WAPOL PROJECT
sustainable flame retardants

Fire reaction modelling of sustainable flame retarded polymers

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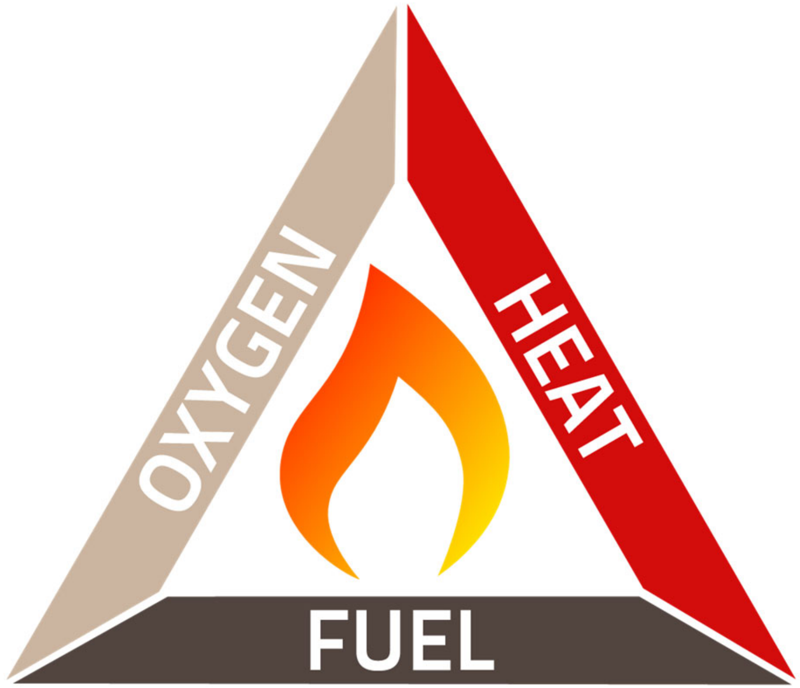
Summary

- Burning mechanism in polymers
- Flame retardant actions
- Fire reaction characterization and modelling

Burning mechanism in polymer

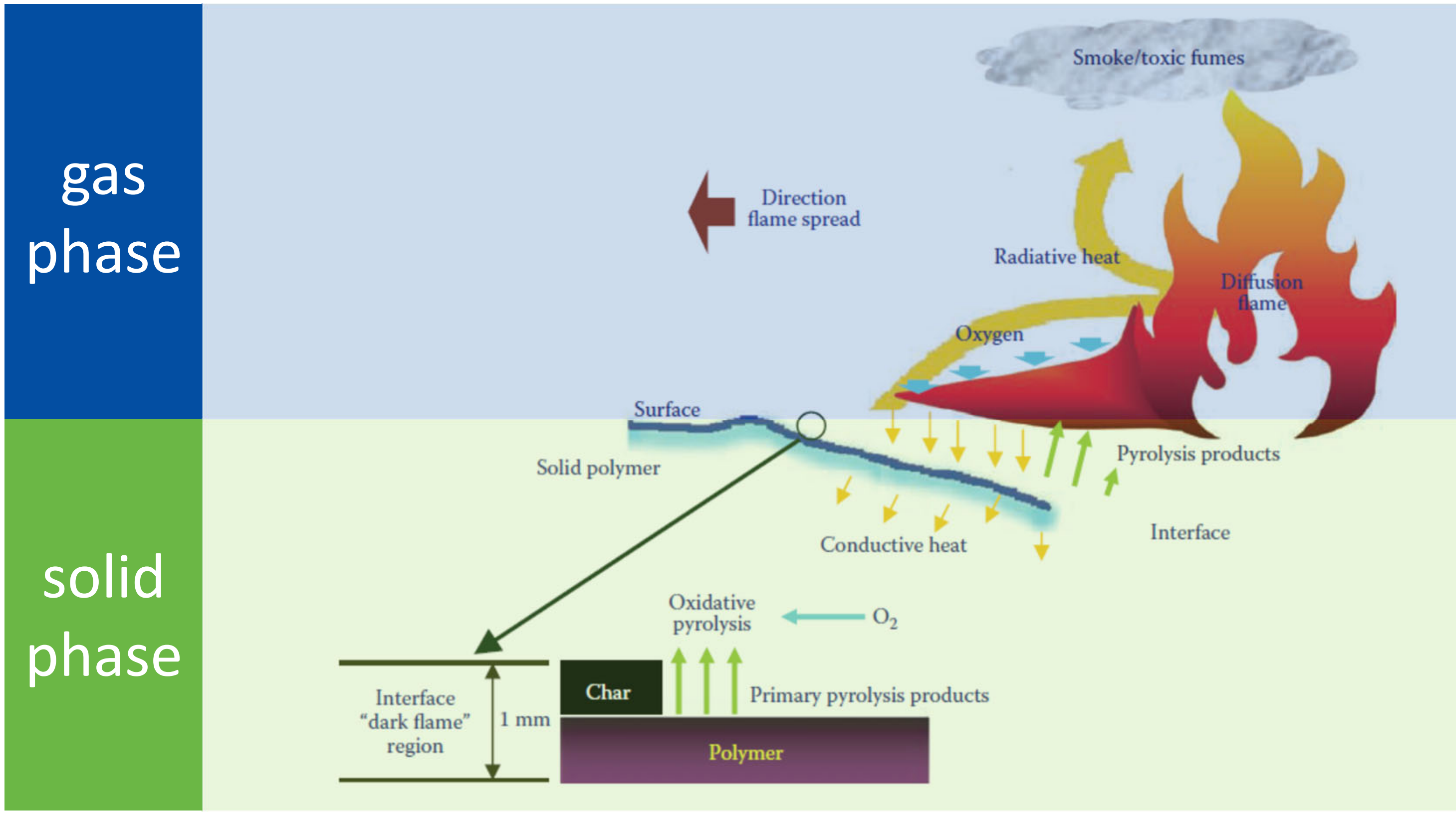
- One generally accepted definition of combustion or fire, is a process involving rapid oxidation at elevated temperatures accompanied by the evolution of heated gaseous products of combustion, and the emission of visible and invisible radiation.

- The Fire Triangle is a simple model for understanding the ingredients necessary for most fires.
- A fire naturally occurs when the elements are combined in the right mixture:
  - fuel-oxidizing agent within the flammability limits
  - the temperature above the ignition temperature or in presence of a suitable ignition source, such as a spark
- The fire is prevented or extinguished by removing any one of them.



Fire Triangle

Burning mechanism in polymer



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Fire Retardancy of Polymeric Materials: 2nd Edition, CA Wilkie and AB Morgan (editors), CRC Press, Boca Raton, Fl, USA, 2010

Flame retardant actions

Physical

SOLID PHASE

cooling effect, protective layer

GAS PHASE

dilution

Chemical

SOLID PHASE

charring, intumescence

GAS PHASE

Flame (radical reactions) inhibition

Fire reaction characterization

- Manufacturers of plastic products or those who utilize plastic components must assure consumers that their products are reasonably fire-safe
- The necessary standards required for a particular plastic product are chosen based on its intended end-use
- There are several commonly used small scale test for fire reaction:
  - UL94
  - Limiting oxygen index (LOI)
  - DIN 4102-B2
  - ……..

Fire reaction characterization – UL94

https://www.youtube.com/watch?v=EFZ0jSr15BE

Fire reaction characterization-UL94

To meet V0 classification:

1. Gas phase action to stop the flame (t1 and t2)
2. Solid phase action to prevent dripping (t drip)

Need to use FRs mixture

Flammability rating UL 94 V			
Test criteria	V-0	V-1	V-2
Burning time of each individual test specimen (s) (after first and second flame applications)	≤10	≤30	≤30
Total burning time (s) (10 flame applications)	≤50	≤250	≤250
Burning and afterglow times after second flame application (s)	≤30	≤60	≤60
Dripping of burning specimens (ignition of cotton batting)	no	no	yes
Combustion up to holding clamp (specimens completely burned)	no	no	no

Fire reaction characterization-UL94

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Fire reaction characterization-UL94

Let's see an example for PP

	thickness	t1	t2	Cotton ignition	t dripping
F20_M15_N1	3 mm	3s	2s	yes	12s
	1,5 mm	8s	3s	yes	8s

Burning time similar to **V0**

Too short dripping time

V2 classification

Need to find FRs to prevent dripping

Fire reaction characterization-UL94

Checking the literature, it seems that **Nv works well**, so let's try….

	thickness	t dripping	t1	t2	Cotton ignition	UL94
F20_M15_**Nv1**	3 mm	12s	3s	2s	yes	V2
F20_M15_N1_**Nv3**	3 mm	22s	11s	13s	yes	V2
F20_M15_N1_**Nv5**	3 mm	40s	24s	>30s	yes	V2

Dripping time is higher

but also burning time is higher

The action of a FRs mixture is not the sum of the single effect

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Fire reaction characterization - modelling

Development of a statistical model able to predict the results of formulations before their production.

Multiple regression:
technique used to obtain a **hidden or implicit relationship**, starting from the analysis of independent variables.

Indipendent Variables
M, P, N

t_{drip}, t_1, t_2 ← Y

$$Y = C + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \ldots + \beta_p X_p$$

i-th coefficients of
independent variables

Obtained a mathematical relationship that links the **percentage by weight of each additive** (independent variables) to the **burning and dripping time** (dependent variable).

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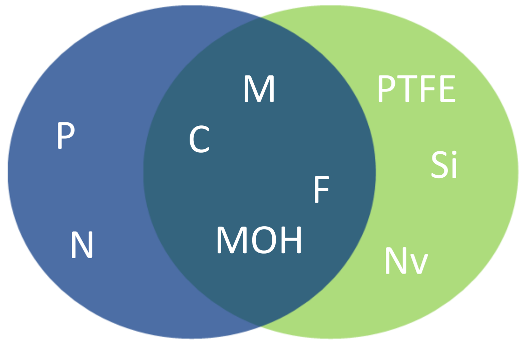
Fire reaction characterization - modelling

	F	M	P	N	Nv	t1_	t2_	t drip_	t1+2_	Probabilità	Prob 2
	%	%	%	%	%	s	s	s	s	3mm	1,5mm
Colonna1	Colonna	Colonna	Colonna	Colonna	Colonna	Colonna	Colonna	Colonna	Colonna	Colonna11	Colonna
composition	60	0	0	0	0	50	50	25	100	0.00	0.00
	0	0	0	0	0	50	50	12	100	0.00	0.00
	0	30	12	0	0	1	1	22	2	0.50	0.00
	0	30	10	0	0	1	2	23	3	0.25	0.00
	0	35	10	0	0	1	1	28	2	1.00	0.00
	0	33	10	0	0	1	1	26	2	1.00	0.00
	0	35	8	0	0	1	2	26	3	0.83	0.00
	0	33	8	0	0	1	3	24	4	0.33	0.00
	0	35	6	0	0	1	4	26	5	0.50	0.00
	0	31	10	0	0	1	2	24	3	0.67	0.00
	0	37	4	0	0	1	5	25	6	0.50	0.00
	0	35	4	0	0	1	6	27	7	0.33	0.00
	0	37	6	0	0	1	3	26	4	0.86	0.00
	0	30	6	1	0	1	1	15	2	0.83	0.50
	0	25	6	1	0	1	1	15	2	0.25	0.25
	0	27	6	1	0	1	1	17	2	0.83	0.43
	10	25	6	1	0	1	1	17	2	0.50	0.50
	0	25	6	2	0	1	1	13	2	0.50	1.00
	0	30	0	2	0	1	1	16	2	0.25	0.40
	0	33	0	2	0	1	1	18	2	0.38	0.60
	10	30	0	2	0	1	1	18	2	0.25	0.80
	0	30	0	5	0	1	2	14	3	0.25	0.60
	0	36	0	2	0	1	1	17	2	0.66	1.00
	0	36	0	3	0	1	1	16	2	0.75	1.00
	20	15	0	1	0	2	3	11	5	0.00	0.00
	20	25	0	5	5	29	45	48	74	0.00	0.00
	10	30	5	5	5	38	44	48	82	0.00	0.00
	0	30	10	5	5	13	36	57	49	0.00	0.00
	0	25	15	5	5	1	10	30	11	0.00	0.00
	0	25	12	5	5	6	9	30	15	0.00	0.00
	30	25	0	5	5	49	50	54	99	0.00	0.00
	0	20	10	5	5	26	22	28	48	0.00	0.00
	0	25	10	5	5	1	33	54	34	0.00	0.00
	0	30	12	3	3	1	11	35	12	0.00	0.00
	0	25	12	3	3	1	7	25	8	0.00	0.00
	0	30	12	0.5	0.5	1	5	27	6	0.00	0.00
	0	25	10	0.5	0.5	2	3	24	5	0.00	0.00
	0	30	10	0.5	0.5	1	4	26	5	0.00	0.00
	0	35	10	0.5	0.5	1	1	29	2	0.00	0.00
	0	28	10	0.5	0.5	1	6	26	7	0.00	0.00
	0	30	8	0.5	0.5	1	5	25	6	0.00	0.00
	0	32	8	0.5	0.5	1	4	28	5	0.00	0.00
	0	32	6	0.5	0.5	1	7	29	8	0.00	0.00
	0	30	6	0.5	0.5	1	7	29	8	0.00	0.00
	10	25	5	1	5	9	23	39	32	0.00	0.00



Exp. trials to get large **dataset**

model development

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Fire reaction characterization - modelling

- An example…

	X_i	β t_{drip}	β t_1	β t_2
	Cost **C**	11,5389	5,1405	6,7203
	F	0,2881	0,7609	0,7377
	M	0,4892	-0,0298	-0,0048
	P	-0,4104	-0,5075	-0,624
	N	-5,3924	-1,003	-1,8867
	Nv	8,4575	3,5442	5,4328
		R^2 = 0.89	**R^2 = 0.89**	**R^2 = 0.93**

Every coefficient describes the influence of each independent variable on the relationship

$$t_{drip} = 11,54 + 0,29F + 0,49M - 0,41P – 5,39N + 8,46Nv$$

Fire reaction characterization - modelling

- At the end, several PP-V0 compositions can be identified without the need of producing and characterizing them

	F	M	P	N	Nv	t1_	t2_	t drip_	t1+2_	Probabilità	Prob 2
	%	%	%	%	%	s	s	s	s	3mm	1,5mm
Colonna1	Colonna	Colonna	Colonna	Colonna	Colonna	Colonna	Colonna	Colonna	Colonna	Colonna11	Colonna
composition	0	27	6	2	0	1	1	16	2	1.00	1.00
	0	40	0	3	0	1	1	15	2	1.00	1.00
	0	32	6	2	0	1	1	13	2	1.00	1.00
	0	41	0	3	0	1	1	15	2	1.00	1.00
	0	42	0	3	0	1	1	15	2	1.00	1.00
	0	33	6	2	0	1	1	13	2	1.00	1.00
	0	34	6	2	0	1	1	13	2	1.00	1.00
	0	43	0	3	0	1	1	16	2	1.00	1.00
	0	44	0	3	0	1	1	16	2	1.00	1.00
	0	35	6	2	0	1	1	14	2	1.00	1.00
	0	36	6	2	0	1	1	14	2	1.00	1.00

Exp. trials have shown that these compositions are really V0

You can now choose the optimal one in terms of

- margin of safety (longer t dripping)
- cost
- mechanical properties
- …….