Phosphinates, the Flame Retardants for Polymers in Electronics

Public
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Development Flame Retardants
ATPG
24.11.2006

Clariant

Exactly your chemistry.

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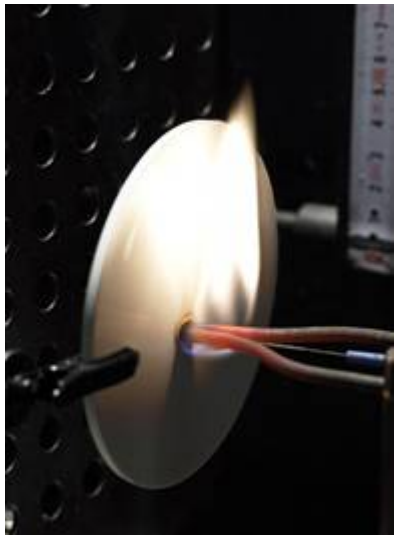
FR Polymers in the E&E Industry – Demanding requirements

- Material properties (selection)
  - small parts, thin wall, low density
  - Surface Mount Technology
  - lead free soldering
  - laser markability / weldability
  - glow wire test



- Lifecycle considerations
  - Reprocessing of production waste
  - Recycling of used materials
  - End of life – environmental properties
  - Total costs

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Phosphinate Flame Retardants

- Properties of Phosphinates
- High temperature Polyamides
  - Lead free soldering
- Polyamide 6 and 66
  - Glow wire test
  - Electrical properties
  - Recycling Study
- Polyester (PBT)
- Epoxy resins
- Conclusion

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Clariant's New Phosphinate Plant

- Properties of Phosphinates
- HT Polyamides
  Lead free soldering
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Phosphinates, a new class of FR Systems

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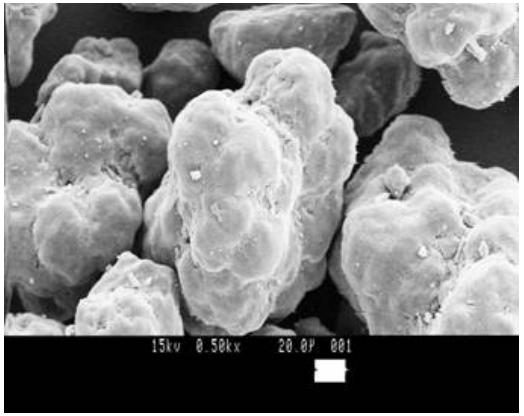
■ Registration is completed in compliance with

- ELINCS inventory (Europe)
- TSCA (USA)
- IECSC (China)
- ENCS (Japan)
- DSL (Canada)
- ECL (Korea)
- HNSO (New Zealand)
- AICS (Australia)



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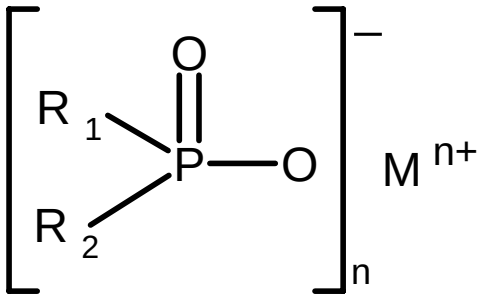
Phosphinates as Flame Retardants

- Thermally stable up to 350°C
- Mineral-like characteristics of metal phosphinate FR system
- decomposes to solid phosphates
- no migration and blooming
- virtually no emissions



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Toxicologic Findings for the Phosphinate

■ Sensitization	non-sensitizing (Guniea pig)
■ Mutagenity	
– Ames-Test	not mutagenic
– Genotoxicity in vivo	no experimental indications
■ Toxicity	
– Daphnia	EC50 > 100 mg/l (48 h, daphnia magna)
– Fish	LC50 > 100 mg/l (96 h, zebra fish)
– Bacteria	EC50 = 1968 mg/l (3 h, activated sludge)
– Algae	NOEC > 180 mg/l (scendenemus subspicatus)

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Phosphinate Based Flame Retardants – A growing number of applications

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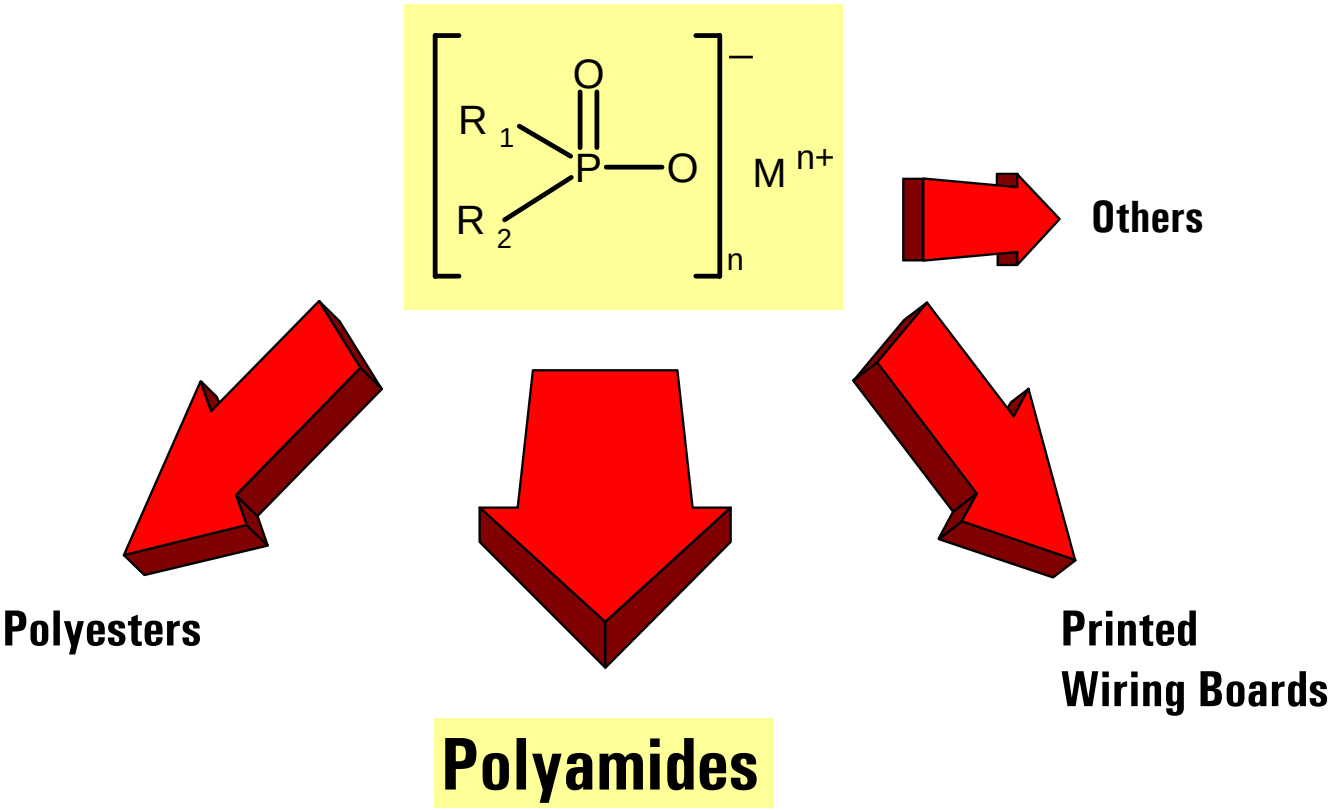

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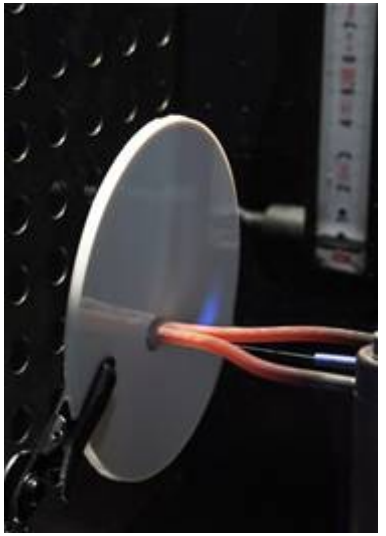
FR Polyamides with Phosphinates

- Coloribility
- CTI 600 V
- good mechanical properties
- low density of compounds
- good flow properties
- high temperature stability
- Laser marking and laser welding possible



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PA-HT Recipes for Comparison

- Compounding on Leistritz ZSE 27 HP – 44D
- PA 6T/66
- 30% Glass fibres
- Without flame retardants
- With Br-PS/ATO/PTFE UL 94 V-0
- With Exolit OP 1230 UL 94 V-0

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Mechanical Properties in PA-HT

- Properties of Phosphinates
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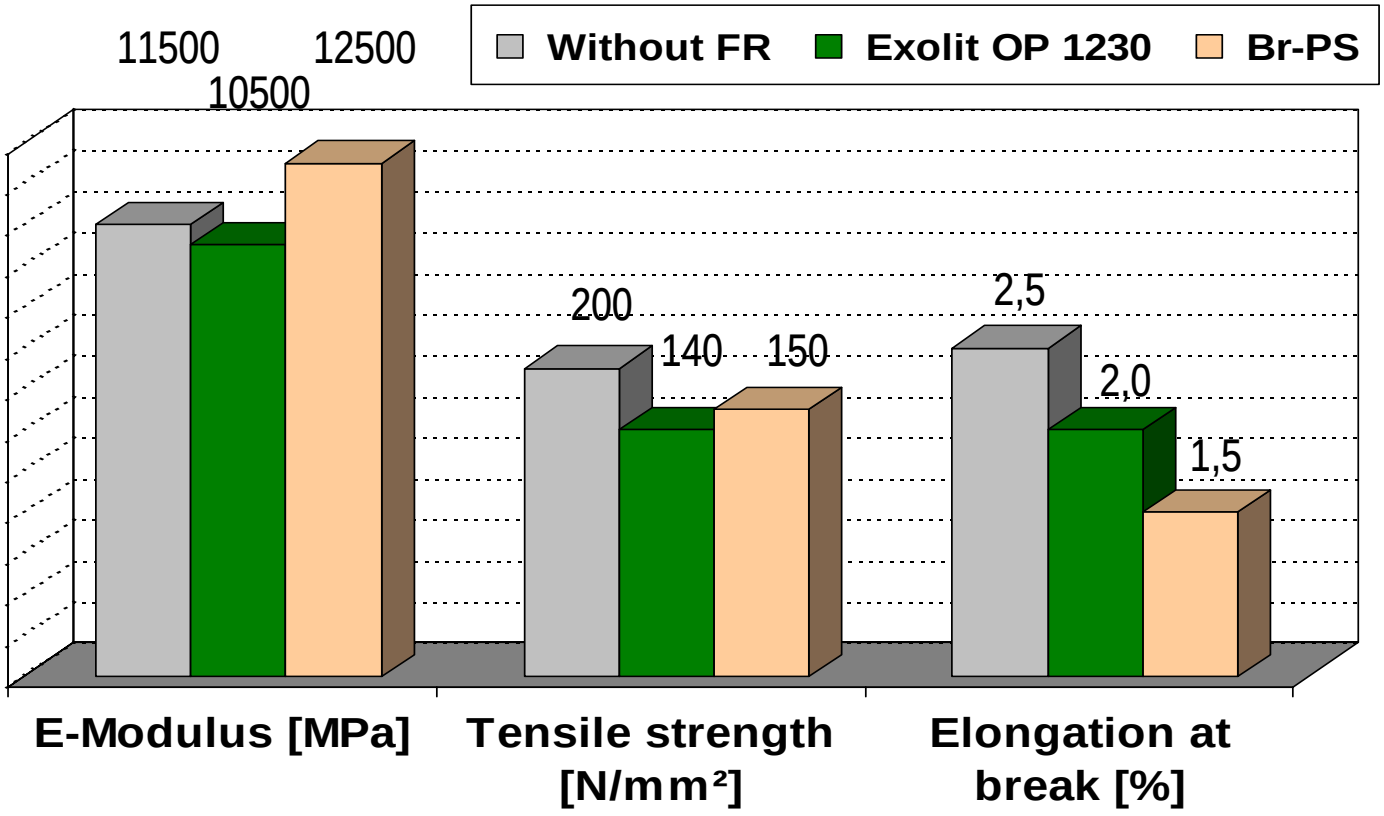
❖ Tensile (dry as moulded)



Mechanical Properties in PA-HT

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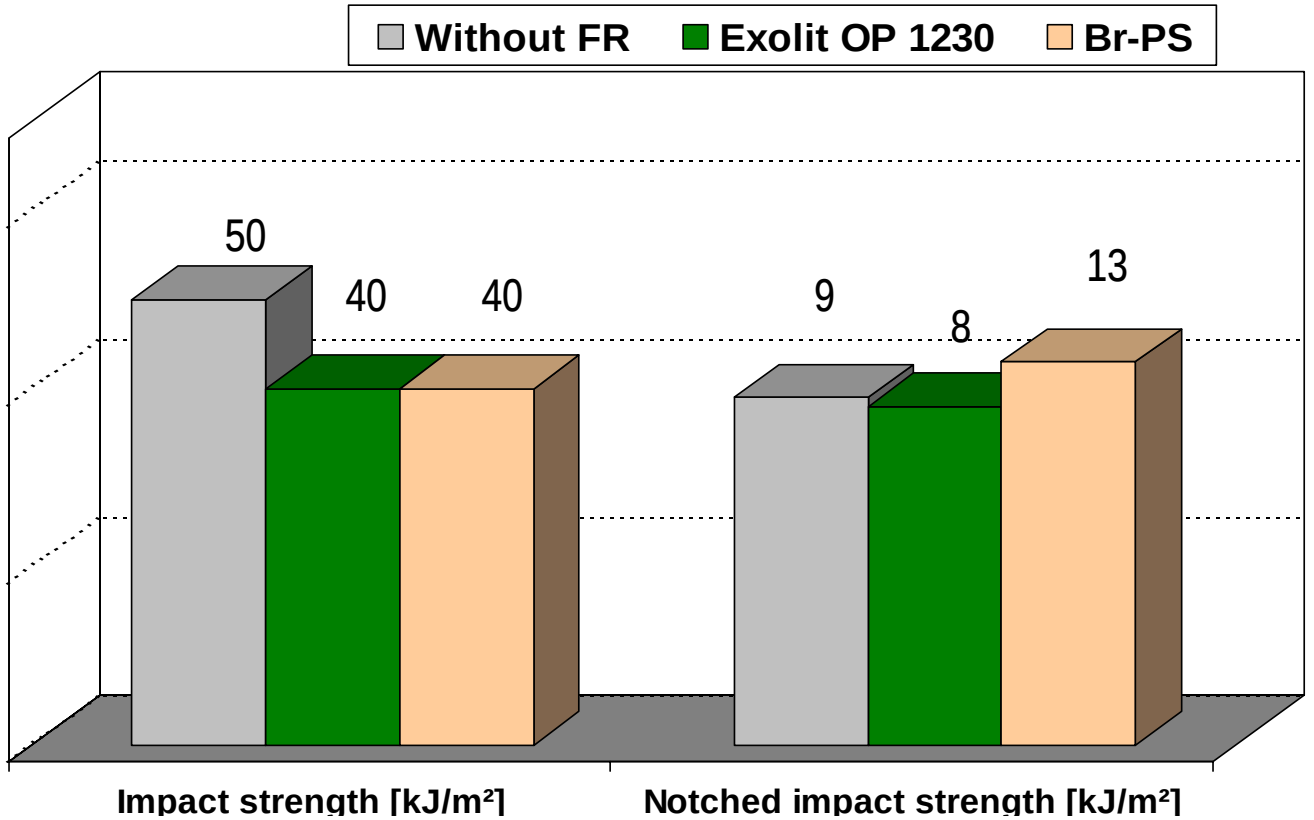
❖ Impact (dry as moulded)



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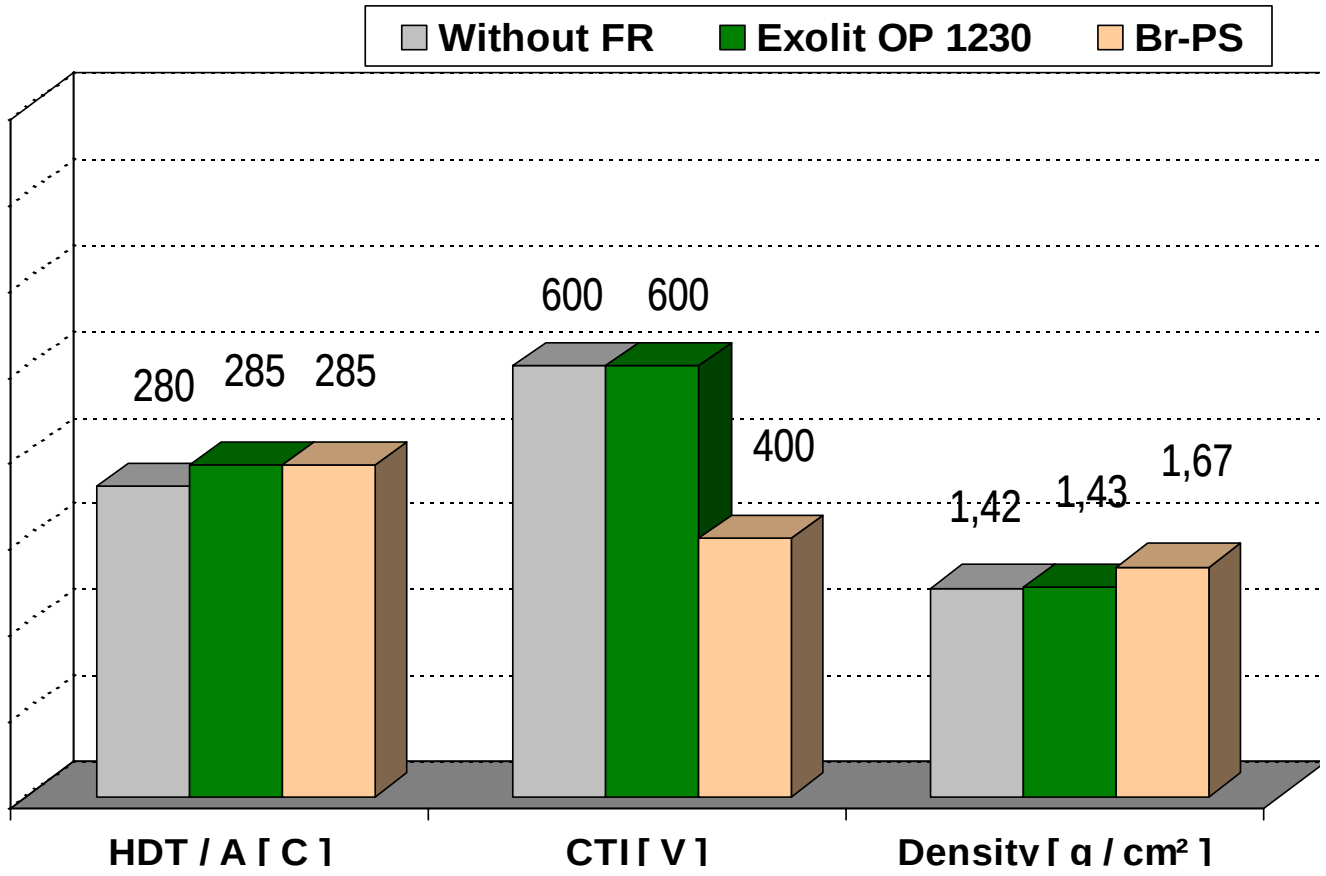
Other properties in PA-HT

- HDT / CTI / Density



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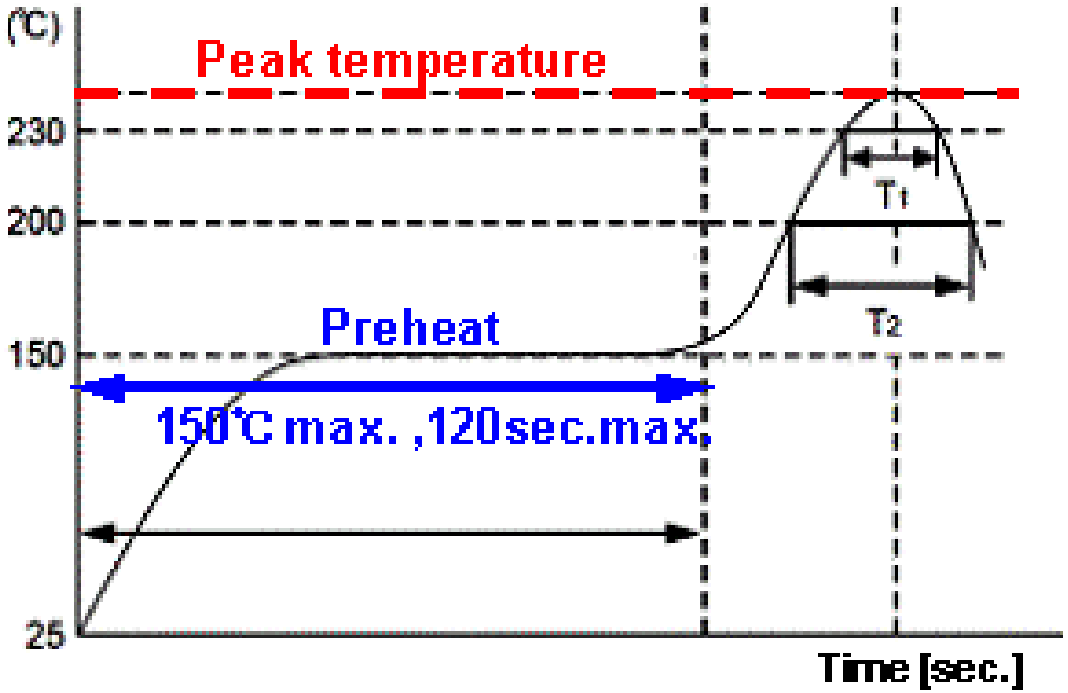
Lead-free Soldering, SMT Technology

- RoHS directive causes switch to lead free solder systems
- 30-50°C higher temperatures
- Reflow oven peak temperature lead-free 250-260°C



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Temperature Profile Reflow Oven

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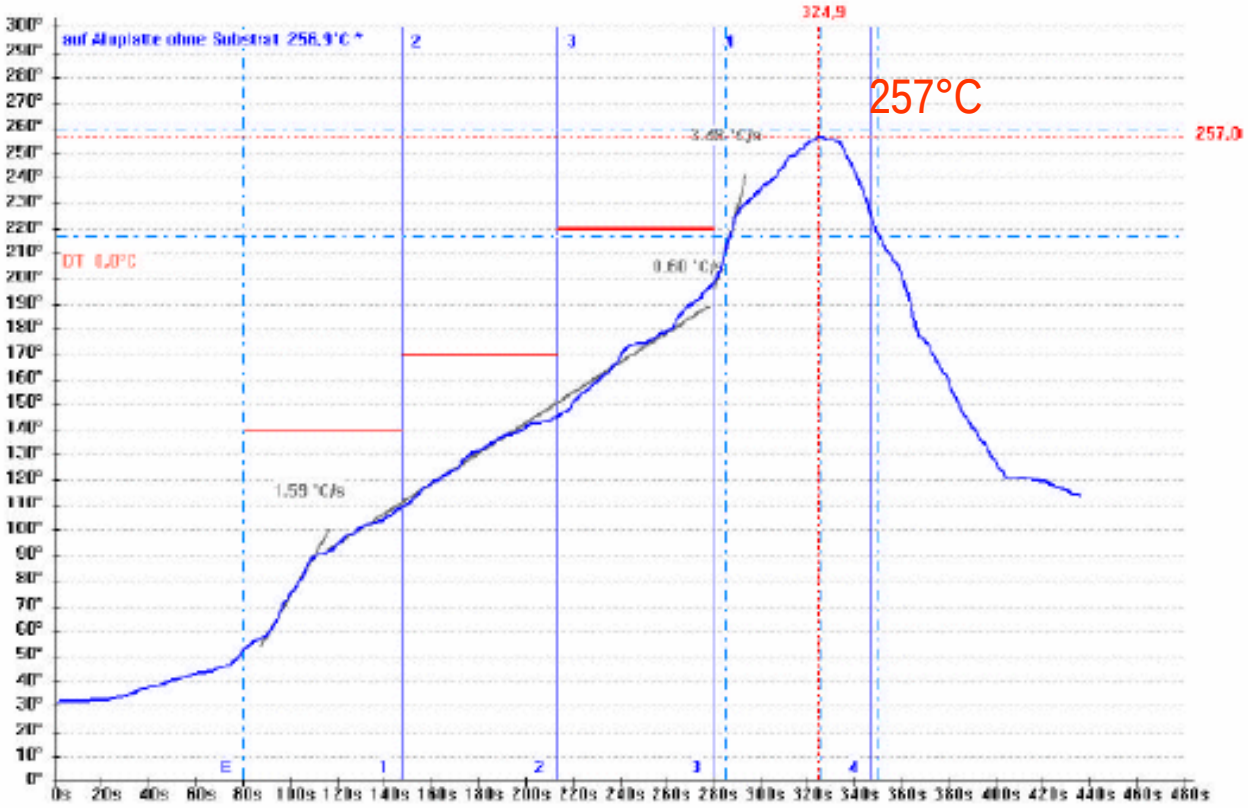
Lötanlage: Heraeus FCI-V/20
Profilname: Profil 71_350°C
Messpunkt: Mitte Aluminiumträger (260 x 180 x 1,5 mm³)



Exolit OP 1230 for lead free soldering

- PA-HT GF30 with 15% Exolit OP 1230

- Storage: JEDEC-J-Std 020C (MSL 2) 85°C / 60% rel. humidity
- Reflow oven 260°C peak temperature
- No blistering, no discolouration

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Exolit OP for High Temperature Polyamides

- good flowability in the injection moulding process
- flame retarded material is stable for lead free soldering
- excellent electrical properties
- high weld line strength
- no blistering tendency
- cost savings versus high performance polymers (LCP, PES)

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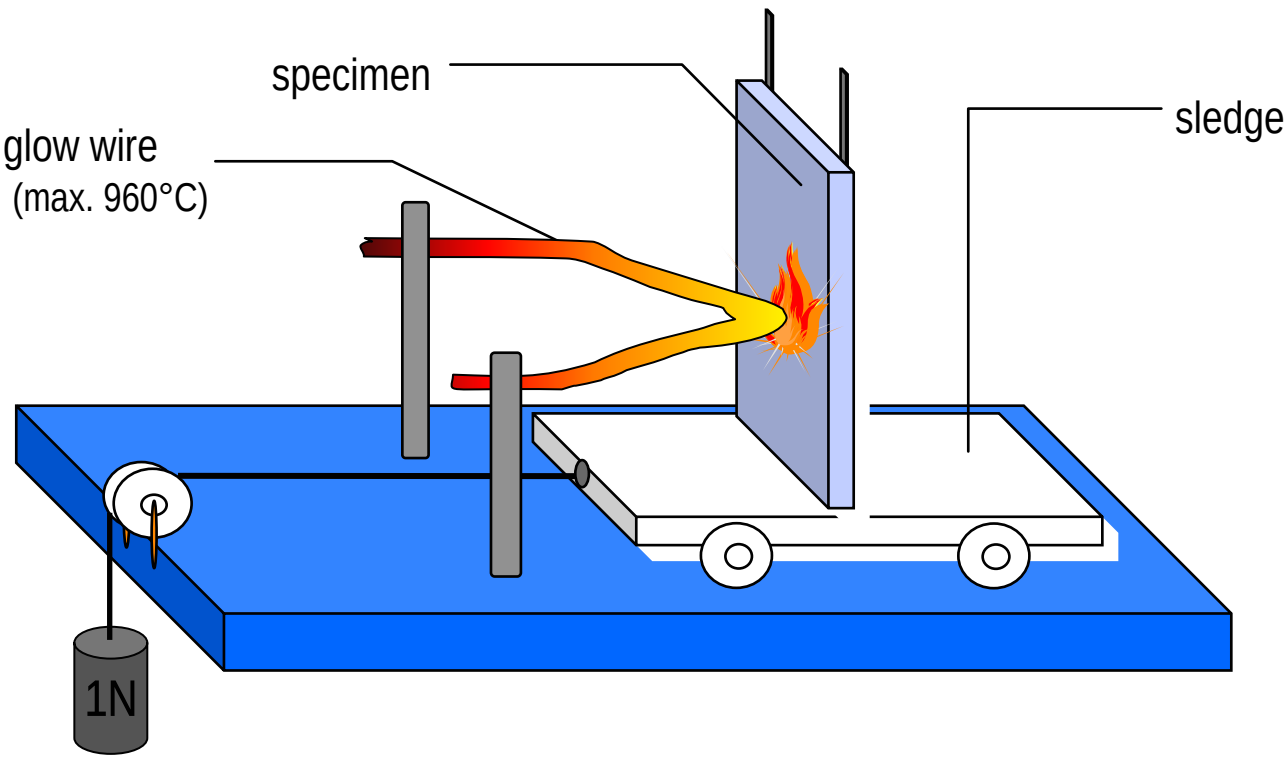
Glow Wire Test IEC 60695

- GWIT no ignition at temperature level (ignition = flame persists > 5 s)
- GWFI extinguishing of the flame within 30s at temperature level



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Glow wire classifications of polyamides containing phosphinate based FRs

	GWFI IEC 60695-2-12	GWIT IEC 60695-2-13
PA 6 Exolit OP 1311	960°C / 1 mm	775°C / 2 mm
PA 66 Exolit OP 1312	960°C / 1 mm	775°C / 2 mm
PA-HT (PPA) Exolit OP 1230	960°C / 1 mm	775°C / 1 mm

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Mechanical Properties in PA 66

Glass fiber reinforced

- Different glass fiber contents
- all recipes contain Exolit OP 1312 and reach UL 94 V-0

Glass fiber content	%	15 %	25 %	35 %	45 %
E-Modulus	MPa	7200	10000	13000	16500
Tensile strength	N/mm²	111	148	155	156
Elongation at break	%	3,4	2,8	2,8	2,1
Impact Strength	kJ/m²	58	64	69	56
Notched Impact Strength	kJ/m²	6,1	8,1	9,1	8,5

Electrical Properties of PA66 GF 30

- Good electrical insulation properties of phosphinate compound

		Without FR	Br-PS-Ato-PTFE	Exolit OP 1312
CTI	V	600	400	600
Volume resistivity	Ωm 10E10	6,6	0,4	4,1
Dielectric Constant	at 10E5 Hz	6,1	5,6	5,5
Dielectrical Strength	kV/mm	38	35	37
Dissipation Factor	at 10E5 Hz	0,0956	0,083	0,0789

IEC 112, 60093, 60250, 60243-1, 60250

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Recycling Study
Flame Retarded Polyamides

- Exolit OP 1312 and Br-PS/Ato in Polyamide 66 GF 30
- Test procedure according to UL
  - Injection molding of compounds (1. pass)
  - Grinding of the test bars
  - Mix 50% of grinded material with 50 % of neat compound
  - Injection molding
  - etc.
- Comparison of 1st , 3rd and 6th pass

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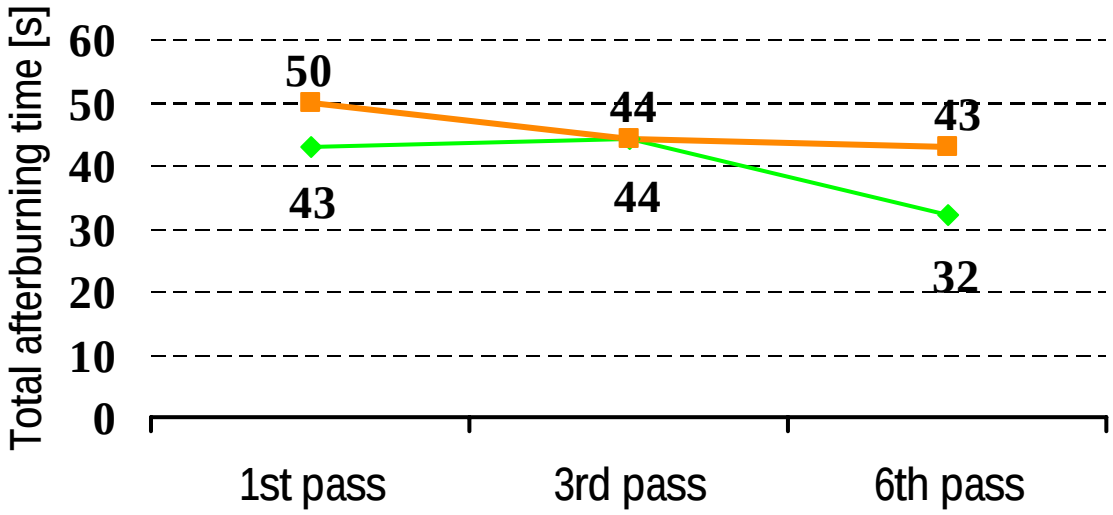
Recycling Study Flame Retarded Polyamides

- UL 94 Performance at 0.8 mm

	Neat Polymer	OP 1312	brom. PS
1st pass	n.c.	V-0	V-0
3rd pass	n.c.	V-0	V-0
6th pass	n.c.	V-0	V-0

- Total afterburning time



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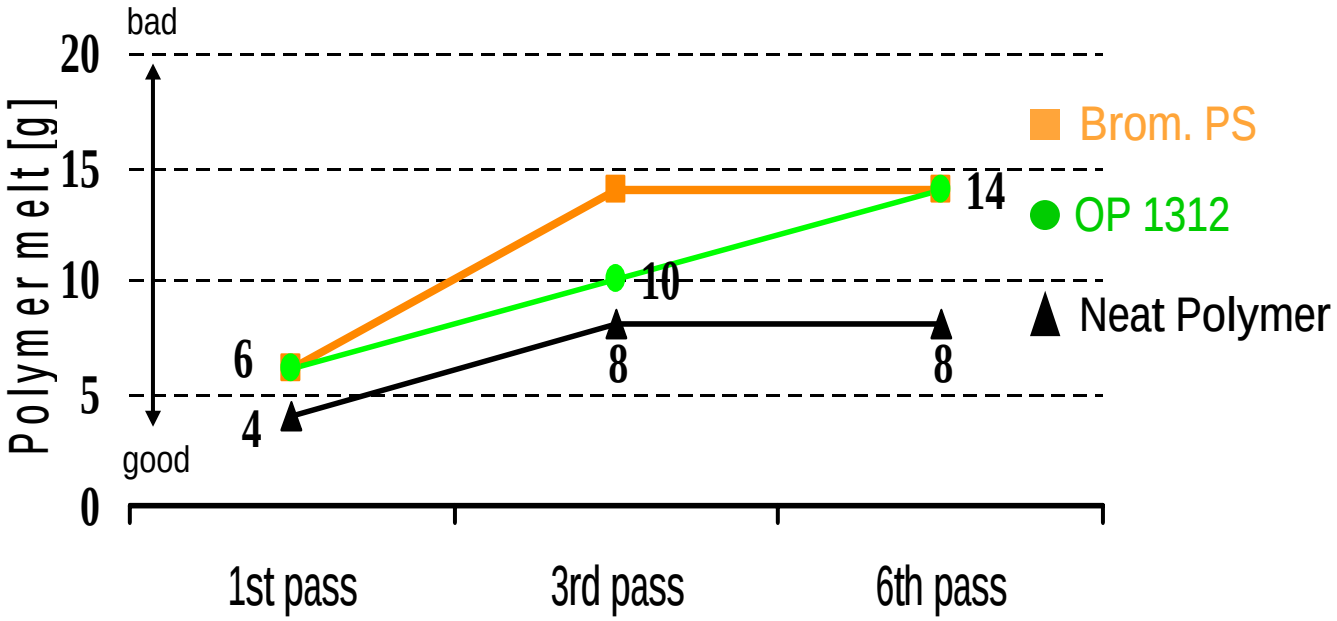
Recycling Study
Flame Retarded Polyamides

- Stability of Polymer melt during injection molding (Internal test)
  - g of Polymer melt flowing out of the die



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Recycling Study
Flame Retarded Polyamides

- Color

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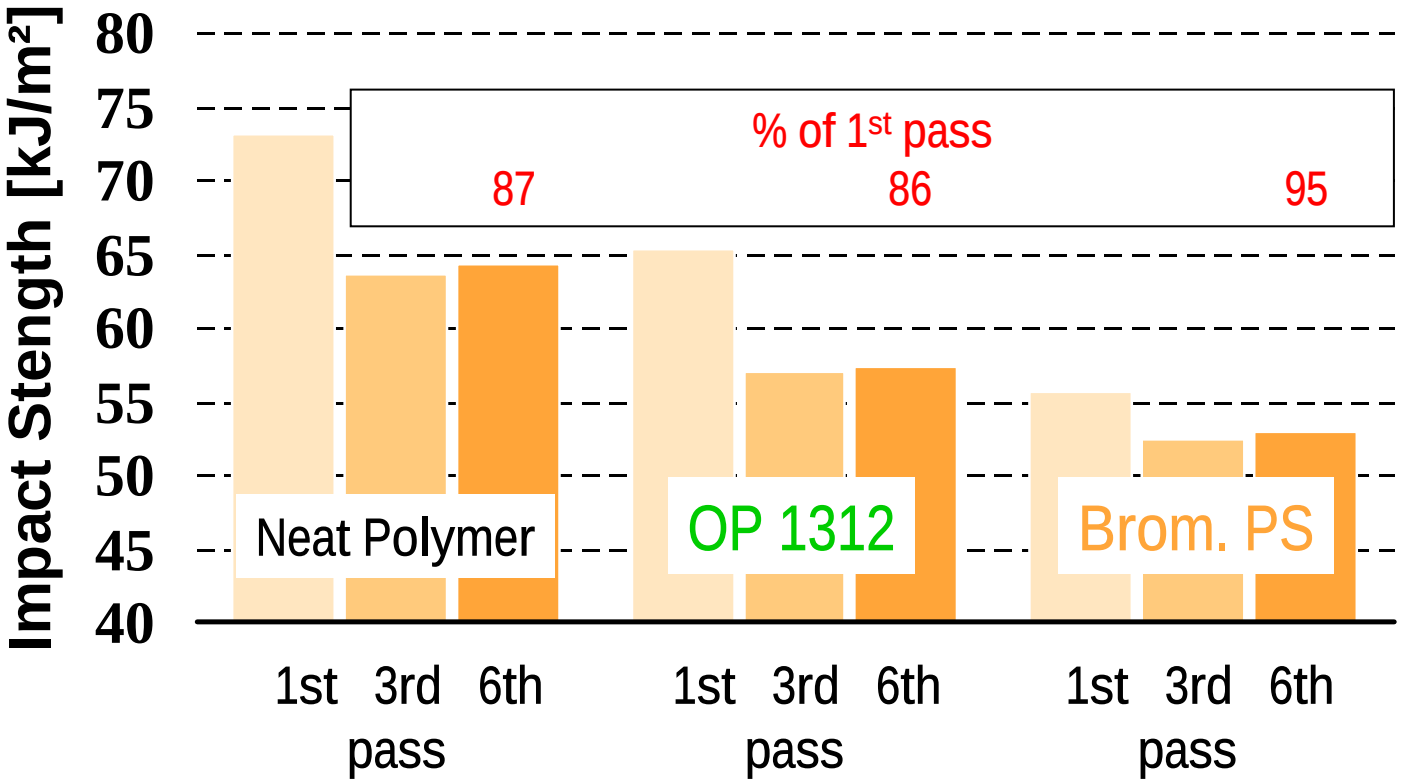
Recycling Study
Flame Retarded Polyamides

- Mechanical Properties
  - Impact Strength (Charpy), dry as mold



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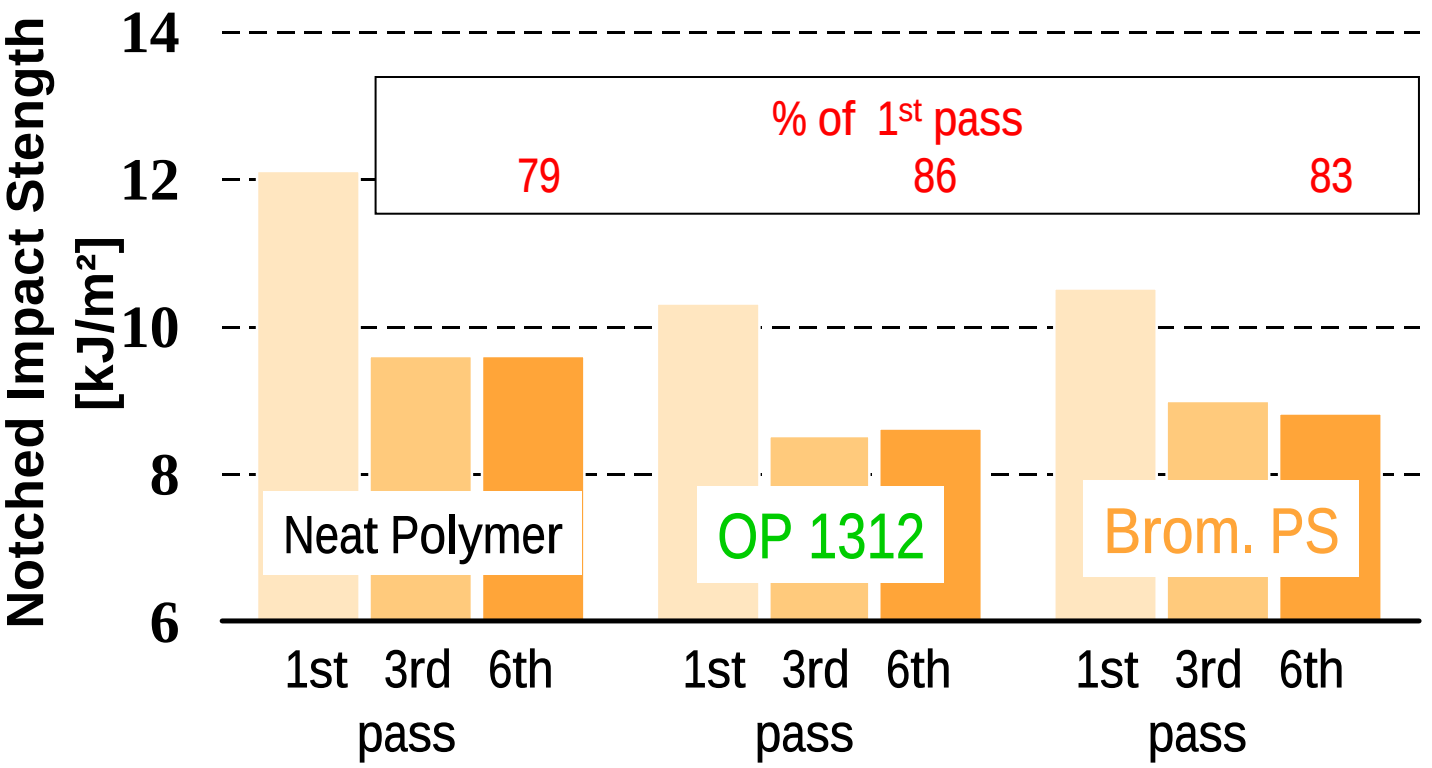
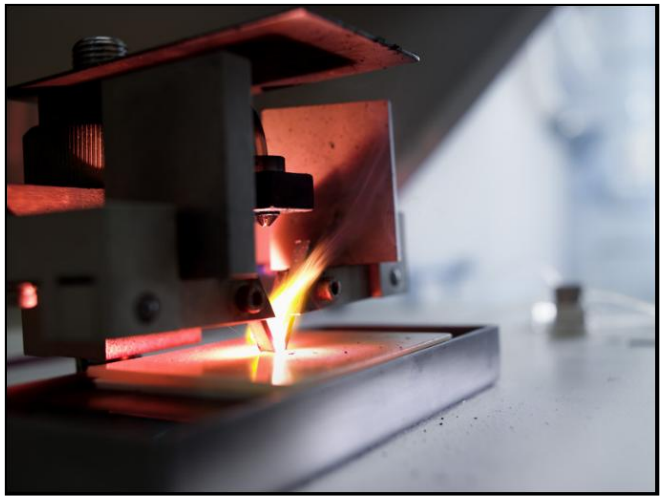


Polyester Applications

- Celanex XFR (PBT, PBT GF)
- Riteflex XFR (TPE-E, COPE)
  - No migration
  - No corrosion of electrical contacts
  - Very good colorability
  - Lower density than Br/Sb system
  - Proprietary: EP 699708 (Ticona)

Ticona



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PBT V-0

Ticona

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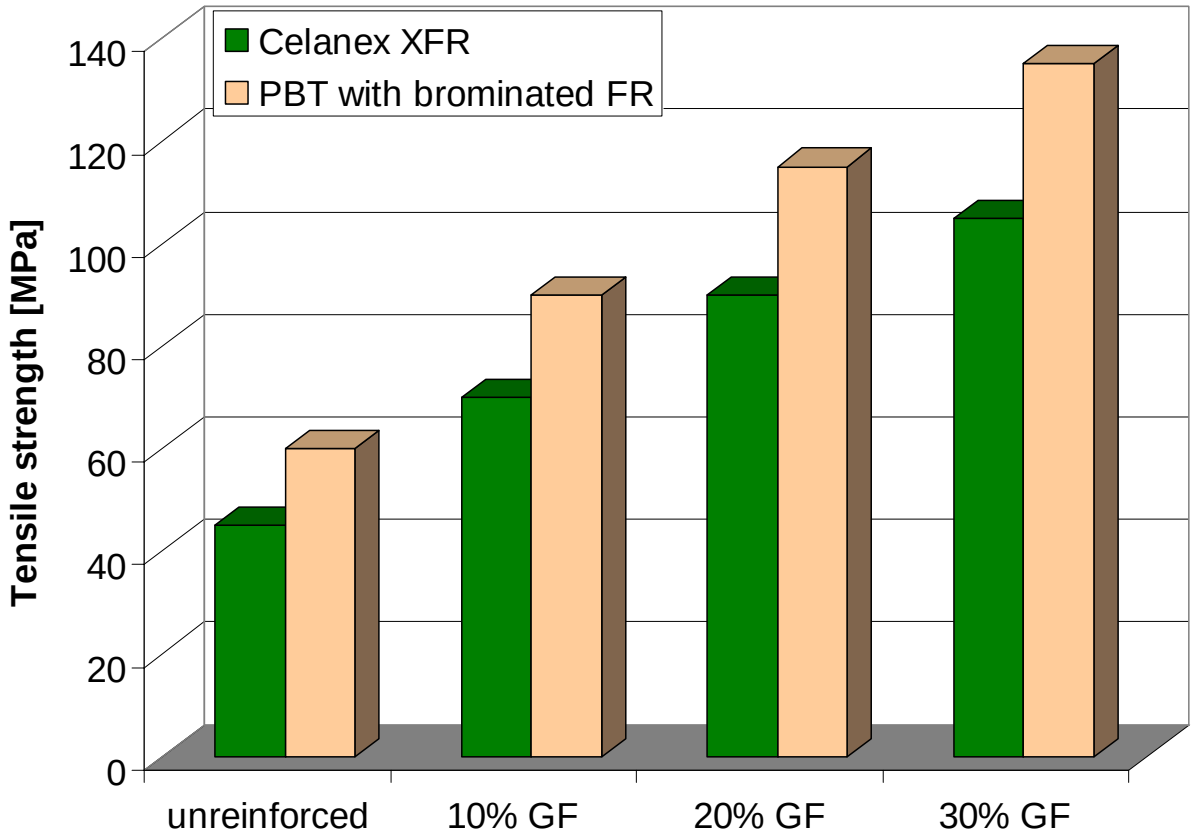
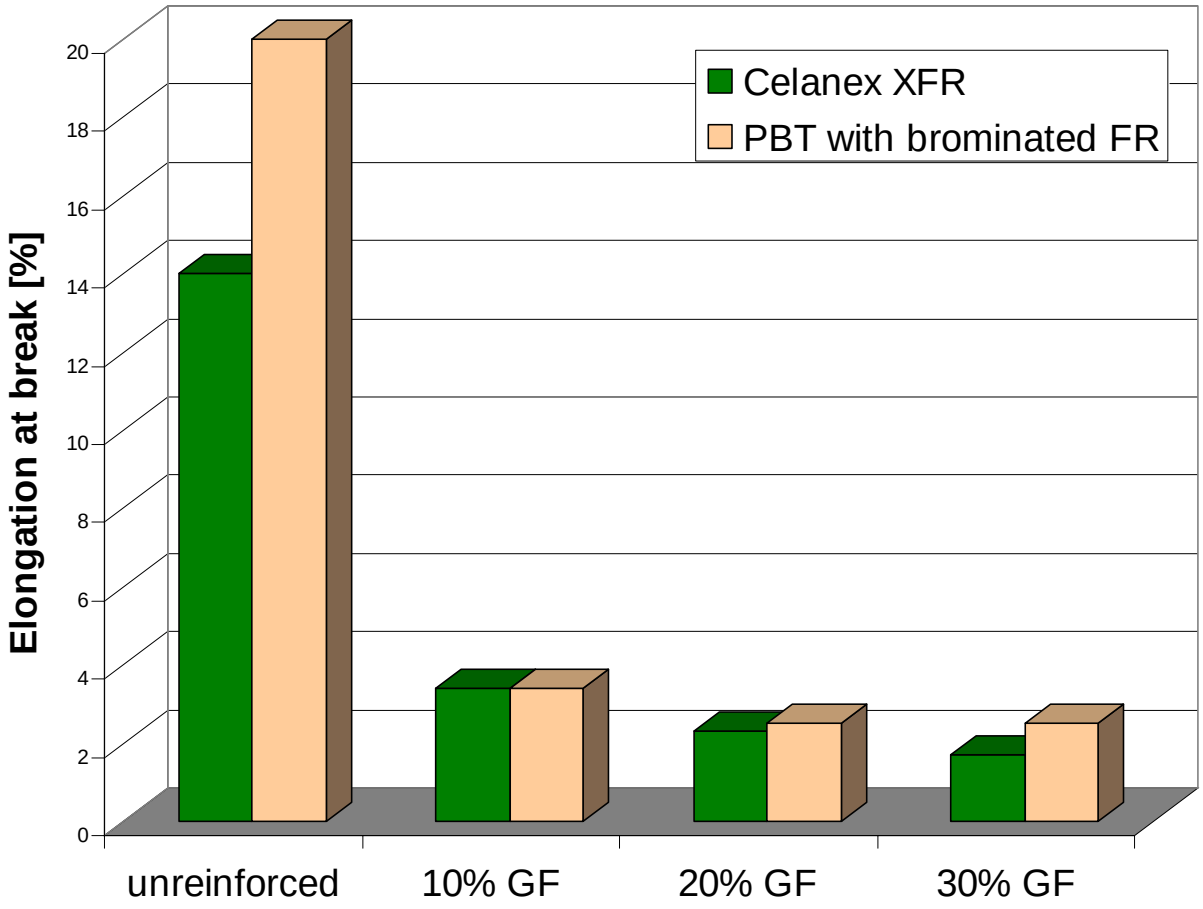
Tensile Strength



PBT V-0

Ticona

- Elongation at Break



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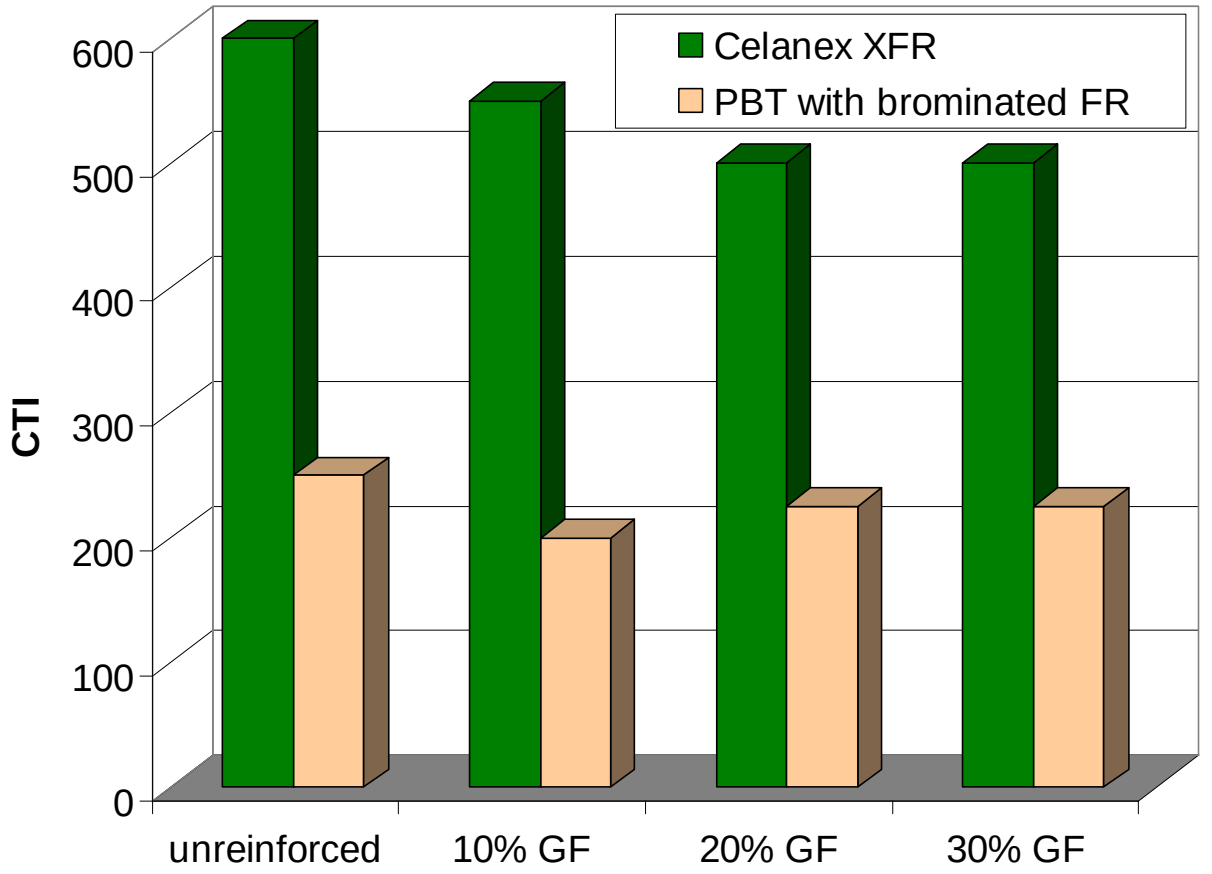
PBT V-0

Ticona

- CTI



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Halogen-free PCB: Technical challenge

A direct drop-in substitue for TBBP-A does not exist (yet):
One must re-formulate with different components

Traditional Varnish composition	Varnish bath (Halogen-free)
Generally a four component system	> 6 components system
– Epoxy Resin (brominated)	– new epoxy resin ?
– Curing Agent	– new curing agent ?
– Accelerator	– new accelerator ?
	– New flame retardants ?
	– Fillers ?
	– Processing additives?
– Solvent (viscosity modifiers)	– Solvent

Challenge: the varnish bath must be **completely reformulated**,
and **individual components** optimized to **customer requirements**.
No industry standards - Each customer with **own recipe, tests & requirements**

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Specific requirements in rigid PCB

Overall requirements and aspects that may be affected by additives:

- No blisters or delamination after PCT
- No decomposition or delamination during soldering (TTD at 260°C/288°C up to 300°C!)
- Chemical resistance against acid, alkali and oxidative substances
- No or low water uptake
- No migration (critical for CAF testing)
- No or little impact on mechanical properties, CTE as low as possible
- No or little impact on Tg
- No or little impact on electrical properties (Dk, Df)
- No or little impact on resin-glass or resin-copper interface
- No impact on resin flow of prepregs for press process
- Optical aspect: no agglomerate for quality inspection

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Pros and cons of Exolit phosphinate in thermosets

Unique properties

- high phosphorus content (23-24 %)
- high thermal stability

  (decomposition @ > 320°C)
- unlike ATH, no influence on Tg after thermal treatment > 220°C
- high moisture resistance: very low solubility in water and lower water absorption than the resin
- no influence on electrical properties like Dk and Df in particular at higher frequencies

Potential technical limitations

- Adhesion properties (critical when dosage >20 phr)
- Curing kinetics can be affected in certain resins
- Resistance vs. strong alcaline conditions (refers to organic component)

Exolit® OP is not a drop-in FR and must be correctly formulated

Exolit OP in thermosets for Electronics

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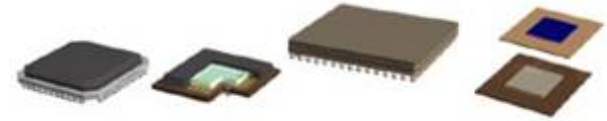
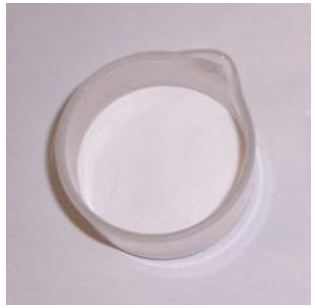
■ Established applications in different electronic materials

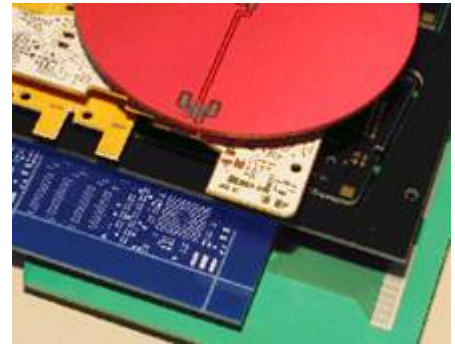
Rigid and flexible PWB

Epoxy moulding compounds





Exolit®
OP 930/935/1230



Others: solder masks, resist inks, adhesives...

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Conclusion

- Halogen-free flame retardant systems will continue to gain importance in the electrical and electronics sector
- The major electrical and electronic equipment manufacturers will switch globally to halogen-free systems
- The new, highly effective metal phosphinates will fill an important gap in halogen-free flame retardation of engineering plastics such as PA and PBT
- In demanding PCB application, metal phosphinates have proven themselves as a suitable synergist (performance chemical)

They will help companies meet the challenges they face