Fire retardancy enhancement of unsaturated polyester polymer resin filled with nano and micro particulate oxide additives

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Abstract. In the last years the traditional construction materials, such as wood, glass and steel, have been increasingly replaced by polymer composite materials due to their superior properties. However, this feature has also raised buildings' combustibility fire hazards. Polymer modification with inorganic nanoparticles can be a potential and efficient solution to control matrix flammability without sacrificing other important properties. In this study a new type of unsaturated polyester based composite materials with enhanced fire retardancy are developed, through polymer modification with nano/micro oxide particles and common flame retardants systems. For this purpose, the design of experiments based on Taguchi methodology and analyses of variance were applied. Samples with different material contents and processing parameters resultant from the L9 Taguchi orthogonal array were produced, and their fire properties assessed and quantified by single-flame source and vertical flammability tests. It was found that material and processing parameters have different effects on different properties. Unsaturated polyester composites modified with nano and micro oxide particles showed better fire performance compared to the neat composite improving at least one fire property whatever the nature of the filler. More thorough studies are required in order to improve mix design formulations towards further fire retardancy enhancement.

1. Introduction

Unsaturated polyester composites (UPC) are increasingly replacing traditional materials like wood, glass and metal, in building, furniture, machinery and vehicle components, as well as in other consumer products. However, UPCs are vey susceptible to high temperatures and behave poorly in fire situations [1-3]. This increasing use UPCs and other polymer composite materials has led to a rise of the fire load in buildings resulting in increasing fire hazards. According to statistical data, these materials have contributed to an exponential decrease of 'escape-time' from 17 minutes, in 1977, to 3 minutes, in 2007 [4].

The use of fireproof resins or the incorporation of flame retardant (FR) systems in a polymer matrix partially improves the fire behaviour of composite materials to some extent; however, these solutions usually lead to a reduction in mechanical properties and have a detrimental effect on composite workability and processing [5]. Due to both high specific surface area and reduced dimension, nanomaterials (NM) reduce the mobility of polymer chains, leading to significant changes on volume,

surface and functional properties. Unusual property combinations can be achieved, resulting in a new class of materials for almost every application. Previous research revealed that polymer nanocomposites, with homogeneous nanoparticles dispersion, present improved characteristics over unfilled or micro-filled polymers. Depending on the polymer and nanoparticle nature and content, the main improvements are found in mechanical properties (*e.g.*, toughness and stiffness), and barrier properties such as permeability and solvent resistance. Other interesting results include increased thermal stability and, mainly, the improved ability to promote flame retardancy at very low content levels [6-11]. Therefore, UPC modification with NM can be a potential and effective solution to control flammability of polymers, without significant negative effect on other properties.

As early as the 60's nanosized particles have been investigated for fire retardancy and thermal stability purposes of polymer composites [12]. However, it was after Toyota researchers [13-14] found that the addition of clay to polyamide-6 led to superior mechanical properties and substantial increases on heat distortional temperature that this research subject received significant attention. An exhaustive review of the state of the art in this field can be found in Morgan and Wilkie [7]. The main findings, summarized in the book, as well as ongoing research, clearly show that nanoparticles are in fact the basis for improved FR systems. The majority of research work on the subject of thermal stability and fire retardancy of polymers has been carried out on polymer-clay nanocomposites. Other emerging nanoparticles which have also shown promising effects on polymer thermal degradation are nano-oxides. Most of the few studies focused on this issue show promising results, attesting that nano-oxides incorporation can improve thermal stability and other relevant properties of the final product [10, 15-21]. Synergetic effects between metal nanoparticles, including nano-oxides, and conventional FR additives have also been reported [5, 22-25], and this approach appears to be very promising towards an effective improvement in the flame retardancy of UPCs.

Under this framework, the present study is an effort to develop a new UPC material with improved fire reaction behaviour, through matrix modification with hybrid flame retardant systems based on nano-oxides (alumina and magnesium hydroxide), micro-oxides (silica) and phosphinates. Experiments were planned and conducted according to Taguchi methodology with basis on the L9 Taguchi orthogonal array, with 4 material/processing parameters at three variation levels. Fire reaction properties were analysed and quantified by single-flame source and vertical flammability tests.

2. Materials and methods

2.1. Raw materials and UPC manufacturing

A commercially available unsaturated polyester resin, with trade name Aropol® FS3992 (Ashland Chemical Hispania S.L., Spain) was used as matrix. Physical and mechanical properties of the cured resin, as supplied by the manufacturer, are displayed in table 1.

Table 1. Physical and mechanical properties of cured resin

Property	Method	Values
Heat distortion temperature (°C)	ASTM D 648	90-100
Water absorption (%)	ASTM D 570	0.2
Tensile strength (MPa)	ASTM D 638	50-70
Flexural strength (MPa)	ASTM D790	90-110
Barcol hardness (-)	ASTM D 2583	45
Ultimate elongation (%)	ASTM D 638	3

The phosphinate based flame retardant was Exolit® OP 1240 (Clariant-Químicos, Lda., Portugal) which consists of a fine white grain-based organic phosphonate powder having high phosphorus content. The silica sub-microparticles (SiO_2, 98% purity) were provided by Innovnano (Portugal). The NanoDur® (Al_2O_3, 99.5% purity, Alfa Aesar®) alumina nanoparticles were purchased from Cymit Quimica S.L. (Spain), and magnesium hydroxide nanoparticles (Mg $(OH)_2$, 99% purity) were supplied

by NanoAmor® (USA). All fillers have spherical shape, and some of their physical properties are specified in table 2.

Table 2. Physical characteristics of fillers.

Filler	Specific surface area (m^2/g)	Specific gravity (g/cm^3)	Average particle size (nm)
Al2O3	36	3.60	45
Mg(OH)2	80	2.36	15
SiO2	64	2.69	437
Exolit OP1240	-	1.35	25000-50000

A well determined quantity of filler was manually pre-mixed with the unsaturated polyester resin and accelerator (0.5 wt. %) for a few minutes at room temperature. The mixing process was then completed by ultrasonication (0.5s on/0.5s off) for several minutes. The initiator (1.0 wt. %) was then added and mixed. All the mixtures were poured into a preheated mould (1 h/80ºC) and the samples were then allowed to cure (6 h/80ºC). After de-moulding they were subject to an additional thermal treatment (3 h/80ºC).

2.2. Trial formulations

The design of experiments (DoE) based on a Taguchi methodology was applied to the experiments plan. DoE is an approach for systematically varying the controllable input factors and observing the effects of these factors on the output product parameters. Using Taguchi methodology, the same information provided by an experience plan based on full factorial method can be assessed but with the advantage of requiring smaller number of experiments. This method can also identify the factors and possible interactions between factors that most influence the response, using analyses of variance (ANOVA) [26, 27]. The main objective is to determine the optimal formulations of UPCs modified with nano/micro oxides and phosphinates that result in the best fire reaction properties. In this study the selected control material and processing factors were: type of oxide particle (A) and content (B), phosphinate FR content (C) and total sonication time (D). Each of these factors was run at three variation levels as shown in table 3. The 4^3 full factorial design (4 factors at 3 variations levels) leads to 64 different experiments; however, using a suitable Taguchi orthogonal array, the experimental plan dimension can be significantly reduced. In the present case the L9 orthogonal array was selected, which results in 9 different experiments. The resultant trial formulations are specified in table 4.

Table 3. Design factors and levels.

Levels	Factor A	Factor B (wt%)	Factor C (wt%)	Factor D (min)
1	$Mg(OH)_2$	0.0	0.0	3
2	Al_2O_3	2.5	10.0	15
3	SiO_2	5.0	15.0	9

Table 4. Trial formulations resultant from L9 Taguchi array.

Trials	Factor A	Factor B	Factor C	Factor D
F1	$Mg(OH)_2$	0.0	0.0	3
F2	$Mg(OH)_2$	2.5	10.0	15
F3	$Mg(OH)_2$	5.0	15.0	9
F4	Al_2O_3	0.0	10.0	9
F5	Al_2O_3	2.5	15.0	3
F6	Al_2O_3	5.0	0.0	15
F7	SiO_2	0.0	15.0	15
F8	SiO_2	2.5	0.0	9
F9	SiO_2	5.0	10.0	3

2.3 Fire characterization tests

After UPCs preparation according to trial formulations defined in table 4, the fire properties were assessed by the single-flame source and vertical UL-94 flammability tests performed on two and five specimens, respectively, of each formulation. All specimens were pre-conditioned for 48 hours at 23 °C/50 % RH before being tested.

2.3.1 Single-flame source test. In the single-flame source test carried out according to ISO 11925-2 standard test [28], two test specimens ($250x90x10mm^3$) were subjected to direct action of a small flame for 30 s on the bottom edge (figure 1). The maximum test duration was 1 minute (60 seconds) after flame removal. The classification criteria were based on observations of whether the flame spread reached the 150 mm length marker on the specimen within a given time, and if the filter paper below the specimen ignited due to flaming debris.

2.3.2 UL94-Vertical flammability test. The UL94 (Underwriters Laboratories, USA) test allows the determination of plastics flammability characteristics [29]. The standard classifies plastics according to their burning behaviour in different orientations (horizontal or vertical burning tests) and thicknesses. The vertical method was used in this study. The specimens ($125 \times 13 \times 5$ mm^3) were supported vertically and a flame was applied to the bottom of the specimen (figure 2). The flame was applied for 10 s and then removed until flaming stops, at which time the flame was reapplied for another 10 s and then again removed. On the basis of overall results for a sample of five specimens, materials can be classified as V-0, V-1, V-2 or unrated (U).

Figure 1. ULC specimen (Trial 1) during single-flame source test.

Figure 2. ULC specimen (Trial 4) during vertical UL-94 flammability test.

3. Results and discussion

3.1. Data test results

The single-flame source test results (*i.e.*, ignition time -IT_{SF}-, total length of specimen material destroyed –MD,- and total time of the test –TT-), and the vertical UL-94 test results (*i.e.*, ignition time – IT_{UL} -, after flame times -T_1, T_2-, and correspondent UL 94 classification) are presented in table 5 and 6, respectively. Presented values are average values obtained for two and five specimens and respective standard deviations (when applicable).

Globally, as shown in tables 5 and 6, filler addition improved at least one fire response parameter when compared to unfilled formulation F1, either by increasing the time to ignition (IT_{SF} or IT_{SF}), or decreasing both total length of specimen material destroyed (MD) and combustion times (TT or T_1 and T_2). Trial formulations F5 and F7 showed particularly significant improvements, with much lower combustion times, which led to a V-1 classification for the vertical UL94 test.

Table 5. Single-flame source test results.

Trials	IT_{SF} (s)	MD (mm)	TT (s)
F1	1.0±0.0	16.3±11.3	60.0± 0.0
F2	2.0±0.0	24.5± 7.8	60.0± 0.0
F3	1.0±0.0	10.5±12.0	42.5±24.7
F4	2.5±0.0	14.0± 7.1	41.0± 2.8
F5	1.5±0.0	17.0± 1.4	45.0±12.7
F6	2.0±0.0	19.0± 0.0	60.0± 0.0
F7	2.0±0.7	4.0± 0.0	40.0± 0.0
F8	1.5±0.0	25.5± 4.9	60.0± 0.0
F9	2.5±0.7	11.0± 1.4	60.0± 0.0

Table 6. Vertical UL-94 test results.

Trials	IT_{UL} (s)	T_1 (s)	T_2 (s)	Class
F1	2.0±0.0	281.0±24.4	-	U
F2	3.4±0.3	18.6± 4.6	39.2±23.8	U
F3	2.6±0.4	43.0± 4.2	35.5±27.5	U
F4	2.2±0.4	51.0±30.4	23.0±27.7	U
F5	2.0±0.0	2.2± 2.6	29.5±18.0	V-1
F6	2.5±0.9	333.2±46.3	-	U
F7	2.0±0.7	2.8± 2.2	15.0±21.5	V-1
F8	1.9±0.1	229.0±23.2	-	U
F9	2.5±0.2	56.6±29.7	120.0±20.0	U

3.2. Data treatment and analysis of results

The Taguchi method uses ANOVA to analyse data obtained from implementation of the experimental design. The ANOVA performs the overall variance analysis of a sample set, identifying its origins and assessing the contribution of each variable or factor to the global dispersion.

The various parameters obtained from both single-flame source and vertical UL-94 fire tests can be submitted to statistical treatment with two exceptions: T_2 and TT parameters. During the UL-94 test, great part of the specimens were not submitted to the 2nd flame application because they burned completely during and/or after removal of the 1st flame; on the other hand, in the single-flame source test, the total combustion time computed for F1, F2, F6, F8 and F9 corresponded to the maximum time allowed for this test (60 s). Hence, the parameters submitted to statistical treatment were limited to both ignition times (IT_{SF} and IT_{UL}), 1st after flame time (T_1), and total length of material destroyed (MD).

The results of the analyses of variance for the aforementioned parameters are presented in tables 7 and 8. The results are detailed in terms of sum of squares (SQ), degrees of freedom (dF) quadratic mean deviation (QMD), F-ratio (F_{rat}) and percent contribution to global variation (P). All analyses were performed for a significance level (α) of 5% (or a confidence level of 95%). For this level of significance, the F-test ratio critical value (F_c) is 3.26 for all 4 factors under study.

Response graphics regarding the main effects of each factor on the analysed fire properties are displayed in figure 3.

Table 7. Analyses of variance of single-flame source test results (IT_{SF} and MD).

	Variation Source	SQ	dF	QMD	F_{rat}	P (%)
IT_{SF}	A	1.778	2	0.889	4.00	18.8
	B	0.111	2	0.056	0.25	Rej.
	C	2.778	2	1.389	6.25	32.8
	D	0.444	2	0.222	1.00	Rej.
	Er	2.000	9	0.222		53.3[a]
	Tot	7.111	17			100.0
MD	A	63	2	32.8	0.69	Rej.
	B	382	2	190.9	4.17	23.6
	C	353	2	176.7	3.86	21.3
	D	19	2	9.6	0.21	Rej.
	Er	412	9	45.8		63.3[a]
	Tot	1130	17			100.0

Table 8. Analyses of variance of vertical UL-94 flammability test results (IT_{UL} and T_1).

	Variation Source	SQ	dF	QMD	F_{rat}	P (%)
IT_{UL}	A	0.470	2	0.235	1.27	Rej.
	B	0.226	2	0.113	0.61	Rej.
	C	1.448	2	0.724	3.93	10.0
	D	2.072	2	1.036	5.62	15.7
	Er	6.636	36	0.184		74.7[a]
	Tot	10.852	44			100.0
T_1	A	123157	2	61579	19.5	16.0
	B	68526	2	34263	10.8	8.5
	C	396093	2	198046	62.7	53.5
	D	27214	2	13607	4.3	2.9
	Er	113763	36	3160		19.1[a]
	Tot	728752	44			100.0

[a] Residual error computed as 100% minus the sum of percent contributions relative to all factors (A, B, C and D).
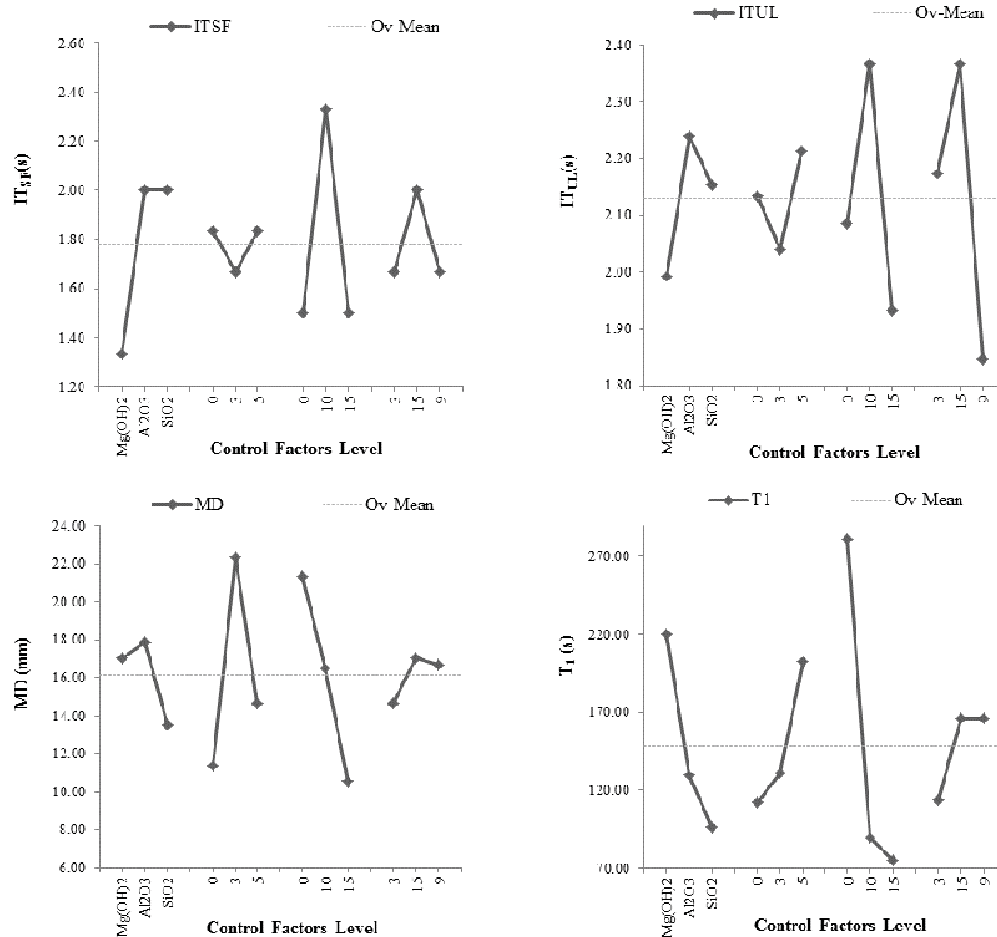
Figure 3. Main effects of material factors on fire reaction properties: time to ignition (IT_{SF} and IT_{UL}), total length of material destroyed (MD) and 1st after flame time (T_1).

As shown in tables 7 and 8, different effects with different relative weights were found for each material factor on the global variation of fire properties under study. The major outputs can be summarized as follows:

a) The oxide particle content (Factor B), for a confidence level of 95%, has no significant statistical effect on global variation of times to ignition regardless of the used fire test. Concerning this target response (*i.e.*, the time to ignition) the null hypothesis is also rejected for the type of oxide particle (Factor A) when the UL-94 flammability test is used. The type of oxide particle, as well as the sonication time (Factor D), have also no relevant effect on how fast the material is destroyed (MD) by fire.

b) Overall based on ANOVA results, it can be stated that the factor with the lowest effect on the analysed fire properties is sonication time (Factor D) whereas the most influential factor is the content of phosphorous based FR (Factor C). For a significance level of 5%, the null hypothesis was rejected for Factor D as regard to MD and IT_{SF} target responses, and the same factor also presented a minor effect (2.9%) on global variation of combustion time (T_1 – UL 94). Although a relatively high value of percent contribution is found for this factor on global variation of IT_{UL} (15%), the high variation due to random error associated to this specific set of experiments (75%) prevents a definite conclusion. On

the other hand, Factor C presented the highest percent contributions to global variations of IT_{SF} and T_1 (32.8% and 53.5%, respectively) and it is the second factor with higher influence on IT_{UL} and MD (10% and 21.3, respectively).

Considering the response graphs, the best combinations of factors' levels leading to an improved response for each analysed property are shown in table 9. For each optimal formulation, the estimated response value (R_{EST}) predicted by Taguchi method and determined according to equation (1), is also presented.

$$R_{EST} = A + \Sigma\,(X_i - A) \tag{1}$$

where A is the global average of all formulations, and X_i represents the marginal mean corresponding to all responses involving factor X with the optimum level (only the material factors with a statistical significant effect on global response are considered).

Table 9. Optimal formulations and estimated response values

Response property	Optimal formulation	Estimated value
IT_{SF}	$A_{2\text{ or }3}\,B_{1\text{ or }3}\,C_2\,D_2$	2.55 s
MD	$A_3\,B_1\,C_3\,D_1$	5.72 mm
IT_{UL}	$A_2\,B_3\,C_2\,D_2$	2.61 s
T_1	$A_3\,B_1\,C_3\,D_1$	0.00 s

4. Conclusions

The Taguchi methodology was used as an alternative approach to the full factorial experimental work plan, to determine material factors' effects on fire properties of polyester composites modified with nano/micro oxides and phosphinates. The following conclusions can be drawn from the investigation:

• It was observed at naked eye that even for the longest used sonication time, filler dispersion was not fully achieved;

• With increasing sonication time a greater content of 'air bubbles' resulted, and the created paths allowing easier flame propagation lead to a poorer burning behaviour;

• The use of nano and/or micro particulate oxide additives improved at least one fire behaviour property. The addition of phosphinate based FR on its own or combined with nano-alumina lead to significant improvements in fire properties, achieving a V-1 rating. This may be an indication of a synergistic effect between the phosphinate compound and nano-alumina.

•The optimized formulations are divergent with respect to some response properties as the factors had different impacts on final results of trial formulations. Nevertheless, it can be stated that 0% to 5% of nano alumina or micro silica particles, in combination with 10% to 15% of phosphinate based FR result in the UPC with overall best fire properties.

The use of nano and/or micro particulate oxide additives may lead to better fire performance than that of unmodified traditional composites, but further studies are required. Additional studies are thus foreseen, to explore the synergistic effect between nano-alumina and conventional FRs, and more thoroughly study the use of these additives (*e.g.,* content, surface treatment), so that products with better fire performance can be obtained.

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