The Optimization of the Smoke Suppressant and Flame Retardant Properties of Flexible PVC

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Synopsis

The combination of mixture diagrams and quality functions can be a straightforward and rapid method of simultaneously optimizing polymer formulations for both flame retardancy and smoke suppression. For a semirigid PVC formulation using a three-component additive mixture it was found possible to raise the limiting oxygen index by over 7 units, while simultaneously reducing smoke production by more than 20%.

INTRODUCTION

Metal oxides are widely used as either flame retardants (FR) or smoke suppressants (SS) for a wide range of combustible organic polymers. In a recent paper we reported the FR/SS effects for a range of inorganic and organometallic iron-containing compounds, including iron oxides, incorporated into a flexible PVC formulation.[1] Antimony and zinc oxides were also studied. Organoiron derivatives were found to possess both FR and SS properties, and ferrocene itself, for example, in a formulation at 1.0 phr (part per hundred of PVC) was found to raise the limiting oxygen index, LOI, by about 3 units while depressing smoke production, as measured by the U.S. National Bureau of Standards (NBS) test, by 28%, whereas the metal oxides studied tended to exhibit either FR or SS properties but not both. Of the iron-containing additives investigated, the oxides were the most effective smoke-suppressants, with an effectiveness similar to the commercial zinc/magnesium oxide preparation Ongard II, although the LOI enhancement (< 2 units) of both these additives is small. On the other hand, antimony (III) oxide is an excellent flame retardant, raising the LOI by 6.8 units at 5.0 phr, but with substantially increased smoke production (+40%). We report here the results of an investigation into the three-component additive system, antimony/iron/zinc oxides, which has used chemometric methods to identify synergic effects and to rapidly develop an optimum formulation for semirigid PVC which has both good SS and good FR properties.

Background Theory

Cullis et al. have extensively used triangular diagrams to represent the LOI response of three-component additive systems for cotton, polystyrene, polypropylene, high-density polyethylene, and an ABS copolymer.[2–7] By keeping

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the total additive level constant, each composition is represented by a point within the triangle, and a polynomial fit (typically fourth order with 15 coefficients) on the data obtained by carrying out measurements on up to 40 different formulations can be used to produce a contour representation, or response surface, of the results. The optimum formulation can then be determined from the position of the maximum in the diagram. Unfortunately the processing and testing of formulations is very time consuming, particularly so if it is desired to simultaneously optimize two parameters such as smoke reduction and flame retardancy. In one study response surfaces were determined for both LOI and smoke density data, but a simultaneous optimization was not carried out.[6] Accordingly, we have developed a more rapid approach based on mixture diagrams. Mixture diagrams have been used for the rapid optimization of three-component high-performance liquid chromatography solvent systems,[8] and the principle is illustrated in Figure 1. For a three-component system, if the response is assumed to be linear, seven coefficients are needed to describe changes in the LOI response

$$\Delta_{\mathrm{LOI}} = A_S W_S + A_F W_F + A_Z W_Z + A_{SF} W_S W_F + A_{SZ} W_S W_Z + A_{FZ} W_F W_Z + A_{SFZ} W_S W_F W_Z \quad (1)$$

where W_S, W_F and W_Z refer to the amounts of antimony, iron, and zinc oxide additives used. The first three coefficients, A_S, A_F and A_Z, describe the linear responses, while the other four coefficients describe the interactions between the additives. In principle only seven measurements are needed to determine all the coefficients, and the simplest approach is, keeping the total additive level constant, to carry out measurements on three single-component formulations, three two-component formulations and one three-component formulation as indicated in Figure 1. The system is then determined, and the coefficients can be used to predict responses for unknown formulations.

In this research we have simultaneously determined the coefficients describing the effect of the additives on smoke production by means of a similar relationship

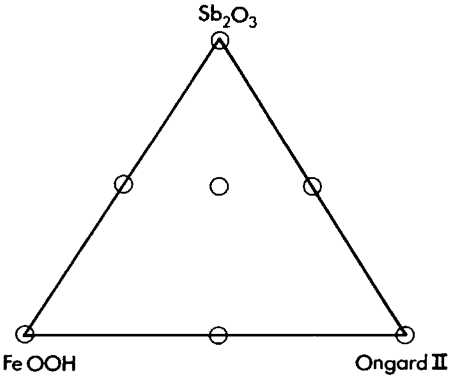

Fig. 1. A mixture diagram for the three-component additive system Sb_2O_3—FeOOH—Ongard II (ZnO). The circles indicate the seven formulations used.

$$\Delta_{\mathrm{NBS}} = B_S W_S + B_F W_F + B_Z W_Z + B_{SF} W_S W_F + B_{SZ} W_S W_Z + B_{FZ} W_F W_Z + B_{SFZ} W_S W_F W_Z \quad (2)$$

Again three coefficients are needed to describe the linear response and four coefficients to describe the interactions.

In order to simultaneously optimize both FR and SS properties, it is necessary to have some quality function, F, which combines both the changes in the NBS smoke density measurements, Δ_{NBS}, and the changes in the LOI response, Δ_{LOI}. Of the functions tested the relationship given by eq. (3)

$$F = \Delta_{\mathrm{LOI}}/\Delta_{\mathrm{LOI}}(\mathrm{max}) + \Delta_{\mathrm{NBS}}/\Delta_{\mathrm{NBS}}(\mathrm{max}) \quad (3)$$

was chosen for simplicity and robustness. By scaling LOI and NBS results to the maximum values obtained in the mixture experiments, equal weight is given to flame retardancy and to smoke suppression, and the function so obtained varies only slowly in the region of maximum response. It is relatively straightforward to write a computer program (or to modify an existing program such as may be found in Ref. 8) to determine the optimum value of F by choosing a suitable step length, say 0.2 phr, to calculate the predicted response for all formulations subject to the restriction of constant total additive level.

EXPERIMENTAL

Materials

A typical semirigid PVC cable formulation was used in this study comprising 100 phr Breon (BP PVC grade S110/10), 30 phr dioctyl phthalate plasticizer, 5 phr tribasic lead sulfate stabilizer, and 1 phr calcium stearate lubricant. The FR/SS additives—iron oxide FeOOH (Bayer-Bayferrox yellow 420), antimony (III) oxide (Anzon-Timinox Red Star) and Ongard II (Cookson ZnO/MgO complex) were all thoroughly powdered and sieved (less than 300 mesh) before compounding into the PVC on a two roll mill. Total additive levels of 5.0 phr were used.

Smoke and Flammability Measurements

Limiting Oxygen Index (LOI) values were determined according to ASTM D-2863-77 for self-supporting specimens (BS 2782 Part 1—method 141b) using the Stanton-Redcroft Flammability Apparatus.

NBS smoke values (ASTM E 662-79) were determined for 1 mm thick samples in the flaming mode using an Aminco Smoke Density Chamber. Values quoted are D_{max} corrected to 7 g of sample burned, averaged over at least two results.

RESULTS AND DISCUSSION

The seven formulations used, the changes in NBS and LOI values relative to an untreated sample of PVC, and the smoke reduction and flame retardancy

TABLE I
Formulations Used and Resulting Changes in Smoke Density Measurements and LOI Responses

W_S	W_F/phr	W_Z	$-\Delta_{NBS}$ (%)	Δ_{LOI}
5.0	0.0	0.0	−32	6.8
0.0	5.0	0.0	49	1.6
0.0	0.0	5.0	48	2.4
2.5	2.5	0.0	18	7.5
0.0	2.5	2.5	12	6.0
2.5	0.0	2.5	60	2.2
1.25	2.5	1.25	16	7.8

TABLE II
Derived Smoke Reduction and Flame Retardancy Coefficients

Smoke reduction coefficients		Flame retardancy coefficients	
A_S	−6.4	B_S	1.36
A_F	9.6	B_F	0.48
A_Z	9.8	B_Z	0.32
A_{SF}	0.64	B_{SF}	0.224
A_{SZ}	1.52	B_{SZ}	0.528
A_{FZ}	1.84	B_{FZ}	0.032
A_{SFZ}	−0.48	B_{SFZ}	0.262

TABLE III
Formulations Optimized for Flame Retardancy and/or Smoke Suppression

				Δ_{LOI}		$-\Delta_{NBS}$	
Formulation	W_S	W_F	W_Z	Pred.	Obs.	Pred.	Obs.
F1	1.6	1.6	1.8	6.9	7.2	36	22
F2	0.0	2.6	2.4	2.2	2.3	60	58
F3	3.2	0.4	1.4	8.1	7.0	5	25

coefficients derived using eqs. (1) and (2) are shown in Tables I and II. Evidence of synergicity between antimony and zinc oxides is evident from the large positive values of 1.52 and 0.528 respectively for the coefficients A_{SZ} and B_{SZ}. Zinc and iron oxides also show synergicity for smoke reduction.

In contrast to the over-determined approach used by Cullis et al.,[2] the present approach is much less time-consuming, but it is also more likely to be prone to errors, yielding results which may be misleading compared to a more comprehensive study. In some cases the optimum range of formulations may be very narrow, as has been found for polypropylene/Cerechlor 70/ferrocene mixtures.[6] This may not be a major limitation since the usefulness of such formulations is limited by their sensitivity to small variations in composition. Possible approaches to the assessment of the likely error are either to make several repetitive measurements for one formulation, or to assess the predictive validity of the derived coefficients. Since the aim of this investigation was to produce effective formulations, we have adopted the latter approach as being more useful, particularly as some of the assumptions of the model (such as linearity of response) can only be considered as of approximate validity.

Table III shows the predicted and observed results for three formulations. One formulation (*F*1) corresponds to the optimized value of the quality function *F* given in eq. (3), using the coefficients given in Table I, whereas formulations *F*2 and *F*3 correspond to formulations predicted to give good smoke suppression or good flame retardancy respectively. Agreement can be seen to be reasonable for this type of measurement, and in particular, it is observed that some very effective formulations are produced.

The effectiveness of these formulations is shown in Figure 2, which compares them with some of the results for the individual additives taken from ref. 1. Rather than the less informative plots of response against additive levels, the data is plotted as Δ_{NBS} vs Δ_{LOI}. In this way the clustering of the data for the different additives, and the effectiveness of the optimum formulation, even though not in exact agreement with the predicted value, are clearly evident. The differences between the observed and predicted values are difficult to interpret, reflecting a combination of experimental error and nonlinearity of response. This is an inevitable limitation of this approach, but it is important to emphasize that the main aim of the rapid development of an effective formulation can be readily achieved. It should also be pointed out that all the additives used in this formulation are relatively cheap. If one additive were expensive

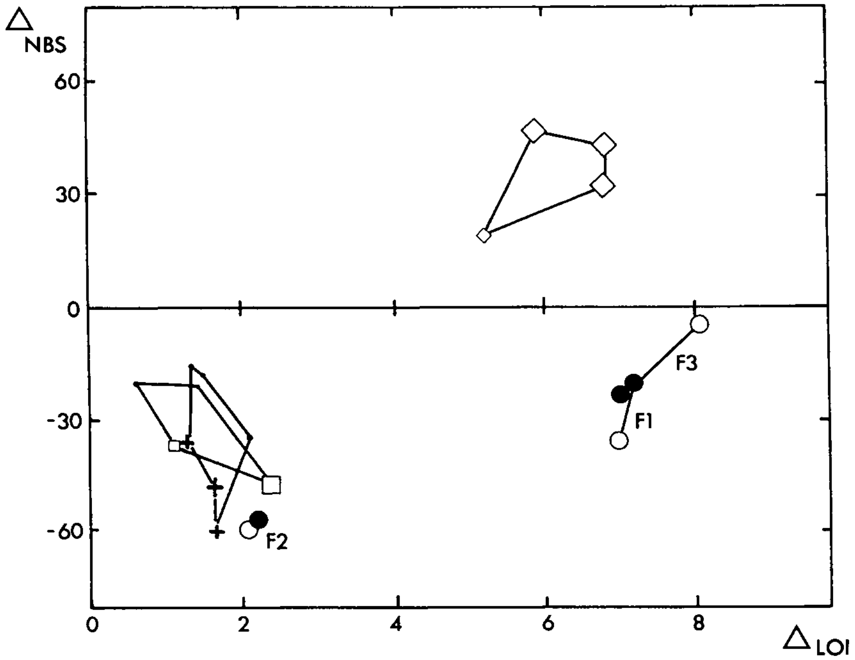

Fig. 2. Change in smoke density, Δ_{NBS}, plotted against change in limiting oxygen index, Δ_{LOI}. □: FeOOH; ◇: Sb_2O_3; and +: Ongard II. ○ – ● - predicted (○) and observed (●) values for the three-component mixture formulations F1–F3. Data for pure components are taken from ref. 1. The size of the data points is proportional to the amount of additive used. The maximum additive levels were 5 pph, while values of 1 pph or less are represented as dots.

then it would be relatively straightforward to modify the quality function F to include a weighting for relative costs.

In conclusion, the use of mixture diagrams together with a flame retardancy/smoke suppression quality function provides a straightforward and rapid optimization method for semirigid PVC additives to produce a formulation with very good flame resistance and low smoke evolution. Despite the apparent limitation of an assumed linear response, the predictions of the simple model used are both reasonable and useful. Although more precise information could be gained by using higher order polynomials to fit the data, the time required to prepare samples and make sufficient measurements can be prohibitive. An intermediate approach could be to use an extension of the present method to study a further range of formulations in the region of the predicted optimum in order to locate more precisely the position of the optimum and investigate its sensitivity to composition.

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