ORIGINAL PAPER

Mechanical and fire retardant properties of EVA/clay/ATH nanocomposites: effect of functionalization of organoclay nanofillers

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Abstract   A new modification process for the preparation of organoclay has been
devised. Functional organoclay nanofillers (FONs) based on the mixing of bentonite
and other inorganic fillers such as fumed silica, aluminium trihydroxide (ATH) and
sepiolite were prepared and employed to obtain composites of ethylene–vinyl
acetate and ATH. These composites were characterised by means of X-ray dif-
fraction, thermogravimetric analysis, mechanical and fire retardant properties. The
results confirmed that the modification process for the preparation of FONs is able
to influence the intercalated structure of the clay, and hence the mechanical prop-
erties and behaviour as flame retardant materials.

Keywords   Organoclay · Nanocomposites · EVA · ATH · Mechanical properties ·
Fire retardant properties

Introduction

Ethylene–vinyl acetate (EVA) copolymers are extensively used in the cable industry
as excellent insulating materials with good mechanical properties. To reduce the
large amount of smoke produced during combustion, metal hydroxides, such as
aluminium trihydroxide (ATH), are added to the polymer. However, the inclusion of
these additives causes the mechanical properties of these materials to decrease
significantly. Thus, the combination of bentonite nanoclay with other inorganic

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fillers during the modification of the nanoclays used as reinforcement of polymer matrices was presented as a new way to improve the thermal stability of polymers, while maintaining the mechanical properties [1].

Addition of modified nanoclays in composites has been presented in recent years as a new option to improve the fire retardant properties in EVA/ATH composites [2, 3]. Some authors [4, 5] have reported that thermal stability and char rigidity were enhanced by montmorillonite (MMT), which acted as a mass and heat transport barrier. According to Hull et al. [6], the char formed during combustion could be broken up due to the water released by the decomposition of ATH. The main idea is to enhance this protective layer by the incorporation of nanoclays. Other authors [7] considered that the amount of ATH could be reduced by the use of nanoclays.

With regards to nanocomposites, the modification treatment of nanoclays has been widely discussed. The modification of nanoclays is necessary to ensure a better balance of the final properties in the nanocomposites. In this sense, ammonium salt surfactants have been chosen as organophilic modifiers for MMT in EVA/MMT/ATH composites in a number of research publications [1, 8, 9].

In our previous work [10], the effect of particle size and surface treatment of ATH filler in EVA/clay/ATH nanocomposites was examined in terms of mechanical and fire retardant properties. It was observed that smaller particle size ATH fillers and silane-coated ATH led to better elongation at break and cone calorimeter test values.

In this work, new modification processes based on the mixing of bentonite nanoclay with other inorganic fillers are described. These new organoclays, that we have called functional organoclay nanofillers (FONs), facilitate the addition of other fillers in nanocomposites during processing and could improve their flame retardant properties due to synergies between the different inorganic fillers. Moreover, the FONs represent an easy way to introduce some inorganic fillers which are difficult to manipulate such as nanoparticles of fumed silica. We used these FONs as new modified fillers in EVA-based composites with ATH in order to improve their fire retardant properties.

Experimental part

Materials

Sodium bentonite clay (Na-BNT) from Tolsa S. A. (Spain) was used as raw material. The bentonite content is 92 % smectite. Mica, gypsum, quartz, and felspar are impurities. After purification, Na-BNT had a cation exchange capacity (CEC) of 96 mequivalents per 100 g and a specific surface area of 50 $m^2 g^{-1}$. The modifier was a dimethyl-dihydrogenated tallow ammonium or 2M2TH (tallow = mixture of fatty acids originated from bovine fat) from Kao Corporation S. A. Nanocomposites obtained with this surfactant had shown optimal properties previously [11]. The secondary inorganic fillers were ATH from Albemarle Corporation (Martinal 104 LE), silica (SiO_2) from Cabot Corporation (Cabosil M5), and sepiolite (SEP) from Tolsa S. A. The properties of ATH, SiO_2 and SEP are shown in Table 1. The polymer matrix used for the compounding of nanocomposites is formed by an EVA

Table 1 Properties of ATH, SiO$_2$, and SEP particles

Properties	ATH	SiO$_2$	SEP
Specific surface area (BET) (m^2/g)	3–5	200	320
Density (g/cm^3)	2.4	2.2	2.0–2.3
Particle shape	Platelet, pseudo-hexagonal	Spherical	Fibril
Dimension	Particle size: 2.2–5.2 μm	Average particle (aggregate) length: 0.2–0.3 μm	Length: 200–2,000 nm Width: 10–30 nm Depth: 5–10 nm

copolymer containing 18 wt% of vinyl acetate (VA) from ExxonMobil Chemical (Escorene UL-00218), a maleic anhydride grafted polyethylene (PE-*g*-MA) from DuPont (Fusabond E226) and an antioxidant from Ciba (Irganox 1010). This polymer blend is an industrial formulation used for cable applications in which EVA copolymer is the major component.

Preparation of FONs

A suspension of Na-BNT was obtained by means of the addition of 10 wt% of Na-BNT in water at room temperature for 24 h. The suspension was stirred at 70 °C for 20 min using a high speed turbine. The modifier 2M2TH had been previously dispersed in water at 70 °C. The amount of 2M2TH was equivalent to 85 % of the CEC of the bentonite. The solution was added by dripping it into the Na-BNT suspension under vigorous stirring. The blend was heated at 80 °C for 1 h and then washed in water. Washing allows the elimination of the excess of modifier. The BNT–2M2TH was dispersed in water at 80 °C. A dispersion of the second inorganic filler in water was obtained mixing them together and stirring for 24 h. This solution was added to the BNT–2M2TH and was stirred for 24 h at room temperature, and then a high speed stirring was applied for 20 min to ensure homogeneity and dispersion of the particles. The obtained FON suspension was dispersed and washed using a 50/50 (vol/vol) ethanol/water mixture. Finally, the FON was dried by spray drying (atomization) in a Rotatory Spray Dryer NIRO 2267, with an inlet temperature of 300 °C and an outlet temperature of 120 °C. FONs based on SiO$_2$, ATH, and SEP as second inorganic fillers were named FON1, FON2, and FON3, respectively. Preparation and characterisation of these FONs has been previously described [1]. In addition, a portion of BNT–2M2TH kept as reference was washed and dried using the same method than that for the FONs.

Preparation of EVA/FON/ATH composites

EVA/FON/ATH composites were obtained in a Leistritz 27 GL twin-screw extruder operating at 150 °C and 200 rpm in co-rotating mode. The formulation and concentration of all the nanocomposites and composites are listed in Table 2. They were produced by a two-step process: in the first one, nanocomposites of EVA/bentonite (95/5 wt%) were obtained by adding the appropriate amounts of polymer

Table 2 Formulation and concentration of the nanocomposites and composites

Sample	EVA matrix	BNT–2M2TH	BNT–SiO$_2$ (FON1)	BNT–ATH (FON2)	BNT–SEP (FON3)	ATH
EVA/BNT–2M2TH	95	5	–	–	–	–
EVA/BNT–2M2TH/ATH	41	5	–	–	–	54
EVA/FON1	95	–	5	–	–	–
EVA/FON1/ATH	41	–	5	–	–	54
EVA/FON2	95	–	–	5	–	–
EVA/FON2/ATH	41	–	–	5	–	54
EVA/FON3	95	–	–	–	5	–
EVA/FON3/ATH	41	–	–	–	5	54

matrix and functional organoclay through the main and side feeders, respectively; in the second step, ATH was incorporated through a side feeder, where the final proportions of EVA/bentonite/ATH composites were 41/5/54 wt%. Pellets of nanocomposites were compression-moulded into test samples by using a Schwabenthan Polystat 200T hydraulic press compression mould.

Characterisation

Thermogravimetric analysis (TGA) was used to study the thermal stability of the composites in N$_2$ under a heating rate of 10 °C/min, using a Thermogravimetry Analysis Mettler Toledo Model TGA851. The gallery distance of bentonite and FONs was evaluated by measuring the X-ray reflection by X-ray diffraction (XRD) in a Philips X'Pert MPD using Cu Kα radiation. The tensile strength (TS) and elongation at break (Eb) were evaluated according to UNE-EN 60811-1-1. The Young modulus (E) was measured according to UNE-EN ISO 527-1. The mechanical properties were measured using an Instron machine model 5500R60025. The fire retardant properties were characterised by UL94 tests, limiting oxygen index (LOI) and cone calorimeter. The UL94 tests were realised according to ASTM D-635/97 (horizontal) and ASTM D-3807/96 (vertical) using five specimens in each test. The LOI values were measured in accordance with ASTM D2863/77 (five specimens were tested) in a Stanton Redcroft with a FTA module. The cone calorimeter was realised according to ISO 5660 in a Fire Testing Technology with a heat flux of 50 kW m^{-2} using three specimens of 100 × 100 × 5 mm, and conventional data were determined (time of ignition, heat release rate, and total heat release, THR).

Results and discussion

XRD analysis

XRD patterns of pristine and modified bentonite, and also EVA/clay and EVA/clay/ATH were analysed in order to estimate the effect of clay modification and
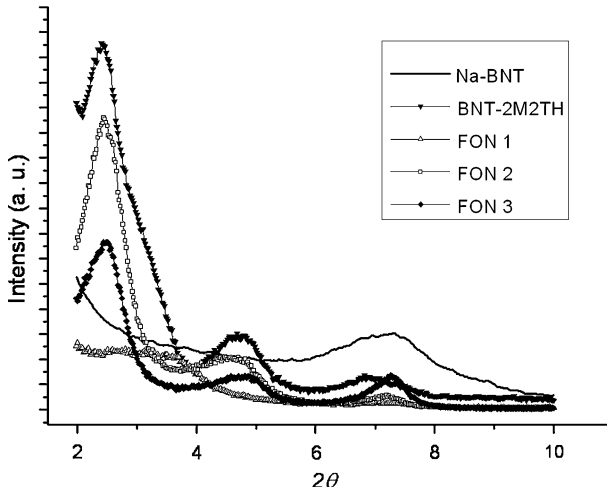
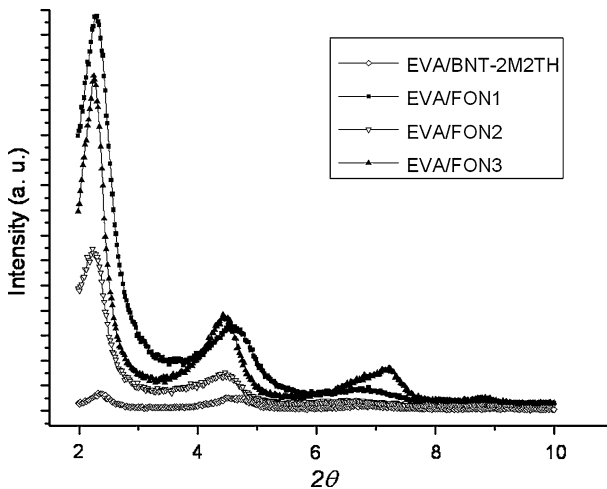**Fig. 1** XRD patterns of pristine bentonite and modified bentonites

Fig. 2 XRD patterns of EVA/bentonite nanocomposites

extrusion process on the interlayer spacing (*d*). XRD patterns of bentonites, nanocomposites and composites are shown in Figs. 1, 2, and 3, respectively. Values of 2θ at small angles and the corresponding interlayer spacing (inferred from Bragg law) are collected in Table 3. These results showed that the initial basal space of Na-BNT was increased around 200 % due to the modification process with 2M2TH. Similar values were shown by the FONs, except for the FON1, because its corresponding peak was not observed in the X-ray pattern, probably due to a low percentage of surfactant incorporated during modification. On the other hand, the increment of the interlayer spacing when each organoclay was added to the matrix
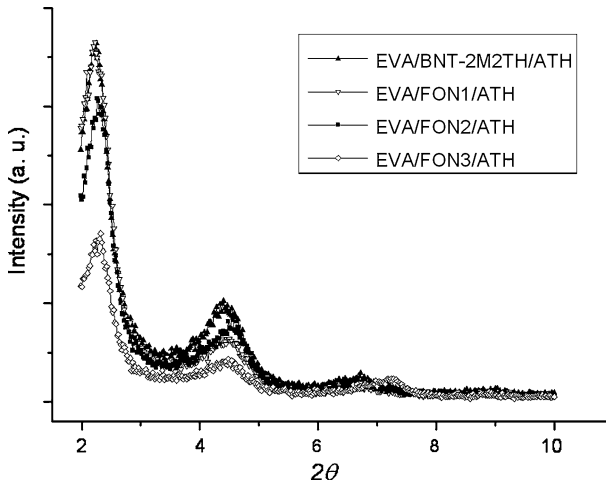
Fig. 3 XRD patterns of EVA/bentonite/ATH composites

could be related to the shear effect produced during the extrusion process. When ATH was incorporated during the second extrusion step, the interlayer spacing was increased in composites with BNT–2M2TH and especially in FON1. This result is believed to be related to the two-step processing, reflecting a good dispersion and interaction between the polymer matrix and the organoclay, and also the presence of smaller aggregates. However, it was not observed in composites with FON2 or FON3, where the interlayer spacing remained nearly unchanged, probably due to the bigger size of the particles.
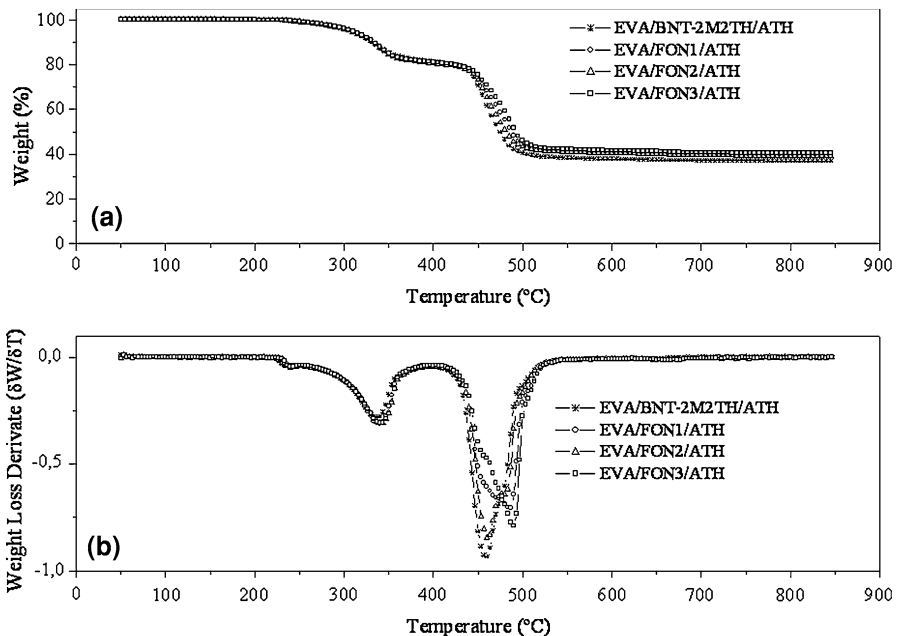
TGA

The TGA thermograms and weight loss derivative curves (DTG) of EVA/clay/ATH composites are shown in Fig. 4. Data extracted from these curves are summarised in Table 4: residue (char at 800 °C), $T_{5\%}$ (temperature at 5 % of sample weight loss) and T_{max} (temperature at maximum decomposition rate). Although the inorganic component of the composite represented 51 % of the total weight, the low proportion of the char was related to the residue left by ATH and clay. The small difference between EVA/BNT–2M2TH/ATH and the rest of the composites is due to the total volatilisation of the unique organic modifier.

In TGA curves, three transitions were observed. The first decomposition was associated to the beginning of the degradation of ATH [10]. The $T_{5\%}$ values were similar in all the samples because the initial decomposition was associated with ATH and EVA degradation. After that, the EVA matrix decomposes in two main steps, as explained elsewhere [11, 12]. The first transition (peak temperature: 340 °C) was principally influenced by the dehydration reaction of the ATH, and there was no difference among them. However, the second degradation was produced at different temperatures. Composites of EVA/BNT–2M2TH/ATH and EVA/FON2/ATH showed a peak temperature around 460 °C, which is related to the

Table 3 Gallery distances (*d*) measured by XRD for organoclays, nanocomposites and composites

Material	2θ (°)	d (nm)
Na-BNT	7.90	1.21
BNT–2M2TH	2.42	3.65
EVA/BNT–2M2TH	2.36	3.74
EVA/BNT–2M2TH/ATH	2.24	3.94
FON1	–	–
EVA/FON1	2.28	3.87
EVA/FON1/ATH	2.20	4.01
FON2	2.46	3.59
EVA/FON2	2.24	3.94
EVA/FON2/ATH	2.28	3.87
FON3	2.46	3.59
EVA/FON3	2.26	3.91
EVA/FON3/ATH	2.28	3.87

Fig. 4 Thermogravimetric analysis of EVA/BNT–2M2TH/ATH and the EVA/FONs/ATH composites **a** TGA thermograms and **b** weight loss derivate curves

decomposition process of ATH; the protective layer generated through the calcination was destroyed by the water evaporated during the TGA experiment [6]. On the other hand, a similar second degradation than virgin EVA was shown at higher temperature ($T_{\max}$ around 490 °C) in EVA/FON1/ATH and EVA/FON3/

Table 4 Residue and decomposition temperature of EVA/clay/ATH composites

Sample	Residue (%)	$T_{5\%}$ (°C)	T_{max} (°C)
EVA/BNT–2M2TH/ATH	37.03	305	458
EVA/FON1/ATH	39.34	308	485
EVA/FON2/ATH	39.29	307	460
EVA/FON3/ATH	40.41	309	490

ATH composites, probably due to a compensation between the acceleration caused by ATH and the protective effect of silica and SEP in these composites.

Mechanical properties

Generally, reinforcements such us nanoclays, being much stiffer and stronger than the polymer, usually increase its modulus and strength. The TS and Eb have a high sensitivity to (1) the interfacial adhesion between organoclay and polymer, and (2) the ability of the polymer chains to line up in response to an applied effort. Therefore, measuring these properties provides relevant information that may be related to the morphology of the composites. TS, Eb, and E of EVA and EVA/clay/ATH are summarised in Table 5.

Elastic properties (TS and Eb) were diminished and the stiffness (E) was increased when the fillers (organoclay and ATH) were added to the polymer matrix, due to the restriction of the polymer chain movement and their reinforcing effect. Regarding the composites, TS was practically the same for all the materials, whereas EVA/BNT–2M2TH/ATH and EVA/FON1/ATH showed higher Eb values, probably related to a good dispersion and interaction between matrix and particle, as seen in XRD, supporting the idea of smaller aggregates in these composites. On the other hand, lower values of Eb were measured in materials with the lowest interfacial spacing showed in XRD.

A low interfacial spacing could represent the presence of big aggregates, that act as defects in the material and stress concentrated zones [13, 14], producing a reduction in Eb. The higher amount of ATH in EVA/FON2/ATH and the bigger size of ATH in comparison to SiO_2, make the Eb lower in EVA/FON2/ATH than in EVA/FON1/ATH. On the other hand, the lower value of Eb observed for EVA/FON3/ATH may be related to the fact that the fibril structure of SEP in FON3 could form a network within the matrix that makes the movements of the polymer chains

Table 5 Mechanical properties of EVA and EVA/clay/ATH composites

Sample	TS (MPa)	Eb (%)	E (MPa)
EVA	18 ± 1	845 ± 35	78 ± 3
EVA/BNT–2M2TH/ATH	9 ± 1	150 ± 15	284 ± 2
EVA/FON1/ATH	10 ± 1	156 ± 18	331 ± 6
EVA/FON2/ATH	10 ± 1	120 ± 22	328 ± 5
EVA/FON3/ATH	11 ± 1	90 ± 20	331 ± 6

more difficult [15] and reduces the elasticity of the composite. With regards to the modulus, the composites elaborated with FON organoclays exhibited higher E values in comparison to the EVA/BNT–2M2TH/ATH composite, so a better reinforcement was obtained by the combination of inorganic fillers and bentonite.

Fire retardant properties

UL94 burn test and cone calorimeter were performed to evaluate the fire retardant properties of the composites. The results are summarised in Table 6. All the composites were rated as HB and V0 in the horizontal and vertical UL94 test, respectively, which is indicative of an improvement in the fire retardant properties. Also, LOI values (minimum oxygen concentration needed for combustion) were improved due to the high amount of ATH, but there was no difference among the FONs used. However, variations in fire retardant properties dependent on the clay's modification process cannot be extracted from these techniques. For this reason, cone calorimeter test was carried out as it is more sensitive to the composition of the sample tested. Due to the poor fire retardant behaviour of EVA matrix observed during the UL-94 test and the high pHRR value (above 2,000 kW m^{-2}) reported elsewhere [16], cone calorimeter test was not carried out for pure EVA.

Peak of heat release rate (pHRR) values were comparable, except for EVA/FON2/ATH, where the pHRR was slightly higher than for the other composites. These results suggest that the synergistic effect is greater for bentonite with silica (FON1) and with SEP (FON3) than for bentonite with ATH (FON2). This is an expected effect in the case of bentonite with SEP taking into account that both inorganic fillers are phyllosilicates and have analogous chemical composition. However, the differences between the pHRR may be also influenced by the specific combustion mechanism of the different inorganic fillers used (silica, ATH, SEP). The time of ignition was improved in all the FON-based composites, especially in EVA/FON1/ATH, where a greater flame retardant effect has been achieved by the presence of silica. On the contrary, the THR of the FON-based composites was higher than that for the BNT–2M2TH composite, probably due to the presence of the second inorganic filler. It would be worth noting that EVA/FON3/ATH showed the lower THR among the FON-based composites, confirming the synergistic effect between bentonite and SEP explained above.

Table 6 Fire retardant properties of EVA and EVA/clay/ATH composites

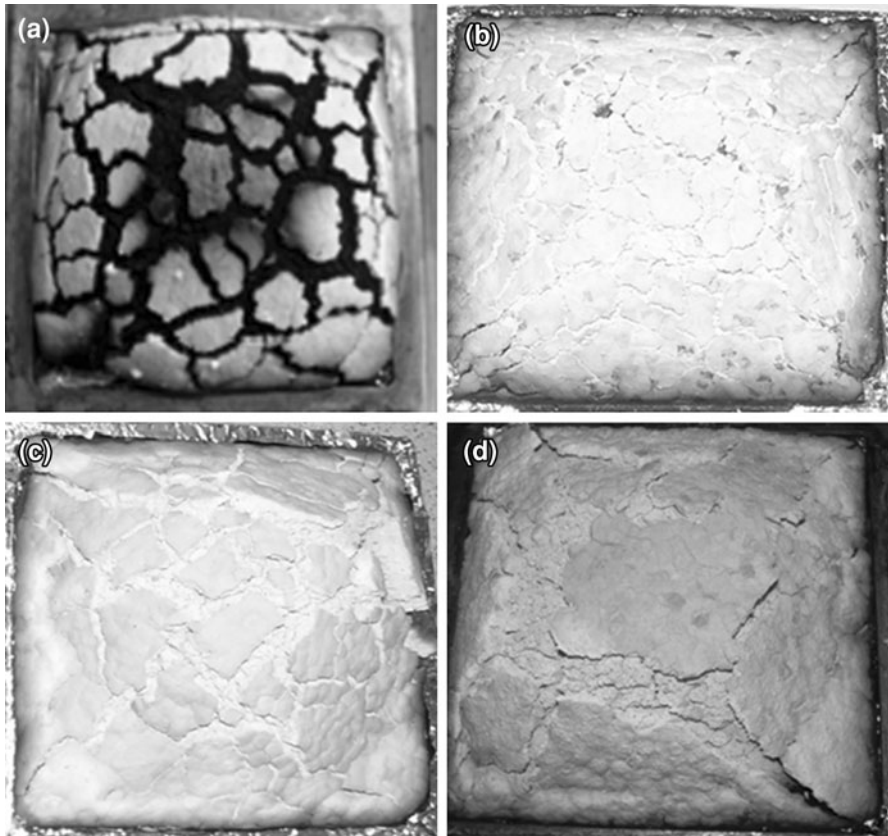| Sample	UL94 test		LOI (%)	Cone calorimeter		
	UL94H	UL94V		$t_{ignition}$ (s)	pHRR (kW m^{-2})	THR (MJ m^{-2})
EVA	Fail	Fail	20	–	–	–
EVA/BNT–2M2TH/ATH	HB	V0	30	53	152	92
EVA/FON1/ATH	HB	V0	31	112	157	168
EVA/FON2/ATH	HB	V0	31	88	174	151
EVA/FON3/ATH	HB	V0	32	87	154	132

Fig. 5 Images of composite samples after Cone Calorimeter test: **a** EVA/BNT–2M2TH/ATH, **b** EVA/FON1/ATH, **c** EVA/FON2/ATH, and **d** EVA/FON3/ATH

In addition, the morphology of the char formed during the cone calorimeter test (Fig. 5) varied depending on the composition. The residual char was more uniform and rigid for those composites based on FONs. In the EVA/BNT–2M2TH/ATH composite, deeper cracks were observed, reflecting a poor stability of the residual char. In EVA/FON3/ATH composite, a uniform and rigid layer was formed, so the contribution of SEP to forming a more rigid layer of char much was evidenced, possibly due to the fibril structure of this type of clays.

Conclusions

Composites of EVA/clay/ATH with different organoclay functionalizations were created and characterised. The new modification process using bentonite and other inorganic fillers led to an increase of the interlayer space of nanoclays within the composite, an improvement in stiffness with a reduction in toughness, and also, an enhancement in flame retardant properties. Overall, the silica-based functional

organoclay (FON1) showed to be the best nanofiller option to improve the mechanical and fire retardant properties of EVA/clay/ATH composites.

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