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Optimisation of the effect of colemanite as a new synergistic agent in an intumescent system

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Abstract

An intumescent system including ammonium polyphosphate (APP) as an acid source and blowing agent, pentaerythritol (PER) as a carbonific agent and colemanite as a synergistic agent is used to enhance flame retardancy of polypropylene (FR-PP). In order to investigate the synergism between colemanite and the flame retardant materials (APP and PER), D-optimal mixture design was employed. The limiting oxygen index (LOI) and amount of residue (AoR) were accepted as response 1 and response 2, respectively. Applying D-optimal strategy, 18 experiments were performed. Filler content was fixed at 30 wt% of total amounts of flame retardant PP composites. Constraints were determined according to the ratio of APP/PER ranging between 1 and 3. Statistical analysis of the cubic model revealed that lack of fit (LoF) was not significant for the cubic and linear model for both responses. The model suggested an optimum composite formulation with concentration levels 65% of APP, 28% of PER and 7% of colemanite that gives an LOI of 40.3. The experimental LOI and AoR of optimum formulation were achieved as 39.3 and 21.4 with 2.5% and 2.2% errors, respectively.

Keywords: Colemanite; Intumescent system; D-optimal mixture design; Polypropylene

1. Introduction

In recent years, polymeric composites are widely used in the production of new engineering materials. It is perceived as the reflection of technological development. Meanwhile the polymeric composites are promising, due to their economically versatile applicability and good mechanical properties. They are used in many applications, such as housing materials, transport and electrical engineering. Due to the increasing demands on polymers, the development of safe and environmental flame retarded polymers has great importance. Many types of flame retardants are added to polymers to reduce their flammability. Flame retardants are defined as chemical compounds that modify pyrolysis reactions of polymers or oxidation reactions implied in the combustion by slowing down or inhibiting them [1–4]. Many types of flame retardants are used in consumer products. They are mainly phosphorus, antimony, aluminium and boron-containing compounds, chlorides and bromides [5,6].

Borates (such as colemanite, ulexite, kernite, etc.) find a variety of applications in industry including glass, ceramics and detergents. Colemanite ($2CaO \cdot 3B_2O_3 \cdot 5H_2O$) is the most important calcium and boron containing commercial borate mineral with 5 mol crystal water. Borates are also used in manufacturing high-tensile strength glass fibre materials used in a range of products. Boron is important in many speciality glasses such as heat resistant domestic Pyrex glass and optical glass. Boron imparts a low thermal expansion level. Boron compounds are used as flame retardants where they reduce flammability by melting and preventing contact of oxygen with the burning surface. Sodium borates and boric acid are used in cellulose materials such as timber, particle board, paper, wood fibre, and cotton products. Anhydrous borax is used in the manufacture of flame retardant fibreboard.

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In plastics, zinc borate is the most widely used borate compound [7–11]. Presently, two or more flame retardants are used for obtaining synergism. A synergist may be defined as a case in which the effect of two components taken together is greater than the sum of their effects taken separately [12]. The addition of inorganic fillers (i.e. zeolite, clay, etc.) in thermoplastic polymers with combination of ammonium polyphosphate and pentaerythritol leads to a significant improvement in their fire retardant performance.

In this study, the aim was to investigate synergistic effect of colemanite on our intumescent flame retardant system and to develop flame retardancy of polypropylene. The intumescent flame retardant system was ammonium polyphosphate (APP) as an acid source and blowing agent, pentaerythritol (PER) as a carbonific compound and colemanite as a new synergistic agent. The formulations of flame retardant polypropylene matrix composite were prepared according to the 18-run D-optimal mixture design. The purpose was to find the best flame retardance performance of composites corresponding to limiting oxygen index (LOI) value and amount of residue after thermal treatment.

2. Theory

In mixture experiments, the factors are the components or ingredients of a mixture so their levels are not independent. This means that mixture factors are expressed as the fraction of total amount of their experimental ranges. In many mixture designs, there are restrictions on the component proportions x_i that prevent the experimenter from exploring the entire simplex region. These restrictions take the form of lower (L_i) and upper (U_i) constraints on the component proportions. The general form of the constrained mixture problem is:

$$\sum x_i = 1 \quad \text{and} \quad L_i \le x_i \le U_i \tag{1}$$

In this type of design where the components have both upper and lower bound constraints, the feasible region is no longer a simplex; instead, it will be an irregular polytope. D-optimal design procedure would be useful for this type of design since the experimental region is not of a standard shape. In these types of designs, it would be convenient to simplify the situation by introducing pseudo-components defined as:

$$x_i' = \frac{x_i - L_i}{\left(1 - \sum_{j=1}^{p} L_j\right)} \tag{2}$$

Therefore, pseudo-components allow the use of simplex type designs when lower bounds are employed in the experimental design.

D-optimal criterion selects design points from a list of candidate points so that the variances of the model regression coefficients are minimized. D-optimal design is a computer generated design, which maximizes the determinant of the $\mathbf{X}'\mathbf{X}$ matrix, where $\mathbf{X}$ is the extended design matrix. Geometrically, this corresponds to laying out mixture experiments so that as large an experimental region as possible is well mapped [13–16].

In mixture problems, the purpose of performing mixture experiments is to model the behaviour of the mixture in terms of a mathematical equation so that prediction of the response can be made empirically. There are linear, quadratic, special cubic and full cubic mixture models employed in mixture experiments. The mixture model assumed to be appropriate in this experimental design is the full cubic model that has the general form:

$$E(y) = \sum_{i=1}^{p} \beta_i x_i + \sum \sum_{i<j}^{p} \beta_{ij} x_i x_j + \sum \sum_{i<j}^{p} \delta_{ij} x_i x_j (x_i - x_j) + \sum \sum_{i<j<k} \sum \beta_{ijk} x_i x_j x_k \tag{3}$$

The first term represents the linear terms with coefficients β_i. The second quadratic term represents either synergistic or antagonistic effects or simply interactions. Higher order terms are necessary in mixture models because the phenomena studied may be complex. The full cubic model, which contains special cubic terms and coefficient at thirds of the edges, is selected since the purpose of the mixture design is the optimisation of the response. Response surface methodology is a collection of statistical methods that are useful for the modelling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimise this response [13–16].

In the literature, APP/PER/natural and synthetic zeolite intumescent systems in PP are studied and it is stated that intumescent material should be around 30 wt% to obtain satisfactory improvements in flame retardancy and the rest should be PP [17]. Therefore concentration of PP was kept constant at 70 wt% in the experimental design procedure. The remainder was used as the mixture design matrix for three components: X_1 (A), X_2 (B) and X_3 (C) designating APP, PER and colemanite, respectively. The constraints of these three input variables were selected in accordance with prior knowledge so that APP/PER ratio would be between 1 and 3. Another constraint was the amount of colemanite, which was adjusted so that total amount of colemanite would not exceed 5 wt% in the mixture. The constraints employed in terms of actual components can be seen in Table 1. APP/PER/colemanite formulation accounting for 30 wt% in the whole mixture was treated as 100% in the mixture design. These restrictions imposed on the mixture component proportions yielded an irregular polytope shape. The dependent variables are LOI and amount of residue (AoR) of formulations.

Table 1
Constraints for controllable input variables

Variable	Lower limit (wt%)	Upper limit (wt%)
X_1:A (APP)	0.42	0.75
X_2:B (PER)	0.21	0.50
X_3:C (colemanite)	0	0.17

3. Experimental

3.1. Materials

Colemanite having particle size below 50 μm was supplied by Eti Madencilik Co. Exolit 422 ammonium polyphosphate (APP) ($n > 1000$), having soluble fraction in water below 1%, and average particle size of 15 μm was supplied by Clariant. Pentaerythritol (PER) was supplied by Merck Co., and polypropylene (PP) MH 418 was supplied by PETKİM A.Ş. Design Expert 6.0 trial version software was used for analysing the D-optimal mixture design data.

3.2. Compounding

Polypropylene matrix composites were prepared by blending of PP pellets, flame retardant materials (APP and PER), and colemanite by using a Haake Polydrive mixer. Colemanite and APP were dried in an oven at 120 °C overnight. Samples were mixed at 60 rpm screw speed at 190 °C for 10 min. At first, polypropylene was melted at 190 °C in the plastograph for 2 min and then, colemanite, APP and PER, respectively, were added. Mixed materials were pressed with a Carver hot press at 190 °C and 100 bar, into sheets having dimensions of 15 × 15 × 0.3 cm. Composites were cut by bar shaped hollow die punch with dimensions of 125 × 6.5 × 3 mm for LOI test.

3.3. Limiting oxygen index test

A standard test method for measuring the minimum oxygen concentration to support candle-like composition of composites was constructed according to ASTM D-2863. The minimum concentration of oxygen in a mixture of oxygen and nitrogen flowing upward in a test column that support combustion was measured under equilibrium conditions of candle-like burning. The gas flow rate in the column was adjusted by a Cole Parmer flowmeter (A-3227-30) to 4 ± 1 cm/s.

Initial concentration of oxygen was determined arbitrarily. If the specimen burns rapidly, concentration of oxygen is reduced below the oxygen concentration of air. If the specimen does not burn at the selected concentration, concentration of oxygen is increased gradually.

3.4. Thermal analysis

TGA of composites were carried out using SETERAM Thermal Gravimetric Analyser from room temperature to 800 °C at a heating rate of 10 °C/min. Dry air was used as a carrier gas with a constant flow rate during analysis. Alumina pans were used for sample holder.

4. Results and discussion

4.1. Flammability test

Applying D-optimal strategy, the mixture design foresaw 18 experiments. In addition to 10 runs to fit the cubic model, 4 additional runs were performed for the estimation of lack of fit and 4 of these runs were replicated for the estimation of pure error. The program used the vertices, the edge centres, third of edges, interior points and the overall centroid as the candidate points and revealed the 18 run design as shown in Table 2.

Analysis of variance (ANOVA) could be useful for not only checking the adequacy of a regression model in terms of an LoF test, but also to estimate the magnitude of main and interaction terms by employing an F-test. The ANOVA table for the cubic model is shown in Table 3.

The overall model, individual mixture components and interaction terms were tested by means of F-test and significance. First, second and higher order terms are displayed on

Table 2
D-optimal design in terms of actual components

Std	Run	Type	Component 1 A:X_1 (APP) wt%	Component 2 B:X_2 (PER) wt%	Component 3 C:X_3 (colemanite) wt%	Response 1 LOI (%)	Response 2 AoR (%)
18	1	Vertex	0.75	0.25	0.00	32	22.01
16	2	Vertex	0.42	0.50	0.08	31	17.52
3	3	Vertex	0.75	0.25	0.00	32	17.40
4	4	Vertex	0.63	0.21	0.17	33	24.62
15	5	Vertex	0.50	0.50	0.00	28	15.97
13	6	AxialCB	0.60	0.28	0.12	38	24.26
1	7	Vertex	0.42	0.50	0.08	31	17.73
17	8	Vertex	0.42	0.42	0.17	29	15.69
10	9	Vertex	0.42	0.42	0.17	29	20.32
6	10	CentEdge	0.52	0.31	0.17	35	22.26
5	11	Interior	0.66	0.29	0.05	40.5	19.34
14	12	AxialCB	0.50	0.38	0.12	34	21.05
2	13	Interior	0.52	0.42	0.06	34.5	15.00
11	14	CentEdge	0.63	0.38	0.00	30	17.29
9	15	Vertex	0.50	0.50	0.00	29	14.86
7	16	Vertex	0.75	0.21	0.04	35	27.22
8	17	ThirdEdge	0.67	0.21	0.12	34	19.35
12	18	Center	0.58	0.35	0.08	38	17.90

Table 3
Analysis of variance of LOI response for mixture cubic model

Source	Sum of squares	DF	Mean square	F value	Prob > F	
Model	207.95	9	23.11	73.98	<0.0001	Significant
Linear mixture	65.09	2	32.55	104.21	<0.0001	
AB	1.01	1	1.01	1.04	0.0601	
AC	5.08	1	5.08	16.26	0.0038	
BC	1.05	1	1.05	18.99	0.0024	
ABC	16.08	1	16.08	51.49	<0.0001	
AB(A−B)	13.11	1	13.11	41.98	0.0002	
AC(A−C)	1.11	1	1.11	37.87	0.0003	
BC(B−C)	1.04	1	1.04	14.58	0.0051	
Residual	1.02	8	0.31			
Lack of fit	2	4	0.5	4	0.1041	Not significant
Pure error	0.5	4	0.13			
Cor total	210.44	17				

the ANOVA table in Table 3. Overall model is also defined as significant with a P value less than 0.0001. Terms with a P value greater than 0.1 were discarded from the model. The LoF stands for error terms due to discarded and disregarded parameters which may affect the overall model. Therefore, the LoF value is desired to be insignificant. For this system, the LoF for the cubic model was found insignificant ($P > 0.05$). The interactions of A and B with C were significant. F value of AB which indicates interactions among APP and PER is not significant. However, since the P value of AB (0.0601) is not so far from 0.05, this term can be added in the model equation. The colemanite interacted with APP and PER individually according to lower P value of AC and BC. The synergism between colemanite and flame retardant additives was proved by the P value of ABC which is smaller than 0.0001, indicating that there is interaction between them. The LOI is defined as:

$$\begin{aligned}\mathrm{LOI} = {} & 28.39\mathrm{A} + 36.73\mathrm{B} + 151.65\mathrm{C} - 11.30\mathrm{AB} - 227.49\mathrm{AC} \\ & - 253.32\mathrm{BC} + 505.60\mathrm{ABC} + 47.37\mathrm{AB}(\mathrm{A}-\mathrm{B}) \\ & + 205.61\mathrm{AC}(\mathrm{A}-\mathrm{C}) + 132.31\mathrm{BC}(\mathrm{B}-\mathrm{C}) \end{aligned} \tag{4}$$

in terms of pseudo-components and

$$\begin{aligned}\mathrm{LOI} = {} & -52.82642\mathrm{A} + 430.15715\mathrm{B} + 5139.25078\mathrm{C} \\ & - 641.18178\mathrm{AB} - 8816.65894\mathrm{AC} - 9354.93885\mathrm{BC} \\ & + 9579.97964\mathrm{ABC} + 897.51909\mathrm{AB}(\mathrm{A}-\mathrm{B}) \\ & + 3895.89557\mathrm{AC}(\mathrm{A}-\mathrm{C}) + 2506.91659\mathrm{BC}(\mathrm{B}-\mathrm{C}) \end{aligned} \tag{5}$$

in terms of actual components.

Several R-squared statistics were computed to validate the model. The R-squared coefficient of determination and adjusted R-squared of the cubic model were 0.9881 and 0.9748, respectively. The R-squared statistics measures the proportion of total variability explained by the model. The adjusted R-squared term, on the other hand, reflects the impact of increasing and decreasing the number of model terms. In other words, adjusted R-squared may not increase with the addition of insignificant terms whereas R-squared statistic does. Close values of R-squared and adjusted R-squared are desirable as observed in this particular case. The prediction error sum of squares (PRESS) statistic is a measure of how well the model will predict new data. A low value of PRESS indicates that the model is likely to be a good predictor. The value of PRESS of cubic model was 23.09 and total sum of squares was 19 746.5. Thus, The predictive capacity of the regression model was calculated as 0.9988 according to Eq. (6). Therefore, we could expect this model to explain about 99.88% of variability in predicting new observation. The prediction R-squared, which explains the variability that the model would predict in a new data set, is 0.89. All R-squared values revealed satisfactory results in terms of quality of experimental data and the model.

$$R^2_{\mathrm{prediction}} = 1 - \frac{\mathrm{PRESS}}{\mathrm{SS}_T} \tag{6}$$

"Adeq Precision" measures the signal to noise ratio. A ratio of 27.578 indicates an adequate signal since a ratio greater than 4 is desirable. Design expert facilitates adequacy of the model by providing normal probability plots, plots of residuals versus fitted data and outliers. Fig. 1 is the normal probability plot of residuals and resembles a straight line since the underlying error distribution is normal. This means that normality assumption is valid for the proposed model. Residuals intensified in the middle of straight line indicated that data distributes normally. There is no significant deviation from the straight line which could also be accepted as an indicator of outliers. Fig. 2 is the plot of residuals versus predicted values testing the assumption of constant variance regardless of the size of the response. The residuals should be structureless not revealing any obvious pattern. The results of the residuals are structureless proving the assumption of homogeneity of variances. Fig. 3 could also be used to estimate outliers considered to have a value above 3 or below −3.

Fig. 4 illustrates the trace plot of LOI for flame retardant system which indicates how the response changes with the proportion of each component while keeping all the others

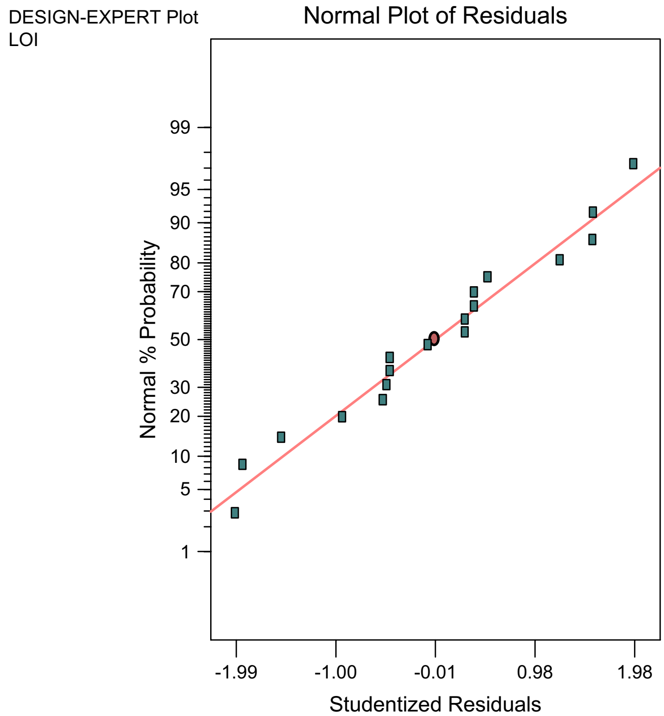

Fig. 1. Normal probability versus studentized residuals for checking normality of residuals of LOI.

constant. The graph indicates that increment in proportion of APP improves LOI of flame retardant composites until the critical level. However, decrease of the proportion of colemanite and PER improves the LOI values of flame retardant composites.

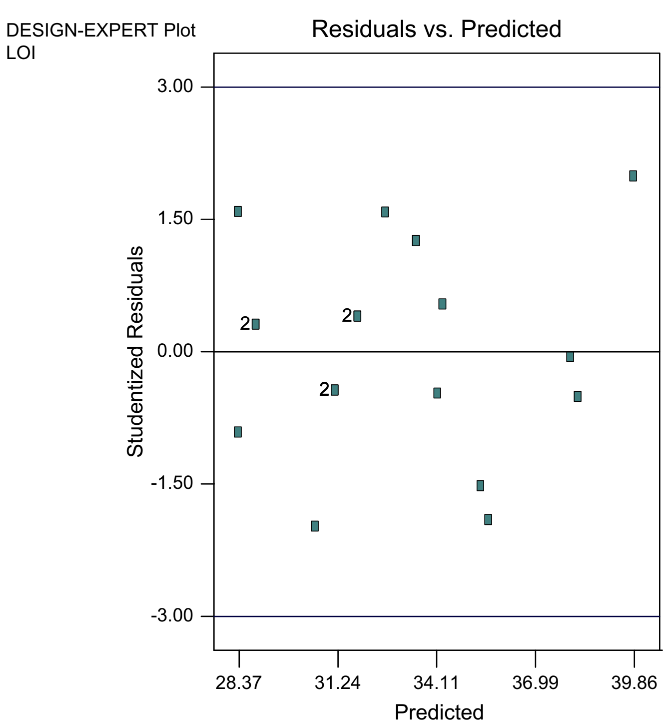

Fig. 2. Studentized residuals versus predicted values for checking constant error.

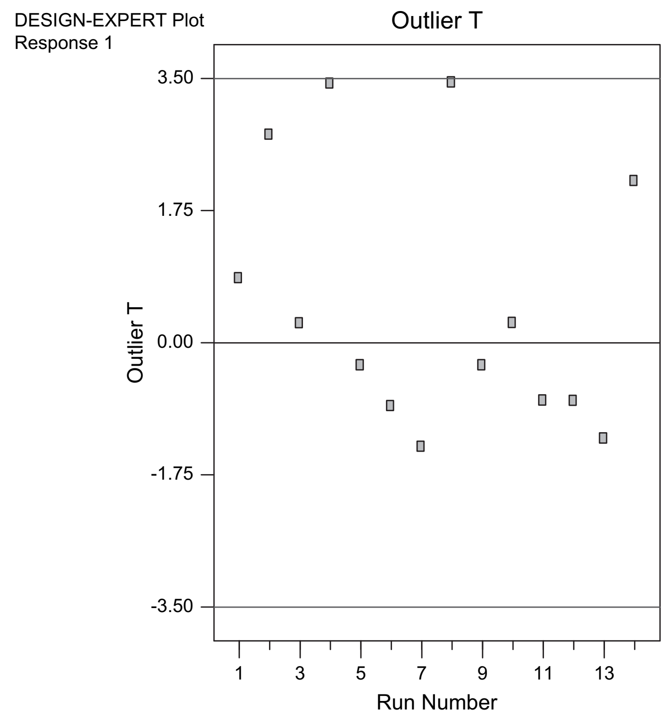

Fig. 3. Outlier *t* versus run order for looking outliers of LOI response.

Contour plot of limiting oxygen index response is shown in Fig. 5 in order to understand the influence of ingredients on response and the interaction amongst them. The feasible region for this study is the unshaded region that covers maximum LOI responses. A peak which is provided by maximum LOI values is near the edge of APP. Therefore Fig. 5 indicates that the amount of APP has an important role in the improvement of flame retardancy performance of

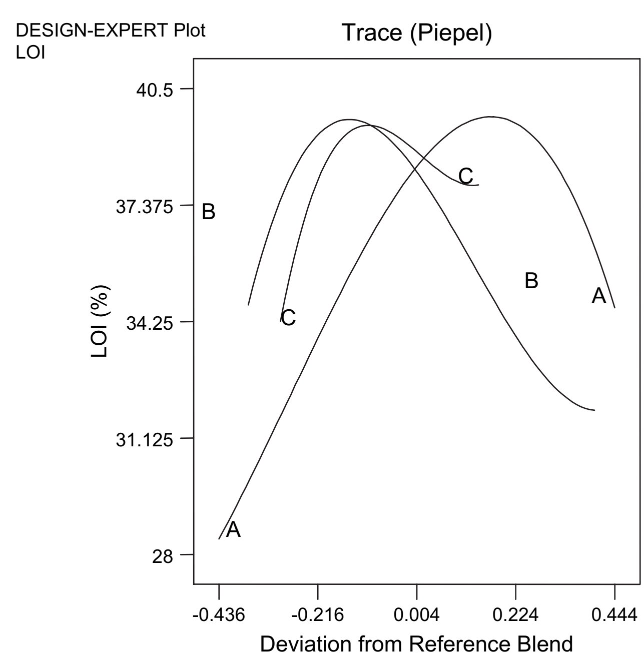

Fig. 4. Trace plot for LOI of intumescent flame retardant system.

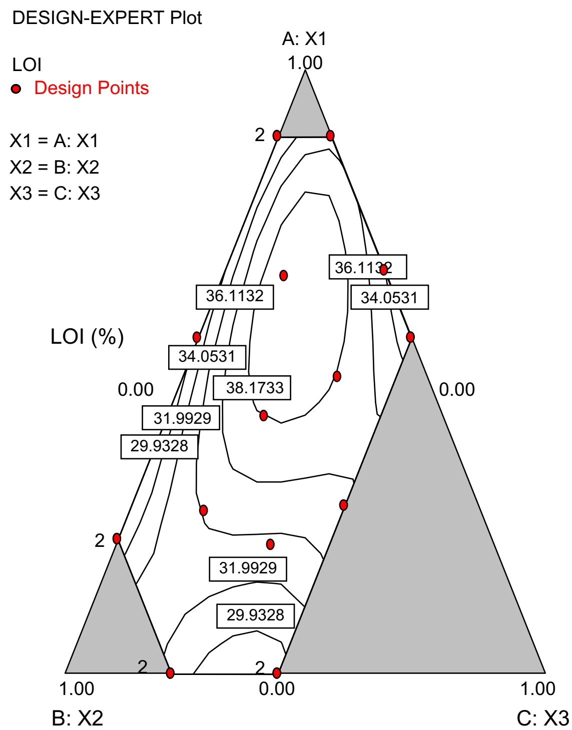

Fig. 5. Contour plot of LOI response.

composite. On the contrary, any increment in the concentration of colemanite and pentaerythritol in formulation decreases the response drastically. The three-dimensional response surface is plotted to find out the optimum combination of ingredients for maximum LOI values. Hill shape is clearly observed in Fig. 6. The model suggested the optimum LOI is achieved as 40.28 at 65% of APP, 28% of PER and 7% of colemanite with the desirability of 0.983. An experiment

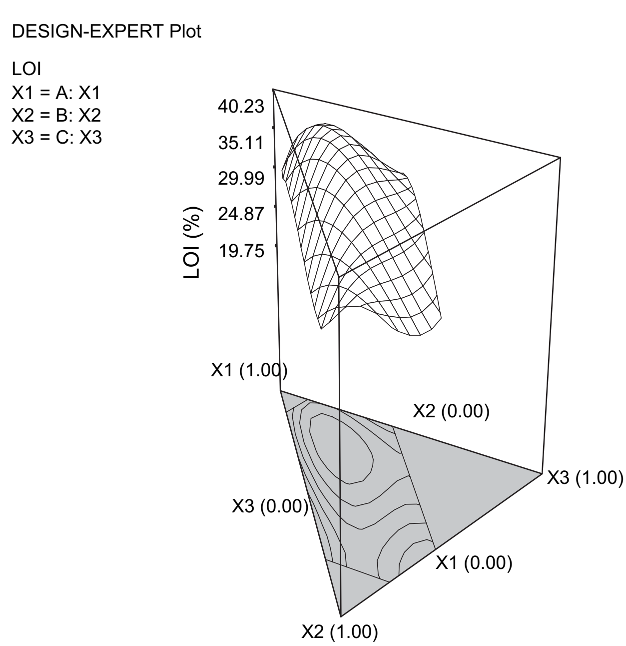

Fig. 6. Response surface plot of LOI response.

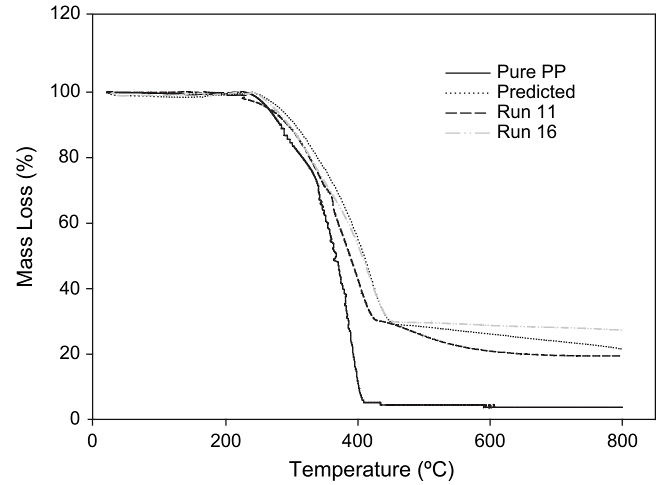

Fig. 7. TGA thermograms of composites and pure PP.

conducted with the suggested formulation found out the LOI value of 39.33 which was very close to the estimated LOI value (40.28).

4.2. Thermogravimetric analysis

Fig. 7 illustrates the TGA thermograms of some composites representing the rest of composites. The thermograms of flame retarded composites shifted through the higher temperature according to pure PP. The amount of residue of composites was higher than that of the pure PP.

The ANOVA table for the thermal gravimetric analysis of composites is given in Table 4. In this case linear mixture components are significant model terms. The individual mixture components affected the thermal behaviour of composite without any interaction between them. The LoF was not significant for the linear model (P-value $\gg$ 0.05). The final linear mixture model equation for response 2 (amount of residue, AoR) was

$$AoR = 26.50A + 3.71B + 38.71C \quad (7)$$

in terms of actual-components and

$$AoR = 21.71A + 13.28B + 26.23C \quad (8)$$

in terms of pseudo-components.

Table 4
Analysis of variance of AoR response for mixture linear model

Source	Sum of squares	DF	Mean of square	F value	Prob > F	
Model	119.43	2	59.72	9.34	0.0023	Significant
Linear mixture	119.43	2	59.72	9.34	0.0023	
Residual	95.87	15	6.39			
Lack of fit	74.11	11	6.74	1.24	0.4544	Not significant
Pure error	21.77	4	5.44			
Cor total	215.30	17				

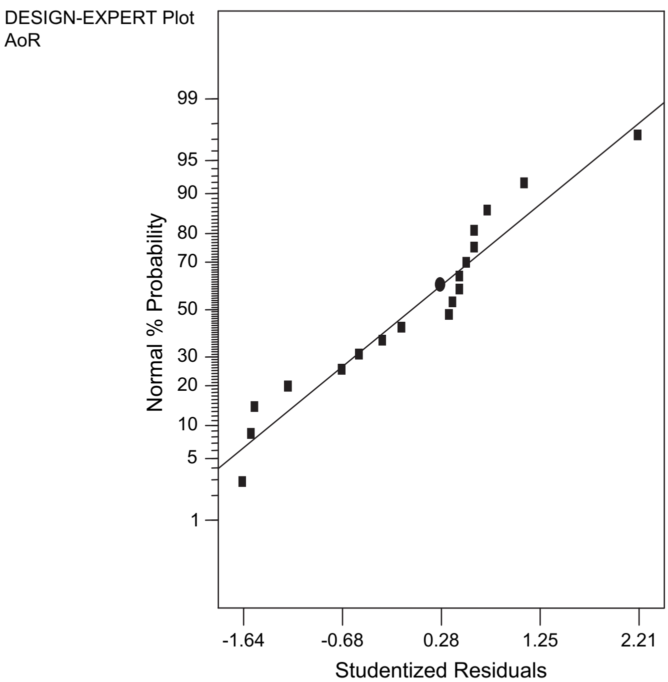

Fig. 8. Normal probability plot of residuals of AoR response.

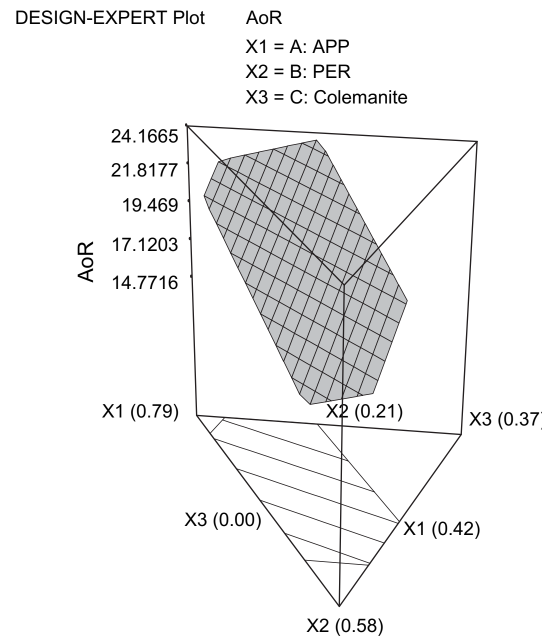

Fig. 10. Three-dimensional response surface plot of AoR response.

R-squared and adjusted *R*-squared values of model were 0.5547 and 0.4953, respectively. Although, the adjusted *R*-squared value was 0.4953, it was in reasonable range.

Normal plot of residuals is shown in Fig. 8. On normal probability plots, residuals accumulated in the middle of straight line. There are more data on the left end of straight line than the right end of line. This means data illustrate left skewed distribution. The plot of outlier *t* versus run order is shown in Fig. 9. There are no any outlier data between −3 and 3 values. The structureless and random distribution with discernible pattern also reveals that the test does not depend on the time and constant variance was provided.

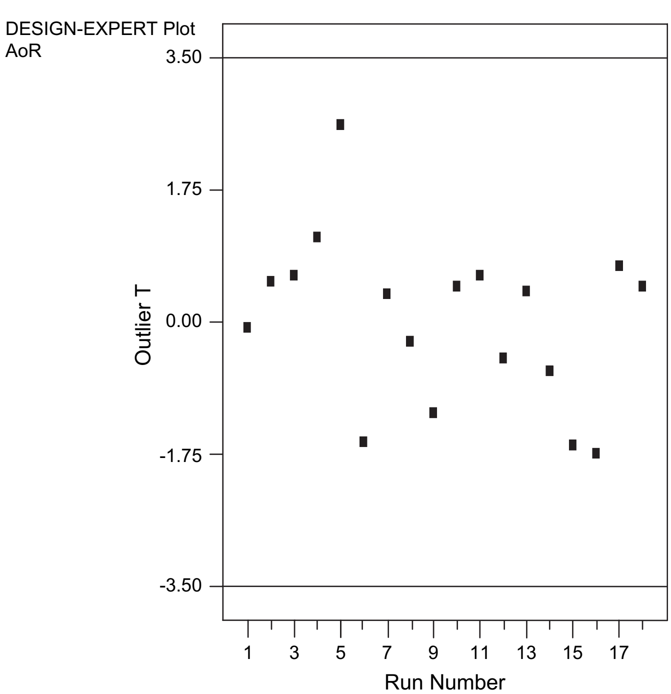

Fig. 9. Outlier *t* versus run order for looking outliers of AoR.

The three-dimensional surface plot of the amount of residue response is shown in Fig. 10. The response of AoR depends on directly thermal degradation behaviour of components. Minerals such as colemanite do not lose big parts of mass during thermal treating. The increment concentration of APP in formulation also causes to increase the AoR. Since the AoR model does not have any quadratic or interaction terms, the three-dimensional surface plot is a flat response surface. This situation was expected for this intumescent formulation, since the main flame retardant additive was APP and other components were only co-additives.

5. Conclusion

D-optimal mixture design indicated that combination of colemanite, APP and PER affected the LOI values as well as flammability of polypropylene matrix composites. Adjusted *R*-squared value revealed that the overall model would explain new data 97.5% confidently. Model adequacy also indicated that outlier was not observed and homogeneity of variances was satisfied. The interactions of APP and PER with colemanite are also significant. The interactions of APP and PER with colemanite individually are not as much as the interaction of three of them together. This is an evidence for synergism between colemanite and flame retardant additives.

D-optimal mixture design suggested a linear model according to AoR of composites after thermal processing with 0.0023 *P* value. In fact, a linear relation between components indicated which component actually affects the degradation of composites during heating. The regression model equation also includes the dominant components on flame retardancy of composite which were APP and colemanite. These components acted as inhibitor and reinforced the composite structure during degradation process.

Colemanite decomposes to CaO and B_2O_3 at 600 °C. Borax (B_2O_3), which is widely used in the glass industry, is incorporated in order to improve thermal resistance of glass. In this study, our results indicated that colemanite showed promise as a new synergistic agent with interacting flame retardant additives. It may be concluded that when heat is applied to the composites, colemanite decomposes to CaO and B_2O_3 which can react with flame retardants or form a thermally resistant layer on the surface of composites. In order to explain the role of colemanite in the mixture, X-ray photoelectron spectroscopy (XPS) and NMR analysis should also be performed.

The optimum flame retarded polypropylene matrix composites were determined according to LOI response. The cubic model suggested the optimum LOI as 40.3 for concentration of APP at 65%, PER at 28% and colemanite at 7%. The suggested combination provided 39.3 LOI with a 2.5% error. AoR of optimum formulation was calculated as 20.9 by using regression equation for actual components. Experimental AoR at the optimum formulation was achieved as 21.4.

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