

## Article

# Influence of the Process of Synthesis of Zeolites from Volcanic Ash in Its Synergistic Action as a Flame-Retardant for Polypropylene Composites

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**Abstract:** In this research, the influence of natural zeolites obtained from the volcanic ash of the Ubinas volcano has been studied as synergistic agents in a flame-retardant system (composed of ammonium polyphosphate, pentaerythritol, and polypropylene). Four zeolites were synthesized from volcanic ash, including those that had been calcined and those that had not. These were then placed in an alkaline solution at three synthesis temperatures. Zeolites were characterized through X-ray diffraction, specific surface area by nitrogen adsorption analysis (Brunauer–Emmett–Teller) and scanning electron microscopy. Polypropylene matrix composites were prepared with ammonium polyphosphate, pentaerythritol and zeolites at 1, 5 and 9%. Its thermal stability and fire resistance were evaluated by thermogravimetric analysis, limiting oxygen index, vertical burning test and cone calorimeter and its morphological structure by scanning electron microscopy. It was determined that the synthesis temperature and the use of calcined and without calcined volcanic ash have an influence on the characteristics of the zeolites and on its synergistic action.

**Keywords:** zeolite; volcanic ash; flame-retardant; polypropylene

## 1. Introduction

Polypropylene is a thermoplastic polymer that is widely used for application in textiles and plastics due to its low cost and high chemical resistance in acidic and alkaline environments [1]. However, being a petroleum derivative, it tends to be flammable, so the use of flame-retardant additives is required for its application [2].

Flame retardants are chemical compounds that are incorporated into plastics or textiles in order to reduce or stop their flammability [3]. Among the flame-retardant additives include intumescent fire systems that are characterized by forming an expanded carbonaceous layer on the polymer surface when thermal degradation begins. In addition, this intumescent system is characterized for being environmentally friendly compared with other traditional flame retardants such as those containing halogen [4,5]. An intumescent flame-retardant system is composed of an acid source, a charring agent, a blowing agent and additionally, synergistic agents can be used. The acid source is responsible for promoting

the dehydration of a carbonizing agent, while the carbonizing agent provides the carbons that will constitute the carbonaceous layer. Flame retardants can be minerals, phosphorus-based compounds, bromides, and chlorides. The most used and efficient are phosphorous formulations like ammonium polyphosphate and triphenyl phosphate [6]. However, its disadvantage is that if the polymer does not contain reactive groups, the addition of a carbonized co-additive is required to contribute to the carbonization, which can be a polyol such as pentaerythritol (PER). Thus, the use of PER with ammonium polyphosphate (APP) in several types of research has demonstrated an improvement in flame-retardant properties [4,5,7]. Furthermore, it has been seen that adding other compounds, in addition to the retardant additives, improves their activity, since these compounds, known as synergistic agents, improve the action of the flame-retardant additives [8,9]. As synergistic agents for polypropylene matrix composites, an improvement in flame-retardant properties was obtained using natural zeolites; in other studies, volcanic ash, rice husk ash, and heat-treated solid waste were used [8]. The zeolite, volcanic ash and rice husk are characterized by having abundant silica and alumina in their composition, which is the reason why other authors have used volcanic ash and rice husk as a source of raw material to synthesize zeolites [10–13]. Although these authors have carried out the synthesis of these natural zeolites, their flame-retardant activity has not been determined.

According to Wei et al. [14], the  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  have shown a flame retardant activity, but it is needed a high quantity of them; they probe that  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  had increased the thermal stability of the ammonium polyphosphate, pentaerythritol and polypropylene (APP-PER-PP). Thus, knowing the predominance of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in the zeolite is probably that the zeolites have a positive effect in flame retardant additives, as was determined by Feng et al. [7], who use the zeolites type A in a polypropylene-flame retardant composite (PP/FR) and determine its proficient synergistic action in flame-retardant additive as like a smoke inhibitor. Wang et al. [15] used the zeolites type 4A and 13X like synergistic agents in cooperation with APP and the flame-retardant activity in wood-plastic composites improved. Wu et al. [16] studied the synergistic effect between different zeolites such as type 3A that has a superior flame-retardant activity against APP, and the X zeolite had an upper affinity for  $\text{CO}_2$  molecules and an enhanced adsorption capacity than type A. In addition, the 13X zeolite had an outstanding activity as a smoke inhibitor.

Furthermore, considering that the volcanic ash, collected from the Ubinas volcano, when it was used as a synergistic agent in the polypropylene matrix, had good results as a synergistic agent of APP and PER [8]. Therefore, the aim of the present research was to determine whether the different synthesis conditions such as the use of calcined and without calcined volcanic ash, in an alkaline solution of NaOH at three reaction temperatures (120, 150, and 180 °C) during 12 h, affect their flame-retardant activity as a synergistic agent. For this, the textural and morphological characterization of the synthesized zeolites has been performed through the nitrogen adsorption analysis (Brunauer–Emmett–Teller method) and Scanning electron microscopy. Then, the polypropylene matrix was prepared with ammonium polyphosphate (APP) and pentaerythritol (PER), which was characterized by thermogravimetric analysis, scanning electron microscopy, limiting oxygen index, vertical burning test (UL-94), and cone calorimeter.

## 2. Materials and Methods

The zeolites (Z1, Z2, Z3, and Z4) were synthesized from volcanic ash that was collected from Ubinas volcano, located in Moquegua (Peru) whose composition is depicted in Table 1. The conditions of synthesis were at 1.5 M NaOH solution, at different temperatures (120, 150 and 180 °C) during 12 h of reaction time as indicated in Table 2.

**Table 1.** Chemical composition of volcanic ash.

| Oxides                         | (%)   | Oxides                         | (%)  | Oxides                        | (%)  |
|--------------------------------|-------|--------------------------------|------|-------------------------------|------|
| SiO <sub>2</sub>               | 51.3  | SO <sub>3</sub>                | 7.3  | P <sub>2</sub> O <sub>5</sub> | 0.16 |
| K <sub>2</sub> O               | 1.84  | Fe <sub>2</sub> O <sub>3</sub> | 3.8  | others                        | 0.09 |
| Al <sub>2</sub> O <sub>3</sub> | 26.19 | MnO                            | 0.05 | P.F. *                        | 3.53 |
| CaO                            | 4.92  | TiO <sub>2</sub>               | 0.8  |                               |      |

\* P.F.: Loss to fire.

**Table 2.** Conditions of zeolite synthesis.

| Sample Code | Temperature (°C) | NaOH Molarity (M) | Time (h) |
|-------------|------------------|-------------------|----------|
| Z1          | 120              | 1.5               | 12       |
| Z2          | 150              | 1.5               | 12       |
| Z3          | 180              | 1.5               | 12       |
| Z4 *        | 120              | 1.5               | 12       |

\* The zeolite Z4, the volcanic ash before being taken to the Teflon liner, was calcined in the stove at 500 °C for 4 h and the following procedure was the same.

### 2.1. Materials and Process

The volcanic ash collected was dehydrated and ground in a mono planetary mill at 450 rpm for 25 min until a powder with a particle size of 75 µm was obtained. Subsequently, 10 g of the volcanic ash was weighed, which was placed into a Teflon liner with 60 mL of NaOH (1.5 M) and taken to a batch reactor. The batch reactor was put into the oven at a temperature of 120, 150, or 180 °C for 12 h.

After the reaction time ended, the sample was left to rest for two days in order to optimize the crystals' growth and their stabilization and then the sample was washed with 500 mL of distilled water in a beaker and left to rest for a day for its sedimentation. Then the vacuum filtration of the sample was proceeded to eliminate the greatest amount of water and finally dried on the stove at 100 °C for 3 h. The dried sample was placed in a labeled bottle.

### 2.2. Characterization of the Zeolites

The four natural zeolites (Z1, Z2, Z3 and Z4) were characterized, their structural phases of the zeolites were achieved by X ray diffraction (XRD) using a Bruker (D8 Avance Davinci, Lille, France) diffractometer with CuKα (λ = 0.1542 nm) radiation operated at 40 kV, 40 mA with a 2θ range from 5° to 90° and a 0.6°/min scan rate. Textural analysis for the precursors were performed by adsorption and desorption isotherms of nitrogen at 77 K in an ASAP 2020 Micromeritics apparatus (Brunauer–Emmett–Teller method) and the specific surface area (S<sub>BET</sub>) was determined by Brunauer–Emmett–Teller (BET) analysis.

The morphology of the zeolites was observed using an EVO MA10 (Carl Zeiss) Scanning Electron Microscopy (SEM) at 3.0 kV, 50 µm, and 10 µm.

### 2.3. Synthesis of Polypropylene Composites

The retardants additives used were the Exolit AP 422 ammonium polyphosphate (APP) supplied by Clariant Plastics & Coatings S.A.C (Lima, Peru), Charmor PM 15 pentaerythritol (PER) was provided by Perstop Group from Ohio (United States). Polypropylene (PP 5707N) was provided by Saudi Basic Industries Corporation (Sabic) from Houston (United States).

The natural zeolites were used to prepare the plates using a micro extruder (DSM Research micro-twin-screw model, Xplore, Lille, France). To prepare the mixture of zeolites with flame retardant additives and polypropylene, the micro extruder was heated at 185 °C and when the set temperature was achieved, the polypropylene was poured into it for 4 min, then the PER was poured and mixed with the PP for 2 min, then the APP for 3 min and finally the other zeolites for 6 min. The mixing speed was set at 50 rpm.

Finally, to give a certain shape to the extruded mixture, it is placed in the Heated platen press (Fontaine LabEcon300 Junior, Lille, France) at two temperatures, 100 °C is set for the mold and 190 °C for the transfer system. The extruded mixture was subjected to those temperatures while being crushed at a pressure of 10 kN for 4 min, after of 20 kN for 2 min and 40 kN for 3 min. It was obtained plates with the dimensions of  $100 \times 100 \times 3 \text{ mm}^3$  that were used in the calorimetric cone test and other plates with the dimensions of  $100 \times 10 \times 3 \text{ mm}^3$  for the Limiting oxygen index (LOI) and Vertical burning test (UL-94).

Table 3 shows the formulations of the polymeric matrix; it should be noted that the APP:PER ratio of 2:1 has been used and in all samples, the following concentration was kept: 70% of PP, 20% of APP, 10% of PER and 1%, 5% and 9% of zeolites.

**Table 3.** Composition of samples and the flame retardancy composites.

| Sample      | PP (wt%) | APP (wt%) | PER (wt%) | Z1 (wt%) | Z2 (wt%) | Z3 (wt%) | Z4 (wt%) |
|-------------|----------|-----------|-----------|----------|----------|----------|----------|
| PP_FR       | 70.0     | 20.0      | 10.0      |          |          |          |          |
| PP_FR_Z1-1% | 69.3     | 19.8      | 9.9       | 1.0      |          |          |          |
| PP_FR_Z1-5% | 66.5     | 19.0      | 9.5       | 5.0      |          |          |          |
| PP_FR_Z1-9% | 63.7     | 18.2      | 9.1       | 9.0      |          |          |          |
| PP_FR_Z2-1% | 69.3     | 19.8      | 9.9       |          | 1.0      |          |          |
| PP_FR_Z2-5% | 66.5     | 19.0      | 9.5       |          | 5.0      |          |          |
| PP_FR_Z2-9% | 63.7     | 18.2      | 9.1       |          | 9.0      |          |          |
| PP_FR_Z3-1% | 69.3     | 19.8      | 9.9       |          |          | 1.0      |          |
| PP_FR_Z3-5% | 66.5     | 19.0      | 9.5       |          |          | 5.0      |          |
| PP_FR_Z3-9% | 63.7     | 18.2      | 9.1       |          |          | 9.0      |          |
| PP_FR_Z4-1% | 69.3     | 19.8      | 9.9       |          |          |          | 1.0      |
| PP_FR_Z4-5% | 66.5     | 19.0      | 9.5       |          |          |          | 5.0      |
| PP_FR_Z4-9% | 63.7     | 18.2      | 9.1       |          |          |          | 9.0      |

PP: Polypropylene; FR: Flame-retardant (APP:PER), Z1, Z2, Z3, and Z4: zeolites

#### 2.4. Characterization of Polypropylene Composites

The thermal degradation of the composites was carried out using a Discovery Series thermogravimetric analyzer (TGA) in aTA INSTRUMENTS, (Lille, France) from room temperature to 800 °C at a heating rate of 10 °C/min. Nitrogen was used as a carrier gas with a constant flow rate during analysis.

The morphology of the composites was tested in an EVO MA10 (CARL ZEISS) SEM operated at 5 kV.

Several tests were made to characterize the flammability properties for the different samples:

The Limiting oxygen index (LOI) is the minimal percent concentration of oxygen that remains flame combustion of the sample for 3 min or consumes a length of 5 cm of the sample. This measurement is defined in the context of standard ASTM D2863 [17]. The LOI measurement was performed on a Fire Testing Technology equipment instrument (East Grinstead, UK) on sheets ( $100 \times 10 \times 3 \text{ mm}^3$ ).

The Vertical burning test (UL-94) is a test that allows measuring the ability of a material to extinguish the flame after ignition and its dripping behavior in response to a small open flame or radiant heat source under controlled laboratory conditions. It was carried out using a Fire Testing Technology equipment according to ASTM D3801 [18], IEC 60695-11-10 [19], IEC 60707 [20], ISO 1210 [21] with barrels of  $100 \times 10 \times 3 \text{ mm}^3$ . The barrels are ignited by a blue flame of 20 mm. The burner that generates the flame is supplied with methane gas having a flow rate of 100 mL/min. For each formulation, five specimens were tested.

The Cone calorimetric test (CCT) was done using a CCT (Fire Testing Technology, East Grinstead, UK) according to ISO 5660. Each specimen, with the dimensions of

$100 \times 100 \times 3 \text{ mm}^3$ , was wrapped in aluminum foil and exposed horizontally to an external heat flux of  $35 \text{ kW/m}^2$  and  $50 \text{ kW/m}^2$  with 35 mm of separation. All samples were run in triplicate and the average value was reported.

### 3. Results and Discussion

#### 3.1. Material Characterization

Table 4 shows the textural properties of the zeolites where it is clearly observed that the synthesis conditions, that is, the temperature variation, affect its textural properties. It should be noted, by Almirón et al. [8], that volcanic ash from the Ubinas volcano, which was used as raw material for the synthesis of zeolites, has a pore size of  $430.8 \text{ \AA}$ , a pore volume of  $82.0 \text{ mm}^3/\text{g}$ , a micropore area of  $1.2 \text{ m}^2/\text{g}$  and  $2.06 \text{ m}^2/\text{g}$  of  $S_{\text{BET}}$ . For Z1 to Z3, it is clearly observed that the increase of the temperature has an influence on the increase of the pore size and the micropore area, and a remarkable decrease of the  $S_{\text{BET}}$ . If we compare Z4 to Z1, it is clear that the calcination of Z4 at  $500 \text{ }^\circ\text{C}$ , then the setting in the oven at  $120 \text{ }^\circ\text{C}$ , leads to an increase the pore size, the micropore area and the  $S_{\text{BET}}$ . Therefore, it can be deferred that the exposure of the volcanic ash with NaOH solution at different temperatures has caused the amorphous and less stable components to be eliminated, which causes a greater generation of crystallization that results in a variation in its textural properties as reported [22,23]. In addition, these changes in their textural properties also have been seen in their morphology that as shown in Figure 1.

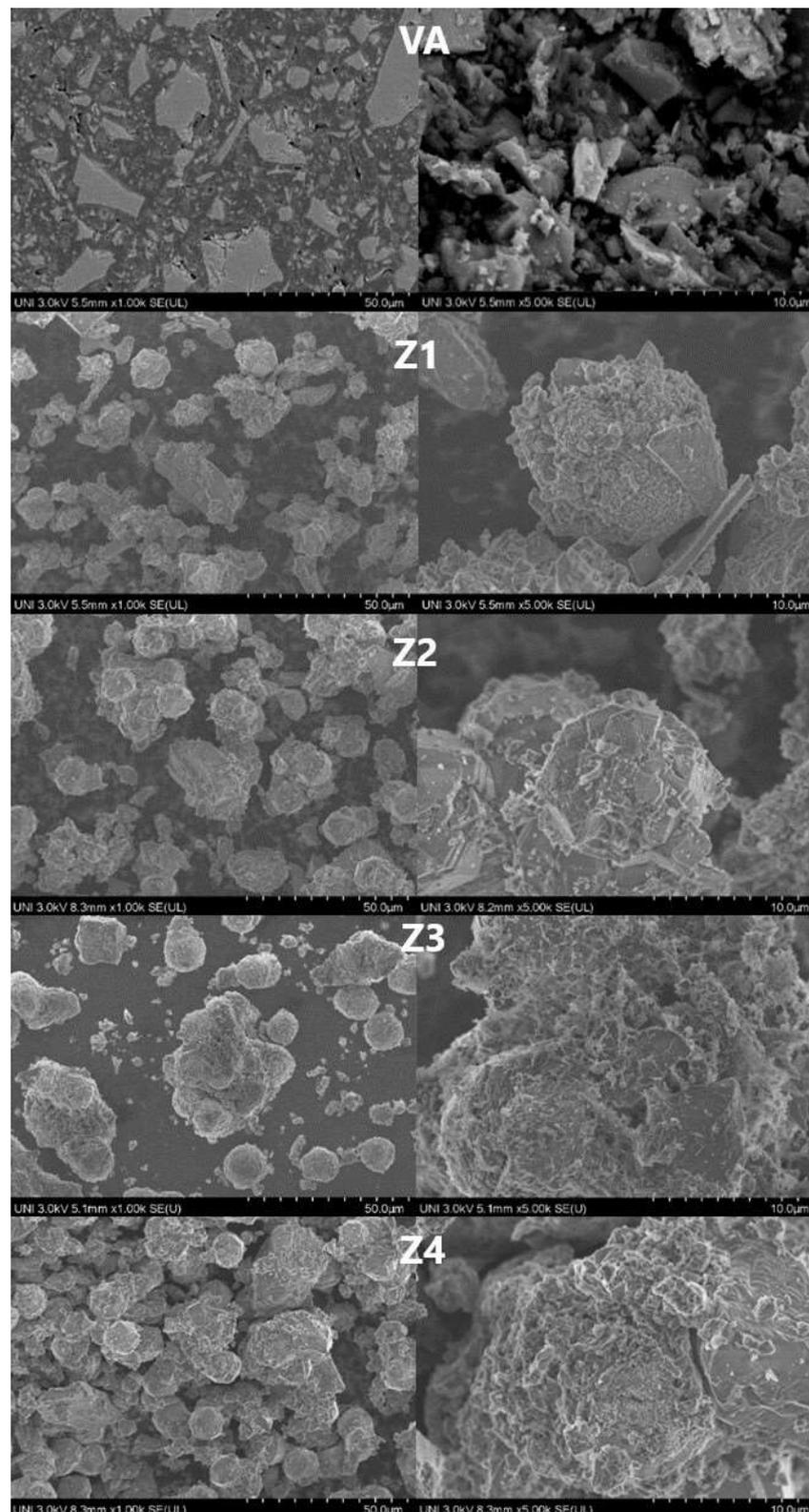
**Table 4.** Textural properties.

| Samples | Temperature ( $^\circ\text{C}$ ) | Pore Size ( $\text{\AA}$ ) | Pore Volume ( $\text{mm}^3/\text{g}$ ) | Micropore Area ( $\text{m}^2/\text{g}$ ) | $S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ ) |
|---------|----------------------------------|----------------------------|--|--|--|
| Z1      | 120                              | 66.49                      | 38.26                                  | 0.13                                     | 27.85                                      |
| Z2      | 150                              | 96.84                      | 47.12                                  | 8.08                                     | 25.91                                      |
| Z3      | 180                              | 146.81                     | 39.70                                  | 8.60                                     | 11.43                                      |
| Z4      | 120                              | 76.89                      | 37.90                                  | 6.26                                     | 30.56                                      |

It is worth mentioning that as the synthesis temperature increased, the pore size has also increased, being the highest value obtained of the Z3 zeolite (synthesized at  $180 \text{ }^\circ\text{C}$ ), which was also observed in zeolites synthesized from fly ash when its synthesis temperature varied [24]. However, when increasing the temperature, the  $S_{\text{BET}}$  of the Z3 zeolite decreases, reaching a value of  $11.43 \text{ m}^2/\text{g}$ ; this is probably due to the fact that the textural properties are affected not only by the temperature but also by the molar concentration of the solution [23,25]. It is important to mention that Z1 and Z4 zeolite have the same synthesis temperature; however, the values of its textural properties vary, because volcanic ash has undergone calcination at  $500 \text{ }^\circ\text{C}$  for the synthesis of Z4 zeolite, and it is known that the calcination at  $500 \text{ }^\circ\text{C}$  causes that organic and volatile material to be removed without altering the framework of the zeolites and in this case the synthesized zeolite showed an improvement in the absorption and thermal properties [22,23].

Comparing the  $S_{\text{BET}}$  values of synthesized zeolites using several sources as raw material, we have obtained  $10.80 \text{ m}^2/\text{g}$  at  $150 \text{ }^\circ\text{C}$  using fly ash and NaOH solution [16],  $348 \text{ m}^2/\text{g}$  using rice husk ash with aluminum foil and sodium hydroxide at  $100 \text{ }^\circ\text{C}$  for 15 h of reaction [13]. Zeolites used as flame-retardants like X zeolite have a surface area of  $622 \text{ m}^2/\text{g}$  [23], zeolite type A with  $355 \text{ m}^2/\text{g}$  [24] and zeolite type 13X with  $440 \text{ m}^2/\text{g}$  [25]. It is important to mention that in cases whose  $S_{\text{BET}}$  values are high, there is a control of the Si/Al ratio that favors a greater surface area.

SEM analysis is depicted in Figure 1. As can be seen in Figure 1, there is a difference between the morphology of volcanic ash and the natural zeolites synthesized from them.



**Figure 1.** Micrographs of volcanic ash (VA) and the zeolites (Z1, Z2, Z3 and Z4).

In addition, Figure 1 shows that the morphology of the zeolites synthesized from volcanic ash is very similar between them, having a form of loose crystals with a pseudo-spheres form; this same morphology was observed by Liu et al. [25] at the same reaction time of 12 h. Therefore, it can be corroborated what is indicated by Liu et al. [25] who

has established that the reaction time has an influence on the morphology of the synthesized zeolites while the reaction temperature and molarity of the solution affect the crystal formation and size distribution [25].

It is worth noting that the natural zeolites, Z1 and Z2, show a mix of pseudo-spherical and rough particles with smooth cubic crystals; while the Z3 and Z4 zeolites have a rougher-looking structure, which corroborates the aforementioned, that is, the increase in temperature influences the morphology as well as the reaction time [25]. Liu et al. [25] obtained pseudo-spherical and rough morphology, as in the present research, at reactions greater than 8 h, while smooth cubic crystals were obtained at 4 h. Therefore, these changes in morphology correspond to the transformations of the natural zeolite that occur as a consequence of increasing the temperature, reaction time and molarity of the NaOH solution [23,25].

Figure 2 shows the diffractogram of the four zeolites synthesized from volcanic ash. It is clearly seen how the variation of the reaction temperature influences on the peaks present in the zeolites, so that for Z1 zeolite a greater crystallinity is observed than with Z4, which has more amorphous phases. This is due to the calcination process of the volcanic ash that has affected the characteristics of the zeolite obtained. Additionally, it is observed that Z1 and Z3 zeolites are the ones with the highest crystallinity, in addition, the peaks that show the Z1 and Z3 are similar, while the Z2 and Z4 also show similar peaks.

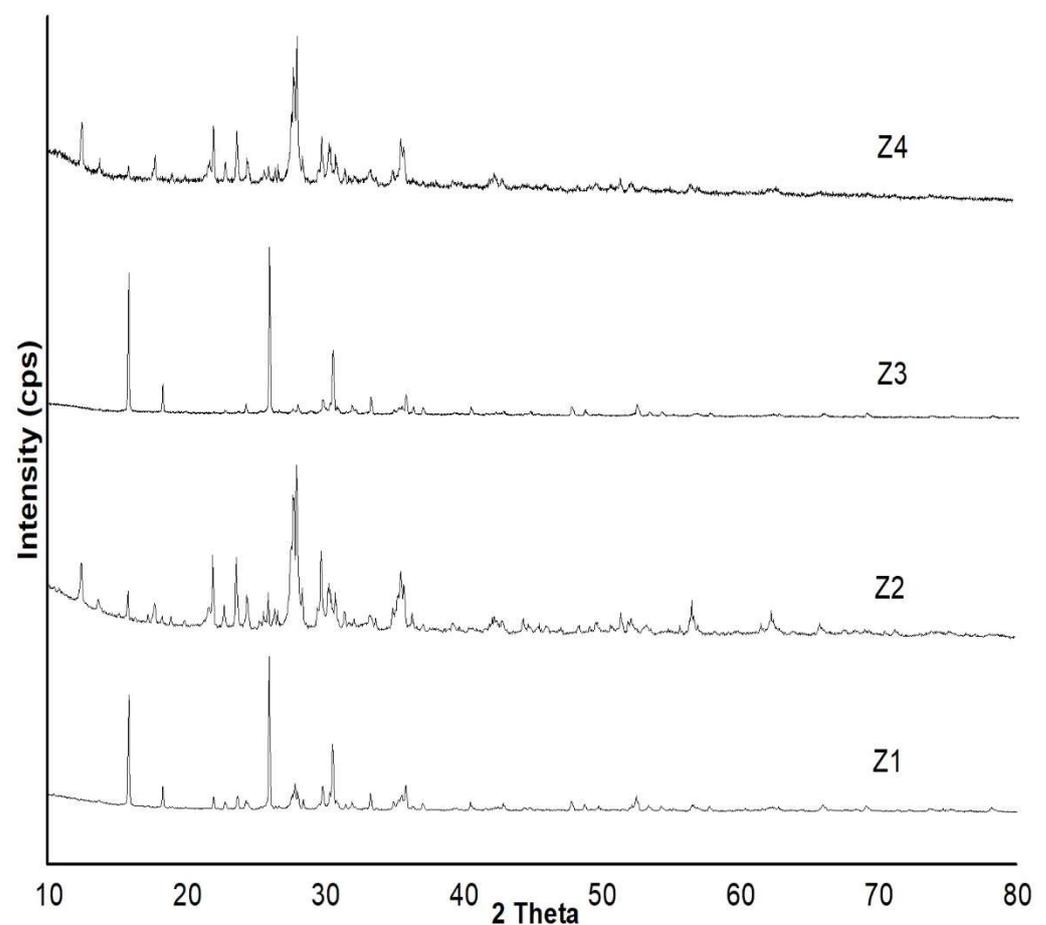


Figure 2. XRD pattern of zeolites: Z1, Z2, Z3 and Z4.

The Z1, Z2 and Z3 zeolites show peaks  $2\theta$  at  $15.8^\circ$  which corresponds to the presence of zeolites, Z1 and Z3 have presented peaks at  $26^\circ$  and  $30.6^\circ$  that also correspond to the zeolites. The Z2 sample contains zeolite and plagioclase according to the following peaks

at 28° and 35.5° [26,27]. Z4 zeolite exhibits zeolites due to the presence of peaks at 21.9° and 35.4° and plagioclase at the peaks at 28° and 23.6° [26,27].

### 3.2. Characterization of Polypropylene Composites

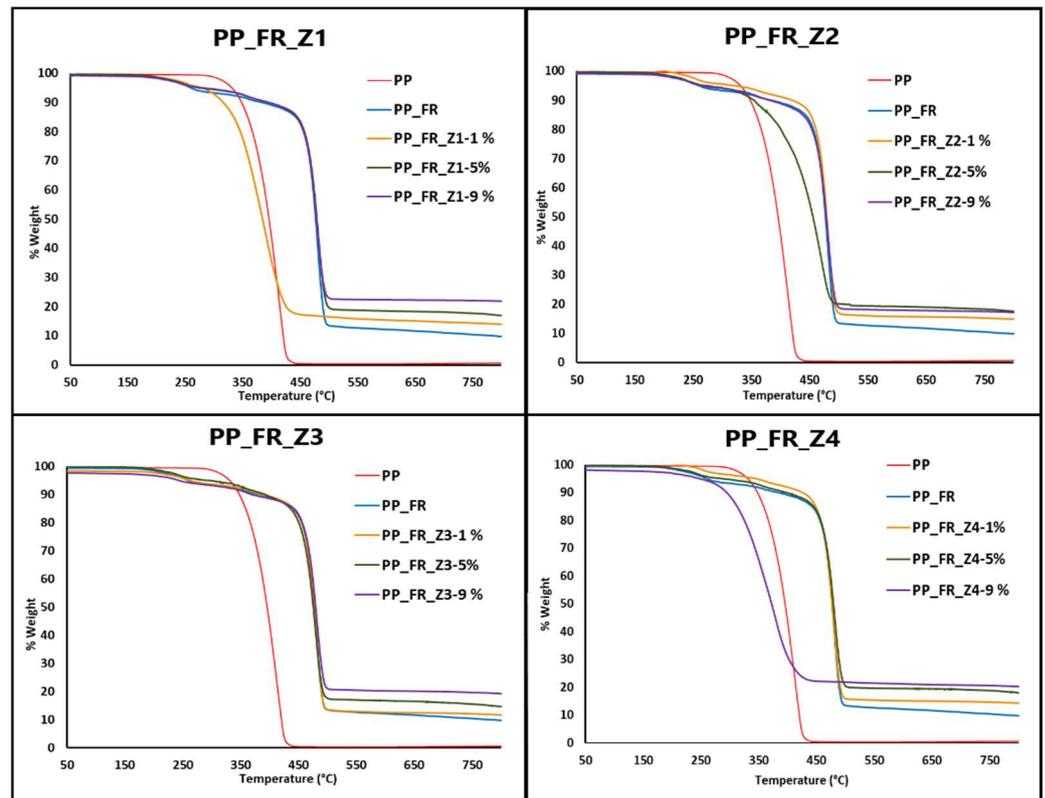
TGA data is shown in Table 5, as observed for the four groups of polymeric matrices using the four types of natural zeolites, the thermal degradation initiation temperature ( $T_{\text{onset}}$ ) decreases compared to PP, which begins its degradation at 293 °C, and it decreases to 184 °C with APP:PER retardants. This is consistent with the expected behavior since initially, both APP:PER begin their degradation before PP to form the carbonaceous protective layer [8].

**Table 5.** Onset and maximum temperature (°C) of samples and residue at 800 °C (%).

| Samples     | $T_{\text{onset}}$<br>(°C) | Average<br>$T_{\text{onset}}$ | $T_{\text{max}}$<br>(°C) | Average<br>$T_{\text{max}}$ | Residue (%) at<br>800 °C |
|-------------|----------------------------|-------------------------------|--------------------------|-----------------------------|--------------------------|
| PP          | 293                        |                               | 445                      |                             | 0.0                      |
| PP_FR       | 184                        |                               | 481                      |                             | 9.8                      |
| PP_FR_Z1-1% | 164                        | 173                           | 383                      | 427                         | 13.9                     |
| PP_FR_Z1-5% | 179                        |                               | 419                      |                             | 16.9                     |
| PP_FR_Z1-9% | 176                        |                               | 480                      |                             | 21.9                     |
| PP_FR_Z2-1% | 209                        | 187                           | 482                      | 478                         | 14.9                     |
| PP_FR_Z2-5% | 160                        |                               | 469                      |                             | 17.1                     |
| PP_FR_Z2-9% | 192                        |                               | 483                      |                             | 17.8                     |
| PP_FR_Z3-1% | 195                        | 185                           | 481                      | 462                         | 11.7                     |
| PP_FR_Z3-5% | 174                        |                               | 423                      |                             | 19.3                     |
| PP_FR_Z3-9% | 185                        |                               | 482                      |                             | 20.6                     |
| PP_FR_Z4-1% | 219                        | 177                           | 480                      | 428                         | 14.3                     |
| PP_FR_Z4-5% | 126                        |                               | 423                      |                             | 18.0                     |
| PP_FR_Z4-9% | 187                        |                               | 382                      |                             | 20.3                     |

If we compared the four groups of zeolites, the PP\_FR\_Z1 composite (synthesized at 120 °C) starts its degradation earlier, while the others slightly later without reaching the  $T_{\text{onset}}$  of PP. Besides, the temperature at one sample lost maximum of its weight ( $T_{\text{max}}$ ) is higher than the value of PP, which indicates the effectiveness of adding FR\_Zeolite [9].

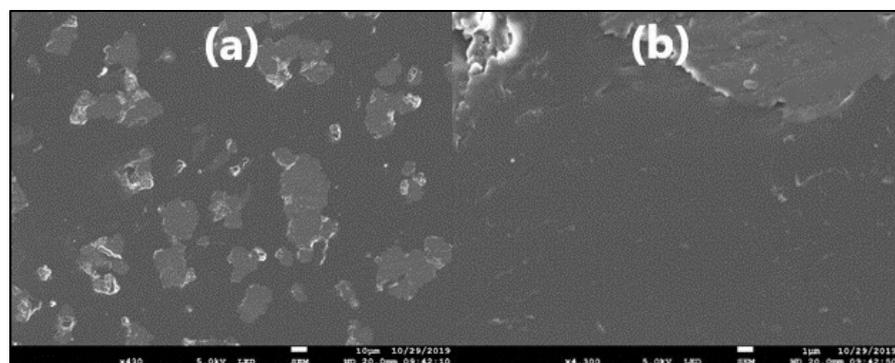
This is clearly seen in Figure 3, where the curves of the polymer matrices using the retardants and zeolites have been moved to the right side. However, if we compare the four groups of the polymer matrices (FR\_Zeolite), there are values close to and lower than the  $T_{\text{max}}$  of PP\_FR composite. It is worth mentioning that this same behavior was observed using natural zeolites from tuffs provided by the company Enli Madencilik (Izmir, Turkey), with APP:PER:PP [6] and with volcanic ash (PP\_FR\_CV) [8]. The advantage of using the FR\_Zeolite can be corroborated since the percentage of residual mass has increased for all samples, which can be clearly seen in Figure 3 and also that when synthesizing them from volcanic ash its thermal properties improved because there has been a variation in the  $T_{\text{onset}}$  and  $T_{\text{max}}$  (164.99 and 430.35 °C, respectively) of the composites with volcanic ash [8].



**Figure 3.** TGA thermograms of PP, PP\_FR and PP\_FR\_Zeolite composites using the Z1, Z2, Z3 and Z4 zeolites.

Additionally, Figure 3 shows how the concentration of the zeolites used in the PP matrix composites has an influence on their thermal properties, being the concentrations at 5% and 9% of zeolites generating the highest residual mass.

Figures 4–6 show the micrographs of the composites PP\_FR and PP\_FR\_Zeolite at 1%, 5% and 9%, respectively. If the mentioned figures are compared, it can be seen that there is a difference between the three concentrations of the zeolites used (Z1, Z2, Z3 and Z4). It should be noted that these figures correspond to polymeric mixtures before being subjected to flame tests.



**Figure 4.** Micrographs of the composites of PP\_FR at  $\times 430$  (a) and  $\times 4300$  (b).

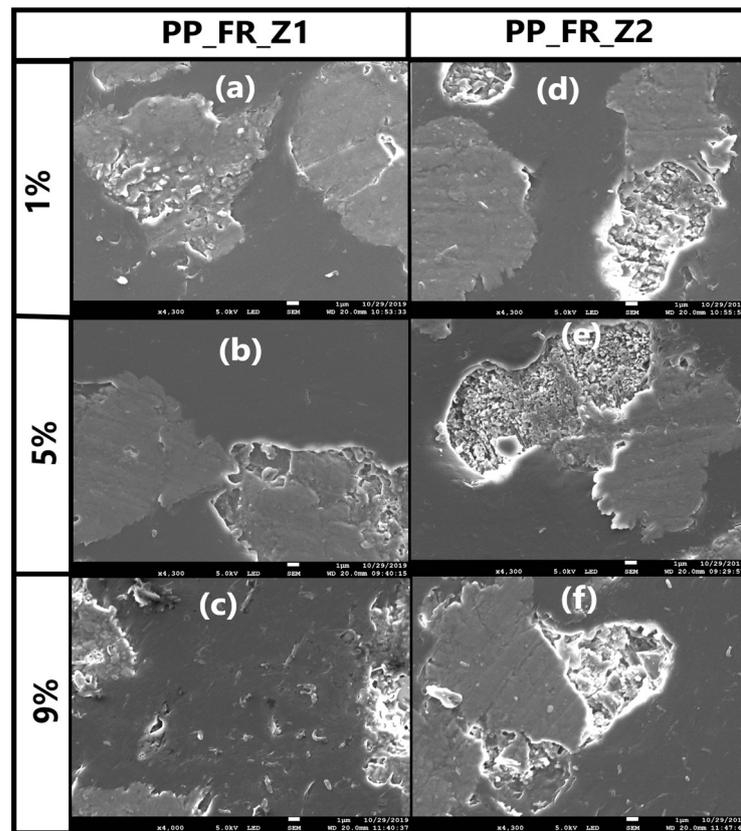


Figure 5. Micrographs of the composites of PP\_FR\_Z1 y PP\_FR\_Z2 composites at  $\times 4300$  (1  $\mu\text{m}$ ).

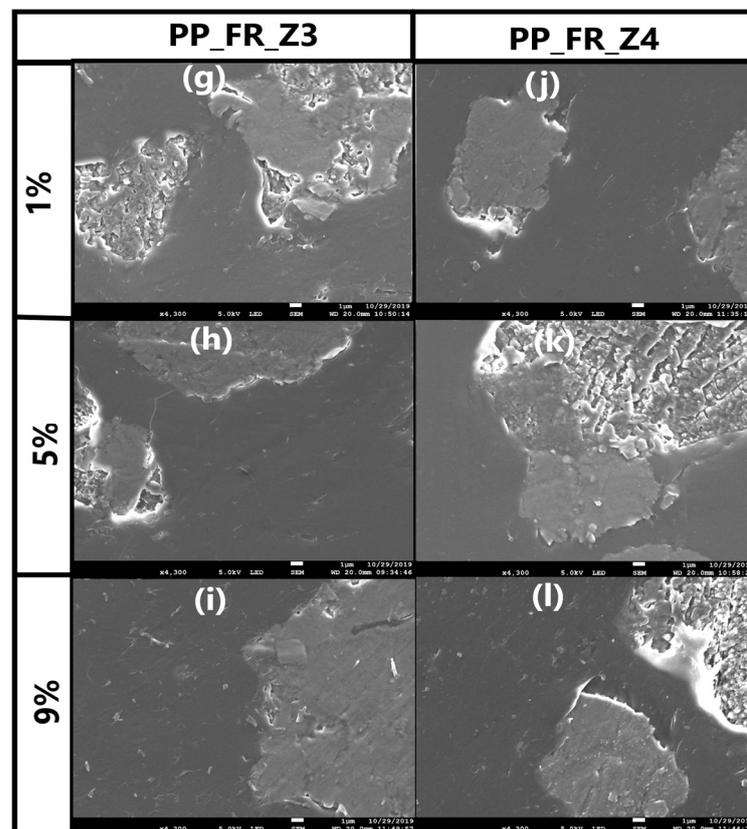


Figure 6. Micrographs of the composites of PP\_FR\_Z3 y PP\_FR\_Z4 composites at  $\times 4300$  (1  $\mu\text{m}$ ).

In Figure 4b, the PP\_FR composite shows a flat structure and without protrusions in the structure. The micrographs of the PP\_FR\_Z1-1% (Figure 5a), PP\_FR\_Z2-1% (Figure 5d) and PP\_FR\_Z3-1% (Figure 6g) composites show a morphology with interruptions (not continuous or smooth), which allows for differing the concentration of the zeolite used affects the morphology of the synthesized polymer matrices. However, for PP\_FR\_Z4-1% (Figure 6j), it is observed that unlike PP\_FR\_Z4-5% (Figure 6k), its structure is smoother with few areas that have a discontinuous structure.

In Figure 5, the same structure between PP\_FR (Figure 4b), PP\_FR\_Z1-5% (Figure 5b), PP\_FR\_Z2-5% (Figure 5e) and PP\_FR\_Z3-5% (Figure 6h) composites is shown while a discontinuous, not the smooth structure is observed in the PP\_FR\_Z4-5% composite (Figure 6k), which could be an indication that the morphology of the Z4 zeolite, which was rough in appearance, affects the interaction of the zeolite with the APP.

In Figures 5c,f and 6i,l, the PP\_FR\_Zeolite composites at 9% are observed, showing for the four types of polymer matrices a non-smooth morphology with interruptions in their structure. Therefore, it is confirmed how the concentration of the zeolite to be used interferes in the morphology of the structure of the polymeric matrix, as well as the synthesis process of the zeolite being more evident for the PP\_FR\_Z4 composites at 1%, 5%, and 9% where the Z4 zeolite was used, which, before being used, the volcanic ash was subjected to a calcination process, while for the rest of the zeolites, the volcanic ash did not go through the calcination stage.

### 3.3. Flammability Tests

Table 6 shows the LOI values of pure polypropylene and polypropylene matrices composed by the flame-retardant additives (FR) and the zeolites at 1%, 5% and 9% of concentration. The use of zeolites synthesized from volcanic ash has increased the LOI values of PP (19%) and PP\_FR (36%), which is an indication that zeolites act as synergistic agents of flame-retardants (APP:PER). Likewise, it is shown that volcanic ash has improved its thermal properties as they have been transformed into zeolites due to the fact that for the four synthesized groups, LOI values were higher than the PP\_FR\_Volcanic ash composite with LOI values of 34, 37 and 41% at 1, 5 and 9% of volcanic ash concentration, respectively [8].

**Table 6.** LOI values and UL-94 testing results of PP\_FR composites.

| Samples     | LOI | UL-94 |
|-------------|-----|-------|
| PP          | 19  | NT *  |
| PP_FR       | 36  | V-0   |
| PP_FR_Z1-1% | 42  | V-0   |
| PP_FR_Z1-5% | 45  | V-0   |
| PP_FR_Z1-9% | 44  | V-0   |
| PP_FR_Z2-1% | 39  | V-0   |
| PP_FR_Z2-5% | 44  | V-0   |
| PP_FR_Z2-9% | 44  | V-0   |
| PP_FR_Z3-1% | 39  | V-0   |
| PP_FR_Z3-5% | 46  | V-0   |
| PP_FR_Z3-9% | 44  | V-0   |
| PP_FR_Z4-1% | 40  | V-0   |
| PP_FR_Z4-5% | 46  | V-0   |
| PP_FR_Z4-9% | 45  | V-0   |

\* NT: No tested.

If we compare the LOI value of the four types of natural zeolites, these values are very close to each other, having in all cases the lowest LOI value with the zeolites at 1% of concentration and the highest LOI value at 5% of concentration. The LOI value of 46%

obtained with the PP\_FR\_Z3-5% and PP\_FR\_Z4-5% composites, while with the PP\_FR\_Z1-5% and PP\_FR\_Z2-5% composites were 45% and 44%, respectively; which indicates that probably at 5% of zeolites concentration, it is the optimum one to be used as a synergistic agent of APP:PER since at higher values a disparity between swelling behavior and the carbonization function of APP:PER over PP is likely to occur [7]. This decrease in LOI value with the increasing of the synergistic agent concentration has also occurred with 4A zeolite, which was used as a synergistic agent in the APP-CNCA-DA-PP polymer matrix composite and it was obtained an LOI value of 32.4% [7] and, as in our case, an UL-94 V-0 rating, being the LOI value obtained in this research higher. Wang et al. [15] used the 4A zeolite and as its concentration in the polymer matrix increased, the LOI value decreased, not happening for the 13X zeolite whose LOI value was maintained with increasing its concentration. This corroborates that in the case of 4A zeolite and Z1, Z2, Z3, and Z4 zeolites, happen an esterification reaction between the polymer and retardant additive. This behavior of the 4A zeolite was also observed by Demir et al. [6].

It should be noted that as shown in Table 6, all the natural zeolites used (at 1, 5, and 9% concentration) as synergistic agents for PP\_FR are classified as UL-94 V-0, which indicates that the polymer matrices have good flame-retardant properties.

### 3.4. Mass Loss Calorimetry

Table 7 shows the data obtained from the calorimetric cone test at 35 kW/m<sup>2</sup> and at 50 kW/m<sup>2</sup>. In both cases, according to the preliminary results of LOI, the PP\_FR\_Zeolite at 5% zeolite concentration polymer matrix composites were chosen because the highest LOI values were obtained at this zeolite concentration. It should be noted that according to the results obtained at 35 kW/m<sup>2</sup>, it was decided to see the effectiveness of zeolites as synergistic agents at 50 kW/m<sup>2</sup>, whose Heat Release Rate (HRR) curves are shown in Figures 7 and 8, respectively.

**Table 7.** Mass loss calorimeter data of samples at 5% of concentration at 35 kW/m<sup>2</sup> and at 50 kW/m<sup>2</sup>.

| Sample                        | t <sub>ign</sub><br>(s) | t <sub>flaming</sub><br>(s) | pHRR<br>(kW/m <sup>2</sup> ) | S.D. | THR<br>(MJ/m <sup>2</sup> ) | S.D. | t <sub>pHRR</sub><br>(s) | Residue<br>% | S.D. | FIGRA | FPI  |
|-------------------------------|-------------------------|-----------------------------|------------------------------|------|-----------------------------|------|--------------------------|--------------|------|-------|------|
| <b>At 35 kW/m<sup>2</sup></b> |                         |                             |                              |      |                             |      |                          |              |      |       |      |
| PP_FR                         | 51                      | 1806                        | 89.86                        | 2.29 | 96.50                       | 5.43 | 1263                     | 38.9         | 2.3  | 89.86 | 2.29 |
| PP_FR_Z1-5%                   | 39                      | 2518                        | 58.69                        | 1.68 | 83.87                       | 4.01 | 1435                     | 33.3         | 0.9  | 58.69 | 1.68 |
| PP_FR_Z2-5%                   | 49                      | 2692                        | 60.36                        | 4.04 | 92.79                       | 7.64 | 748                      | 37.8         | 1.9  | 60.36 | 4.04 |
| PP_FR_Z3-5%                   | 64                      | 2442                        | 54.65                        | 8.31 | 90.56                       | 0.06 | 2031                     | 44.1         | 1.7  | 54.65 | 8.31 |
| PP_FR_Z4-5%                   | 44                      | 3163                        | 51.60                        | 4.43 | 86.26                       | 7.12 | 1956                     | 42.3         | 3.7  | 51.60 | 4.43 |
| <b>At 50 kW/m<sup>2</sup></b> |                         |                             |                              |      |                             |      |                          |              |      |       |      |
| PP_FR                         | 21                      | 1213                        | 146.29                       | 3.81 | 94.39                       | 2.29 | 708                      | 24.3         | 5.3  | 0.21  | 0.14 |
| PP_FR_Z1-5%                   | 19                      | 1456                        | 98.69                        | 4.59 | 76.91                       | 0.02 | 372                      | 27.7         | 2.9  | 0.27  | 0.19 |
| PP_FR_Z2-5%                   | 19                      | 1456                        | 98.69                        | 4.59 | 77.02                       | 0.06 | 372                      | 27.7         | 2.9  | 0.27  | 0.19 |
| PP_FR_Z3-5%                   | 26                      | 1341                        | 107.28                       | 6.33 | 90.17                       | 1.40 | 539                      | 30.7         | 3.1  | 0.19  | 0.24 |
| PP_FR_Z4-5%                   | 17                      | 3163                        | 101.87                       | 6.82 | 86.73                       | 8.69 | 421                      | 28.5         | 0.01 | 0.24  | 0.17 |

t<sub>ign</sub>: Ignition time, t<sub>flaming</sub>: Flaming time, pHRR: Peak of heat released rate, S.D.: Standard deviation, THR: Total heat released, t<sub>pHRR</sub>: Peak of Heat released rate time, FIGRA: Fire Growth Rate Index, FPI: Fire performance index.

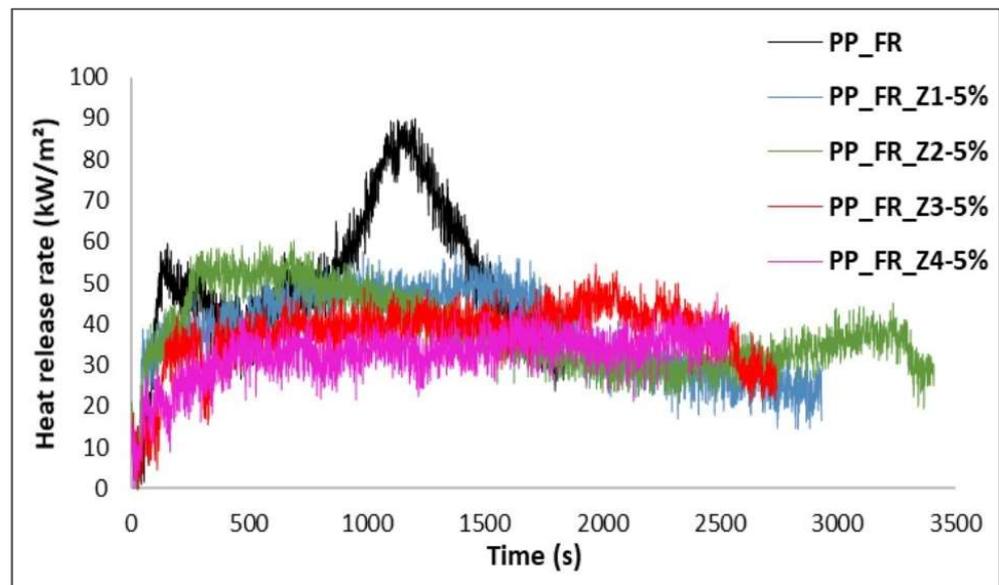


Figure 7. HRR curves for PP, PP\_FR and zeolites composites at 5% of concentration and at 35 kW/m<sup>2</sup>.

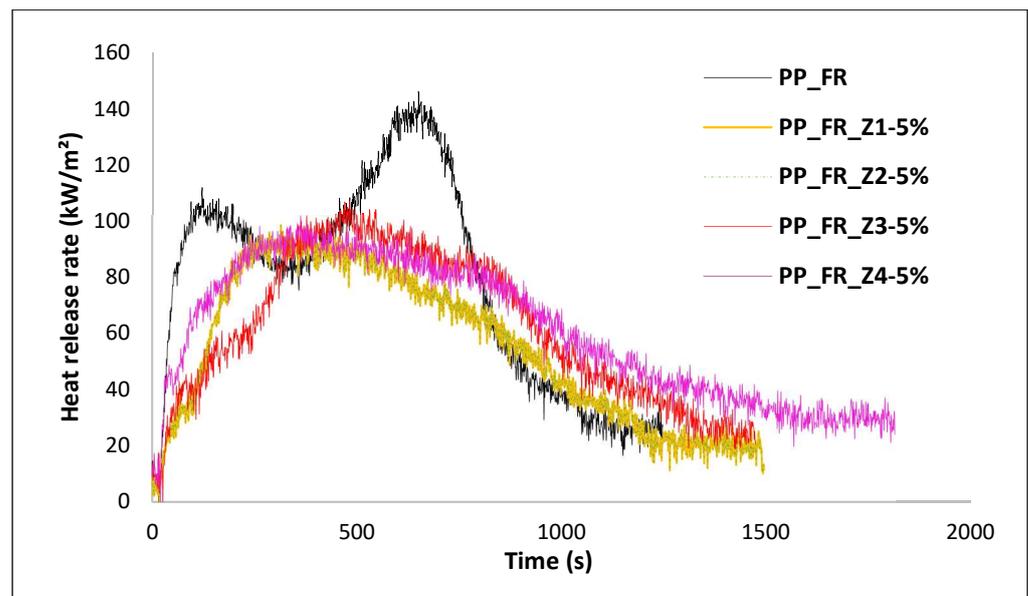


Figure 8. HRR curves for PP, PP\_FR and zeolites composites at 5% of concentration and at 50 kW/m<sup>2</sup>.

The values of Total heat released (THR) and the peak of Heat released rate (pHRR) are considered important parameters to characterize the flammability of the materials under study [16,28].

According to the Mass Loss Calorimeter results shown in Table 7 and Figure 8, it is clearly seen how the THR and pHRR values decrease when the zeolites are used within the polymer matrix composites, which is a confirmation of the synergistic action of the zeolites that favor in the flame-retardant properties of the APP:PER for PP, besides its use favors the prolongation of  $t_{\text{flaming}}$ .

Among the synthesized zeolites, Z3 and Z4 have the lowest pHRR value (54.65 kW/m<sup>2</sup> and 51.60 kW/m<sup>2</sup>, respectively) at 35 kW/m<sup>2</sup>. However, the THR value for the PP\_FR\_Z1-5% composite is the lowest with a value of 83.87 MJ/m<sup>2</sup>. It is followed by the PP\_FR\_Z4-5% composite with a value of 86.26 MJ/m<sup>2</sup> and then the PP\_FR\_Z3-5% composite with a value of 90.56 MJ/m<sup>2</sup>. Nevertheless, the  $t_{\text{ign}}$  of the PP\_FR\_Z1-5% composite is the lowest (39 s), this due to the fact that the PP\_FR\_Z1-5% composite presents a  $T_{\text{onset}}$  lower than PP\_FR

(Table 5). For the rest zeolites, Z2 and Z4 have the same behavior with the  $t_{\text{ign}}$ , which is also less than the value of APP:PER (Table 7). This is due to its thermal properties and also that during the time before ignition the formation of the carbonaceous layer occurs.

The PP\_FR\_Z3-5% composite is the one with the longest  $t_{\text{ign}}$  (64 s), which is favorable to reduce the flammability of materials, besides a low HRR and THR [15]. Therefore, this value would make that despite the fact that the THR is  $90.56 \text{ MJ/m}^2$  (occupying the third place among the zeolites used), it would cause that PP\_FR\_Z3-5% has the best flame-retardant property. This is corroborated with the Fire Growth Rate Index (FIGRA), and Fire performance index (FPI) values obtained, which are 0.027 and 1.16. Considering that the FIGRA is an important parameter to estimate the rate of fire spread and the size of a fire, therefore, the greater FIGRA value, the faster the spread of fire [9] and the FPI, which is the ratio between the  $t_{\text{ign}}$  and the pHRR, which at a higher value means that there is a lower risk of fire [16]. As the PP\_FR\_Z3-5% composite complies with both parameters, it is the one with the best flame-retardant activity, followed by the PP\_FR\_Z4-5% composite. These results agree with those obtained in the LOI test.

Likewise, Table 7 also shows that the  $t_{\text{ign}}$  of the composites at  $50 \text{ kW/m}^2$  is less than the PP\_FR; therefore, they maintain the same behavior shown at  $35 \text{ kW/m}^2$ . It should be noted that despite the fact that the pHRR values for the PP\_FR\_Z3-5% and PP\_FR\_Z4-5% composites show values of  $107.28 \text{ kW/m}^2$  and  $101.87 \text{ kW/m}^2$ , respectively, which are higher among the group of zeolites. The PP\_FR\_Z3-5% composite shows a FIGRA value of 0.199 and an FPI of 0.24, indicating that this zeolite has the best flame-retardant activity, even better than the PP\_FR\_Z4-5% composite. This behavior of showing a higher pHRR and obtaining a FPI value indicating that this is the best flame retardant has also been observed in samples with melanin-APP-Zeolite 3A [16].

If the HRR curve shown in Figures 7 and 8 are compared, the HRR curves obtained at  $50 \text{ kW/m}^2$  present values and peaks closer to the PP\_FR sample; that is, these values are higher than those obtained at  $35 \text{ kW/m}^2$ , as well as, a lower  $t_{\text{flaming}}$ .

#### 4. Conclusions

- Four types of zeolites were synthesized from the volcanic ash collected by the Ubinas volcano (Moquegua, Peru). It was determined that synthesis temperature and alkaline solution have influenced on the textural properties and morphology of the synthesized zeolites, showing a variation in the  $S_{\text{BET}}$ , pore size, pore volume and micropore area values.
- In the morphology, the presence of amorphous (Z4 zeolite) or crystalline phases (Z1 and Z3 zeolite) has been observed and in all synthesized zeolites, there are peaks corresponding to the presence of zeolites. Differences in morphology are also observed, being mostly pseudo-spherical and rough particles with the presence of cubic structures, as well. Polypropylene matrix composites were synthesized with APP, PER and zeolites at 1, 5 and 9% and the TGA, LOI, UL-94 and calorimetric cone tests were carried out, showing that the synthesized zeolites act as synergistic agents in the flame-retardant activity of APP:PER:PP. The PP matrix composite at 5% zeolites concentration showed the best flame-retardant activity, obtaining a LOI value of 46%, a FIGRA value of 0.19 and FPI of 0.24 at  $50 \text{ kW/m}^2$  for the PP\_FR\_Z3-5% composite. This was corroborated in the SEM images where the composites at 5% showed smooth and continuous structures (without holes), except for PP\_FR\_Z4-5%. In addition, the V-0 classification was obtained in the UL-94 test for all PP matrix composites. Therefore, the improvement of the synergistic action of zeolites synthesized from volcanic ash was verified, which in previous studies did show a synergistic action, being Z3 zeolite at 5% the best of the four despite that its  $S_{\text{BET}}$  ( $11.43 \text{ m}^2/\text{g}$ ) was the lowest among the four zeolites.

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## Abbreviations

|                      |   |
|----------------------|---|
| APP                  | Ammonium polyphosphate  |
| APP:PER:PP           | Ammonium polyphosphate, pentaerythritol and polypropylene                             |
| APP-CNCA-DA-PP       | Ammonium polyphosphate, halogen-free oligomeric triazine derivative and polypropylene |
| BET                  | Brunauer–Emmett–Teller method   |
| CCT                  | Cone calorimetric test  |
| FIGRA                | Fire Growth Rate Index  |
| FPI                  | Fire performance index  |
| HRR                  | Heat Release Rate   |
| LOI                  | Limiting oxygen index   |
| PER                  | Pentaerythritol   |
| pHRR                 | Peak of Heat released rate  |
| PP/FR                | Polypropylene and Flame-retardant   |
| $S_{\text{BET}}$     | Specific surface area   |
| SEM                  | Scanning Electron Microscopy  |
| $t_{\text{flaming}}$ | Flaming time  |
| THR                  | Total heat released   |
| $t_{\text{ign}}$     | Ignition time   |
| $T_{\text{max}}$     | Temperature at one sample lost maximum of its weight                                  |
| $T_{\text{onset}}$   | Thermal degradation initiation temperature  |
| $t_{\text{pHRR}}$    | Peak of Heat released rate time   |
| UL-94                | Vertical burning test   |
| XRD                  | X ray diffraction   |

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