



“Gheorghe Asachi” Technical University of Iasi, Romania



THE EFFECT OF MONTMORILLONITE CLAY AND FIRE RETARDANTS ON THE HEAT OF COMBUSTION OF RECYCLED ACRYLONITRILE-BUTADIENE STYRENE

Tudor Mihai Simionescu, Alina Adriana Minea*

Gheorghe Asachi Technical University of Iasi, Faculty of Materials Science and Engineering,
41 Prof. Dimitrie Mangeron Bd., Iasi, Romania

Abstract

The combustion behavior of several polymers was studied with a cone calorimeter, while the samples were based on a recycled acrylonitrile-butadiene styrene (ABS) and as additives were considered: organic montmorillonite (OMT) and a mixture of two fire retardants (FR).

The samples structure and thermal properties are characterized by means of Scanning electron microscopy (SEM), X-ray Powder Diffraction (XRD) and Energy-dispersive X-ray spectroscopy (EDX) and cone calorimeter. The main objective of this article is to study the effect of OMT and FR adding into a recycled ABS combustion behavior. Results show that the addition of the fire retardants into the reABS+OMT matrix created a relevant effect on the phase morphology of the samples while the nanocomposite and fire retardant improves the thermal stability of reABS matrix, as measured by cone calorimeter. If it refers to peak heat release rate (PHRR), one can see a reduction in PHRR when FR and OMT are added to the reABS matrix. More precisely, the PHRR decrease is about 263% if 1% OMT and 18% FR are added to the samples. The sole addition of clay in polymers decreases significantly the peak heat release rate, while FR addition plays a relevant role.

Key words: acrylonitrile butadiene styrene (ABS), effective heat of combustion, fire retardant, mass loss, montmorillonite

Received: February, 2019; Revised final: March, 2019; Accepted: April, 2019; Published in final edited form: November, 2019

1. Introduction

The acrylonitrile butadiene styrene (ABS) is one of the most flammable and most studied materials in the open literature (Du et al., 2010; Kim et al., 2005; Mao et al., 2016; Marquis et al., 2013; Singh and Ghosh, 2014; Wu and Lang, 2016) and is extensively used as an engineering thermoplastic due to its favorable properties that consist of good mechanical properties, chemical resistance and good processing features (Ciuca et al., 2017; Sen et al., 2019). The most important disadvantage of ABS is its high flammability, and therefore there is a need to increase its thermal stability (Du et al., 2010; Kim et al., 2005). Lately, the recycled ABS is getting an increased attention due to the high need of recycling. However,

the main issue is its poor thermal stability, the same as for the pure ABS. To get an improvement of ABS fire properties one has to consider to add clays and fire retardant materials in the matrix. On the other hand, one of the most important equipment for fire testing is the cone calorimeter, which was developed in the early 1980's (Marquis et al., 2013) and was acknowledged as a reference instrument to estimate the fire behavior and its corresponding characteristics needed to be considered during a possible fire scenario.

Polymer/clay nanocomposites are of high interest in the current research due to the change of ABS fire properties in a favorable manner, even if low proportions are added (less than 5% wt), as was affirmed in the literature (Lu et al., 2015). Furthermore, clay addition to the polymer matrix goes

* Author to whom all correspondence should be addressed: e-mail: aminea@tuiasi.ro; Phone: +40723455071

to fire properties augmentation and improves its thermal stability.

The decreased flammability of polymer/clay systems is mainly due to the formation of a physical barrier layer on the polymer surface that acts like a shield alongside heat exposure and obstructs diffusion of volatiles throughout thermal degradation (Gilman et al., 2000; Kashiwagi et al., 2004; Wang et al., 2002). Dispersion of clays into the polymers can be considered of maximum importance for fire retardant properties improvement. On the other hand, it is believed that the clay nanomorphology does not play any noteworthy role to get improved flame retardant properties if nanodispersion of clay is attained (Isitman and Kaynak, 2010; Samyn et al., 2008).

Adding clay in polymers mainly decreases the peak heat release rate (PHRR), consequently, clay ought to be employed in synergistic mixtures with other traditional flame retardants (FR) to accomplish the best flame retardant properties (Lu et al., 2015; Wang et al., 2002). Wang et al. (2002) prepared ABS-MMT nanocomposites using a melt intercalation technique by blending ABS and organophilic clay (OMT). The thermo gravimetric study shows that the pyrolysis of ABS is divided into two steps: i) OMT (5 wt.%) will enhance the formation of char and, ii) improve the thermal stability of ABS matrix (Wang et al., 2002). In regard to flame retardants, few works are published in regard to ammonium polyphosphate (APP) efficiency on non-charring and self-charring polymers (Laoutida et al., 2009; Sypaseuth et al., 2017), and the major role of APP in the condensed phase was demonstrated. On the contrary, the efficiency of diethyl aluminum phosphinate (AlPi) have been less considered (Laoutida et al., 2009).

On the other hand, fire analysis is of much importance in the forthcoming years when we are facing an increase of this kind of devastating events (Akburak et al., 2018; Tahir et al., 2017; Tahir et al., 2018; Tahir et al., 2019). For example, Tahir et al. (2017) reviewed recent literature relating pure and doped/composite WO₃ catalyst and discussed about the optimization of the parameters affecting the degradation efficiency of various dyes. Alternatively, XRD analysis as well as other scanning methods (for example, SEM) are of crucial importance when dealing with fire-resistant materials (Tahir et al., 2018).

In this paper several reABS-OMT-FR samples were obtained by compounding and their structure, EDX and XRD pattern was analyzed. Plus, a thermal analysis was pursued in terms of cone calorimeter while effective heat of combustion is discussed for each sample.

2. Experimental work

2.1. Materials

Recycled ABS was used as matrix for the experimental study, while two types of EXOLIT where used as fire retardants and montmorillonite

nanoparticles were considered as fillers. Recycled acrylonitrile-butadiene-styrene copolymer (reABS) was provided by S.C. Romcarbon S.A. (Buzău, România) in granule form. The additives were used in a 1:1 mass proportion and are: ammonium polyphosphate (APP), Exolit® AP422, and aluminium diethylphosphinate (AlPi), Exolit® OP1230, both supplied, in form of white powder, by Clariant (Germany). The use of two types of APP was highly recommended by Clariant due to their previous positive results that were published by Realinho et al. (2018). The organic montmorillonite (OMT) with the commercial name Shelsite 30B Montmorillonite Nanoparticles (Nanoshell) was used as clay for preparing the samples. For obtaining the best experimental results, all the materials were initially dried at 100°C for 24 hours. Compounding was performed at 205 °C for 10 min, at a rotation speed of 60 rpm, using a fully automated laboratory Brabender station (Brabender, Germany). For mechanical description, specimens were prepared by compression molding using a Carver press at 205 °C (with a pre-pressing step of 3 min at 50 atm and a pressing step of 2 min at 150 atm).

The samples configuration was carefully chosen based on current state of the art targeting the study of OMT and FR influence on polymers EHC and mass loss. In this idea, the new materials are prepared by addition of 1-2 % OMT and 15-18% FR in the reABS matrix.

2.2. Measurements and characterization

Scanning electron microscopy (SEM) images were acquired using a Hitachi SU 8230 Scanning Electron Microscope (Hitachi Ltd. Japan) while the EDX test was accomplished with Rigaku SmartLab X Ray Diffractometer (Rigaku Americas Holding Company, Inc.) using Bragg-Brentano geometry – BB method. XRD analysis was carried out using Cu K α radiation ($\lambda=0.15406$ nm). The identification of the phase was made by referring to the International Center for Diffraction Data - ICDD (PDF-2) database.

Cone calorimeter mass loss tests were performed under ISO 13927 recommendations using a FTT cone calorimeter (FTT Inc, UK). Specimens of 100 x100 x 4mm were covered in aluminum foils and were irradiated at a heat flux of 50 kW/ m², 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 of tests and the orifice plate coefficient (device specific) was calibrated with a methane burner.

3. Results and discussion

3.1. SEM analysis

In order to investigate the detailed dispersion status fillers and clay into the polymer matrix, SEM

analysis of the nanocomposites were carried out and the outcomes are revealed in Fig. 1. Secondary electron (SE) and secondary +backscattering electron images (SE+BSE) were acquired in deceleration mode at different magnification for samples with OMT. In every image, the first one is corresponding to SE mode while the second one is for SE+BSE mode.

The process of addition of the fire retardants into the reABS+OMT matrix created a relevant effect on the phase morphology of the samples, as can be seen from Fig. 1. The fire retardants particle size is

lower than 20 μm while the montmorillonite nanoparticle is nanometer sized (see Fig. 1a and b), thus resulting in a good dispersion of particles in the matrix, as can be clearly seen from Fig. 1. If it compares the SEM results with literature findings (Du et al., 2010; Kim et al., 2005; Mao et al., 2016), the OMT addition determined an enhanced dispersion because of its micro spherical structure. Additionally, an improvement of the surface roughness is observed in Fig. 1 c due to the FR homogenous dispersion into the reABS matrix.

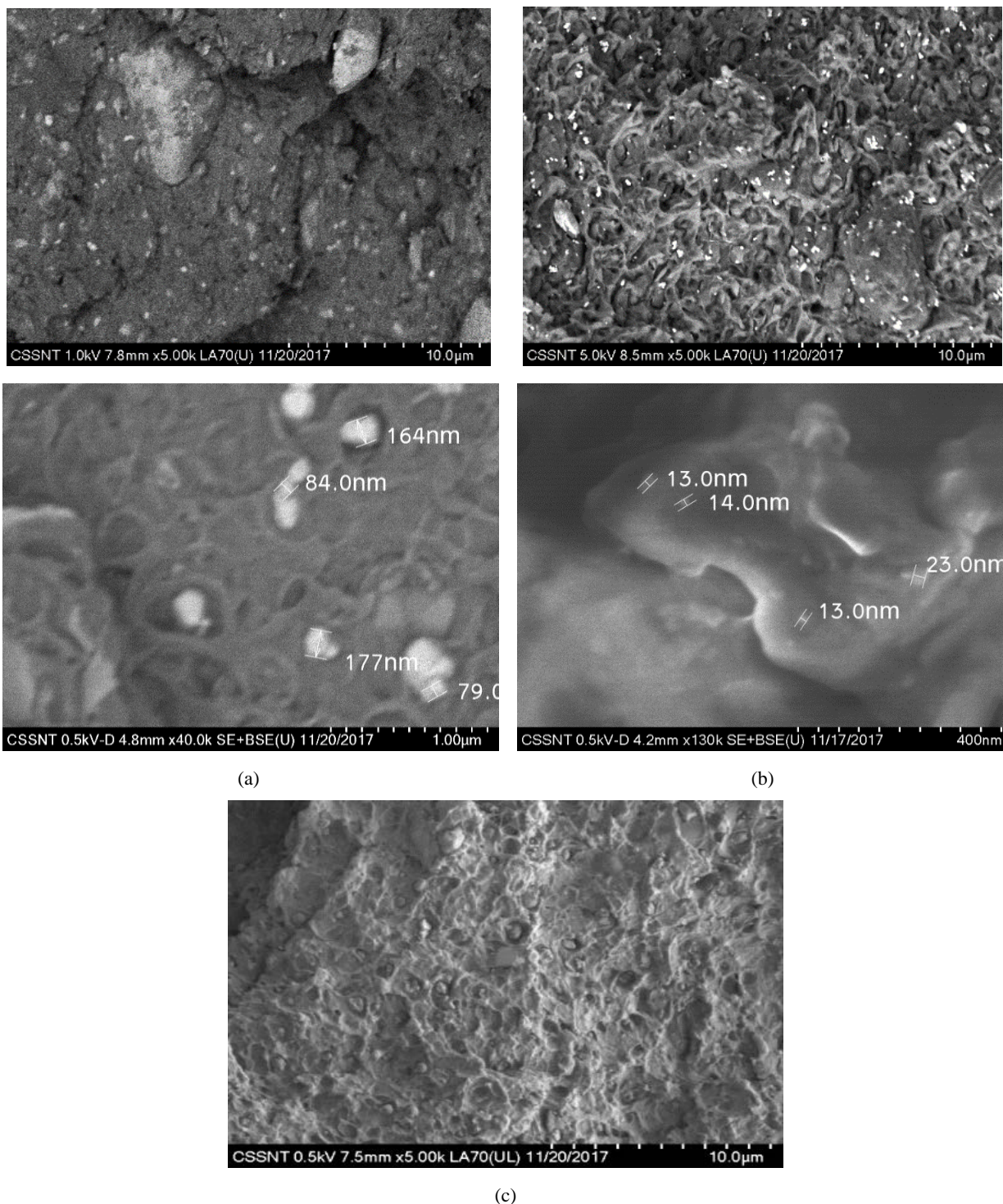


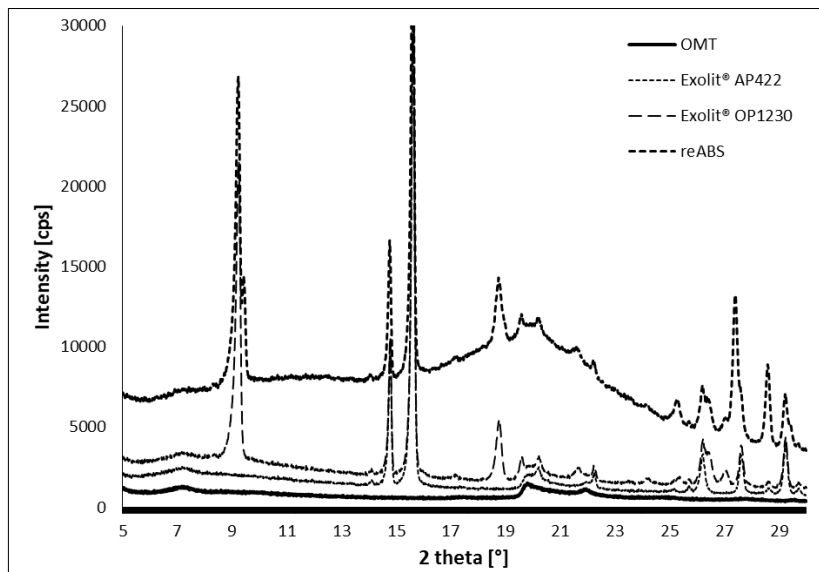
Fig. 1. SEM images of samples: (a) reABS1%OMT15%FR, (b) reABS1%OMT, (c) reABS

3.2. XRD analysis

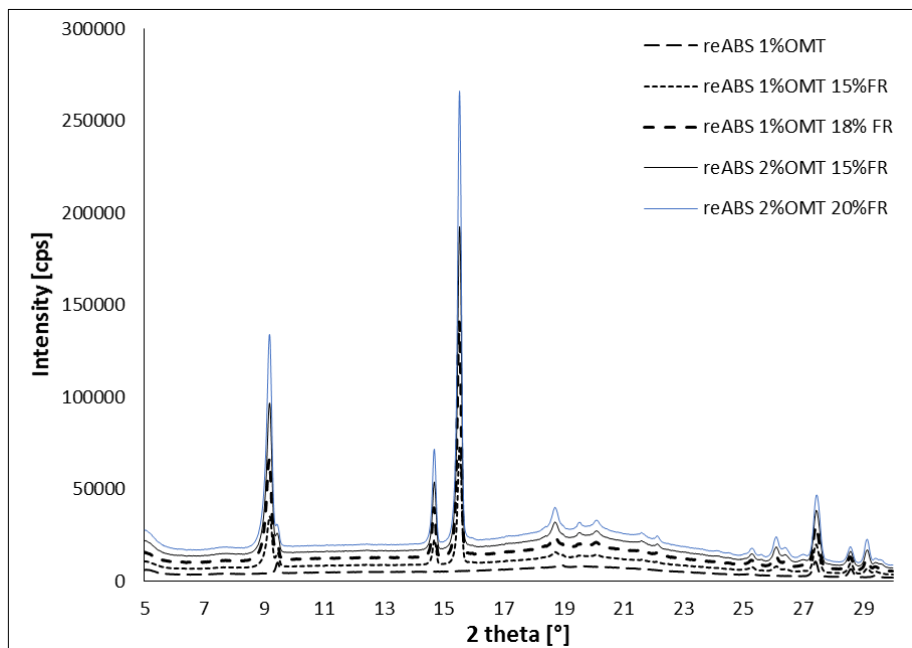
XRD analysis was employed to evaluate the dispersability of OMT and FR in the reABS matrix (see Fig. 2). The observation of dispersion and distribution of OMT and FR is of support in understanding the mechanism for the morphological change with the addition of clay and fire retardant. Previous researches (Lu et al., 2015; Mao et al., 2016; Weng et al., 2016) demonstrated that the OMT mixed with ABS goes to an intercalating structure and, in some particular cases, an exfoliated one. More precisely, Ma et al. (2008) noticed a delaminated structure with some ABS molecular chains

intercalated.

Weng et al. (2016) found peaks corresponding to (001) plane reflections of the clay and an average basal spacing of 1.4 to 2.4 nm of montmorillonite while Lu et al. (2015) noticed the absence of the diffraction peaks meaning that an exfoliated structure tends to apply to PA56-clay. Wang et al. (2003) studied a montmorillonite – ABS nanocomposite and concluded that it is difficult to draw complete conclusions about the structure from XRD analysis, such as how many layers constitute a multiplayer stack. In case of using organic montmorillonite, the interlayer spacing depends on the organic modifier, as well as the preparation technique



(a)



(b)

Fig. 2. XRD pattern of studied samples: (a) basic samples: OMT, Exolit and reABS, (b) manufactured samples: reABS + OMT and reABS + OMT + FR

In conclusion, as one can notice from the present results depicted in Fig. 2a, a diffraction angle was noticed for reABS at 7.71° corresponding to an interlayer spacing of 1.15 nm. In the case of OMT, the diffraction angle was noticed at 7.2° corresponding to 1.23 nm spacing, which is lower than that for the pure reABS. As was also noticed in the literature (Wang et al., 2003), the increase in inter planar spaces goes to a decrease in mechanical strength, as was also noticed in the present experimental study. Plus, Fig. 2b depicts the diffraction angles for the manufactured samples and it can notice a similar angle for all the reABS-OMT-FR mixtures, while the inter planar spacing is increasing if compared to the reABS. However, the diffraction peaks are broad which indicates that the crystallite size is very small. The XRD pattern shows that reABS is crystalline.

3.3. EDX analysis

The EDX analysis reveals the composition of the recycled ABS. As it is known, the chemical composition of ABS, OMT and considered FR are as follows:

- ABS: (C8H8·C4H6·C3H3N)n;

- OMT: (Na,Ca)_{0.33}(Al,Mg)₂(Si₄O₁₀)(OH)₂·nH₂O;
- AP422: NH₄PO₃;
- OP 1230: ((C₂H₅)₂PO₂)₃Al.

As can be noticed from Table 1, the reABS contains, besides of regular ABS chemical elements, other elements like: Al, Si and Ti, which are coming from the recycling process. Plus, in Tables 2- 4 are the EDX analysis results for the OMT and OMT+FR samples. EDX analysis offers also the possibility of checking the chemical distribution and its uniformity into the sample, as can be noticed in Fig. 3.

Analyzing data from Fig. 3 it can clearly affirm that during the manufacturing process, all the chemical elements were uniformly distributed, assuring good properties.

3.4. EHC analysis

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 (Du et al., 2010; Kim et al., 2005; Mao et al., 2016; Singh and Ghosh, 2014; Wu and Lang, 2016).

Table 1. Results of EDX analysis for the reABS

reABS	Statistics	C	N	O	Mg	Al	Si	Ti
	Max	94.24	0.00	4.37	0.13	4.02	0.15	0.28
	Min	92.05	0.00	3.73	0.05	1.60	0.05	0.04
	Average	93.34	0.00	3.92	0.09	2.41	0.08	0.16
	Standard Deviation	1.09	0.00	0.30	0.03	1.11	0.05	0.10

Table 2. Results of EDX analysis for the reABS 1%OMT

reABS 1%OMT	Statistics	C	N	O	Na	Mg	Al	Si	Ca	Ti
	Max	88.74	1.19	8.65	0.03	0.12	3.80	0.41	0.04	0.07
	Min	87.56	0.00	6.58	0.02	0.07	2.65	0.30	0.01	0.00
	Average	88.35	0.48	7.33	0.02	0.09	3.31	0.34	0.02	0.05
	Standard Deviation	0.53	0.57	0.91	0.01	0.02	0.49	0.05	0.01	0.03

Table 3. Results of EDX analysis for the reABS 1%OMT 15%FR

reABS 1%OMT 15%FR	Statistics	C	N	O	Na	Mg	Al	Si	P	Ca	Ti
	Max	81.04	4.56	21.45	0.04	0.28	3.45	0.78	4.31	0.06	0.43
	Min	64.70	0.76	11.83	0.01	0.11	2.08	0.44	2.32	0.01	0.19
	Average	74.06	2.70	15.97	0.03	0.15	2.78	0.55	3.42	0.04	0.29
	Standard Deviation	7.10	1.78	4.21	0.01	0.09	0.75	0.15	0.82	0.02	0.10

Table 4. Results of EDX analysis for the reABS 1%OMT 18%FR

reABS 1%OMT 18%FR	Statistics	C	N	O	Na	Mg	Al	Si	P	Ca	Ti
	Max	76.55	2.02	17.32	0.03	0.08	3.42	0.56	5.62	0.13	0.26
	Min	73.44	0.00	14.69	0.02	0.06	2.26	0.31	3.49	0.03	0.09
	Average	75.19	0.90	15.64	0.03	0.07	2.97	0.42	4.51	0.08	0.19
	Standard Deviation	1.30	1.04	1.24	0.01	0.01	0.51	0.11	0.93	0.04	0.08

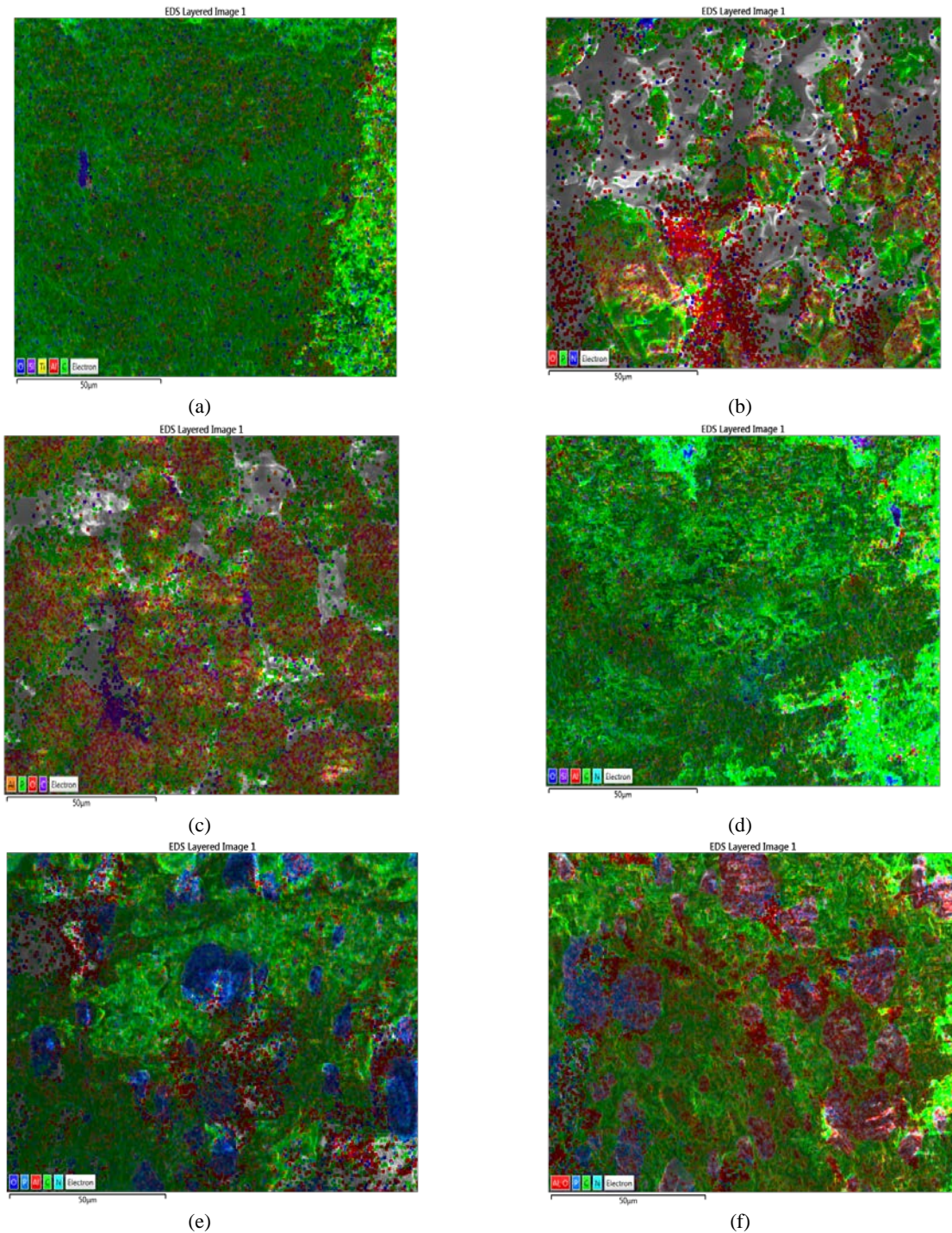


Fig. 3. Elements distribution into the matrix for prepared samples: (a) reABS, (b) APP; (c) AlPi; (d) reABS 1% OMT; (e) reABS 1% OMT 15% FR; (f) reABS 1% OMT 18% FR

In this research, cone calorimeter tests were steered with an irradiation of 50 kW/m² to investigate the fire performance of all manufactures products. The cone-calorimeter test results are summarized in Fig. 4 in terms of THR (total heat released per unit area during the entire test for the tested thickness of product) and in Fig. 5 for PHRR (peak heat release rate) while residue values are depicted in Table 5. The maximum value of heat release rate occurs when the materials is burning most intensely and can be defined by Eq. (1):

$$PHRR = \max(HRR) \tag{1}$$

If it discusses the results from Fig. 4, one can notice that adding 1% OMT it obtains a THR decrease of 7% of reABS+OMT samples, due to a better dispersability of OMT at lower weight concentrations, as was noticed also by Singh and Ghosh (2014) as well as other research groups (Wu and Lang, 2016). On the other hand, Zhuge et al. (2011) incorporated MMT clays into carbon nanofiber nano paper and noticed also that THR decreased dramatically with increasing weight fraction of MMT and attributed this phenomenon to the MMT layer structure that serves as a barrier to mass and heat transfer. The same

phenomenon was noticed by Ahmed et al. (2017) which added 1% and 3% MMT into neat polystyrene. Nazare et al. (2006) studied the flammability parameters of silicate layered polyester resin and found that the incorporation of the nanoclay did not alter the effective heat of combustion. Nevertheless, as the nanoclay filling was enlarged, there was a decrease in PHRR, THR, and FIGRA (Nazare et al., 2006) indicating enhanced fire retardancy.

Actually, adding MMT is lowering the total heat release rate due to their structure, but mixing

MMT and FR goes to a higher efficiency due to physical barrier effect (Ahmed et al. 2017) and the same effects were noticed in our experiments. If it refers to PHRR (Fig. 5), one can see a reduction in PHRR when FR and OMT are added to the reABS matrix. More precisely, the PHRR decrease is about 263% if 1%OMT + 18% FR are added to the samples. As was also noticed in the literature (Lu et al., 2015), the addition of clay in polymers decreases significantly the peak heat release rate, while FR addition plays also a relevant role in heat release rate.

Table 5. Manufactured samples and corresponding residue mass

Sample	Sample mass [g]	Mass burnt [g]	Char mass [g]
reABS	39.39	38.75	0.64
reABS 1%OMT	40.59	38.91	1.68
reABS 1%OMT 15%FR	44.05	38.12	5.93
reABS 1%OMT 18% FR	43.44	37.74	5.70
reABS 1%OMT 20%FR	44.60	36.70	7.90
reABS 15%FR	43.80	39.10	4.70
reABS 2%OMT	41.60	38.92	2.68
reABS 2%OMT 15%FR	43.60	36.70	6.90
reABS 2%OMT 18% FR	44.00	36.40	7.60
reABS 2%OMT 20%FR	43.50	35.30	8.20

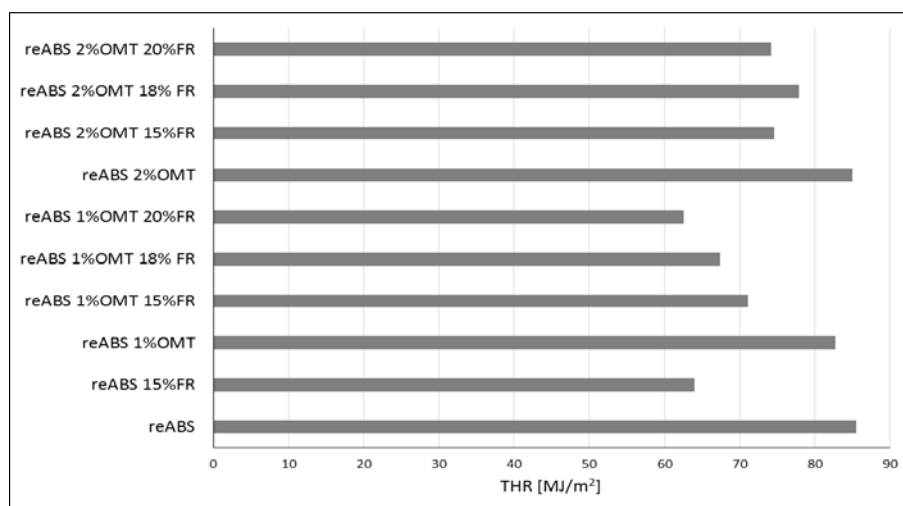


Fig. 4. Cone calorimeter test results for THR

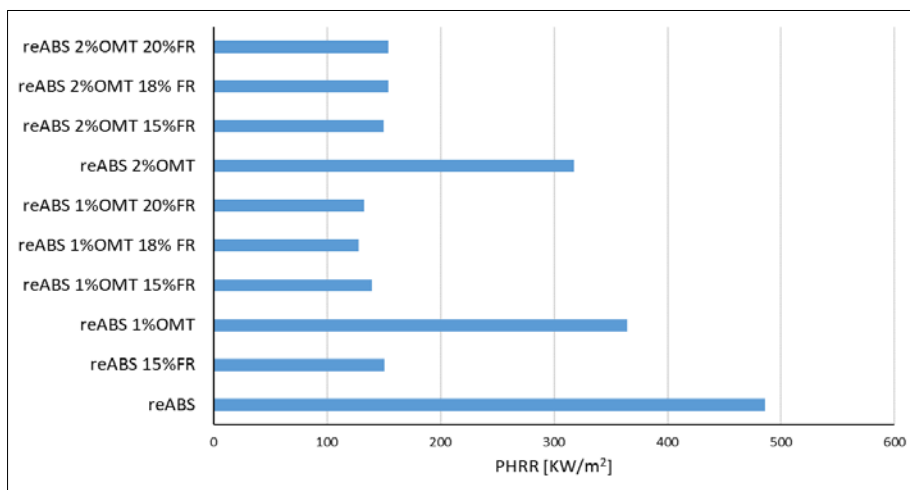


Fig. 5. Cone calorimeter test results for PHRR

The effective heat of combustion (EHC) at a specific burning time t is characterized as given by Eq. (2):

$$EHC = HRR(t) \tag{2}$$

while the maximum EHC is defined as the ratio between PHRR and the maximum specific loss rate. Mass loss and specific mass loss are defined by Eqs. (3-4).

$$\Delta m = \frac{m_{in} - m_{fin}}{t} \tag{3}$$

$$m = \frac{\Delta m}{A} \tag{4}$$

where A is the sample area.

Fig. 6 depicts the experimental data calculated for the samples specific mass loss rate over time while in Fig. 7 is plotted EHC variation in time. One can

notice that the pure reABS has the highest mass loss rate followed by the samples with OMT only. The combustion appears very quick for ABS samples with a high effective heat. Addition of organic montmorillonite delays the combustion while the fire retardant influence is higher, as is depicted in Fig. 7.

Finally, the results for maximum effective heat of combustion calculated with Eq. (5) are depicted in Table 6.

$$\max(EHC) = \frac{PHRR}{\max(m)} \tag{5}$$

If it looks to Table 6 one can notice that the PHRR is decreasing when organic clay is added by 25 % while fire retardant addition to the ABS-OMT matrix reduces the PHRR by almost 70%. Plus, 2%OMT + FR in the reABS copolymer goes to a substantially decrease (i.e. aprox. 80%) in maximum specific mass loss rate.

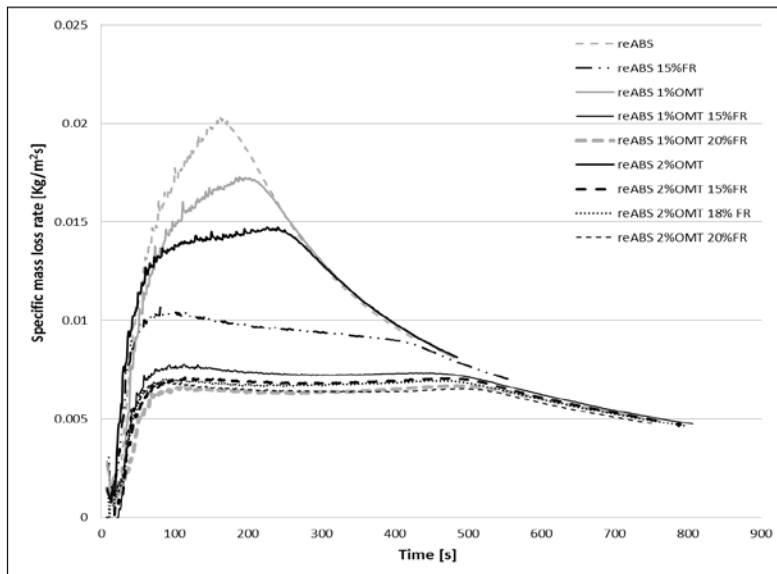


Fig. 6. Specific mass loss rate for studied samples

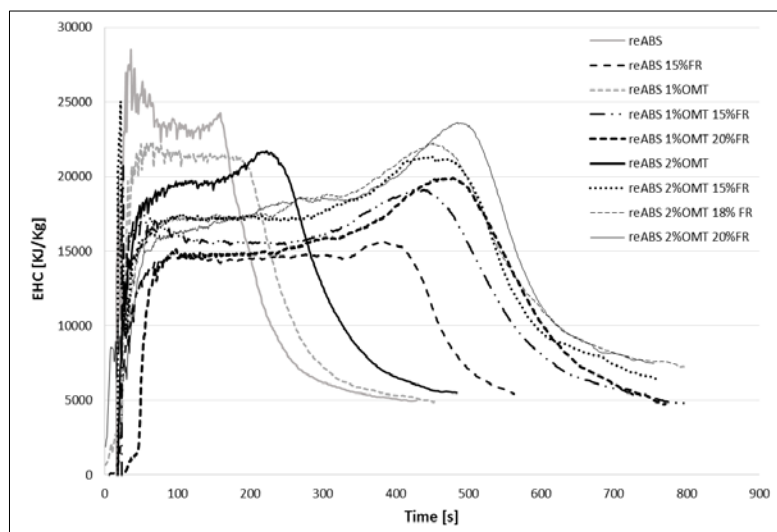


Fig. 7. EHC for studied samples

Table 6. Maximum EHC for studied samples

	<i>Maximum specific mass loss rate</i>	<i>PHRR</i>	<i>Maximum EHC</i>
reABS	0.03271	486.05	14859.10
reABS 15%FR	0.01063	150.92	14198.14
reABS 1%OMT	0.03059	364.38	11910.37
reABS 1%OMT 15%FR	0.00777	139.75	17984.91
reABS 1%OMT 20%FR	0.00670	132.76	19806.96
reABS 2%OMT	0.01473	317.29	21543.52
reABS 2%OMT 15%FR	0.00709	149.69	21128.91
reABS 2%OMT 18% FR	0.00701	154.26	22000.13
reABS 2%OMT 20%FR	0.00691	154.15	22302.70

Plus, the reABS with 1%OMT and 20%FR gets the best thermal results. These outcomes confirm the major improvement in fire properties of the reABS by adding OMT and fire retardants.

One of the main novelties of this research is the original combination between reABS and organic montmorillonite and the combination of the two fire retardants (that was used very rarely in the literature, as was explained before). This experimental study reveals also the relevance of combining OMT with different FR in order to attain a better behavior in a fire scenario.

4. Conclusions

In this research, several new materials based on reABS-OMT-FR were prepared and studied by the means of SEM, XRD and EDX. Plus, cone calorimeter was employed to analyze the fire behavior and especially the effective heat of combustion. Conclusion can be summarized as:

✓ In case of using organic montmorillonite, the interlayer spacing depends on the organic modifier, as well as the preparation technique

✓ EDX analysis confirmed that during the manufacturing process, all the chemical elements were uniformly distributed.

✓ Adding 1% OMT in the reABS it obtains a 7% decrease of THR, due to a better dispersability of OMT at lower weight concentrations.

✓ If it refers to PHRR, one can see a reduction in PHRR when FR and OMT are added to the reABS matrix. More precisely, the PHRR decrease is about 263% if 1%OMT + 18% FR are added to the samples. The addition of clay alone in polymers decreases significantly the peak heat release rate, while FR addition plays a relevant role.

✓ The combustion appears very quick for ABS samples with a high effective heat and the addition of organic montmorillonite delays the combustion while the fire retardant influence is rather important.

As a conclusion, it might affirm that future investigations are needed in order to completely describe all the mechanisms that are involved in a possible fire scenario. Nevertheless, the current investigation mainly revealed the benefits of adding OMT and a combination of two fire retardants on a recycled ABS matrix.

Nomenclature

A	Sample area [m ²]
EHC	Effective heat of combustion [kJ/kg]
HRR	Heat release rate [kW/m ²]
\dot{m}	Specific mass loss rate [kg/s m ²]
m_{fin}	Final mass after burning during 1 second [g]
m_{in}	Initial mass of the specimen [g]
Δm	Mass loss [g/s]
PHRR	Peak heat release rate [kW/m ²]
t	Time [s]
THR	Total heat release [MJ/m ²]

Abbreviations

ABS	Acrylonitrile butadiene styrene
AlPi	Aluminium diethylphosphinate
APP	Ammonium polyphosphate
EDX	Energy-dispersive X-ray spectroscopy
FR	Flame retardant
MMT	Montmorillonite
OMT	Organic montmorillonite
PC	Polycarbonate
reABS	Recycled acrylonitrile butadiene styrene
SE	Secondary electron
SE+BSE	Secondary + backscattering electron images
SEM	Scanning electron microscopy
XRD	X-ray Powder Diffraction

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