

Article



# Fire Properties of Acrylonitrile Butadiene Styrene Enhanced with Organic Montmorillonite and Exolit Fire Retardant

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**Abstract:** In this paper an experimental investigation on fire retardancy of a new polymer nanocomposite derived from organic montmorillonite and exolit fire retardant in an acrylonitrilebutadiene-styrene copolymer by analyzing the flammability and fire behavior is described. The samples were prepared by melting and mixing nanocomposites and fire retardant in different concentrations in an acrylonitrile-butadiene-styrene base polymer. It was found that using only one component (organic montmorillonite or fire retardant) the burning stops in 10 s on the sample. Confirmation of synergy in flammability by combining both montmorillonite and flame retardants was noticed and is discussed regarding the flame-retardant mechanisms assessed by means of the Limiting oxygen index (LOI), UL 94, and cone-calorimeter methods. The acrylonitrile-butadiene-styrene preparation with 15–20 wt% fire retardant and 1–2 wt% organic montmorillonite reached a UL-94 V-0 classification, contrasting with the pure acrylonitrile-butadiene-styrene with 1–2 wt% organic montmorillonite formulations, which completely burned. Finally, the samples showed a very good synergy going to a higher reduction of the peak heat release rate and to a minimum mass reduction, as obtained from cone calorimeter tests.

Keywords: acrylonitrile-butadiene-styrene; limiting oxygen index (LOI); flame retardant; nanocomposites

# 1. Introduction

Polymers are known for relative high flammability, most often accompanied with the production of smoke during combustion. ABS (acrylonitrile-butadiene-styrene) generates heavy smoke and soot with lack of char formation. Consequently, improving the fire-retardant behavior of polymers is of critical importance for specialists. Many authors have combined ABS with different fire retardants [1–12] as well as different clays in order to enhance the synergy between the components [13]. One of the most used clays is the organic montmorillonite (OMT) [13].

Several researchers tried to reduce the polymers' combustibility by adding different fire retardants. For example, Pour et al. [14] added multilayer graphene particles in concentrations of up to 5% and noticed a reduction of 30% in the heat release rate of the polycarbonate ABS, while commercially available flame retardants for ABS are halogen and silicon-containing [15]. Nevertheless, the use of halogen containing fire retardants is rare at this moment due to their negative influence on human health and the environment [16–18]. Later there has been an increase in using montmorillonite due to its excellent compatibility with ABS (acrylonitrile-butadiene-styrene) was noticed by Bardziński [19].

On the other hand, one can use the organic modified montmorillonite (OMT) obtained by ion exchange between montmorillonite and  $C_{16}$  in water, according to Gilman et al. [20]. Meri et al. [21] developed a mixture between polycarbonate, ABS, and montmorillonite nanocomposites obtained by melt compounding in a twin-screw extruder and noticed an increase in mechanical properties of the ABS. Khobragade [22] performed a review on flame retarding performance of different materials and concluded that triphenyl phosphate based materials are the most appropriate as fire retardants. However, it is indicated in the literature that the integration of a quite low quantity of nanoclay (organomodified) in the polymer matrix generates a protective layer throughout combustion [23–25]. In this context, the clay addition on the material surface acts as a shield that restricts the heat transfer into the material, as well as the volatilization of combustible degradation products and oxygen diffusion into the material [22]. Montmorillonite received lately increased attention due to its exclusive nanoscale layered structure and high aspect ratio, thus enhancing the mechanical, thermal and flame-retardant properties [22–25].

Xia et al. [26] performed an experimental study on fire behavior involving ABS, montmorillonite, and ammonium polyphosphate (APP) as fire retardant by melting at 175 °C. A change in LOI (limiting oxygen index) values was observed on increasing the OMT content to 2% while on increasing it to higher values the benefits were not obvious. With this idea, the conclusion was that OMT alone cannot effectively enhance the flame retardancy of ABS [26]. Similar studies were conducted by Lu et al. [27], Despinasse and Schartel [28] and Yoon et al. [29], who also noticed that there was no noteworthy modification in flame retardancy for the mixtures containing only clays, indicating that another FR (fire retardant) is needed to be added to the material.

Multicomponent flame retardant systems containing aluminum diethylphosphinate (AlPi) in thermoplastic styrene–ethylene–butylene–styrene elastomers have been investigated in terms of oxygen index, UL 94, cone calorimeter, and mechanical testing by Langfeld et al. [30]. The authors found that, by adding the fire retardant, an oxygen index of up to 27 vol% was obtained together with a horizontal burn rating in UL 94 with immediate self-extinction and the peak heat release rate decreased by up to 85%. As a conclusion, such AlPi based multicomponent systems have become a good alternative for fire retardant materials.

Ramani and Dahoe [31] studied the effect on flame retardancy on polycaprolactam composites with the combination of aluminum diethylphosphinate and organically modified montmorillonite nanoclay. The outcome of their study was that by combining both flame retardants, the result was an enhanced effect when compared with their application on a separate basis. Guo et al. [32] studied the influence of modified ammonium polyphosphate (APP) on the flame retardancy of wood floor composite by cone calorimetry and noticed a synergetic effect between APP and the composite followed by a good improvement on the overall flame retardancy of the multicomponent material. Similar results were outlined also by other research groups (please see for example Realinho et al. [1], Xia et al. [26], Lu et al. [27], Despinasse and Schartel [28], Ma et al. [33]).

Nevertheless, some contradictory information was found in the open literature, some authors noticed a decrease in thermal stability by adding OMT [29–36] while other experimental research proved a thermal stability enhancement [37,38]. An explanation for these contradictory results may be related to the nanoparticle dispersion in the polymer matrix, as well as with the nanoparticle dimensions and chemical compatibility.

Therefore, according to the literature recommendations, in this research a recycled ABS (reABS) was acquired and improved by adding 1%–2% organic montmorillonite and 15%–20% fire retardants. The nanometer sized montmorillonite clay particles can enhance surface integrity and provide advantages over the thermal properties of the composites, while the Exolit fire retardants [1,6] are well known for their capability to decrease the heat released in a fire. These new developed materials were tested with regard to their fire properties by means of the Limiting oxygen index (LOI), UL 94, and cone calorimeter methods. The overall aim was to improve the global properties of ABS by taking into account two directions: costs (by replacing ABS with recycled: reABS) and fire behavior (by adding

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reABS 2% OMT 15% FR

reABS 2% OMT 18% FR

reABS 2% OMT 20% FR

both OMT and FR (fire retardant) to get better fire resistant properties). This study is of relevance for many areas like the automotive industry, electronics, civil engineering etc due to the large usage of ABS for component manufacturing and due to this material exposure in a possible fire scenario.

#### 2. Materials and Methods

An acrylonitrile-butadiene-styrene copolymer (ABS), with the commercial name of Rocadur RABS 52, was provided by S.C. Romcarbon S.A. (Buzău, România) in granule form with a density of 1.03 kg/m<sup>3</sup>. Two phosphorus fire retardant (FR) additives were considered: an ammonium polyphosphate (APP), Exolit<sup>®</sup> AP422, and an aluminum diethylphosphinate (AlPi), Exolit<sup>®</sup> OP1230, both supplied, in the form of white powder, by Clariant (Germany) with the properties shown in Table 1, as per given by the manufacturer. The two FRs were used in manufacturing the samples in a 1:1 proportion, as was recommended by the manufacturer. In addition, nanoparticles of organic montmorillonite (OMT) with the name Shelsite 30B Montmorillonite Nanoparticles (Nanoshell) was used as clay for preparing the samples. The OMT properties are as follows: particle dimension—less than 80 nm; purity—99%, pH—8–9; humidity—less than 2% and density—2.8 g/cm<sup>3</sup>.

	Exolit OP 1230	Exolit AP 422
Chemical formula	$[(C_2H_5)_2PO_2]_3Al$	(NH <sub>4</sub> PO <sub>3</sub> ) <sub>n</sub>
Phosphor content, %	23.3%-24%	31%-32%
Humidity, %	max 0.2%	max 0.25%
Density, g/cm <sup>3</sup>	1.35	1.9
Decomposing temperature, °C	>300	>275
Particle dimension	20–40 µm	17 µm

Table 1. Properties of fire retardant materials.

Several formulations were prepared (see Table 2) and all the materials were first dried at 100 C for 24 h than were mixed at a blending temperature of 205 °C in a Brabender mixing chamber (Brabender, Germany), with a rotating rate of 60 rpm applied for 10 min. The materials final composition was chosen according to the open literature [1-5] and with the scope to determine the most favorable minimum addition of OMT and fire retardants in order to get the best fire properties. The specific specimens used for further tests were obtained at 205 °C in a Carver press over three minutes at a pressure of 50 atm and two minutes at 150 atm. For better accuracy of results, 2–3 specimens were manufactured for each composition and tests were performed on 2–3 samples, while the average values were used for the results discussion.

Table 2. Prepared samples.					
Specimen	Recycled Acrylonitrile- Butadiene-Styrene, reABS (wt%)	Organic Montmorillonite, OMT (wt%)	Exolit OP 1230 (wt%)	Exolit AP 422 (wt%)	
reABS	100.0	-	-	-	
reABS 1% OMT	99.0	1.0	-	-	
reABS 15% FR	85.0	-	7.5	7,.5	
ABS 1% OMT 15% FR	84.0	1.0	7.5	7.5	
ABS 1% OMT 18% FR	81.0	1.0	9.0	9.0	
ABS 1% OMT 20% FR	79.0	1.0	10.0	10.0	
reABS 2% OMT	98.0	2.0	-	-	

83.0

80.0

78.0

Limiting Oxygen Index (LOI) of ABS and its nanocomposites were measured using an Oxindex type equipment manufactured by the Hungarian Polymer Research Institute in compliance with

2.0

2.0

2.0

7.5

9.0

10.0

7.5

9.0

10.0

standards ASTM D2863 (i.e., Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index)) and ISO 4589 (i.e., standard for Determination of burning behaviour by oxygen index). Tests were performed on sheets with a size of  $120 \times 10 \times 4$  mm<sup>3</sup> and were based on the lowest oxygen gas concentration that still sustains combustion of the sample.

The UL-94 tests were performed according to Standard for Tests for Flammability of Plastic Materials for Parts in Devices and Appliances, (i.e., ASTM D3081 and ASTM D635, respectively) with sample dimensions of  $120 \times 10 \times 4$  mm<sup>3</sup> under a flame of 50 kW.

UL-94 test results are classified by burning rate, from the least flame-retardant to the highest one as [1–6]:

- HB: slow burning;
- V-2: burning stops in 30 s on a vertical sample; drops of flaming particles are allowed.
- V-1: burning stops in 30 s on a vertical sample; drops of particles permitted as long as they are not in flame.
- V-0: burning stops in 10 s on a vertical sample; drops of particles acceptable as long as they are not in flame.
- 5VB: burning stops in 60 s; no drops acceptable; samples may develop a hole.
- 5VA: burning stops in 60 s; no drops permitted; samples may not present a hole.

The mass loss calorimeter tests were performed following the ISO 13927 procedures (i.e., standard for Plastics — Simple heat release test using a conical radiant heater and a thermopile detector) using an FTT cone calorimeter instrument made by FTT Inc (East Grinstead, UK). Square specimens  $(100 \times 100 \times 4 \text{ mm}^3)$  were covered in aluminum foil and were irradiated at a heat flux of 50 kW/m<sup>2</sup>, conforming to a fire scenario. The heat release rate (HRR) and total heat release (THR) were determined. Additionally, heat release values and mass reduction were uninterruptedly logged throughout burning. The calibration was achieved prior to tests and the orifice plate coefficient (device specific) was calibrated with a methane burner.

Finally, a regression analysis was performed by fitting the experimental data in Table Curve 3D software [39] and an equation to fit all data was proposed, as is described further on.

### 3. Results and Discussion

The LOI and UL-94 tests results are summarized in Table 3 where it can be seen that adding solely 15% FR to the reABS affected the nanocomposites LOI, by increasing it by 7%. Pure reABS showed an HB type behavior (i.e., slow burning) at burning and a LOI value of 18.5%, which is in agreement with the studies conducted by Realinho et al. [1] and Jian et al. [6]. When the FR content was as low as 15 wt%, the LOI value increased to 25.5% indicating a significant influence of FR on LOI (Limiting oxygen index).

Specimen	LOI [%]	Behavior at Burning after First Ignition	<b>Drop Type</b>	UL 94
reABS	18.5	burnt completely	burning drops	HB
reABS 15% FR	25.5	burned 10 s	burning drops	V-2
reABS 1% OMT	20.8	burnt completely	burning drops	HB
reABS 1% OMT 15% I	FR 25.8	burned 9 s	no burning drops	V-1
reABS 1% OMT 18% I	FR 27.7	burned 2 s	no drops	V-0
reABS 1% OMT 20% I	FR 28	burned 0 s	no drops	V-0
reABS 2% OMT	22	burnt completely	burning drops	HB
reABS 2% OMT 15% I	FR 27	burned 1 s	no drops	V-0
reABS 2% OMT 18% I	FR 28.3	burned 0 s	no drops	V-0
reABS 2% OMT 20% I	FR 28.7	burned 0 s	no drops	V-0

Table 3. Limiting Oxygen Index (LOI) and UL 94 tests results.

The maximum LOI value observed, 28.7%, was for the nanocomposites reABS 2% OMT 20% FR. Thereafter, the LOI value for the nanocomposite with 18–20 wt% FR was nearly constant while the influence of OMT is rather important. In addition, as can be seen from Table 3, the material composition plays an important role and there is a synergy between adding OMT and FR as is reported in the literature [13]. Adding just one component, OMT or FR, does not give a clear advantage on burning rate, as can be seen from Table 3, where better results in terms of burning are obtained for the samples with both OMT and FR. Furthermore, it can be noted that the addition of OMT maintains the reABS behavior at burning (i.e., HB—slow burning [6]), while the addition of 15% FR gets a V-2 rating. On the other hand, when the percentage of FR increases, the burning rate increased to V-0. The only exception is reABS 1% OMT 15% FR that obtained a V-1 score for the burning rate, even though the LOI result was rather good. In this context, the addition of both OMT and FR to enhance the reABS behavior at burning can clearly be recommended.

The cone calorimeter is the most significant bench scale tool in the fire testing area being the most helpful for fire safety researchers to quantitatively examine the materials flammability [7,8]. In this research, cone calorimetric tests were run with a heat flux of 50 kW/m<sup>2</sup> to investigate the fire performance of reABS and the respective configurations are reported in Table 2. The cone-calorimeter tests results are summarized in Table 4 and Figures 1–6, where:

- TTI is the time taken for the specimen to ignite at 50 kW/m<sup>2</sup> flux;
- THR is the total heat released per unit area during the entire test for the tested thickness of product;
- PHRR is the peak heat release rate;
- Residue is measured as percentage;
- Effective heat of combustion is the energy produced per kg of the product. It is averaged over the length of the test;
- FIGRA is the growth rate of the burning intensity, HRR, during a test and is calculated as the maximum value of the function (heat release rate)/(elapsed test time).

Specimen	Total Heat Released Per Unit Area, THR (MJ/m <sup>2</sup> )	Peak Heat Release Rate, PHRR (kW/m <sup>2</sup> )	Time to Ignition, TTI (s)	Residue (wt%)	Time to PHRR (s)	Growth Rate of the Burning Intensity, FIGRA(W/s)
reABS	85.52	486.05	24	1.6	152	3.45
reABS 15% FR	64.05	150.92	21	10.7	85	1.74
reABS 1% OMT	82.73	364.38	23	4.1	182	2.23
reABS 1% OMT 15% FR	71.06	139.75	28	13.5	429	0.38
reABS 1% OMT 18% FR	67.37	128.14	33	13.1	430	0.34
reABS 1% OMT 20% FR	62.54	132.76	42	17.7	464	0.33
reABS 2% OMT	84.99	317.29	20	6.4	215	1.66
reABS 2% OMT 15% FR	74.57	149.69	29	15.8	434	0.39
reABS 2% OMT 18% FR	77.85	154.26	30	17.3	429	0.41
reABS 2% OMT 20% FR	74.15	154.15	29	18.9	475	0.38

Table 4. Cone calorimeter test results.

In Table 4, the average standard deviation of all measured mass loss calorimeter values are  $TTI = \pm 3 \text{ s}$ ; PHRR =  $\pm 30 \text{ kW/m}^2$ ; time of PHRR =  $\pm 5 \text{ s}$ ; and residue =  $\pm 0.2\%$ . From Table 4 an improvement of the peak heat release rate (PHRR) is visible when the FR and OMT, or both, were added to the polymer. For example, a decrease around 263% was found for 1% OMT +18% FR, even if the time to PHRR goes three times higher. This substantial decrease agrees with the open literature [6,9,10]. If one compares the experimental data with the state of the art, it can be seen that lower PHRR values were obtained also by other research groups (i.e., 1821 kW/m<sup>2</sup> in reference [1], 574 kW/m<sup>2</sup> in [9] and 930 kW/m<sup>2</sup> in ref. [6]) and the phenomenon can be explained by the reABS initial combustion process (i.e., from its preparation process). More exactly, the initial ignifugation of the recycled ABS clearly revealed the influence of the flame retardants incorporated into the material when they compared the thermal properties of pristine ABS and recycled ABS recovered from monitors, microphones, and mice [40]. Beigbeder et al. [41] analyzed recycled ABS using X-ray diffraction and they identified

brominated flame retardants. Plus, the UL-94 test pointed out that recycled ABS obtained V-0 classification and they concluded that several kinds of flame retardants were used [41].

The decrease of PHRR when 1% and 2% OMT is added to the ABS was registered as 25% and 35% respectively. On the other hand, similar results were attained by Du et al. [42], who added 5% of two types of montmorillonite organically modified and obtained a reduction of PHRR of 39% in the first case and 42% in the second case. They concluded that the process may be influenced by melt viscosity, degradation behavior, and char formation on the sample surface [42]. Therefore, the decrease in PHRR and the increase in TTI proves the synergy between these two components: OMT and FR.

Regarding the THR results, when 1% of OMT is added to reABS a decrease of 4% is noticed and this can be attributed to a better dispersability of OMT at lower weight concentrations, as reported also by Singh and Ghosh [11] and Wu and Lang [9]. Additionally, the experiments performed by Zhang et al. [43] showed a similar behavior of THR when 2% triclay III (oligomerically-modified clay) and 6% of triclay III are added to the ABS matrix [38].

The time to ignition results are in line with the open literature [1,9,11]. For example, Realinho et al. [1] developed a composite with ABS and 25 wt% APP/AlPi and obtained TTI (i.e., for a  $35 \text{ kW/m}^2$  flux) of 30 s for the pure ABS and 25 s for the composite. Wu et al. [9] obtained the same TTI for ABS as that determined in the current work.

As discussion, it can be seen that the TTI test results obtained for ABS in combination with FR are lower for both samples FR-reABS. Specifically, TTI for the reABS 15% FR decreased by 3 s while Realinho et al. [1] registered a time for ABS 25% FR decrease of 5 s, if compared to the TTI for ABS. This occurred due to the weak thermal stability of the FR (in special AlPi) that starts to decompose at a lower temperature than pure ABS [1]. Furthermore, the temperature of degradation of OMT is lower than that attained for ABS, as also Wang et al. [44] observed. Plus, it can see that even if OMT and FR are used separately, weaker TTI times are obtained, if compared with reABS. This appears due to the weak thermal stability of OMT and FR, while when these two components are used together a synergy between them occurs and TTI times of nanocomposites are improved. On the other hand, Zhang et al. [45] who used a cone calorimeter with a heat flux of  $35 \text{ kW/m}^2$ , obtained a time of ignition of 39 s for pristine ABS and 51 s for ABS with 30% APP filler. Other researchers, as Wu et al. [46], obtained a TTI of 24 s for ABS with a 50 kW/m<sup>2</sup> external heat flux, which is in line with our result. A different TTI time for ABS shows that for a comprehensive approach, several factors have to be considered, as for example: the monomers (acrylonitrile, butadiene-styrene) concentration [47], the manufacturing method, the products supplier (i.e., with regard to their purity, chemical composition etc.) or the external heat flux value of the cone calorimeter.

When the residue values are discussed, one can say that the residues of particles act as barriers against heat transport and thus decrease the heating rates of the developed nanocomposites. Additionally, the multilayer silicate heat-shielding layer slows down the escape of volatile products generated from the degrading polymer, as was explained also by Pour et al. [14] and Qin et al. [16]. Precisely, Qin et al. [16] affirmed that the barrier effect of exfoliated layered silicates delays the thermal degradation in the nanocomposite, while Pour et al. [14] noticed the same behavior for graphene layers in an PC/ABS matrix. The same effect of the protective layer formed during combustion was observed by Du et al. [42] which compared two types of organically modified montmorillonite mixed in ABS and noticed similar PHRR for both cases.

From the results in Table 4 it may be seen that the residue increases by adding both OMT and FR to almost 19%, larger values being obtained with the wt% increase of both clay and fire retardant. Nevertheless, the addition of clay to the reABS results in a 155%–296% increase in the residue while on adding the Exolit mixture to the base composite, the residue increases to 560%. Finally, the released heat versus time for reABS and when combined with OMT and FR is shown in Figure 1, while Figures 2 and 3 show the results for reABS with 1% OMT and 2% OMT with different percentages of fire retardant (from 15%–20%). Overall, it can be affirmed that the reABS burning is faster and more violent and this is decreased by adding different amounts of OMT and FR. This behavior was also observed by

Ma et al. [33] who added 2% montmorillonite in ABS and by Realinho et al. [1] who added 25 wt% FR in pristine ABS and obtained a four-times decrease of PHRR.

In Figure 1 it is possible to observe that 15% of FR dramatically decreases the heat release, while OMT is responsible for more modest decreases. In the first case, the FR delays the burning as a consequence of the char layer formation (i.e., the same phenomenon was acknowledged also by Realinho et al. [1]) while adding higher percentages of OMT decreases the heat release (delaying the maximum point) due to migration of the OMT to the specimen surface. This phenomenon was also encountered by other research groups who studied these nanocomposites (see for example [1,42,44]). As a further comment, Du et al. [42] who used 5% modified montmorillonite + ABS, also observed that the montmorillonite tactoids have a tendency to accumulate together on the surface of the burning material and create a compact protective layer. The same phenomenon was noticed by Wang et al. [43] when they tested the thermal degradation of ABS +5% OMT. They noticed that after pyrolysis the nanocomposite forms a char layer with a multi-layered carbonaceous-silicate structure that builds up on the surface of the material during burning and has the capacity to insulate the material and to slow down the volatile products [44]. According to Figure 3, the best results were achieved when both OMT and FR were used, due to the synergy between them in the process of the char progression.



**Figure 1.** Released heat against time for reABS (recycled acrylonitrile-butadiene-styrene) and reABS with fire retardant (FR) and organic montmorillonite (OMT).



**Figure 2.** Released heat against time for reABS with 1% OMT (organic montmorillonite) and different mass percentages of FR.



Figure 3. Released heat against time for reABS with 2% OMT and different mass percentages of FR.

Figures 4–6 present the mass loss against time. It is possible to conclude that the reABS is burnt almost completely (98.4% mass loss) after a relatively short time in comparison with reABS with 15% FR which presents a double burning time and an 89.3% mass loss.



Figure 4. Mass loss against time for reABS with OMT and FR.



Figure 5. Mass loss against time for reABS with 1% OMT and different percentages of FR.

These results are in line with the outcomes of Realinho et al. [1] (i.e., a mass loss of 87.7% when 25% FR is added to pristine ABS). However, the influence of 1%–2% OMT is rather limited. Similar details are shown in Figures 5 and 6, where it can be clearly seen that the addition of FR greatly influences the mass loss reduction. More precisely, the decomposition time increases around 10% and 20% after

adding 1% and 2% OMT, respectively, but when FR is added an increase of 200% is achieved in terms of decomposition time and 89.3% of the mass loss. In this case the mass loss is related to the released heat and fire propagation, as Gilman et al. [12] revealed in their study of materials with OMT and different fire retardants. Table 5 summarizes the results obtained from the figures for different times (after 100, 200, and 300 s), in order to evaluate the influence of OMT and FR on the reABS polymer.



Figure 6. Mass loss against time for reABS with 2% OMT and different percentages of FR.

Specimen	Mass after Burning [%]			
1	100 s	200 s	300 s	
reABS	55.03	4.35	0.74	
reABS 15% FR	76.34	55.79	35.99	
reABS 1% OMT	63.45	15.28	4.16	
reABS 1% OMT 15% FR	82.39	66.29	50.45	
reABS 1% OMT 18% FR	84.29	69.23	55.47	
reABS 1% OMT 20% FR	85.49	71.44	57.35	
reABS 2% OMT	66.41	29.71	6.3	
reABS 2% OMT 15% FR	84.17	68.37	53.2	
reABS 2% OMT 18% FR	84.03	69.2	54.11	
reABS 2% OMT 20% FR	84.33	70.13	55.95	

Table 5. Mass loss after different burning times.

For example, the mass remaining after 300 s burning increases greatly when fire retardant and OMT are added, reaching a maximum mass of 57.35% of the initial weight for ABS + 1% OMT + 20% FR, while all samples with OMT and FR showed good firing behavior. The minimum decrease in the mass loss after 100 s burning was registered for reABS 1% OMT 20% FR (85.49% from initial mass remains after burning), following the same trend as PHRR reduction. As a further observation, even if adding only OMT the mass loss decreases by about 5% and on adding solely FR, 35% is obtained. Combining FR and OMT gave very good results in terms of burning behavior if the data from Table 5 are compared. Since the reduction in PHRR follows the reduction in mass loss rate, this correlation is essential to be noted [43].

Finally, another important parameter derived from the con-calorimeter test is the burning time that reflects the time needed for a specific material to decompose and to generate the volatile materials that sustain the burning process. Figure 7 presents the regression analysis of the experimental results

where the influence on burning time of both the fire retardant and OMT concentration are evident. It can be seen that the influence of FR is bigger than that of OMT, although the best performance is obtained for reABS + OMT + FR (an increase of the burning time up to 30 times). In order to predict the total burning time for the different architectures studied, a regression was found with regard to Figure 7 (see the surface fit) and the following equation was obtained:

$$t = 251.33 + 65.61\varphi_{OMT} + 19.85\varphi_{FR} \tag{1}$$

where the t is the burning time, in seconds, and  $\varphi$  refers to the mass percentage of the nanoparticles of OMT and FR, respectively. The R-squared value for this correlation was calculated as 0.96.



Figure 7. 3D analysis with regard to OMT and FR influence on the burning time.

Montmorillonite has a large industrial value due to its high aspect ratio, plate morphology intercalative capacity, natural abundance, and relatively low cost compared to other nanofillers that have higher price and more sensitive processing [48]. Nevertheless, as can be seen from the overall results from this research, adding small percentages of OMT obtains little benefit on the overall fire properties. On the other hand, a THR decrease of 7% of reABS+OMT samples, due to a better dispersability of OMT at lower weight concentrations was noticed by Simionescu and Minea [49] and also by Singh and Ghosh [11] and other research groups (see for example Wu and Lang, [9]). However, Zhuge et al. [50] incorporated montmorillonite into carbon nanofiber nano paper and noticed that THR decreased radically with the growing fraction of montmorillonite and attributed this phenomenon to the montmorillonite layer structure that functions as a barrier to mass and heat transfer. A similar occurrence was observed by Ahmed et al. [51] who added 1%–3% montmorillonite into polystyrene. Overall, the key effect of OMT is to improve the overall structure of the samples due to the interfacial intercommunication between the polymer matrix and the silicate layers of OMT [11], thus creating the basis for the reABS-OMT-FR synergy as a whole compound. The same synergetic effect was noticed also by other authors, as for example Wang and Wilkie [52] when discussing the utility of nanocomposites in fire retardancy in their comprehensive review.

# 4. Conclusions

OMT and a binary flame-retardant system based on Exolit were used in this paper to flame- retard reABS, and a high flame-retardant level was reached.

Fundamentally, nine ABS flame retardant specimens were developed and the experimental study clearly showed improvements in terms of flame retardancy, such as reduction in peak heat release rate and total heat released compared with the pure reABS. Nevertheless, all formulations showed slightly lower values of time to ignition.

Based on flammability and fire tests of the ABS phosphorus flame retardant specimens, evidence of an important flame retardancy enhancement was noted when both flame retardants and montmorillonite were present in ABS. A combined gas and condensed-phase mode of action was observed during cone calorimeter tests, that led to the higher reduction of PHRR values, in good agreement with the obtained V0 classification under the UL-94 standard. In this context, a correlation was proposed to estimate the total burning time of a reABS-OMT-FR polymer nanocomposite. Finally, the cone calorimeter results revealed that both FR and OMT acted via flame inhibition and a protective flame-retardancy mechanism in the developed polymer nanocomposites.

To conclude, it can be affirmed that the developed and tested materials may constitute a viable alternative to common ABS (i.e., an opaque thermoplastic and amorphous polymer with many real life applications) for the manufacture of components for the automobile industry, as well as construction materials or other parts of domestic equipment (i.e., electronics, cases, toys etc.). The use of improved fire-resistant materials is very important, especially when a serious fire scenario may be involved. Nevertheless, more research is needed to establish the best and cheapest FR–OMT–ABS ratio to attain both economic advantages and an increased security in a fire incident.

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