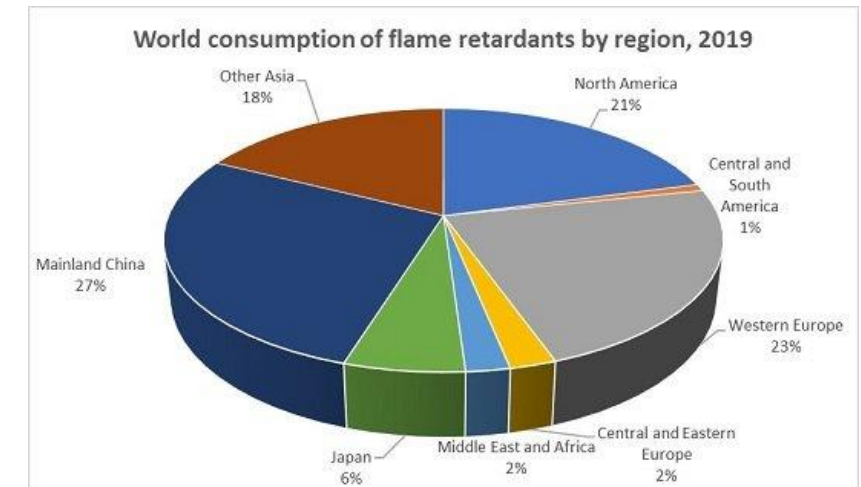
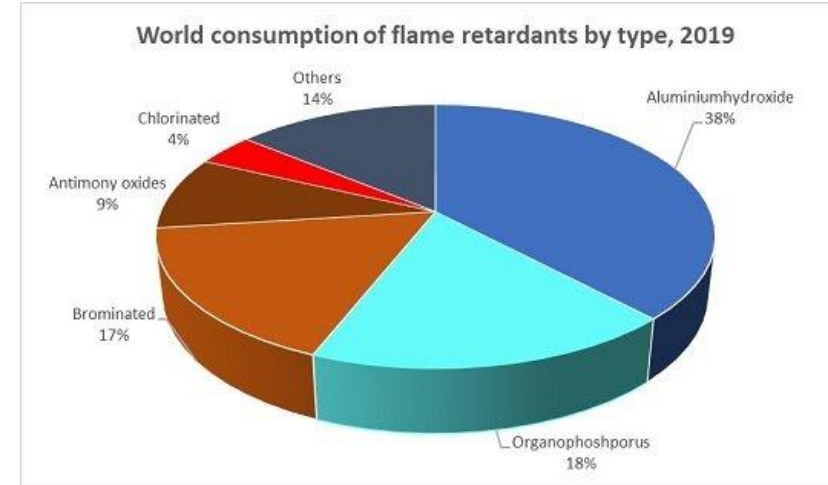


HALOGEN FREE vs HALOGENATED FR have we reached the halfway point?

ARESE 16/10/2022 Micaela Lorenzi
GREENCHEMICALS Srl
Flame Retardants and more

- **FLAME RETARDANTS TODAY'S CONTEST**
- **HALOGENATED AND HALOGEN FREE: THE LAST 3 YEARS**
- **ENGINEERING POLYMERS FR: PA, PBT, PET, PC, PC/ABS, PPO/HIPS, ABS, HIPS. FR formulations**
- **HF VS HALOGENATED: PRICES**
- **HF VS HALOGENATED: RECYCLABILITY**
- **CONCLUSIONS**

- **2,2 MILLIONS/YEAR, WITH GROWTH OF 3%/YEAR.**
- **1/3 ARE HALOGENATED WITH SYNERGIST**
- **50% ASIA, 22% AMERICA, 28% EMEA**
- **IN EUROPE 450.000 MT/YEAR**

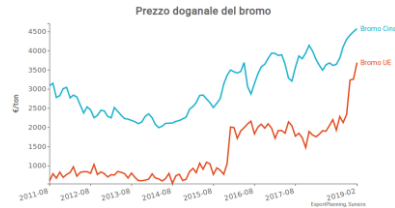


HALOGENS AND ANTIMONY TRIOXIDE CONCERNS

- Endocrine and thyroid disruption
- Impacts to the immune system
- Reproductive toxicity
- Cancerogenic
- Adverse effects on fetal and child development
- Neurologic function

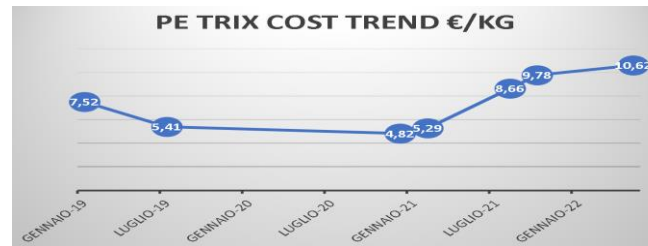
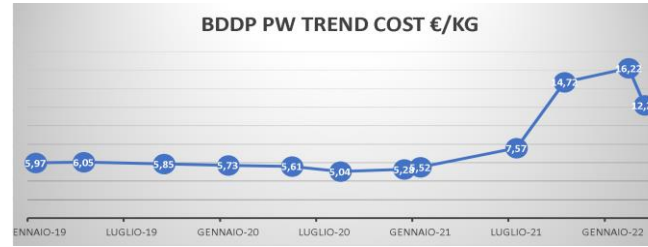
**TRANSPORTATION COST FROM
0,06€/Kg to 1 €/Kg**

BROMINE COST EVEN 100%



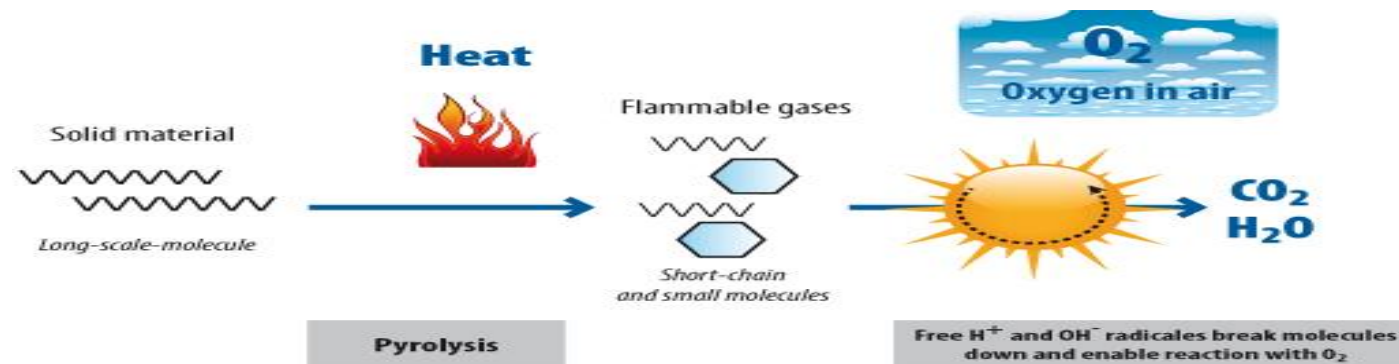
**P MORE STABLE, BECAUSE FOOD
RELATED**

**JUNE 2022 REDUCTION OF
DEMAND, REDUCTION OF PRICES**



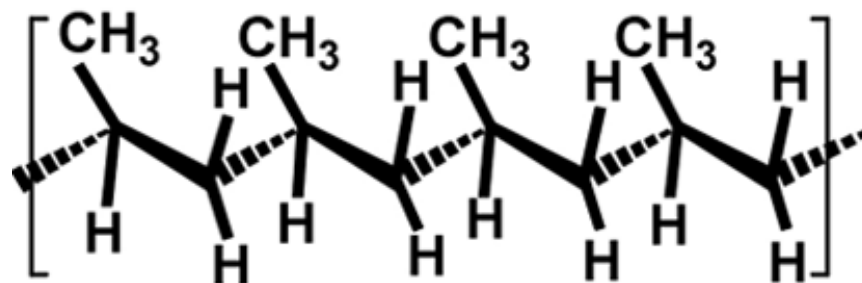
	DPE81	BDDP 68	Sb ₂ O ₃	BDP	HF1000	DEPAL
JAN-20	6,5 €/Kg	4 €/Kg	7,50 €/Kg	3 €/Kg	6 €/Kg	9,5 €/Kg
SEP-22	12 €/Kg	12 €/Kg	10,50 €/Kg	4,5 €/Kg	8 €/Kg	11,5 €/Kg

FLAME RETARDANTS ACTION



MECHANISM	FR TYPE	ACTION	COMBUSTION STEP
WATER DEVELOPMENT	Mg(OH) ₂	Cooling down by water development	Slow down pyrolysis Ignition point increases
GAS PHASE	Bromine, Sb ₂ O ₃ , phosphinates, Pred	Development of not-flammable gases	Breaking down of radical chain degradation
CHAR	Phosphates, phosphonates	Cooling Char formation	Slow down pyrolysis Slow down heat exchange
INTUMESCENT	Ammonia, phosphates	Cooling Char formation Blown up	Slow down pyrolysis Slow down heat exchange
DRIPPING	Bromine, phosphine	Chain scission	Slow down pyrolysis

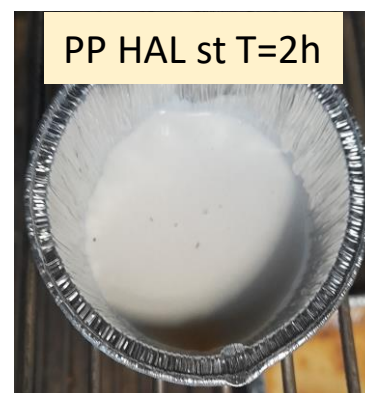
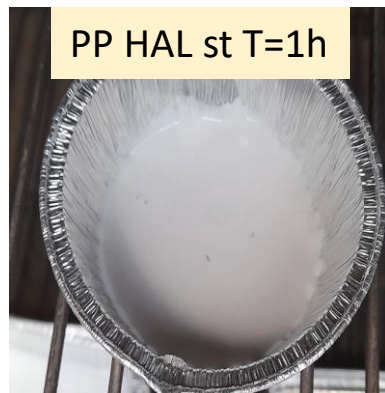
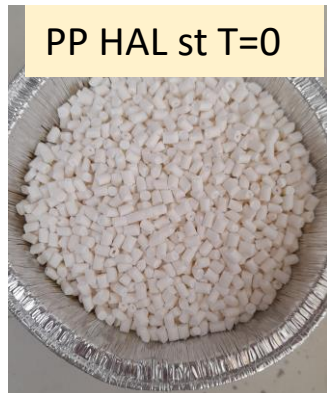
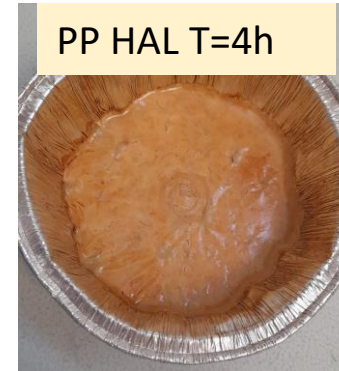
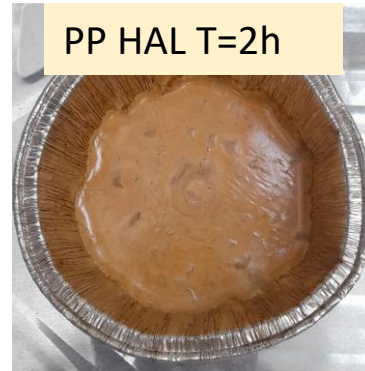
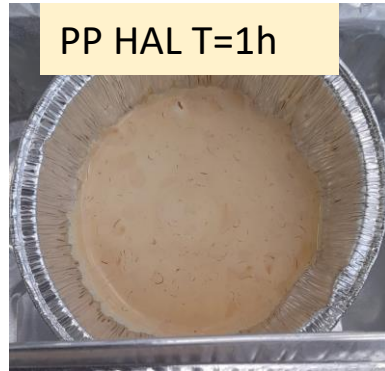
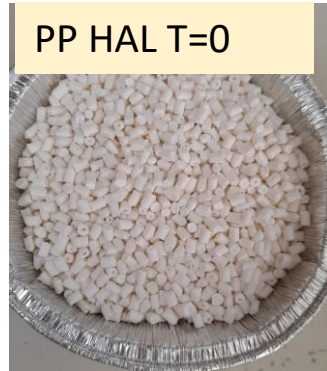
LOI



PE	17
ABS	18
PA	24
PC	27
PP	17

HIGH LOI	BAD FLAME RETARDANT RESISTANCE
<u>N</u> AND <u>O</u> IN CHAIN	ALL FLAMABLE GASES
LOW PROC. TEMP. 200°C-280°C	WIDE RANGE OF FR
NO PRESENCE OF N AND O	BAD CHAR
RADICAL POLYMERIZATION / ZIEGLER NATTA	DRIPPING
CROSS-LINKING ABILITY	VERY BAD

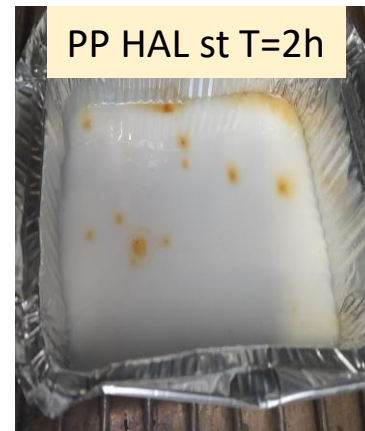
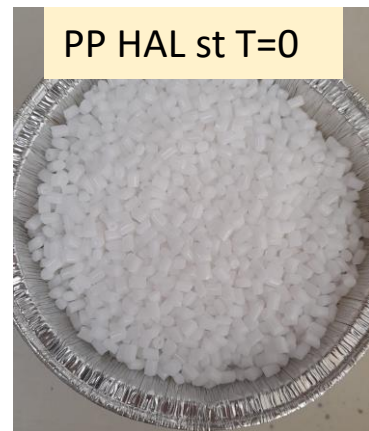
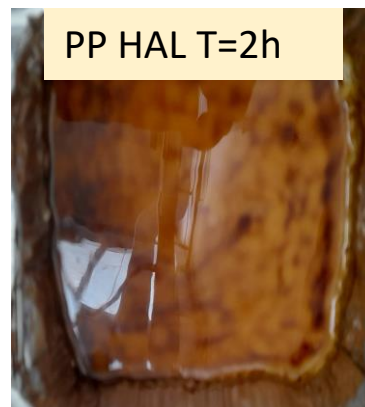
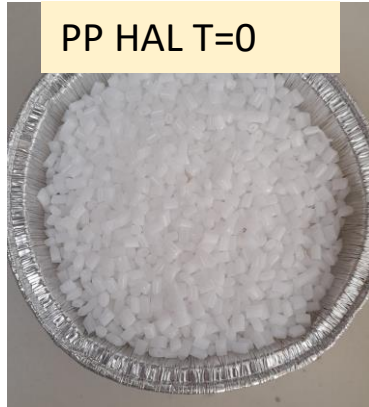
FLAME RETARDANT PACKAGE	TEST	TYPE OF FR	YTD PRICE/Kg	DOSAGE	IMPACT/Kg COMPOUND
GC DPE 81+ Sb ₂ O ₃	UL94 V0	HALOGEN + Sb	12-13 €/Kg	22%	~ 3,01 €/Kg
INTUMESCENT	UL94 V0	HALOGEN FREE	8 €/Kg	27%	~ 2,20 €/Kg
GC BDDP 68+ Sb ₂ O ₃	UL94 V2	HALOGEN + Sb	14-15 €/Kg	4%	~ 0,6 €/Kg
GC DRIPP HF 70	UL94 V2	HALOGEN FREE	13-14 €/Kg	2%	~ 0,4 €/Kg



Compound has been kept at 200 °C for different time.

PP HAL= PP + 22% MB PP DETO 31

PA HAL= PP + 22% MB EVA DETO 31 + MB PO POX 20-4



Compound has been kept at 220 °C for different time.

PP HAL= PP + 6 % MB PP BATO 21

PP HAL= PP + 6 % MB PP BATO 21 + MB PO POX 20-4

PP HAL FREE T=1h



PP HAL FREE T=2h



PP HAL FREE T=3h



PP HAL FREE T=4h



PP HAL FREE st T=1h



PP HAL FREE st T=2h



PP HAL FREE st T=3h



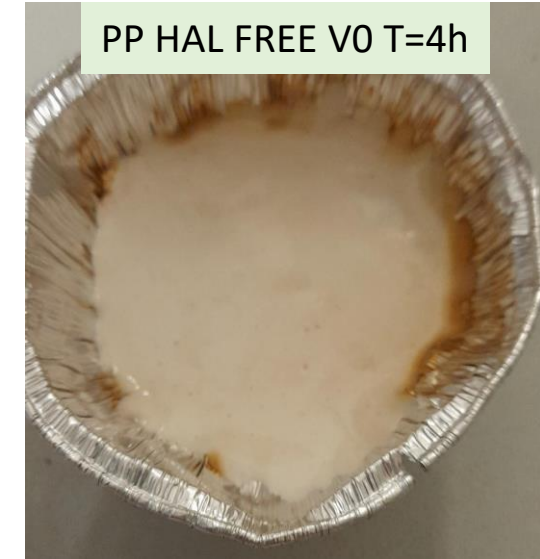
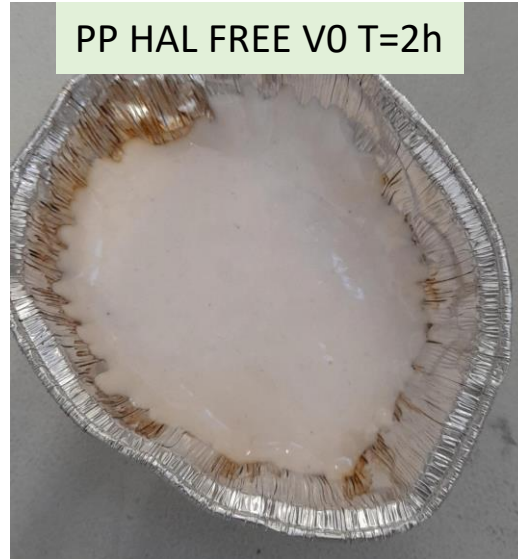
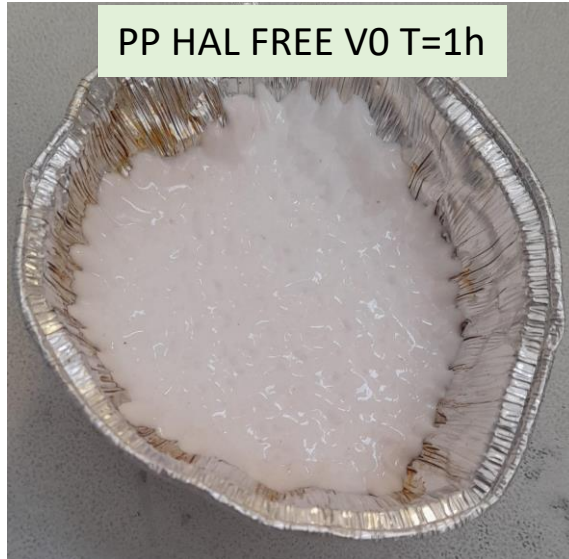
PP HAL FREE st T=4h



Compound has been kept at 220 °C for different time.

PPV2 HALOGEN FREE = PP + 2% GC DRIPP HF 70

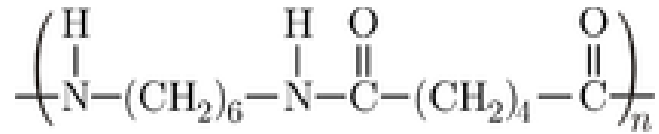
PPV2 HALOGEN FREE= PP + 2% GC DRIPP HF 70 + MB PO POX 20-4



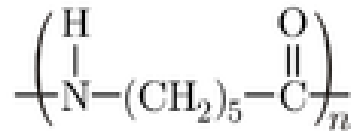
Compound has been kept at 200 °C for different time.

PPV0 HALOGEN FREE = PP + 27 % HF1000 + MB PO POX 20-4

POLYAMIDE



Nylon 66



Nylon 6

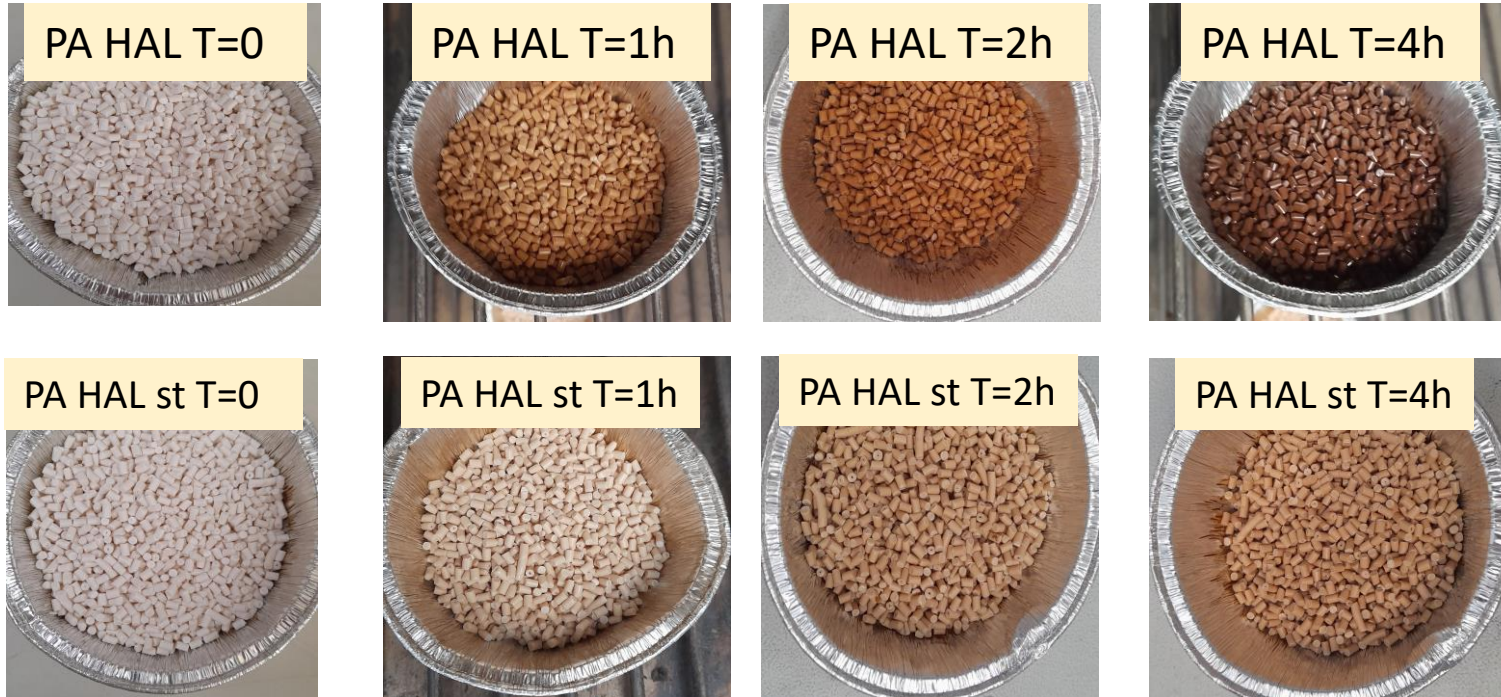
LOI

PE	17
ABS	18
PA	24
PC	27
PTFE	95

MAIN FR FEATURES

HIGH LOI	GOOD FLAME RESISTENCE
N AND O IN CHAIN	LESS FLAMMABLE GASES
HIGH PROCESSING T, 230°C – 280°C	FR MUST BE THERMAL RESISTANT
PRESENCE OF N AND O	CHAR
POLICONDENSATION	DRIPPING
CROSS-LINKING ABILITY	CROSS-LINK

FLAME RETARDANT PACKAGE	TEST	FR TYPE	YTD PRICE/Kg	DOSAGE	IMPACT/Kg COMPOUND
GC DPE 81+ Sb₂O₃	UL94 V0, 30%GF	HALOGEN + Sb	12-13 €/Kg	20%	2,66
GC BPS 67+ Sb₂O₃	UL94 V0, 30%GF	HALOGEN + Sb	14-16 €/Kg	22%	3,52
PHOSPHINATE + PHOSPHATE	UL94 V0, 30%GF	HALOGEN FREE	13-14 €/Kg	18%	2,64



Compound has been kept at 220 °C for different time.

PA HAL= PA66 + 20% MB EVA DETO 31

PA HAL= PA66 + 20% MB EVA DETO 31 + MA PA POX 1171

PA HAL FREE VO T=1h



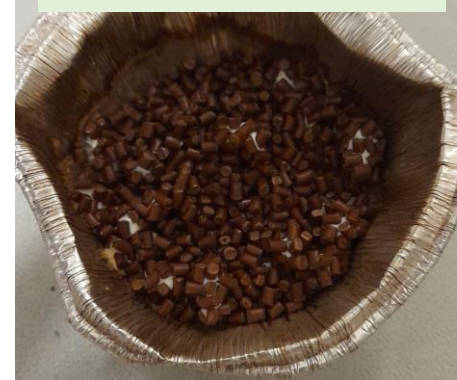
PA HAL FREE VO T=2h



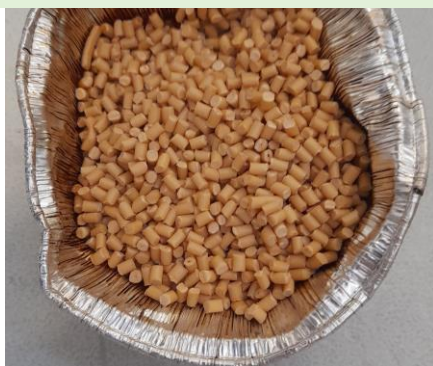
PA HAL FREE VO T=3h



PA HAL FREE VO T=4h



PA HAL FREE VO st T=1h



PA HAL FREE VO st T=2h



PA HAL FREE VO st T=3h



PA HAL FREE VO st T=4h



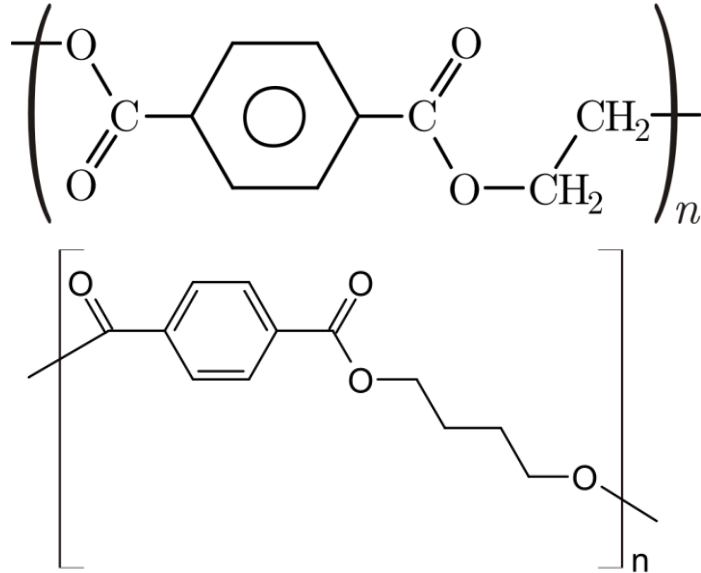
Compound has been kept at 220 °C for different time.

PA HAL FREE= PA66 + 18% PHOSPHINATE/PHOSPHONATE PAP12

PA HAL FREE = PA66 + 18% PHOSPHINATE/PHOSPHONATE PAP12 + MB PA POX 1171

PA HAL= PA66 + 20% MB EVA DETO 31

POLYETHYLEN TEREPHTALATE POLYBUTYLEN TEREPHTALATE



PE	17
ABS	18
PET	25
PBT	23
PC	27
PTFE	95

HIGH LOI

GOOD FLAME RESISTANCE

PRESENCE OF ETEROATHOMS

NOT FLAMABLE GASES

T PROCESS PET 260°C – 290°C
PBT 230°C-270°C

FR MUST BE THERMAL RESISTANT

ETEROATHOMS IN CHAIN

CHAR

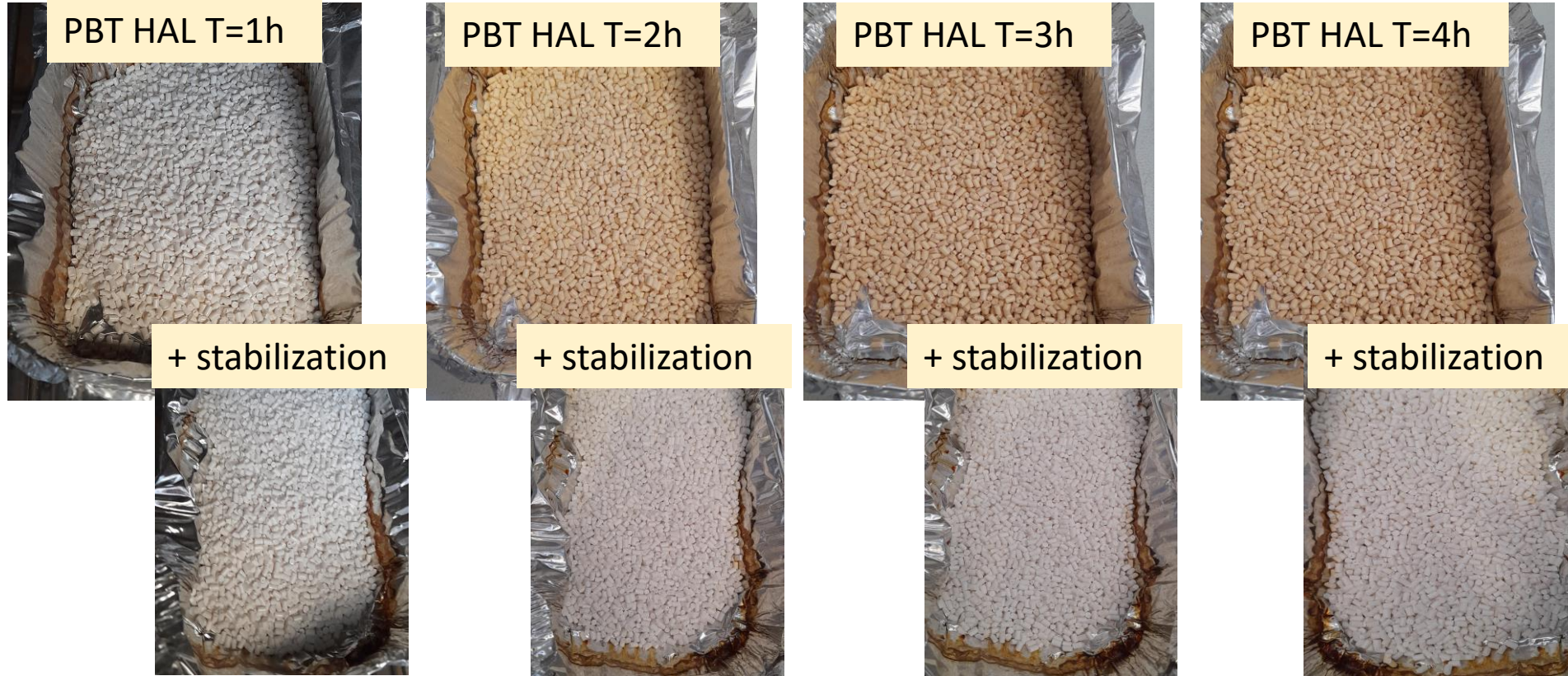
POLYCONDENSATION

DRIPPING

EASY TO CURE

CROSS-LINK

FLAME RETARDANT PACKAGE	TEST	FR TYPE	YTD PRICE/Kg	DOSAGE	IMPACT/Kg COMPOUND
GC DPE 81+ Sb₂O₃	UL94 V0	HALOGEN + Sb	12-13 €/Kg	20%	2,75 €/Kg
GC BPS 67+ Sb₂O₃	UL94 V0	HALOGEN + Sb	14-16 €/Kg	22%	3,61 €/Kg
PHOSPHONATE + PHOSPHATE	UL94 V0	HALOGEN FREE	14-15 €/Kg	25%	3,75 €/Kg



Compound has been kept at 220 °C for different time.

PBT HAL= PBT + 20% MB EVA DETO 31

PBT HAL= PBT + 20% MB EVA DETO 31 + MB EVA POX 900



NOFIA HM1000

Phosphonate omopolymer, 10,5 % P, T_m= 110-120°C

PBT HAL FREE V0 T=1h



PBT HAL FREE V0 T=2h



PBT HAL FREE V0 T=3h



PBT HAL FREE V0 T=4h



Compound has been kept at 220 °C for different time.

PBT HAL= PBT + 15% NOFIA HM1000 + 10% MPP

- **TODAY'S FR MARKET IS DIFFERENT FROM 3 YEAR AGO**
- **IMPROVEMENT IN TECHNOLOGY AND ECONOMICAL CHANGE MAKE HALOGEN FREE MORE INTERESTING**
- **KNOWN HALOGEN FREE FORMULATIONS ARE GENERALLY LESS RECYCLABLE.**
- **SUPER FR BECOMES COMMERCIALY INTERESTING. NOFIA**