Charge and heat transport in halogen-free flame retarded polypropylene compounds

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

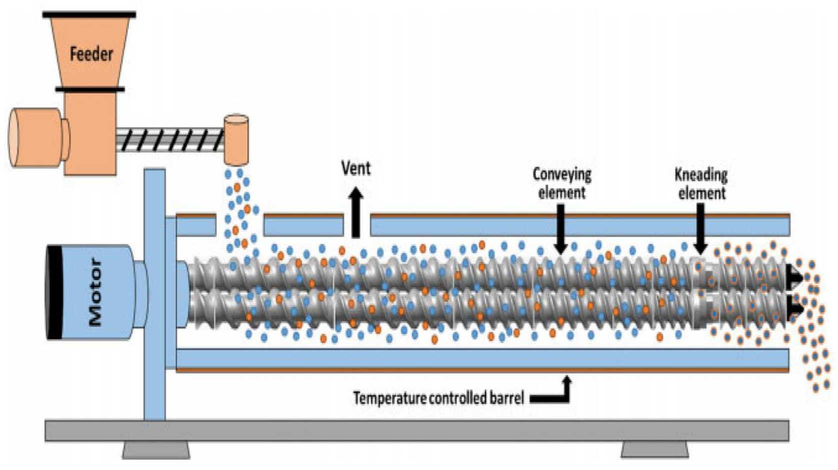
[1] Dielectrics Group, School of Applied Mathematical and Physical Sciences, National Technical University of Athens, Zographou Campus, Athens 157 80, Greece
[2] Laboratory of Polymer Technology, School of Chemical Engineering, National Technical University of Athens, Zographou Campus, Athens 157 80, Greece
[3]EMM. KOUVIDIS S.A. VIOPA Tylissos 715 00, Heraklion, Crete, Greece.
[4]MIRTEC S.A. 76th km Athens – Lamia Nat. Road, Schimatari Viotias, 32009, Greece.

ABSTRACT

Polypropylene (PP) is rising as an alternative polymer for the manufacture of cable protection conduits, replacing traditional PVC pipes[1,2]. However, PP needs to be flame retarded in order to comply with the current stringent EU safety regulations regarding halogen content, smoke density and corrosiveness of released gases (EN50642, EN61034-2, EN60754-2). Herein, four flame retarded (FR) PP formulations (FR1-FR4) were developed by the incorporation of commercial FR additives into PP, by means of melt-compounding. A high impact strength co-polymer (Repsol ISPLEN PB131N5E) was selected as reference PP. The additives used comprised: ammonium polyphosphate, a polymeric triazine derivative (PPM triazine HF) and a N-alkoxy hindered amine resulting in halogen-free formulations FR1 and FR2 (at rather high concentration (20 – 25 wt%). For the low-halogen formulation FR3 (Br<1500 ppm) a mixture of aluminum hypophosphite (AHP) and a phosphorous-bromine salt was used with a low loading level of FR3 (only 2 wt%). Finally, a fourth formulation was developed (FR 4) with a rather high concentration (10%) of another halogen-free FR additive (Aflammit PCO900).

Moreover, additives for UV/Heat protection lead to the development of the second family of the PP FRUV formulations.
The focus of this work lies on the investigation of the effects of the additives on the molecular mobility of the compounds and in the corresponding dielectric and thermal conduction properties by employing Broadband Dielectric Spectroscopy and Thermal Conductivity measurements. Our results show that the compounds with relatively high content of polymeric triazine derivative (FR1 and FR2) exhibit enhanced molecular mobility, which is related to the glass transition of PP, and remarkable charge transport properties due to the high conductivity of the additives. Interestingly, the enhanced charge transport properties are not accompanied by an increased heat transfer capability in the compounds: all compounds are characterized by smaller values of thermal conductivity than neat PP.

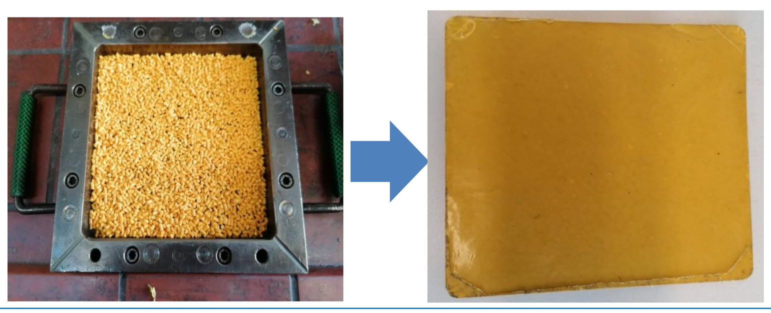
EXPERIMENTAL



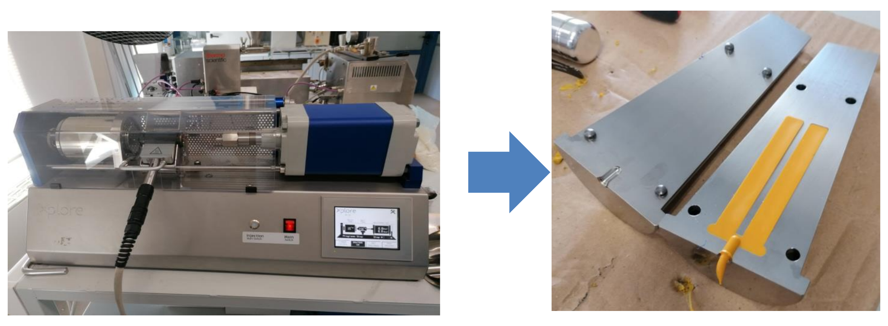
Twin-screw extrusion
(HAAKE Thermo Fischer PTW16, L/D = 25, 190-220 °C, 50 rpm)

FRUV compounds (FR1-FR4)

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

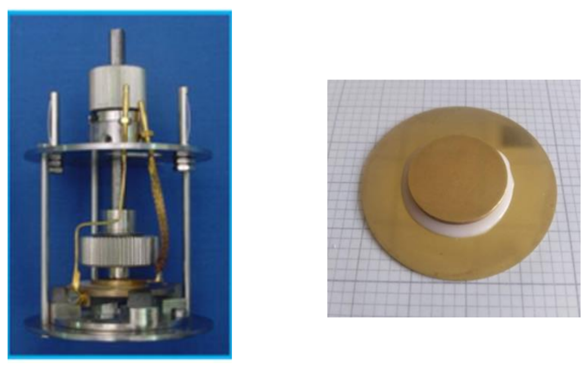


Characterization
- **TGA:** 30-600 °C (10°C/min)
- **DSC, OOT:** 30-300 °C
- **MFR:** 230°C, 2.16 kg
- UL94V Test (ASTM D3801)
- Impact resistance tests



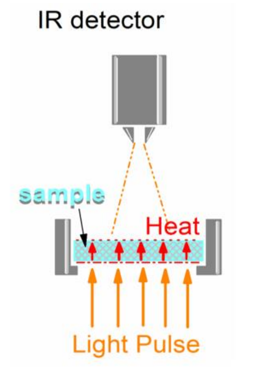
Injection molding
(220 °C, 12 bar)

Broadband Dielectric Spectroscopy



- Frequency range: $f = 10^{-1} – 10^{6}$ Hz
- Temperature range : T = 253-333 K.
- Parallel plate geometry - sample thickness of ~0,8 mm.

Thermal Conductivity Measurements[3]



LFA467 HyperFlash (NETZSCH)

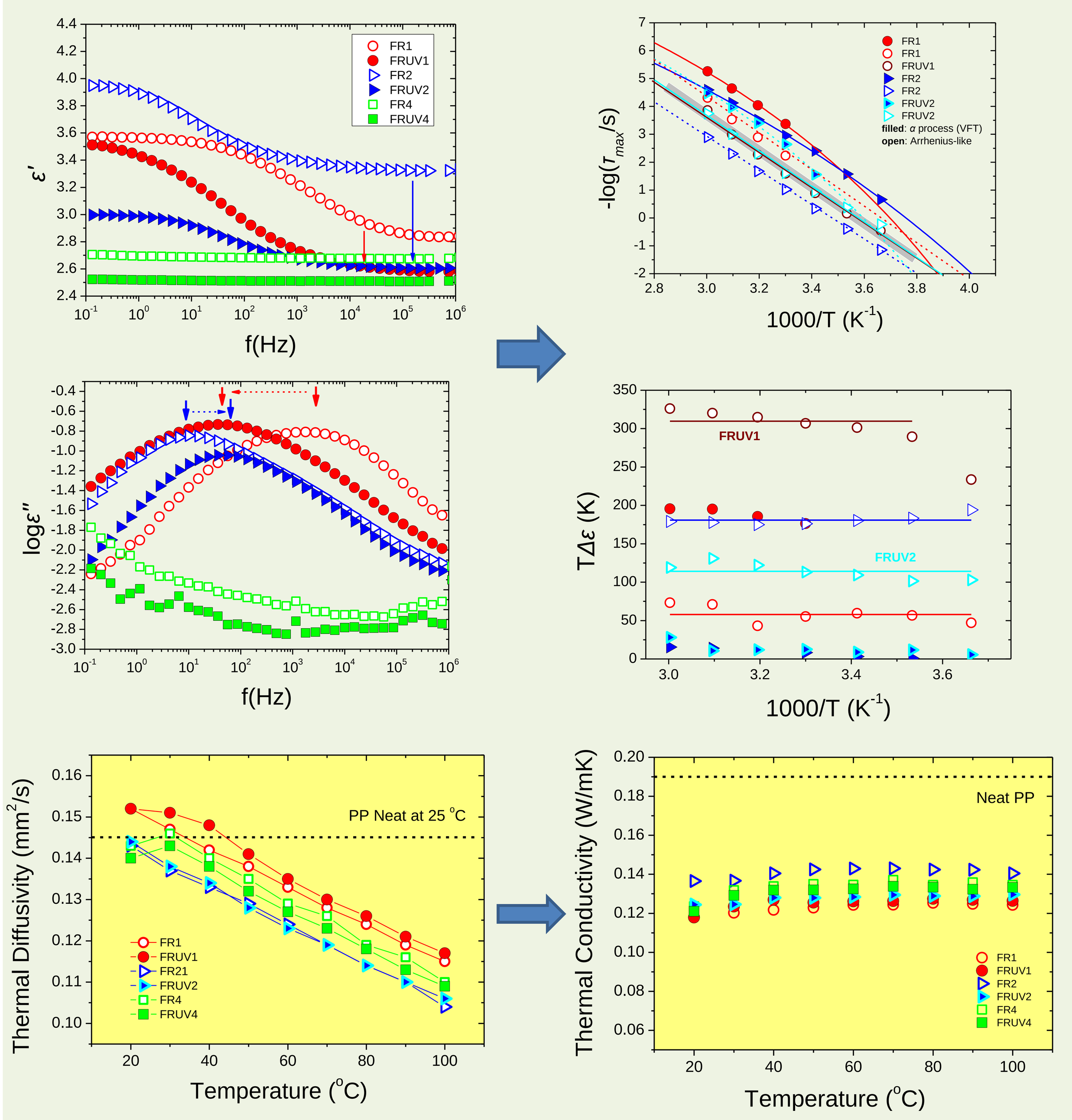
- Measurement of thermal diffusivity
- Temperature range: 293 – 373 K
- Sample thickness of ~1 mm - coating with carbon paint (~μm).

RESULTS AND DISCUSSION

Table 1: Compositions of FRUV compounds

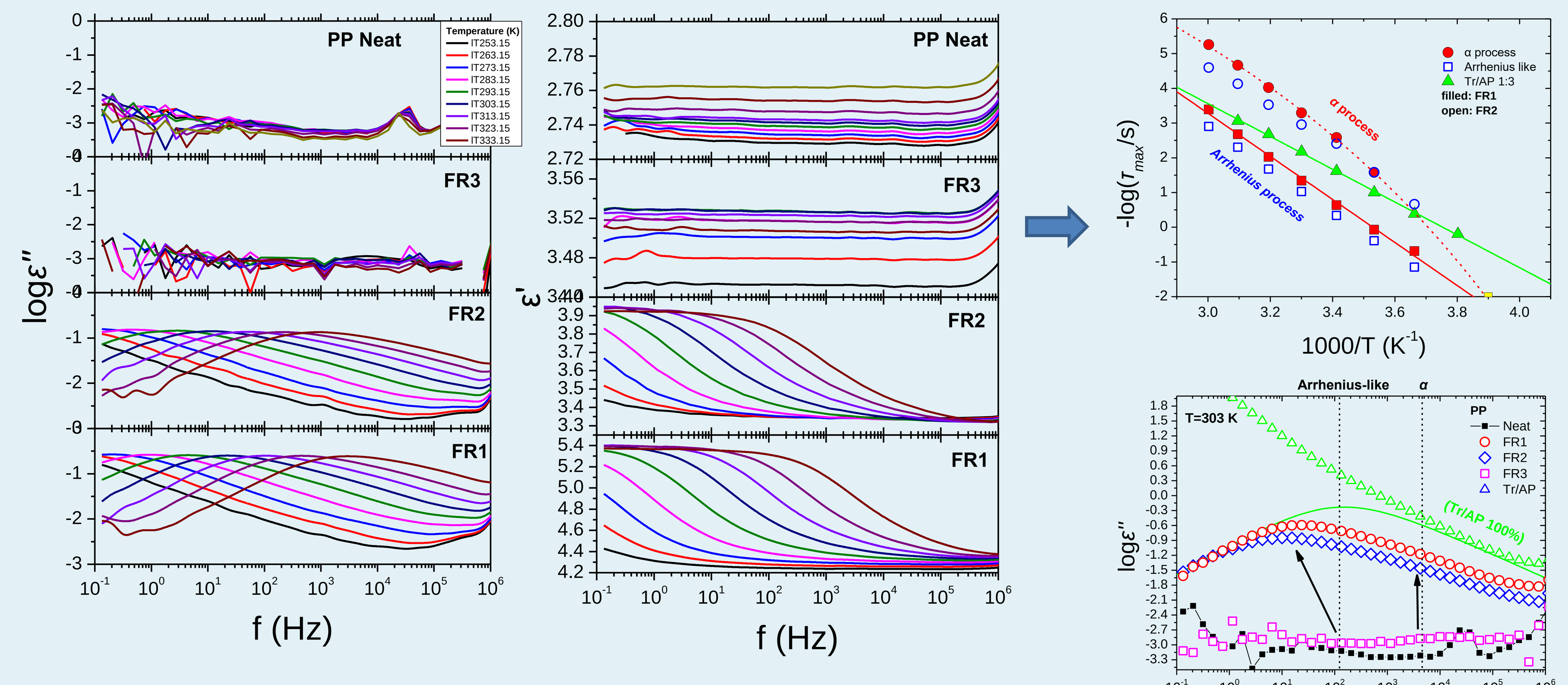
Formulations	FR Additives				UV/heat			Total (wt%)
	PPM Triazine (wt%)	Phosphate (wt%)	Phoslite B114A (wt%)	Phospho-nate (wt%)	HALS-1 (wt%)	HALS-2 (wt%)	Yellow dye (wt%)	
FR1	6.25	18.75			-		-	25
FRUV1	6.25	18.75				0.25	3.5	28.75
FR2	4.75	14.25			1			20
FRUV2	4.75	14.25			1		3.5	23.5
FR3			2					2
FR4				10	1			11
FRUV4				10	1		3.5	14.5

UV/Heat Additives

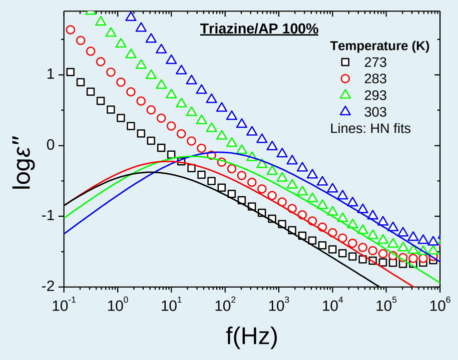


- The samples with the UV related additives show **lower dielectric losses** as well as **lower dielectric permittivity** values
- The presence of UV related additives lead to one Arrhenius-like process governing the dielectric spectra.
- The presence of UV/Heat additives have a **minor impact** on the thermal diffusivity and conductivity of the PP compounds

FR Additives



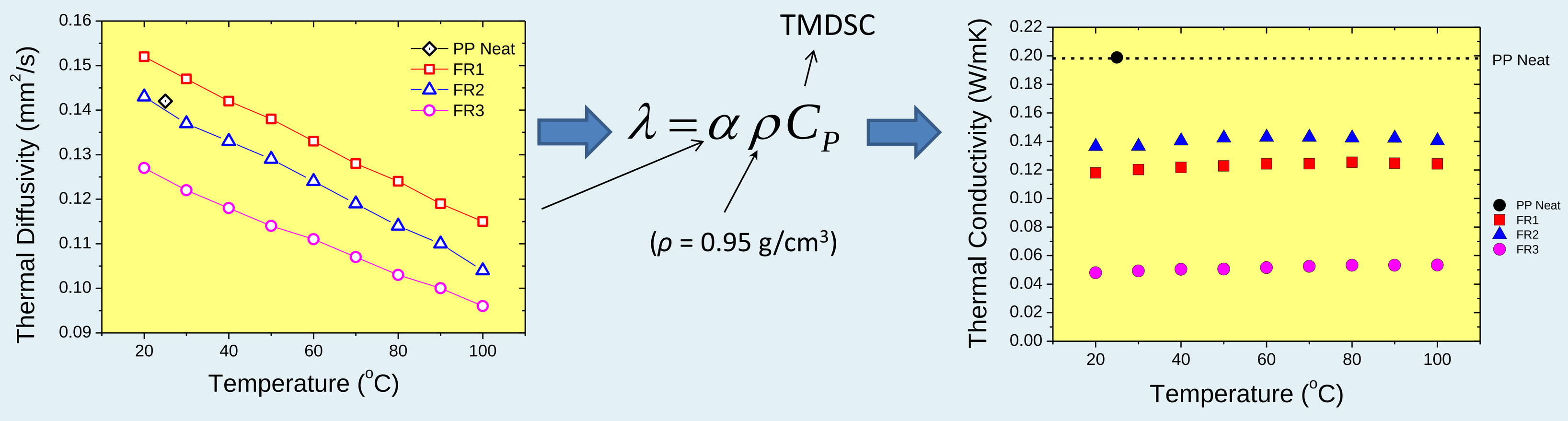
- **Enhanced** molecular mobility in compounds with PPM Triazine as FR additive: a VTF-like process (related to T_g of PP) and an Arrhenius-like process are recorded
- The Arrhenius-like process is related to the presence of conductive Triazine additives



TMDSC

$$\lambda = \alpha \rho C_p$$

(ρ = 0.95 g/cm³)



- The composites exhibit **reduced** thermal conductivity compared to neat PP!

CONCLUSIONS

- The FR additives lead to a more pronounced α process indicating a coupling effect between the dynamics of the PP segments and the molecules of the Triazine additives
- Arrhenius-like process is related to the presence of additives and especially Triazine. UV/Heat additives increase the strength of this process
- The presence of additives lead to lower thermal diffusivity and thermal conductivity values for the compounds.

Enhanced molecular mobility is **not connected** with enhanced heat transport properties

Other molecular mechanism is the crucial one for heat transfer! **(crystallinity?)**

REFERENCES

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