Integrating Flame Retardancy and Weathering Resistance in Halogen Free PP compounds intended for outdoor cable protection conduits

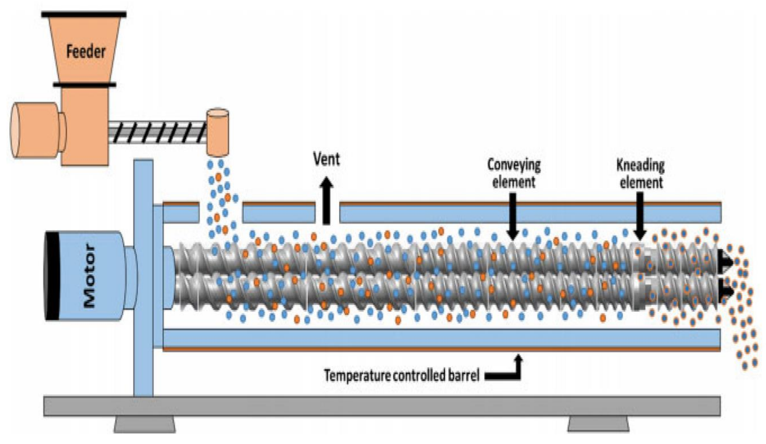
A.D. Porfyris[1], A. Vafeiadis[1], C. Gkountela[1], C. Politidis[2], G. Messaritakis[3], E. Orfanoudakis[3], S. Pavlidou[4], D.M. Korres[1], A. Kyritsis[2], S.N. Vouyiouka[1*]

[1]Laboratory of Polymer Technology, School of Chemical Engineering, National Technical University of Athens, Zographou Campus, Athens 157 80, Greece, (*mvuyiuka@central.ntua.gr)
[2]Dielectrics Group, School of Applied Mathematical and Physical Sciences, National Technical University of Athens, Zographou Campus, Athens 15780, Greece.
[3]EMM. KOUVIDIS S.A. VIOPA Tylissos 71500, Heraklion, Crete, Greece.
[4] MIRTEC S.A., Thiva Branch, 72nd km of Athens-Lamia National Road, 34100, Chalkida, Greece.

ABSTRACT

Cable protection conduits (EN 61386) are typically manufactured from PVC, which exhibits flame retardant (FR) behavior due to the inherent chlorine[1]. PP is rising as a viable alternative[2] as the safety regulations for cables and conduits in most European countries regarding halogen content, smoke density and corrosiveness of released gases (EN50642, EN61034-2, EN60754-2) become stricter. However, PP requires halogen free additivation for flame retardancy in order to comply with these standards. Especially in outdoor electrical installations, additional UV and heat stabilization is required, so as to increase their life cycle performance[4]. **The challenge is to combine FR and UV functionalities at concentrations below 30 wt.% and without any antagonistic effect**[3]. Therefore, 4 different FRUV PP compounds were developed (FR1-FR4), consisting of different commercial organo-phosphorous FRs and commercial light stabilizers such as hindered amines (HALS) or N-alkoxy hindered amine (NOR-HAS).

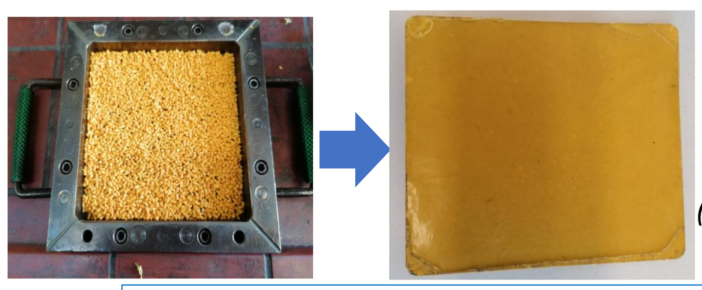
EXPERIMENTAL



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

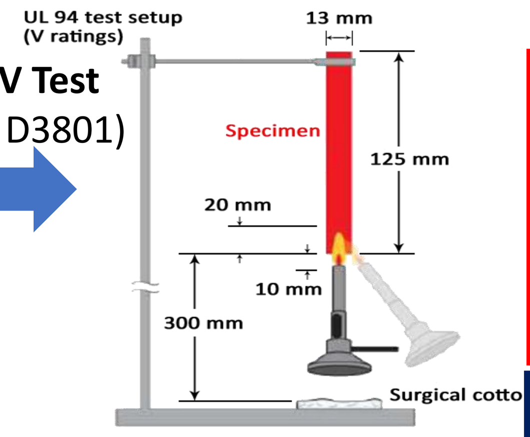
FRUV compounds (FRUV1-FRUV4)

Compression molding
(210 °C, 200 bar, 15 min)



UL94 specimens
(125x13x1.6mm³)

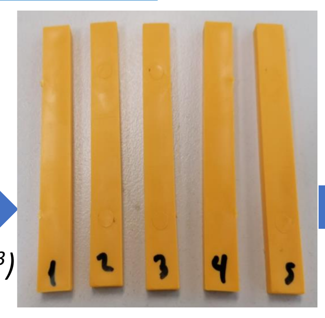
UL94V Test (ASTM D3801)



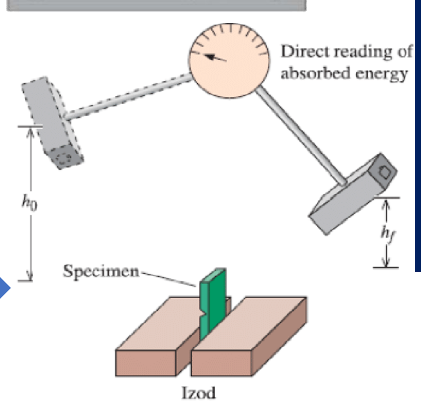
Characterization
- **TGA:** 30-600 °C (10°C/min), Mettler Toledo TGA/DSC1 HT
- **DSC, OOT:** 30-300 °C (10°C/min), Mettler Toledo DSC700, in air
- **MFR:** 230°C, 2.16 kg, Dynisco KAYENESS 4004

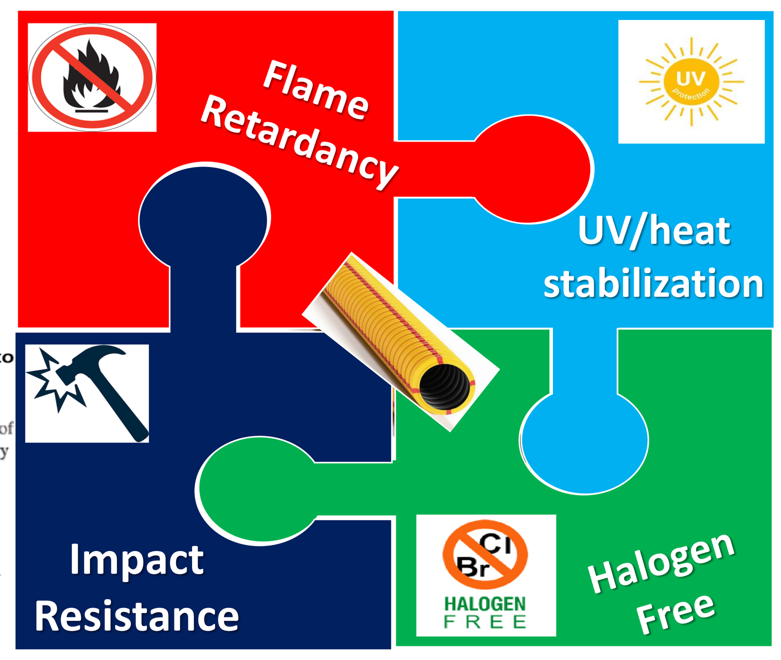
Injection molding
(220 °C, 12 bar)

Impact specimens
(80x10x4mm³)



Izod Impact test (ISO180)

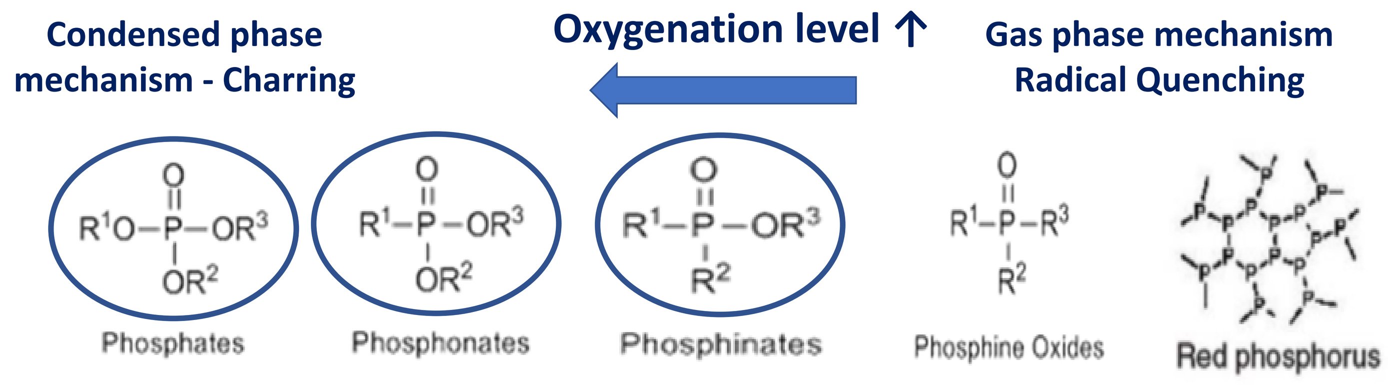




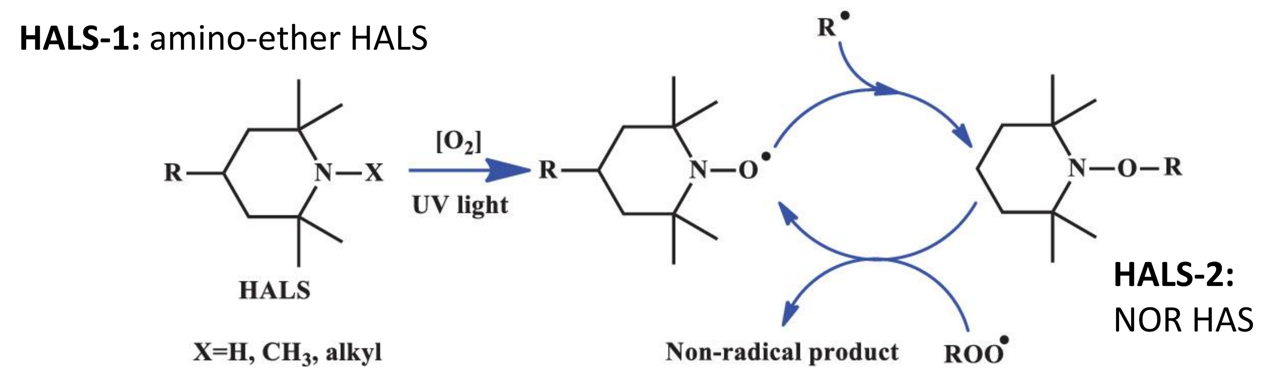
RESULTS AND DISCUSSION

Table 1: Composition of FRUV Compounds

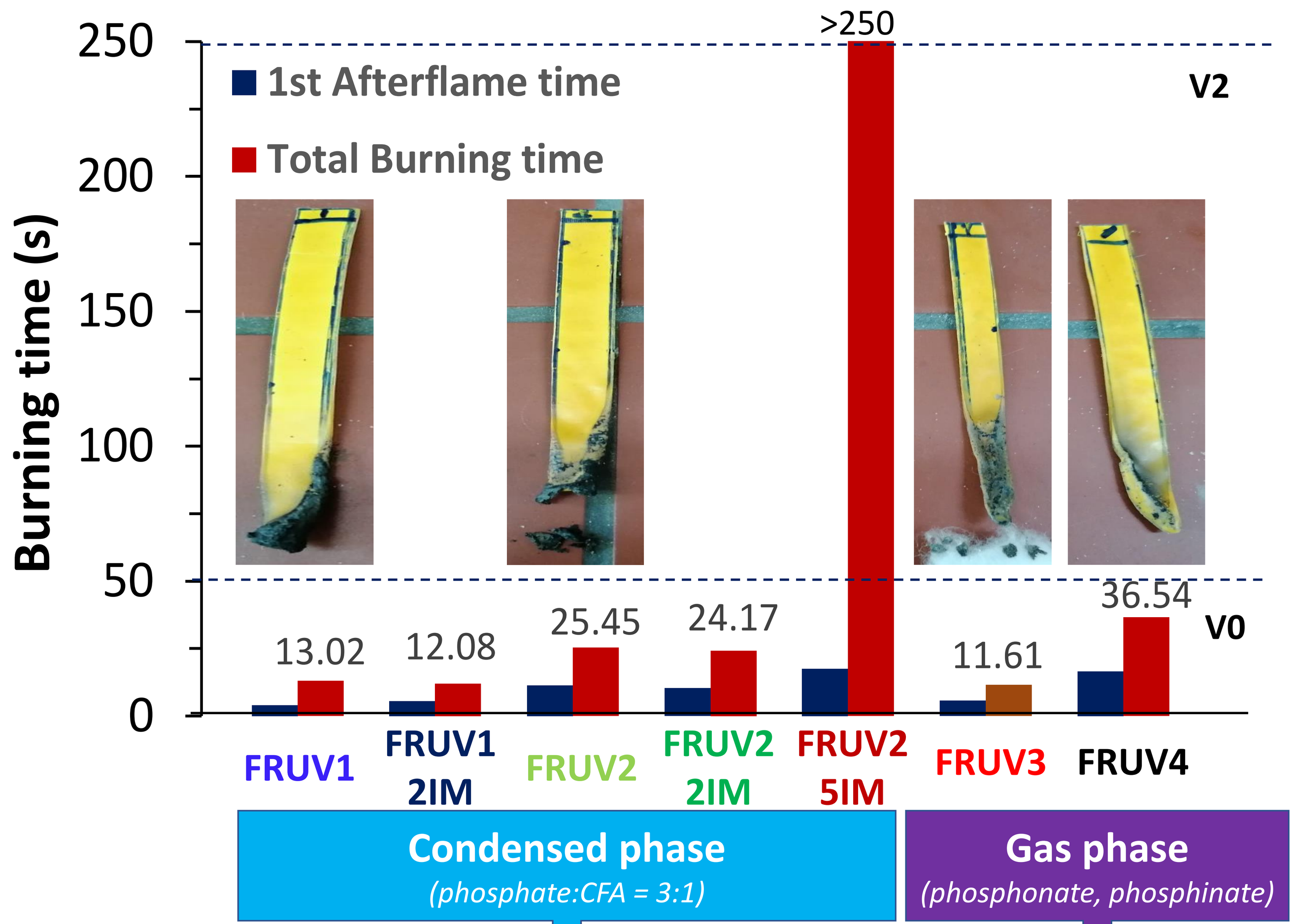
Formulations	CFA [wt%]	Phosphate [wt%]	Phosphonate [wt%]	Phosphinate [wt%]	HALS-1 [wt%]	HALS-2 [wt%]	Yellow dye [wt%]	Impact Modifier (IM) [wt%]	Total Loading [wt%]
PP	-	-	-	-	-	-	3.5	-	3.50
FRUV1	6.25	18.75	-	-	0.25	-	3.5	-	28.75
FRUV1 2IM	6.25	18.75	-	-	0.25	-	3.5	2	30.75
FRUV2	4.75	14.25	-	-	-	1	3.5	-	23.50
FRUV2 2IM	4.75	14.25	-	-	-	1	3.5	2	25.50
FRUV2 5IM	4.75	14.25	-	-	-	1	3.5	5	28.50
FRUV3	-	-	10	-	-	1	3.5	-	14.50
FRUV4	-	-	-	4.5	-	0.5	3.5	-	8.50



Organo-phosphorous Flame Retardants (FRs)



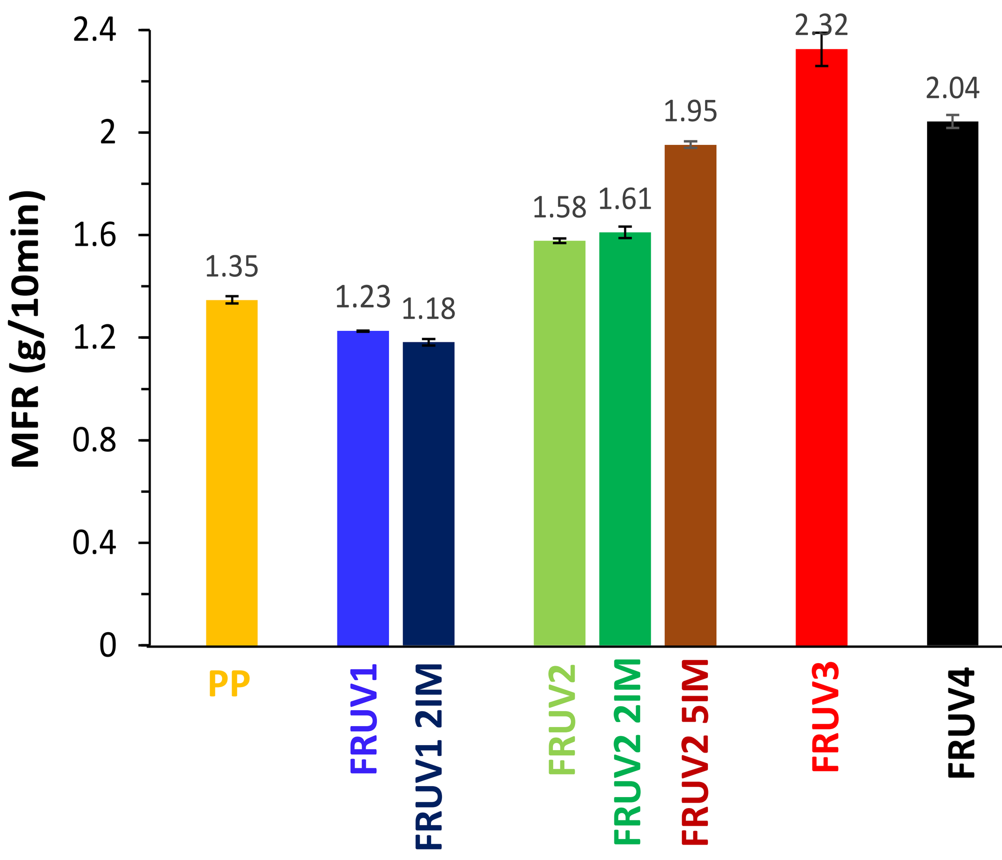
Stabilization mechanism of HALS



FRUV1: highest FR loading (25wt%) → V0
FRUV1 2%IM: Impact Modified FRUV1, retention of V0
FRUV2: reduced FR load to 20 wt.% , flame drips → V2
FRUV2 2% IM: Impact modified FRUV2, retention of V2
FRUV2 5% IM: Increase of IM load → Loss of FR, NC

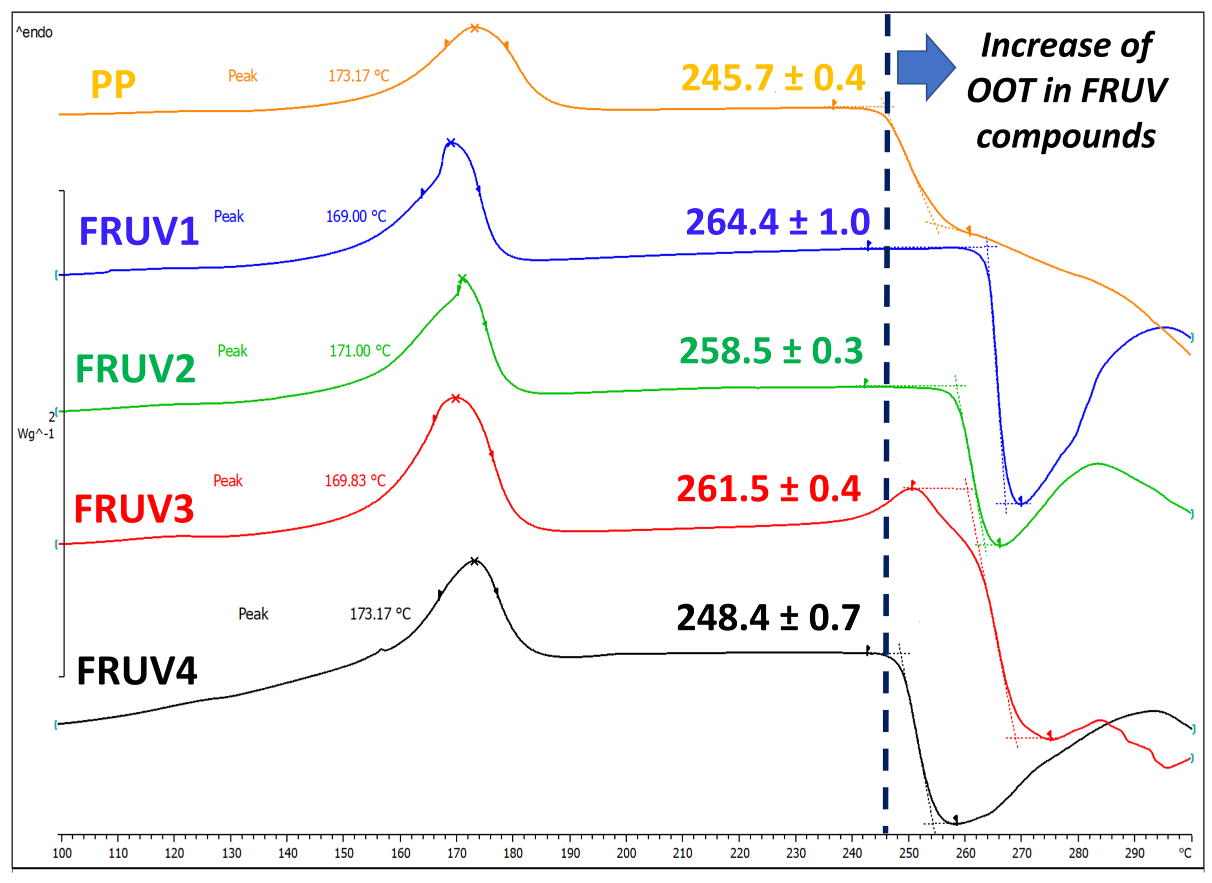
FRUV3: Dripping, no cotton ignition → V0
FRUV4: intense flame dripping → V2

UL94V tests. 5 samples per formulation were measured. Specimens after the burn test



MFR of FRUV compounds. Comparison to neat PP

Acceptable MFR variations → Processability for corrugation extrusion



DSC curves of FRUV compounds in air atmosphere. Determination of OOT

Increased OOT → Prediction of appropriate UV/heat stabilization

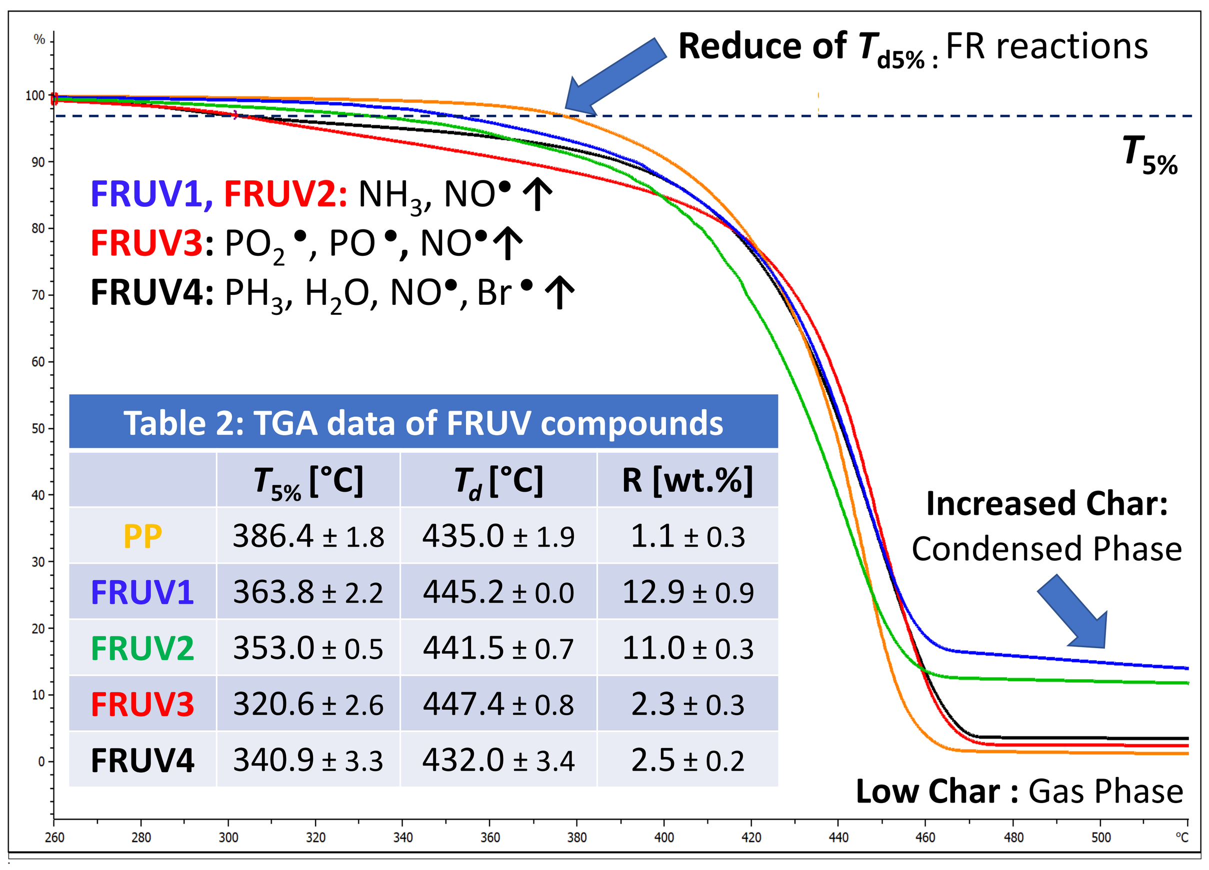
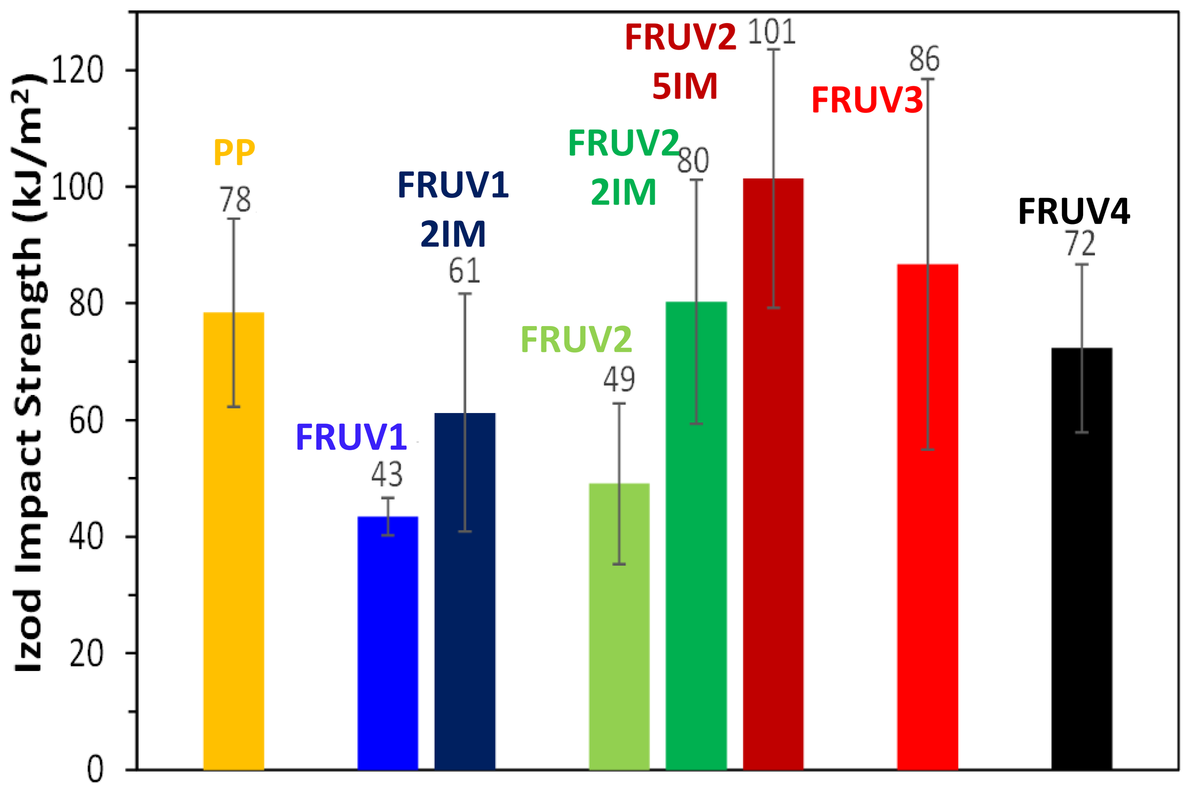


Table 2: TGA data of FRUV compounds

	$T_{5\%}$ [°C]	T_d [°C]	R [wt.%]
PP	386.4 ± 1.8	435.0 ± 1.9	1.1 ± 0.3
FRUV1	363.8 ± 2.2	445.2 ± 0.0	12.9 ± 0.9
FRUV2	353.0 ± 0.5	441.5 ± 0.7	11.0 ± 0.3
FRUV3	320.6 ± 2.6	447.4 ± 0.8	2.3 ± 0.3
FRUV4	340.9 ± 3.3	432.0 ± 3.4	2.5 ± 0.2

TGA curves of FRUV compounds. Mechanistic Insight in FR functionality



Izod impact strength of FRUV compounds. 10 specimens/compound measured.

High FR loadings (FRUV1, FRUV2) → Decrease of Impact Strength Compensation via addition of 2wt% IM

ACKNOWLEDGEMENT

This research has been co-financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (Project: FUVPP - Fireproof and UV/resistant HFLS Cable Protection Pipes based on PP, project code: T2EDK-01466).

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

CONCLUSIONS

Three phosphorous FR additives of different oxygenation level, along with two different HALS types were combined for the FR and UV/heat stabilization of PP. All formulations were pigmented so as to avoid adding UV-absorbers. FRUV1 and FRUV2 consisted of a phosphate (APP) and a CFA, acting as an intumescent system in the condensed phase. The highest FR loading in FRUV1 resulted in V0 class, while in FRUV2, the reduced FR concentration yielded V2, due to observed dripping. On the other hand, in FRUV3 and FRUV4, where a phosphonate and a phosphinate were used as FRs, a gas phase behavior was observed. FRUV3, with the lowest total burning time along with drips that did not ignite the cotton showed V0, unlike FRUV4, where intense flaming drips yielded V2. The addition of HALS in the FRUV compounds promise a fair UV/heat stabilization, as verified by the determined increase in OOT. Regarding the impact tests, a reduced Izod impact strength was determined for the high FR loadings, which was optimized by the addition of 2 wt% impact modifier. All 4 FRUV formulations are halogen free according to EN50642 and are rendered as good candidates for the manufacture of conduits, thus completing the puzzle of properties demanded for such applications.

REFERENCES

[1] A. Cetin; S. Gazme Erzengin; F. Burcu Alp. *Open Chemistry* **2019**, *17(1)*, 980-987.
[2] A.D. Porfyris, et. al. Halogen-Free Flame Retarded PP Compounds designated for cable protection conduits. AMI Fire Resistance in Plastics, 30 November – 2 December **2021**, Düsseldorf, Germany.
[3] C.E. Wilen; R. Pfaendner. *J. Appl. Polym. Sci.* **2013**, *129(3)*, 925-944.
[4] B. Schartel. *Materials* **2010**, *3(10)*, 4710-4745.
[5] T. Tirri et al. *Polym. Degrad. Stab.* **2019**;164:75-89
[6] P. Zhao; C. Guo; L. Li. *J. Therm Anal. Calorim.* **2019**;135:3085-3093

@PolymeReEng