OPTIMIZATION OF A FLAME-RETARDED EVA COMPOSITE

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Introduction:

Many attempts have been made on improving flame retardant properties of EVA/magnesium hydroxide (MDH) composites with the purpose of decreasing filler amount. Among the studied HFFRs, boron and silicon containing additives have shown synergistic effect in combination with MDH, both singularly [1] [2] and when used together [3]. Their main effect is in the solid phase, improving char formation and stability. In this work PDMS and calcium borate are evaluated as co-additives in EVA/MDH composite. A chemiometric approach has been used in order to analyse their influence and the possible synergistic effects [4].

Experimental Design approach

The quaternary system is studied by Mixture Design. The components (independent variables) are expressed as the fraction of total amount and they sum up to one. Some constrains are established (lower and upper boundaries) in order to focus the exploration on the region of interest. A multivariate linear regression model has been used for each response variable.

The aims of the approach are:

- evaluation of possible correlations among FR parameters (PCA);
- modelling mixture behaviour for FR parameters;
- determination of relative importance of the components and interactions on FR properties (statistical analysis);
- possible prediction of "optimal" formulations.

Components and constrains:

- X_1 : natural magnesium hydroxide (MDH) 30-60 wt%
- X_2 : PDMS (Sil) 0-10 wt%
- X_3 : calcium borate (CaB) 0-20 wt%
- X_4 : matrix (EVA28 + 4 wt% coupling agent) 40-70 wt%

MDH + Sil + CaB < 60 wt%

18 - run design
(3 repetitions)

Responses:

Flame retardancy test	Parameter	Importance	Target
LOI	% O_2	++	max
DIN 4102 B2	t_a (s)	++	max
	Dripping	+++	min
	Unstable residue	+++	min
	Stable residue	+++	max
UL94-V	burn rate (cm/min)	+	min
Cone Calorimeter	TTI (s)	+++	max
	pkRHR (kJ/s*m²)	+++	min
	$pkRHR_{time}$ (s)	+	max
	avEHC (kJ/g)	+	min
	Tsmoke (°C)	+	min
	$Tsmoke_{time}$ (s)	+	max
	FPI (m²*s/kW)	++	max
	FIGRA (kW/m²*s)	++	min
	$avRHR_{180}$ (kJ/s*m²)	++	min
	THR (Mj/m²)	+	min

Models quality

Most of the dependent variables show very good (R^2>0.9) and acceptable (R^2>0.8) models.
General results on statistical quality are really positive.

	Response	n° coefficients
R^2 > 0.9 / Adeq Prec > 20	LOI (%O_2)	8
	pkRHR (kJ/s*m²)	4
	$avRHR_{180}$ (kJ/s*m²)	4
	FPI (m²*s/kW)	4
	FIGRA (kW/m²*s)	12
	Tsmoke (°C)	7
	Unstable residue	11
	Stable residue	14
	t_a (s)	4
R^2 > 0.8 / Adeq Prec > 10	TTI (s)	4
	$pkRHR_{time}$ (s)	4
	THR (Mj/m²)	4
	Dripping	4
R^2 > 0.5 / Adeq Prec > 4	burn rate (cm/min)	6
	$Tsmoke_{time}$ (s)	4

Principal Components Analysis

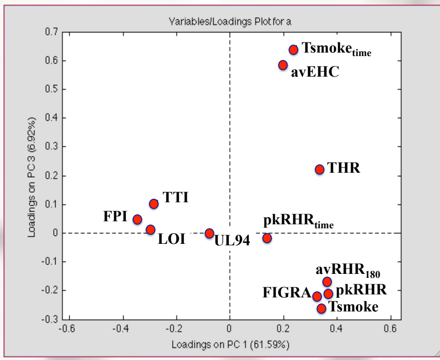

Fig. 1 – PCA plot for the flame retardant parameters.

The PCA study on the responses reveals no important correlations among parameters coming from LOI, UL94 and cone calorimeter. This result is in agreement with previous knowledge.

Statistical analysis on LOI

Regression equation:

$$LOI = 30.5X_1 + 23.4X_2 + 26.2X_3 + 20.6X_4 + 53.5X_1X_2 - 7.6X_1X_4 + 43.1X_2X_3 + 40.7X_2X_4$$

Sil additive is the most influent on LOI due to the interatcion coefficients. These are indicative of synergistic effects of PDMS with the other components (especially MDH).

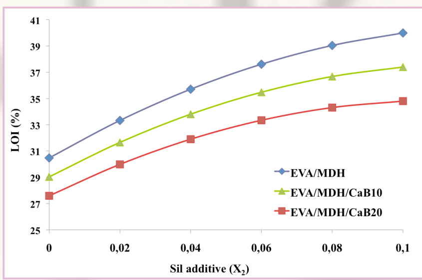

Fig. 2 – LOI regression model as a function of Sil amount at different CaB percentage.

The Sil influence could be observed in reducing afterglow effect (LOI residue without burnt edges)

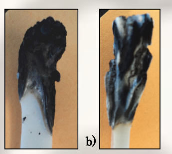

Fig. 3 - LOI residues of the sample (a) EVA/MDH and (b) EVA/MDH/Sil.

a) b)

Statistical analysis on cone calorimeter

Most of the CCT parameters models are described by linear equation
(no statistically significant interactions).

Regression equation for Time to Ignition is:

$$TTI = 77.5X_1 + 48.9X_2 + 66.8X_3 + 49.4X_4$$

MDH is the most influent, followed by CaB. The result points out the positive effect of this kind of fillers on TTI.

Regression equation for peak of Rate of Heat Release is:

$$pkRHR = 152.7X_1 + 99.9X_2 + 151.6X_3 + 364.6X_4$$

PDMS has the weakest contribution (positive effect on RHR). It could be due to the formation of a protective layer on the burning material together with MDH and CaB effect.

Search for optimal formulations

Common property: *stable residue*

Highest LOI value

Highest TTI and pkRHR value

Component	Unit	A (LOI_{opt})	B (CCT_{opt})
MDH	%	50.0	56.0
Sil	%	10.0	1.3
CaB	%	0	2.7
matrix	%	40.0	40.0
desirability		1.000	0.914

The optimal formulations show their compromise property when more than one parameter are optimized.

All the experimental results are are included in the specific 95% confidence interval.

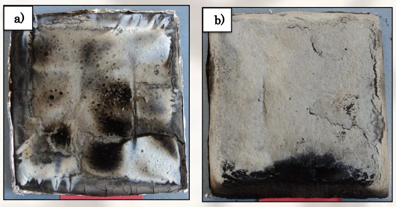

Fig. 5 – Cone calorimeter residues of (a) A-LOIopt and (b) B-CCTopt.

The best cone calorimeter performances are achieved by the formation of a homogeneous char compare to the brittle char of LOI optimal formulation.

Vertical burning tests

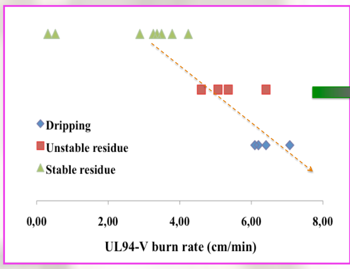

Fig. 4 – Correlation between the formulations residue behaviour during DIN 4102 test and the burn rate in UL94 vertical test.

DIN 4102 B2 test gives useful information about the burning material behaviour (*Dripping, Unstable residue and Stable residue*).

UL94-V burn rate (cm/min): a correlation between the UL94-V burn rate and the stability of burning material from DIN 4102 B2 has been found: slower burn rate corresponds to more stable residue.

Conclusion:

- No significant correlation is found among FR tests and most of the chosen FR parameters are described by models with very good quality.
- Statistical analysis on FR parameters reveals that Sil is the most influent component on LOI because of interaction coefficients, while in CCT most of the parameters are described by linear equations (no significant interactions).
- Optimal formulations with stable residue together with best LOI or CCT performance have been predicted and confirmed by experimental results.

References

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