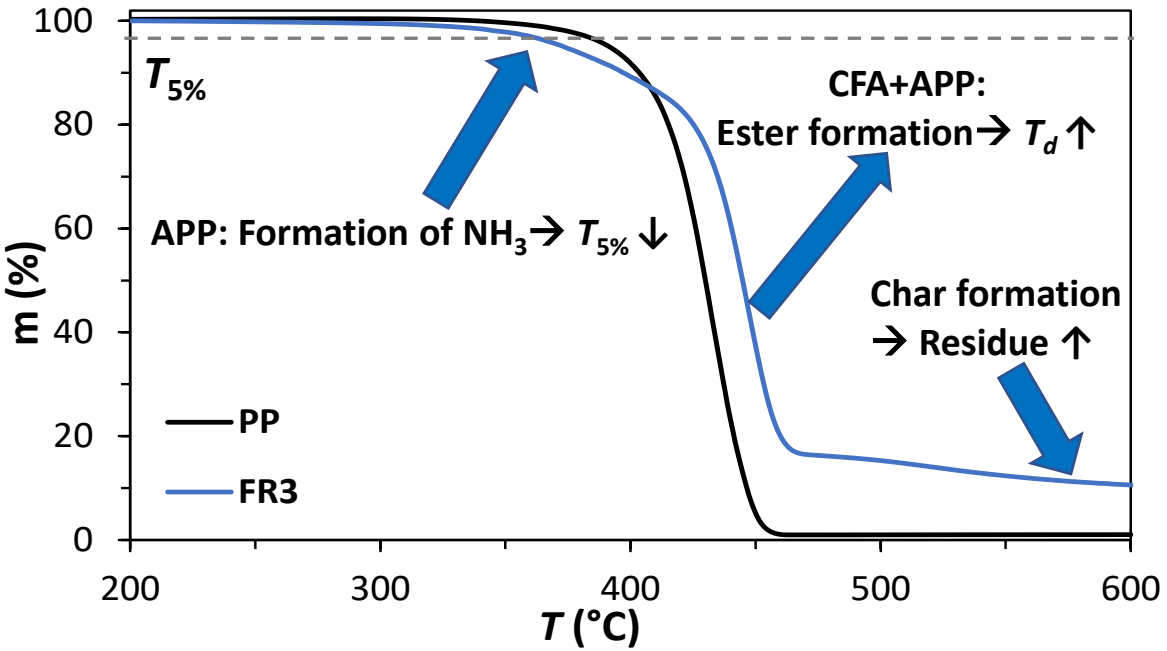
Formulations	CFA	APP	CFA:APP	Radical Generator	Phosphinate FR	Total (%wt.)
Intumescent System						
FR1	5	15	1:3	-	-	**20**
FR2	4	16	1:4	-	-	**20**
FR3	6.25	18.75	1:3	-	-	**25**
FR4	5	20	1:4	-	-	**25**
FR5	5.6	16.9	1:3	-	-	**22.5**
FR6	5.6	16.9	1:3	0.5	-	**23**
FR7	4.75	14.25	1:3	1	-	**20**
FR8	3.8	15.2	1:4	1	-	**20**
Gas Phase System						
FR9	-	-	-	3	-	**3**
FR10	-	-	-	-	2	**2**

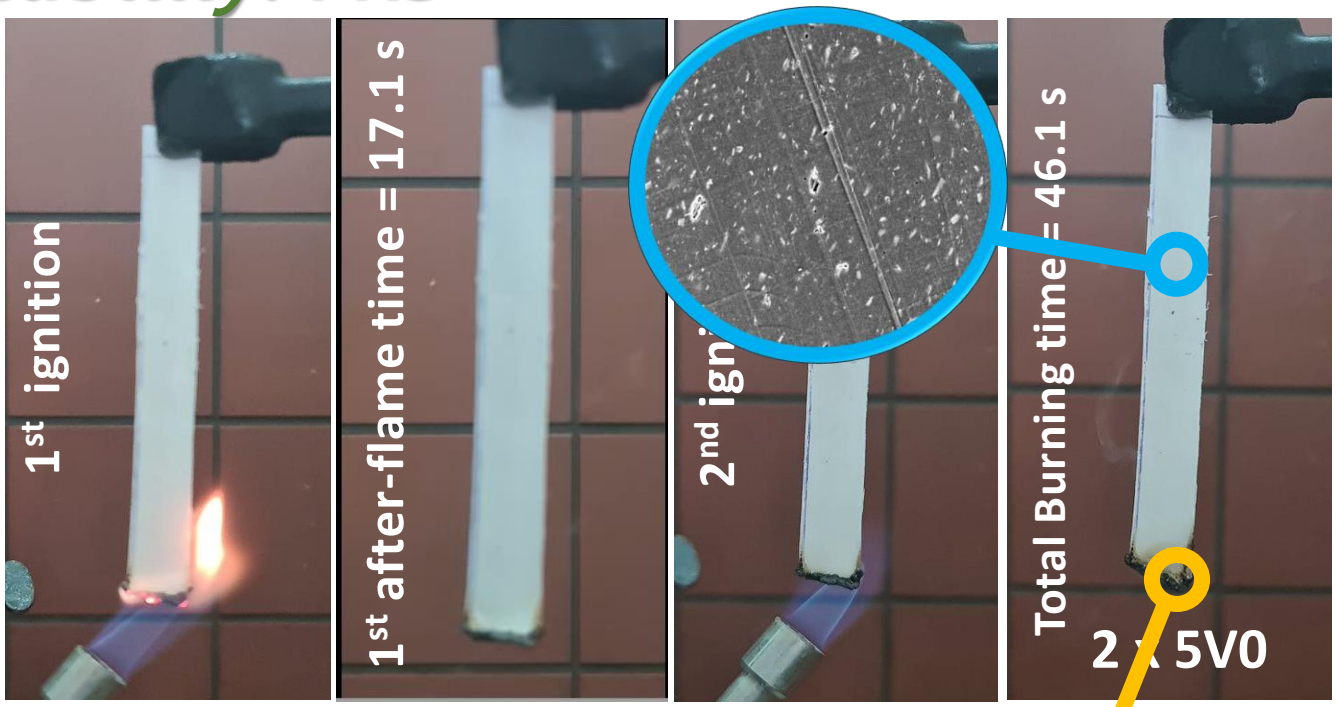
Formulation Development

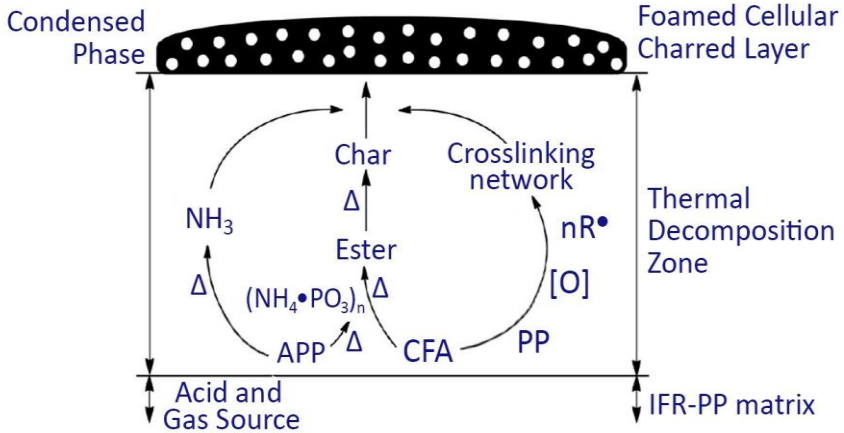
- Parameters: Total loading & CFA:APP ratio
- **UL94** as evaluation tool
- **FR3, FR7, FR10** most promising formulations



Flame retardancy vs thermal stability: FR3





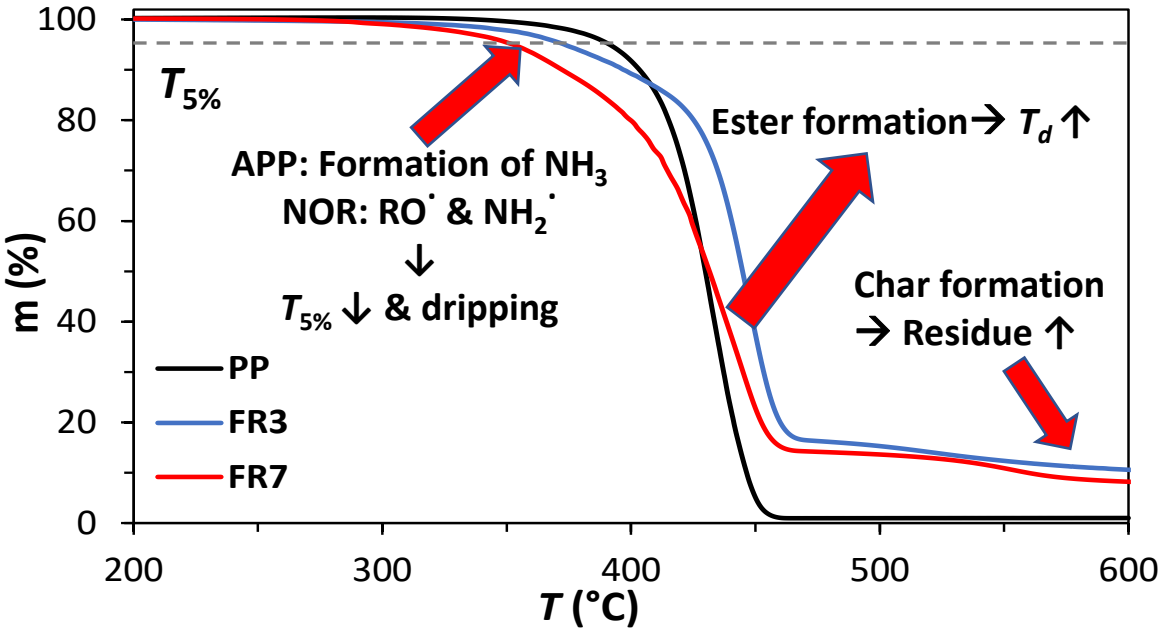


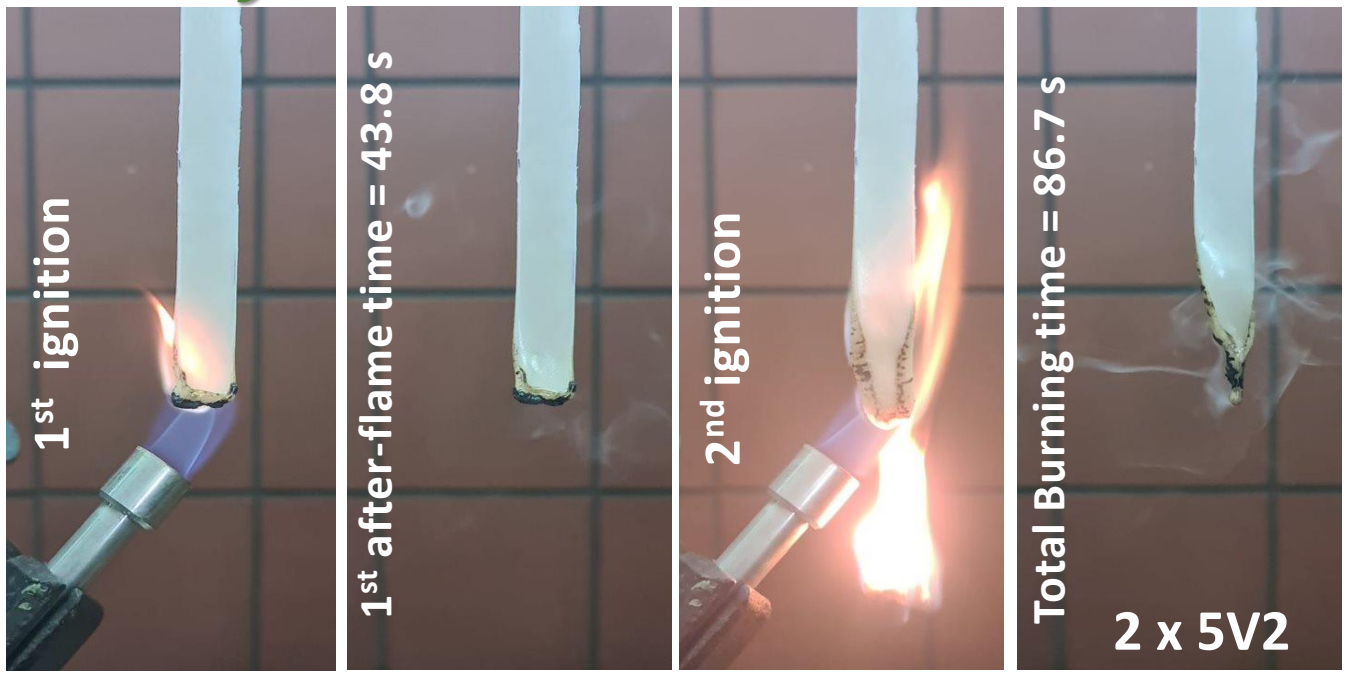
FR3: 25wt.% CFA:APP 1:3

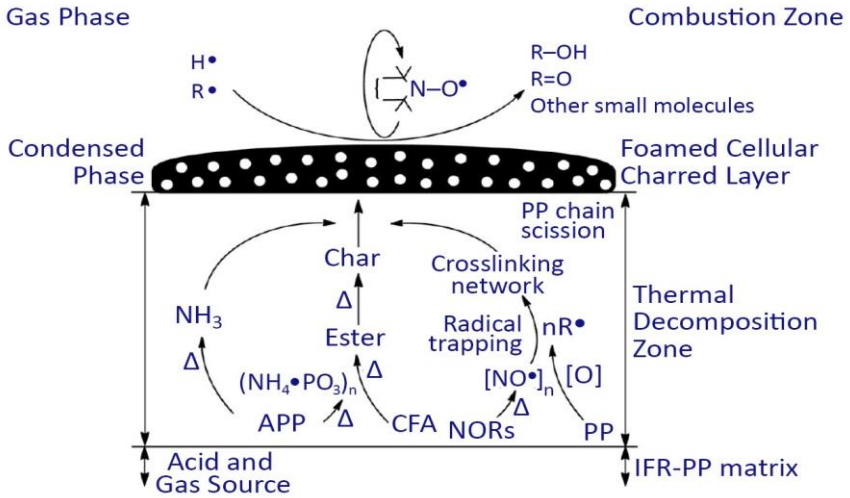
	PP	FR3
$T_{5\%}$ (°C)	391.7 ± 0.1	375.0 ± 1.7
T_d (°C)	433.5 ± 1.2	446.8 ± 0.3
Residue (%)	1.1 ± 0.1	12.0 ± 0.5

- A. S. Luyt et.
- B. Kaul. *Rubb*
- H. Xie et al, *P*
- K. Cao et. al. *In*

Flame retardancy vs thermal stability: FR7







FR7: 19wt.% CFA:APP 1:3 + 1wt.% RG

	PP	FR7
$T_{5\%}$ (°C)	391.7 ± 0.1	351.1 ± 4.7
T_d (°C)	433.5 ± 1.2	444.2 ± 1.8
Residue (%)	1.1 ± 0.1	8.5 ± 0.4

- A. S. Luyt et.al. *Polymers* **2019**;11, 1479.
- B. Kaul. *Rubber Fiber Plastics* **2016**;3:1-9.
- H. Xie et al, *Polym. Degrad. Stab.* **2015**;118:167-177.
- K. Cao et. al. *Ind. Eng. Chem. Res.* **2013**;52:309-317.

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ΕΣΠΑ 2014-2020
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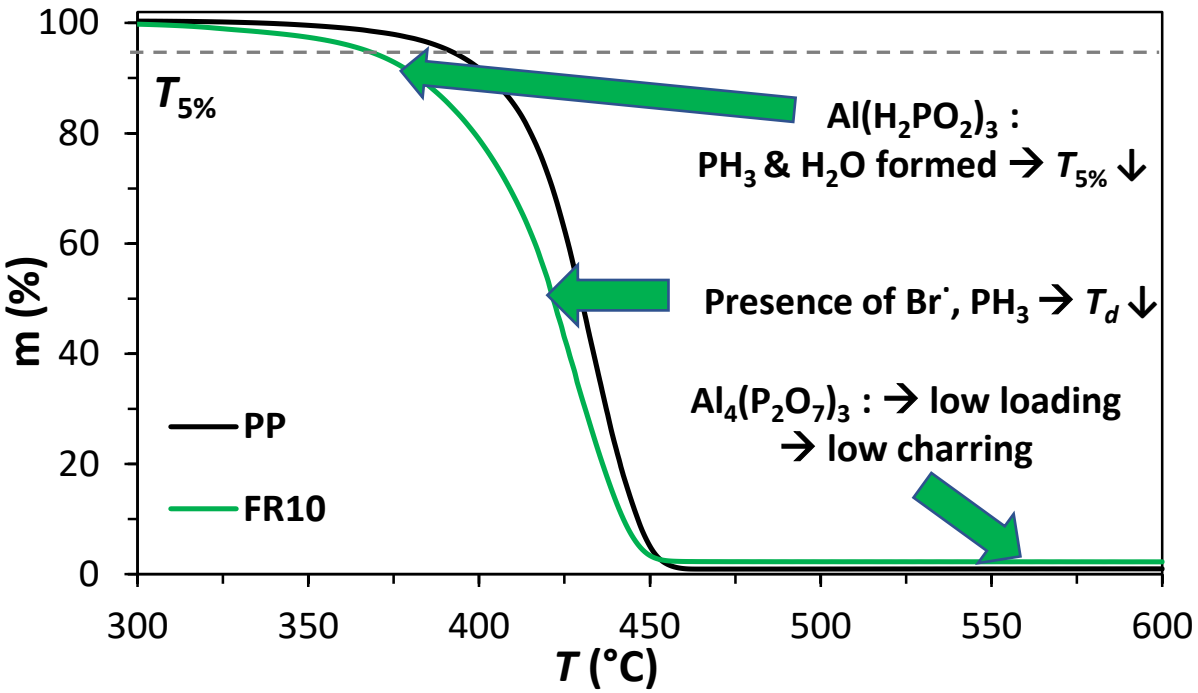
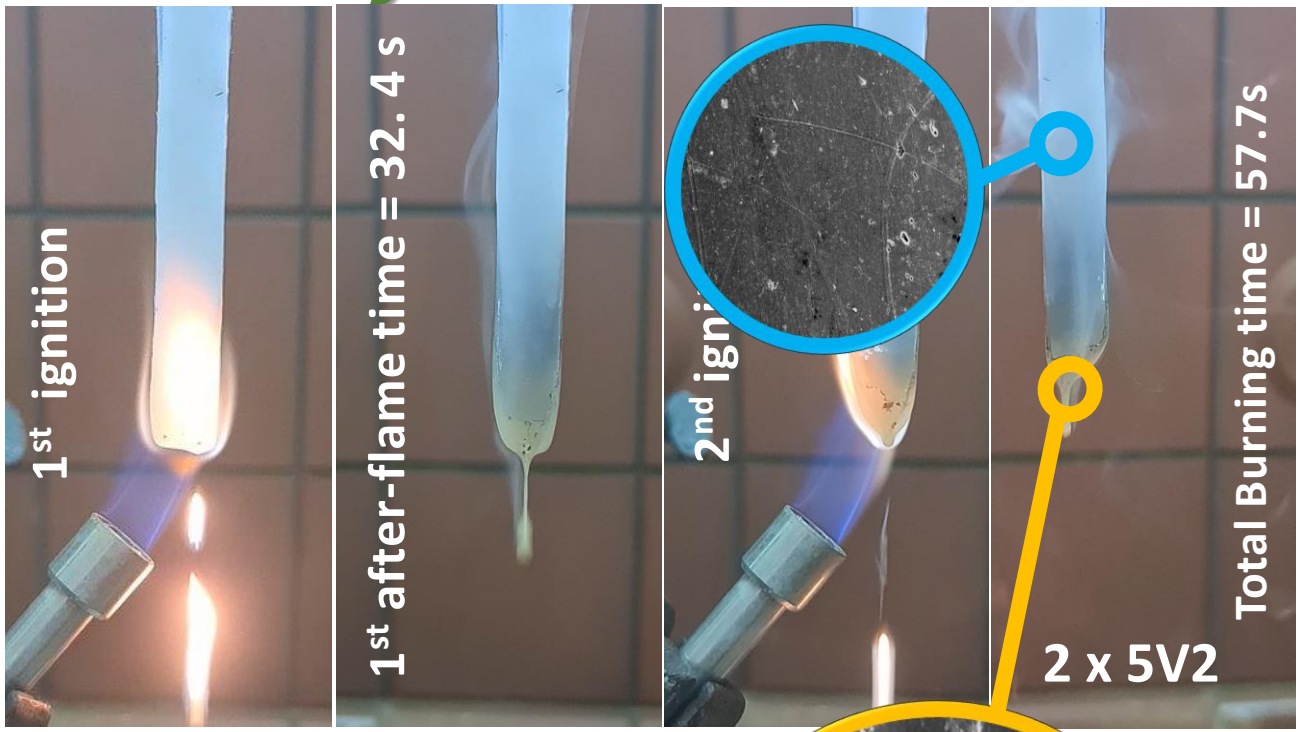
Co-financed by Greece and the European Union

NATIONAL TECHNICAL UNIVERSITY OF ATHENS
Laboratory of Polymer Technology

Flame retardancy vs thermal stability: FR10





$AL(H_2PO_2)_3 + 3O_2 \rightarrow AL(PO_3)_3 + 3H_2O\uparrow$

$2AL(H_2PO_2)_3 \rightarrow AL_2(HPO_4)_3 + 3PH_3\uparrow$

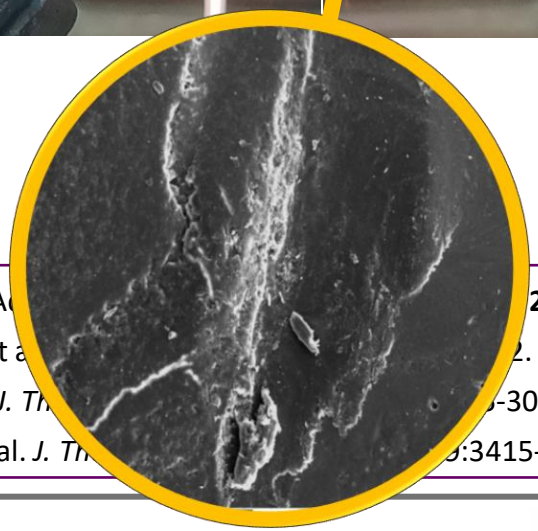
$PH_3 \xrightarrow{O_2} H_3PO_4$

$2AL_2(HPO_4)_3 \rightarrow AL_4(P_2O_7)_3 + 3H_2O\uparrow$

In air

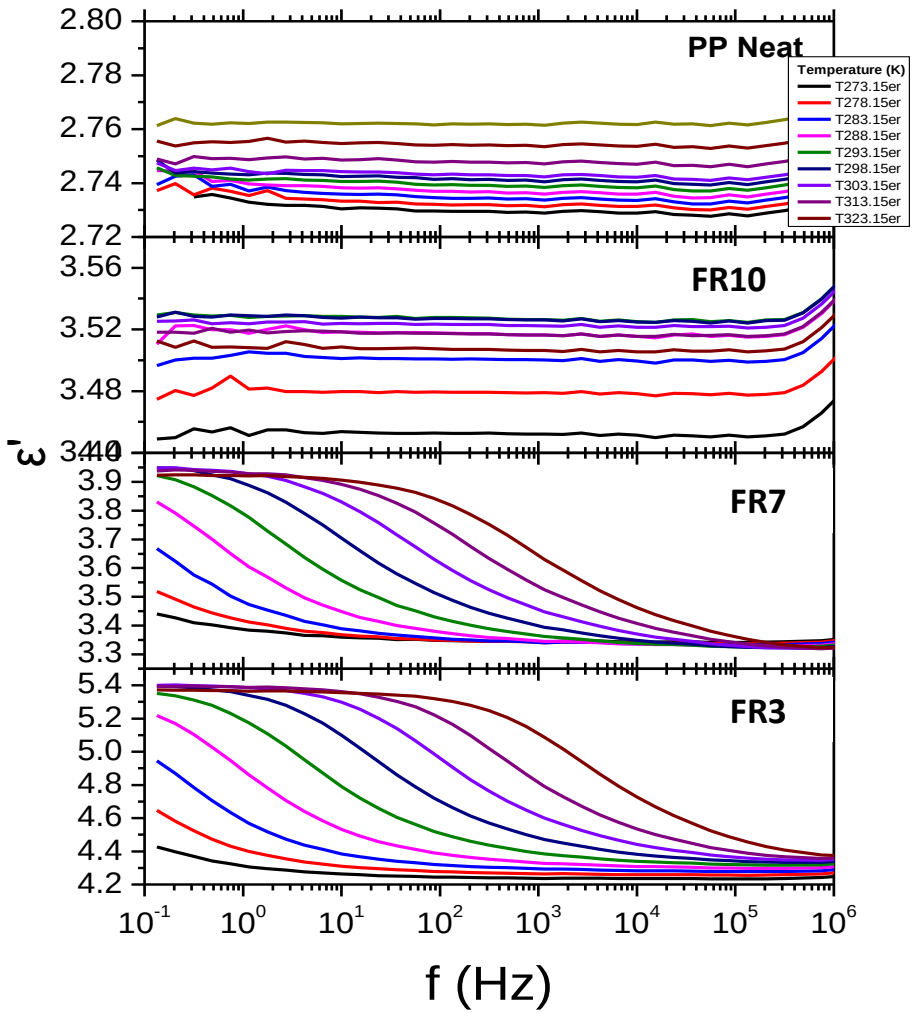
FR10: 2 wt.% phosphinate-based FR

	PP	FR10
$T_{5\%}$ (°C)	391.7 ± 0.1	370.9 ± 3.3
T_d (°C)	433.5 ± 1.2	430.0 ± 3.4
Residue (%)	1.1 ± 0.1	2.5 ± 0.2

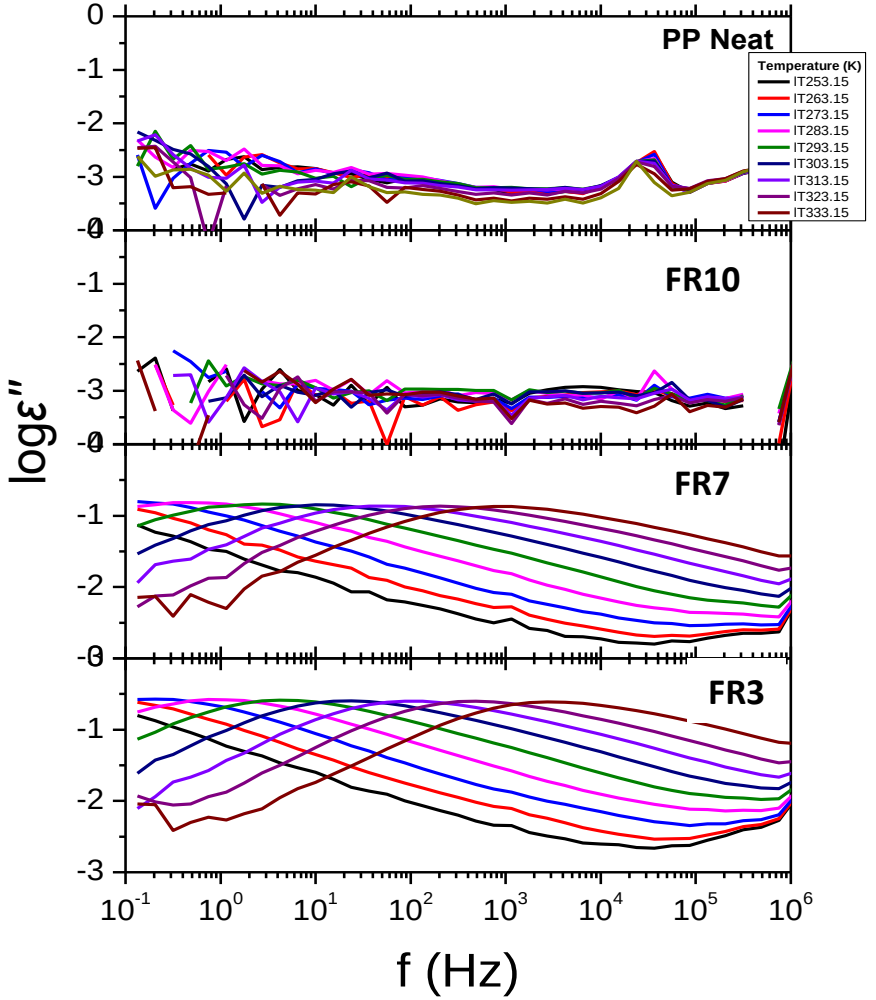


- U. Zucchelli. A… **2007.**
- L. S. Atabek et a… 2.
- P. Zhao et al. *J. Th…* -3093.
- S. Furtana et al. *J. Th…* :3415-3425.

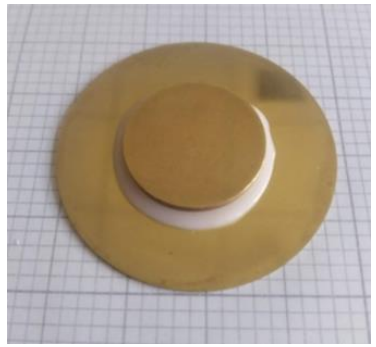
Broadband Dielectric Spectroscopy (investigating the molecular mobility)



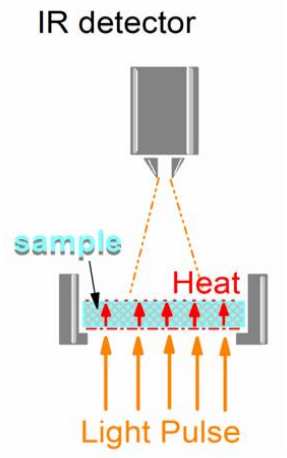
Real part of dielectric permittivity
(polarizability)



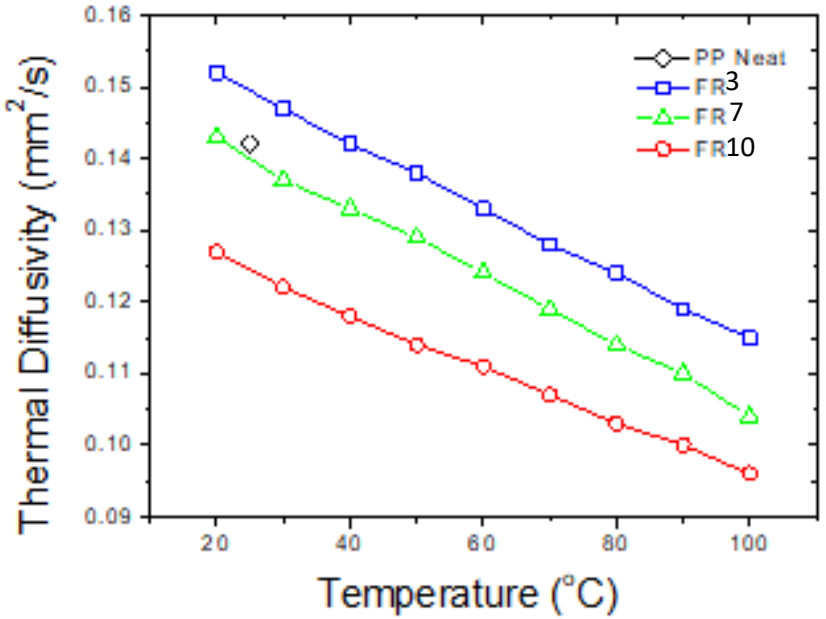
Imaginary part of dielectric permittivity
(dielectric losses)



Thermal diffusivity - conductivity (Laser/Light Flash analysis)

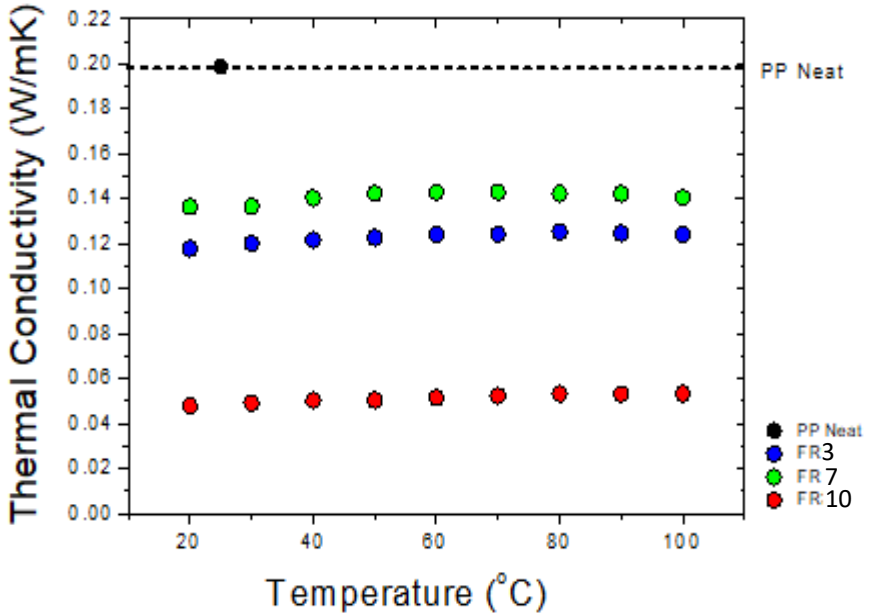


LFA467 Hyper-Flash
(NETZSCH)



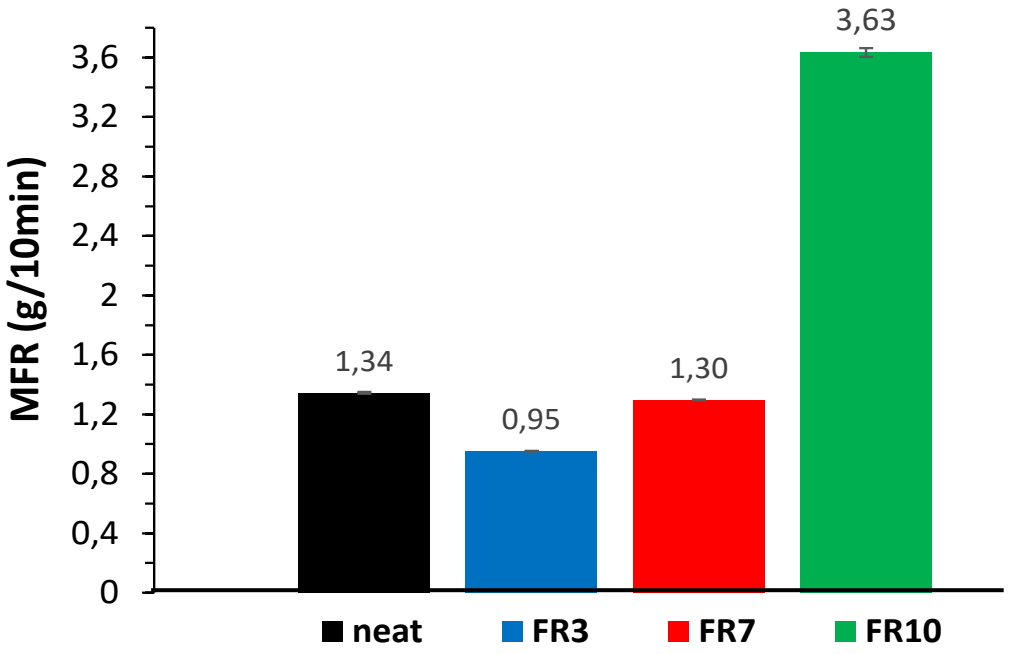
$$\lambda = \alpha \rho C_P$$

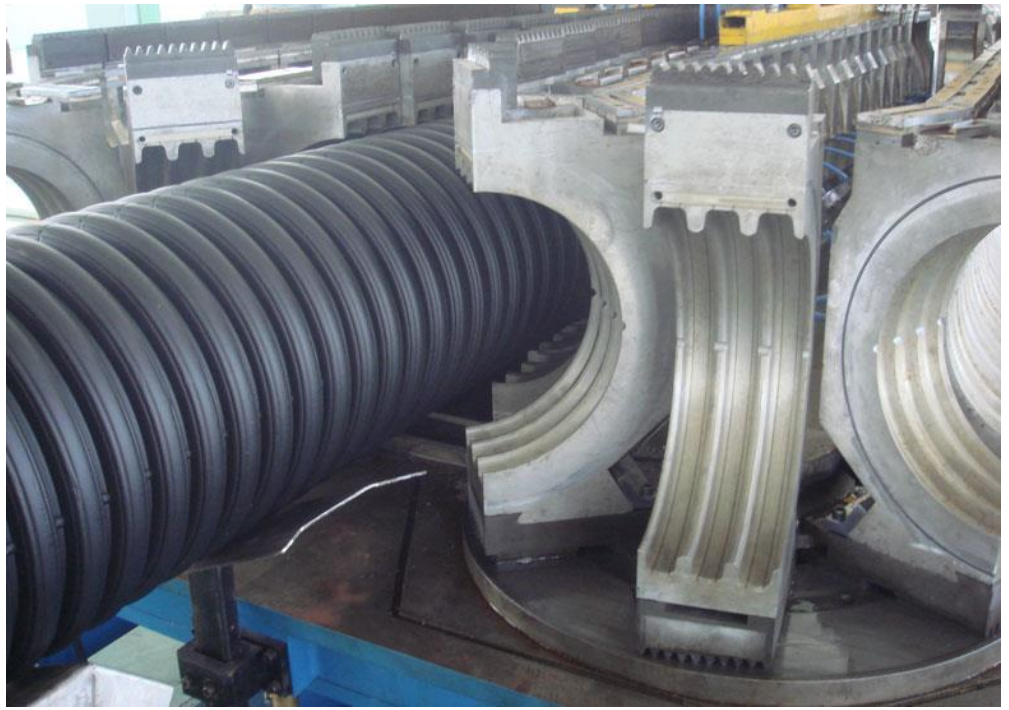
(ρ = 0.95 g/cm³)



Rheological Properties

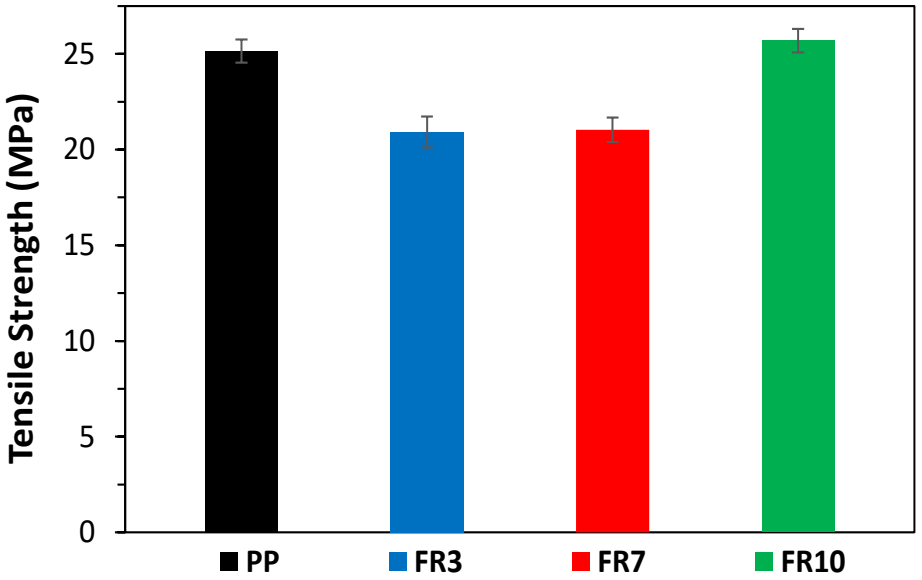
- MFR 230°C, 2.16 kg → Critical processing parameter
- **FR3**: ~30% decrease due to 25% of infusible additives
- **FR7:** Radical generator maintains MFR close to neat PP
- **FR10:** strong increase due to meltable synergic

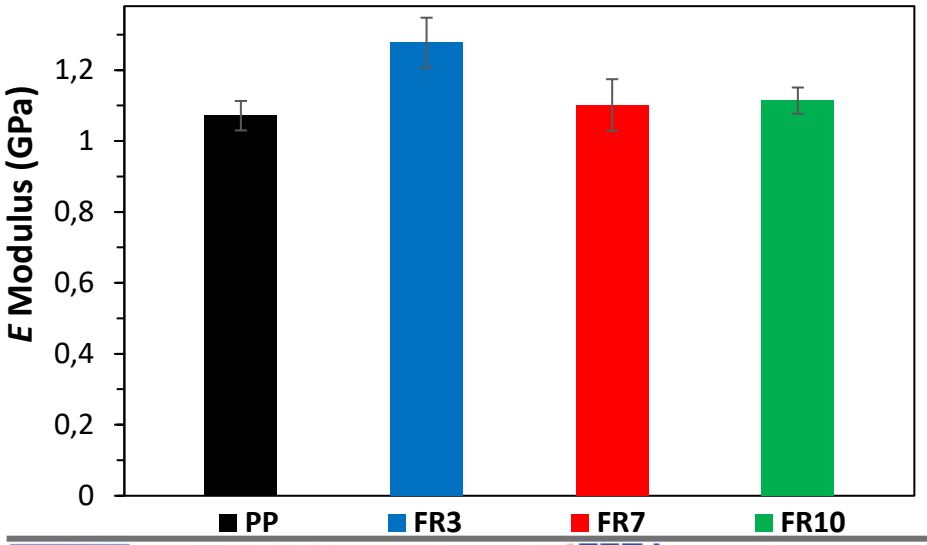


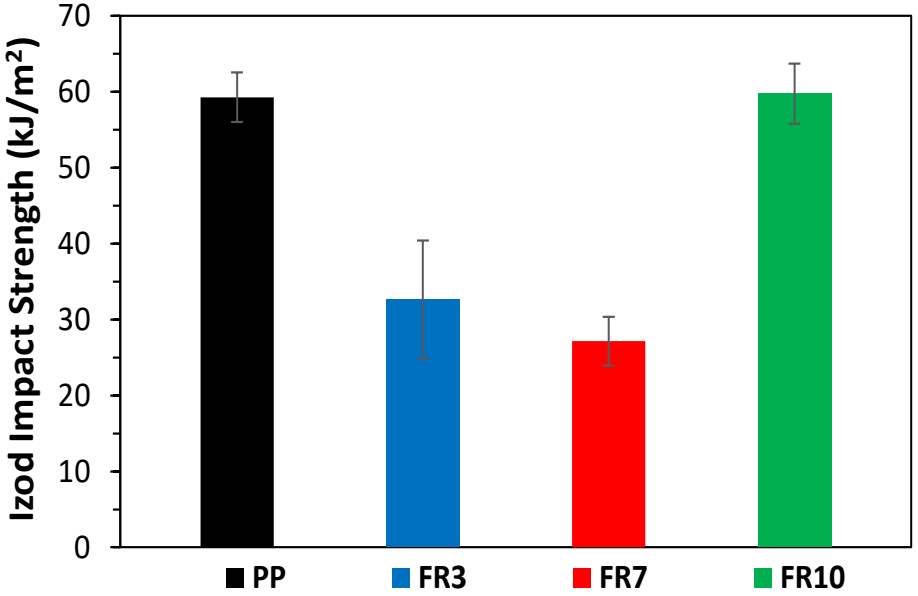


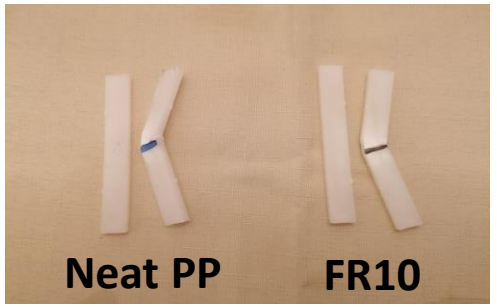
Appropriate Melt strength for corrugation?

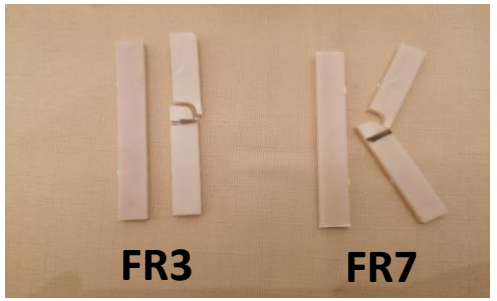
Mechanical Properties







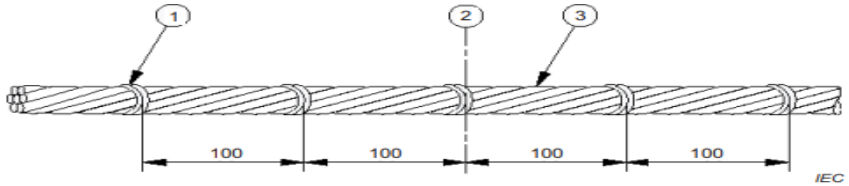




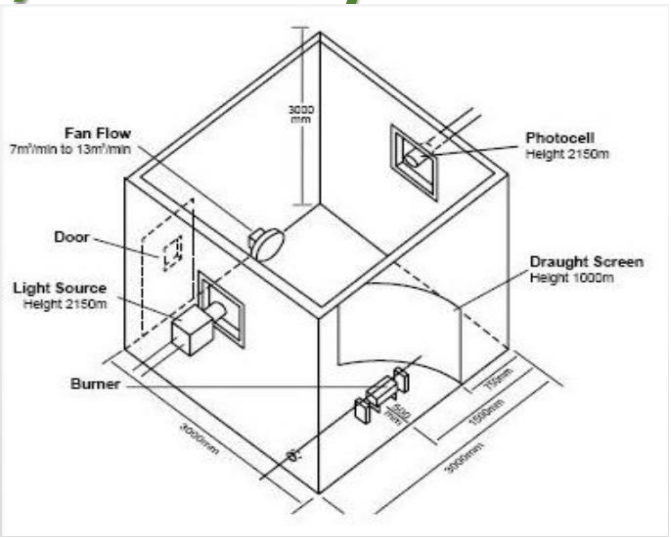
- **FR10**: retention of PP mechanical behavior
- **FR3, FR7:** high FR loadings (25&20 wt.%) → decrease of impact strength → **Brittle materials** → ***Impact modifiers ???***

Smoke Density and Toxicity of FR/PP compounds

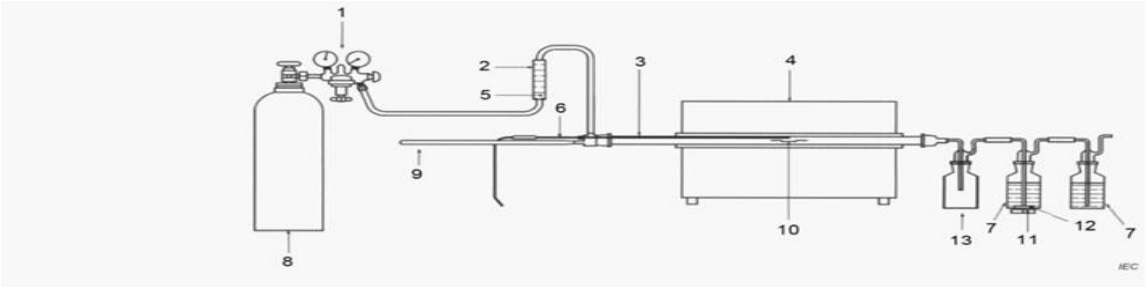
- **Smoke Density (EN61034-2):** visibility >60%



Key
1 wire binder
2 centre
3 number of test pieces = 7



- **Smoke Corrosiveness (IEC 60754-2):** pH of smoke emissions ≥ 4.3



Pending Results

- **Halogen Content (EN50642): Br < 0.15 wt.%**, Cl < 0.15 wt.%, F < 0.3 wt.%, I < 0.3 wt.%, **Total X < 0.4 wt.%**

Conclusions

- Strict fire performance regulations demand **self-extinguishing function**, as well as **low and not toxic smoke** emissions. Need to **change from** traditional **PVC** raw conduit material **to PP → HFLS compounds**
- In **FUVPP** the **FR functionality** is currently studied. At next steps **incorporation of UV/Heat** additives to receive **FR/PP compounds with high resistance to ageing**.
- **2 FR systems**: intumescent system (phosphate-based at 20 and 25 wt%) and gas phase system (phosphinate-based at 2 wt%) → **V0** (25% FR) and **V2** (20, 2 wt%) classifications
- **Increased dielectric looses** for phosphate-based FRs and **decreased thermal diffusivity for** phosphinate-based FR
- **Increased MFR** for phosphinate-based FR → critical for **corrugation** extrusion
- High loadings in phosphate-based FRs → **decreased impact strength**

Further tailoring of FR formulations for end product application and incorporation of UV/Heat additives

Acknowledgements

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http://fuvpp.chemeng.ntua.gr/project.html

European Union
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