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RESEARCH ARTICLE-CHEMICAL ENGINEERING

# Effect of Modified Halloysite/Expandable Graphite Addition on Thermal and Intumescent Properties of the Fire-Resistant Paints for Steel

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**Abstract**
The article presents results of the research on the influence of halloysite and its modified versions in a configuration with expandable graphite on thermal stability, integrity and intumescence of the fire-resistant paints for steel based on the epoxy resin and ammonium polyphosphate/pentaerythritol/melamine (APP/PER/MEL) system. The preliminary scanning electron microscope (SEM) analysis showed that halloysite modified with sulfuric acid (M2) has the best surface expansion. Nanotubes increased their volume and nanoplates were more delaminated. Temperature tests of the fire-resistant paints and subsequent SEM analysis confirmed these results, as a homogeneous structure with 50-fold multiplication was obtained for the sample with modified halloysite M2/expandable graphite, while the sample with pure halloysite/expandable graphite multiplied only 15-fold. Thermogravimetry/ differential scanning calorimetry (TG/DSC) analysis showed that the modified halloysite can significantly change the course of thermograms, even at low addition (7 wt%), and the mass loss can be reduced by up to about 13 wt%. The obtained results showed that the modified halloysite can successfully cooperate with expandable graphite and can be introduced into the intumescent system without deteriorating the physicochemical properties of the coating.

**Keywords** Intumescent coatings · Steel protection · Epoxy resins · Halloysite · Acid modification

## 1 Introduction

A typical intumescent fire retardant coating consists of three main components, i.e. an acidic dehydrating agent (phosphoric and boric acid, as well as their esters and salts), a polyhydric carbonizing component (most often glucose, erythritol and their derivatives) and a foam producing agent (e.g. melamine, urea, chloroparaffin). These substances, together with the intumescent binder and fillers, form a system which, during a fire, due to the synergistic action of individual components, should provide the protected material not only the protection against flames, but also should insulate against excessive temperature rise of the protected material. The most commonly used intumescent ternary system is a combination of ammonium polyphosphate, pentaerythritol and melamine (in an amount up to 25–30 wt%) [1–5]. In addition to delaying the fire progress, such combination reduces the amount of released gases.

Previous studies have shown that protective layers can be modified over a wide range of their functional properties. All fire retardant coatings are based on organic resins, which lose their properties in the temperature range of 300–500 °C. Hence, their low durability under fire conditions is a direct consequence. Therefore, research work is aimed at modifying the carbonization process and preserving the rigidity of the structure. On the other hand, organic resins are elastic enough not to form microcracks in the layers during normal use, i.e. not under the fire conditions. In particular, this applies to metallic structures with high thermal expansion coefficients. In order to extend the fire protection time of intumescent layers, the temperature range at which the hybrid mechanisms that enable the formation of the protective layer take place, must be extended; i.e. induce heat-absorbing reactions and increase the insulating effect of the layers. In this case, the corrosion aspect must also be taken into account. Modern solutions include the use of the substances known as green corrosion inhibitors, among which are walnut fruit

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green husk extract, N-hydroxybenzothioamide, N-doped carbon dots and their derivatives [6–10].

The following ceramic materials are used as auxiliaries in fire protection coating systems: silicate dust (clay, sand, silica) increasing the stiffness of the intumescent coating, fibers (mineral, ceramic, glass) increasing the heat resistance of the coating even up to 1500 ºC, silicon carbide (up to 5 wt. %) which lowers the temperature of the protected substrate, improves thermal stability and integrity of the formed foam, as well as calcium and potassium silicates, titanium oxide, aluminum hydroxide, zinc borate or antimony oxide [1, 2, 11–17]. In turn, the addition of clay nanograins, montmorillonite, nanosilica (in small amounts, up to 5 wt%), by forming thin sintered layers during the contact with fire, reduces oxygen diffusion of the substrates and can prevent cracking, improving corrosion and water resistance [18–21]. Similar effect can be achieved thanks to the addition of aluminum oxide, magnesium aluminate and titanium pyrophosphate nanograins [22]. The addition of zirconium silicate (up to 5 wt%) increases the carbon content in the porous coating after combustion, making it harder [23, 24]. Combining clay minerals together, e.g. kaolin and wollastonite (50:50), and incorporating such an additive into the fire retardant intumescent system containing expanded graphite, the temperature of the porous structure formed is reduced, and its compaction and uniformity are increased [25]. Similar effects can be achieved by combining expanded graphite with a single clay mineral, e.g. with dolomite clay, kaolin clay or vermiculite [26–28].

The advantage of additive fillers, apart from their availability, low price and high compatibility with other components of the intumescent fire retardant coatings, is also the possibility of their modification. Clay minerals and graphite are in the lead among modified fillers. In the case of graphite, its modifications usually lead to so-called expanded graphite, i.e. graphite with pulled apart layers, which is characterized, among others, by increased thermal and chemical resistance. The most commonly used intercalator is concentrated sulfuric acid. Other versions of this method that, for example, increase graphite expansion, include the use of an ultrasonic bath [29], hydrothermal modification [30], where the graphite with sulfuric acid and nitric acid (oxidizer) suspension is kept in an autoclave, or a two-step process—the first step is a suspension of graphite in sulfuric acid and peroxide, and the second step is a treatment of the modified graphite with peroxide and orthophosphoric acid [31]. In turn, the addition of the so-called assistant intercalator (for example ammonium thiosulfate [32], sodium hexametaphosphate [33], sodium tetraborate [34]) improves also the dilability and flame retardancy of the expanded graphite.

Sulfuric acid is also used as an intercalator of the calcined kaolinite [35]. Another clay mineral that is successfully used as a filler in fire retardant coatings and can be modified, is halloysite, i.e. a hydrated tubular aluminum silicate into which various modifying substances can be introduced. The mere addition of pure halloysite decreases rate of combustion of polymer films because of the releasing of water molecules. Modification of halloysite with a suspension of triphenyl phosphate in acetone [36] or benzatriazole in acetone [37] not only enhances the degree of combustion reduction, but also improves the anti-corrosion properties of the coatings with halloysite.

On the basis of the above information, three procedures [32, 35, 36] were selected, with the use of which Dunino halloysite was modified and then, alongside the expanded graphite, was used as a filler in an intumescent fire retardant coating system based on a combination of epoxy resin and ammonium polyphosphate/ pentaerythritol/ melamine. Halloysite was chosen because of its plate-tubular structure, possibility of modification and potential use as a mineral fire retardant. It was checked whether halloysite can be modified using the same methods as for graphite and whether it can be introduced into the intumescent system without deteriorating the structure of the coating. The obtained research results will not only allow to obtain new fire retardant intumescent coatings [38], but will also contribute to the development of the knowledge in the field of halloysite modifications.

## 2 Experimental Section

### 2.1 Materials

The base of the intumescent coatings were epoxy resin CHS-Epoxy 200 V 55 (Spolchemie, Czech Republic) and a standard intumescent system ammonium polyphosphate/ pentaerythritol/ melamine (APP/PER/MEL), where the ammonium polyphosphate AP 422 (Clariant, Germany) was a dehydrating agent (and was also used as a modifier in one of the procedures), pentaerythritol (Sigma Aldrich, Germany) was a carbonizing agent and melamine (Alwernia SA Chemical Plants, Poland) caused foaming. Expandable graphite EG 096 (Sinograf, Poland) and halloysite (Dunino, Poland) were the supporting agents.

The following substances were used to modify the halloysite:

- Sulfuric acid 95% solution (Chempur, Poland),
- Ammonium persulfate (Chempur, Poland).

Distilled water (laboratory purified) and acetone (Chempur, Poland) were used to prepare the modifying suspensions and to wash the modified halloysite samples.

**Table 1** Composition of the intumescent coating

| Substance | [wt %] |
|---|---|
| Epoxy resin | 30 |
| Ammonium polyphosphate | 32 |
| Pentaerythritol | 8 |
| Melamine | 15 |
| Graphite | 8 |
| Halloysite | 7 |

## 2.2 Halloysite Modification

### 2.2.1 Modification with APP and Acetone (M1)

Modification was carried out based on the procedure described by Joshi et al. [36]. First, a 100 mg/ml suspension of halloysite in a concentrated solution of APP in acetone (150 mg/ml) was prepared and stirred for 20 min in the ultrasonic bath. Then, the suspension was mixed for another 20 min on a vortex. The mixing steps were repeated three more times and after that, the suspension was left in a vacuum for about 12 h. Then the suspension was centrifuged, washed 2 times with acetone and the residue powder was dried in ambient temperature.

### 2.2.2 Modification with Sulfuric Acid (M2)

Modification was carried out based on the procedure described by Tang et al. [35]. The suspension of halloysite in sulfuric acid (2.35 g/ml) was heated for 1 h at 90 °C, washed with distilled water and then dried in 100 °C for 24 h.

### 2.2.3 Modification with Ammonium Persulfate and Sulfuric Acid (M3)

Modification was based on the procedure described by Liu et al. [32]. The suspension of ammonium persulfate in sulfuric acid (1.7 g/ml) was stirred for 5 min in the ultrasonic bath. Then halloysite was added, obtaining a new suspension with a concentration of 0.33 g/ ml. The resulting mixture was left to expand for 12 h and after that was dried in ambient temperature.

## 2.3 Samples Preparation

Intumescent coatings samples were prepared by mixing the components together using a Teja high-speed stirrer according to the sequence given in Table 1. This composition was developed based on previous research [39]. Subsequent substances were introduced into the epoxy resin and mixed at a stirring rate of 500 RPM until a homogeneous mixture was obtained. Finally, when all components were introduced into the system, the samples were mixed for another 30 min at a stirring rate of 500 RPM. Before starting the tests, samples were kept for a week in a closed container and stirred daily for 5 min at a stirring rate of 200 RPM. Hardener was not included in any of the compositions.

Samples containing a given halloysite modification are named accordingly to the modification designation, i.e. M1-M3. Reference sample, containing pure halloysite, is denoted as M0.

## 2.4 Methods

Prior the temperature tests, 100 × 50 × 5 mm steel pads coated with a primer paint were covered with the intumescent coatings using a brush to a thickness of 1 mm (measured with the use of digital paint thickness gauge). One single pad covered with paint was prepared for each composition. The pads were then conditioned at ambient temperature for 7 days. Finally, temperature tests were carried out in a high-temperature muffle furnace. The temperature increased from 20 to 500 °C for 1 h, then was 5 min of heating at 500 °C, followed by slow cooling to room temperature.

A Nova Nano SEM 200 scanning electron microscope was used for the observation of the microstructure of halloysite and intumescent coatings after the temperature tests. Charred coating samples after the temperature test were taken directly from the steel plates. All samples were carbon-coated using a Q150T sputter coater and observed in a high.vacuum mode.

A NETZSCH STA 449 F3 thermal analyzer was used to conduct the thermogravimetry (TG) and differential scanning calorimetry (DSC) thermal measurements. Samples, placed in aluminum oxide crucibles, were heated up to 700 °C at a heating rate of 10 °C /min, in air atmosphere. Based on the obtained TG curves, the weight loss the at the individual heating stages was calculated. These results have been linked to the thermal effects determined from the endothermic and exothermic peaks in the DSC curves.

# 3 Results and Discussion

## 3.1 SEM Analysis of Halloysite and Its Modified Versions

Figure 1 shows the SEM microphotographs of the unmodified and modified halloysite. The part showing the microstructure of pure halloysite (M0) shows the plate-tube structure characteristic of the Dunino deposit [40, 41], with clearly visible nanotubes (HNT) of various lengths (outlined in green) and nanoplates (HNP) that predominate. Analyzing the entire Figure, it can be seen that the structure of halloysite modified

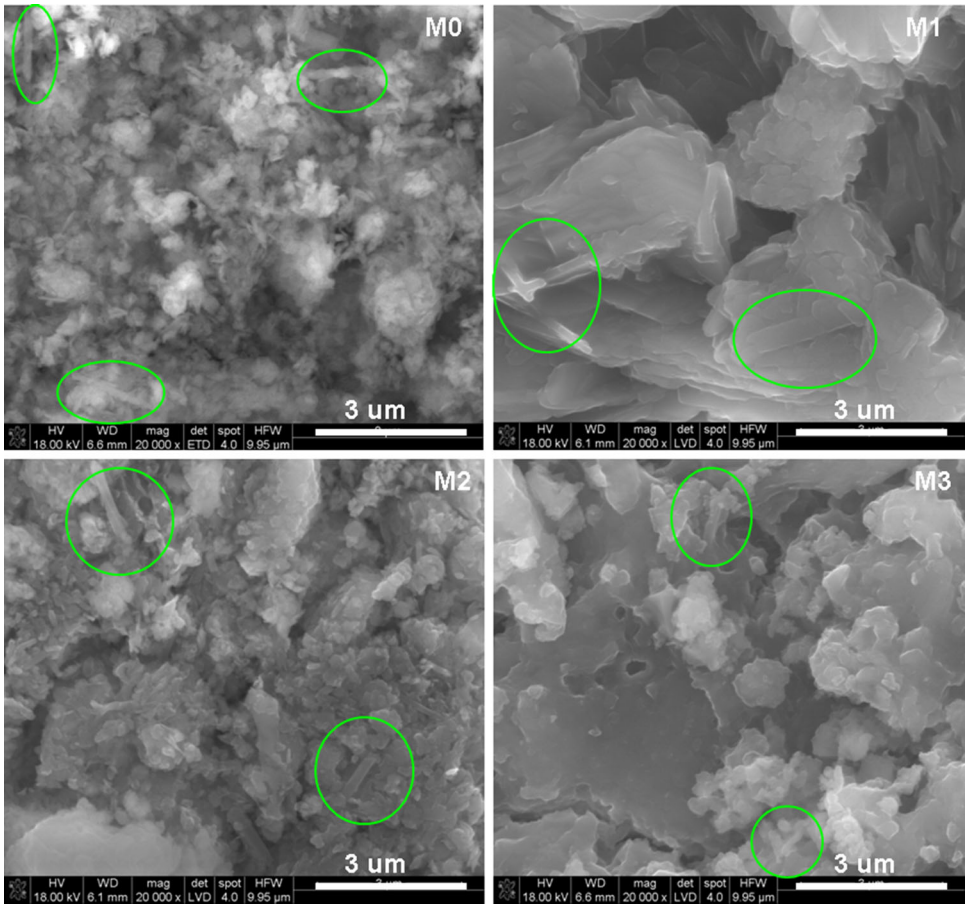


**Fig. 1** The SEM microphotograph of pure halloysite (**M0**) and its modified versions (**M1**- APP and aceton, **M2**- sulfuric acid, **M3**- ammonium persulfate and sulfuric acid)

only with sulfuric acid (M2) is the closest to the microstructure of pure halloysite. Nanotubes and nanoplates can also be seen here, but nanotubes (outlined in green) increased their volume and nanoplates seem to be more delaminated and aggregated. These results are consistent with literature data, which have shown that acid modification of halloysite or kaolinite increases their porosity and causes delamination [35, 42]. In the case of halloysite modified with APP suspension in acetone (M1), numerous interconnected tubes (outlined in green) and individual large plate aggregates are visible. The most different microstructure has halloysite modified with ammonium persulfate and sulfuric acid (M3). The Figure shows a few individual tubes (outlined in green) and single plate aggregates on the sample's surface. Rest is a disordered structure.

### 3.2 Temperature Tests Analysis

Figure 2 shows the intumescent coatings after the temperature test. Coatings differ in their average thickness, as well as in the development of the structure itself. Coating containing pure halloysite (M0) is characterized by the lowest average thickness (15 mm). The resulting intumescent structure is charred, compact and spongy. Its surface is not uniform and smooth, and a inhomogeneous broccoli-type intumescence can be observed. The M1 and M2 coatings are the most homogeneous and have the most uniform surface. They are both compact and spongy. However, the M2 coating is much thicker. It multiplicated 50 times, whereas the M1 coating multiplicated only 30 times. It might seem that opposite should be the case, since APP is also a pore-forming agent and the increased addition of it causes greater intumescence. However, in this case, there was too little of it, and SEM analysis showed that the shape and size of the tubes and plates in the modified with it halloysite did not change, they were even strongly aggregated. The SEM micrograph of the M2 halloysite sample, on the other hand, showed that the reaction with the acid caused an increase in the volume of the tubes and the separation of the plates, what contributed to the fact that during contact with high temperature, halloysite expanded even more, like graphite, and the charred structure was significantly intumescent. The worst result, despite the 30-fold multiplication, was achieved for the M3 modification. The resulting structure was charred and compact, but non-uniform (cracks, clearances to the steel plate). It also shrinked on the sides. In this case, it can be assumed, additionally on the basis of SEM analysis of the modified halloysite,

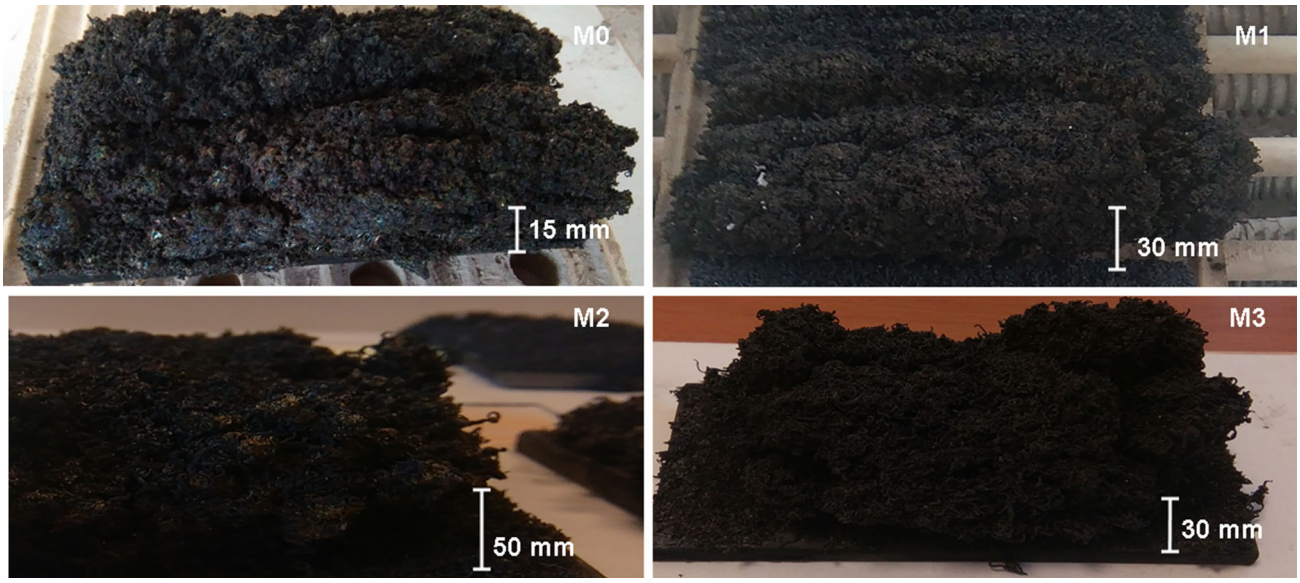


**Fig. 2** Intumescent layers after the temperature test (**M0**- pure halloysite, **M1**- APP and aceton, **M2**- sulfuric acid, **M3**- ammonium persulfate and sulfuric acid)

that the addition of ammonium persulfate, which, like sulfuric acid, is a strong oxidizing agent, caused an excessive expansion of halloysite, resulting in its partial decomposition. Consequently, there was a loss of mechanical strength of the resulting intumescent coating.

### 3.3 SEM Analysis of Intumescent Coatings

SEM microphotographs of the charred intumescent coatings obtained in the temperature test presented in Fig. 3 confirm the considerations included in subSect. 3.2. Loose, highly expanded graphite ribbons can be seen in the SEM micrograph of the ash sample with pure halloysite (M0). Therefore, in a temperature test, a non-uniform intumescence of the broccoli type was obtained on the surface of the charred sample. On the other hand, the SEM micrograph showing the charred intumescent paint with the APP addition (M1) shows a compact structure with single pores. The bubbles visible in the middle part of the figure are phosphate salts formed as a result of the thermal transformations of APP, that is, ammonium polyphosphate. The most uniform structure was presented in the SEM micrograph of an ash of the coating with halloysite modified only with sulfuric acid (M2). It shows single expanded graphite ribbons that are "fused" into the charred intumescent structure. The figure also shows practically no pores. On the other hand, the SEM micrograph of the ash of the coating with the addition of halloysite modified with ammonium persulfate and sulfuric acid (M3) shows a structure similar to the micrograph of the ash of M0 sample, but less developed. Graphite ribbons are less expanded and more porous. They are also more aggregated than in the case of the ash of the coating with the pure halloysite. None of the micrographs show any remnants of the original plate-tube structure of the halloysite. This is due to the fact that, under the influence of temperature, halloysite begins to lose water and turns into so-called metahalloysite with a disrupted structure [40, 41]. It is also influenced by the fact that the addition of halloysite was small, only 7 wt%.

### 3.4 TG/DSC Thermal Analysis

Figure 4 shows the TG thermograms of the analyzed intumescent coatings, while Fig. 5 shows the DSC curves. Only the M1 and M3 curves have similar courses, both in the TG and DSC thermograms. The waveforms of the other two samples differ significantly. When analyzing the TG curves (Fig. 4), it can be noticed that in the case of the M0 sample there is a four-stage weight loss, while in the other three samples this loss consists of three stages. In the case of the M0 sample, the highest weight loss (− 71.45 wt%) was also noted (Table 2). In the case of M1 sample, modified with APP suspension in acetone, the weight loss was not significantly different (− 69.76 wt%). A noticeable difference in weight loss occurred in the case of samples modified with sulfuric acid, i.e. M2 and M3, where the weight loss was at the level of − 58.55 wt% and − 57.79 wt%, respectively.

When analyzing the DSC curves, it is also possible to see some dependencies between the individual curves. At a temperature of about 130 °C, a small endothermic peak appears in the M0 and M2 curves, related to the loss of water by the epoxy resin. It is accompanied by the another endothermic

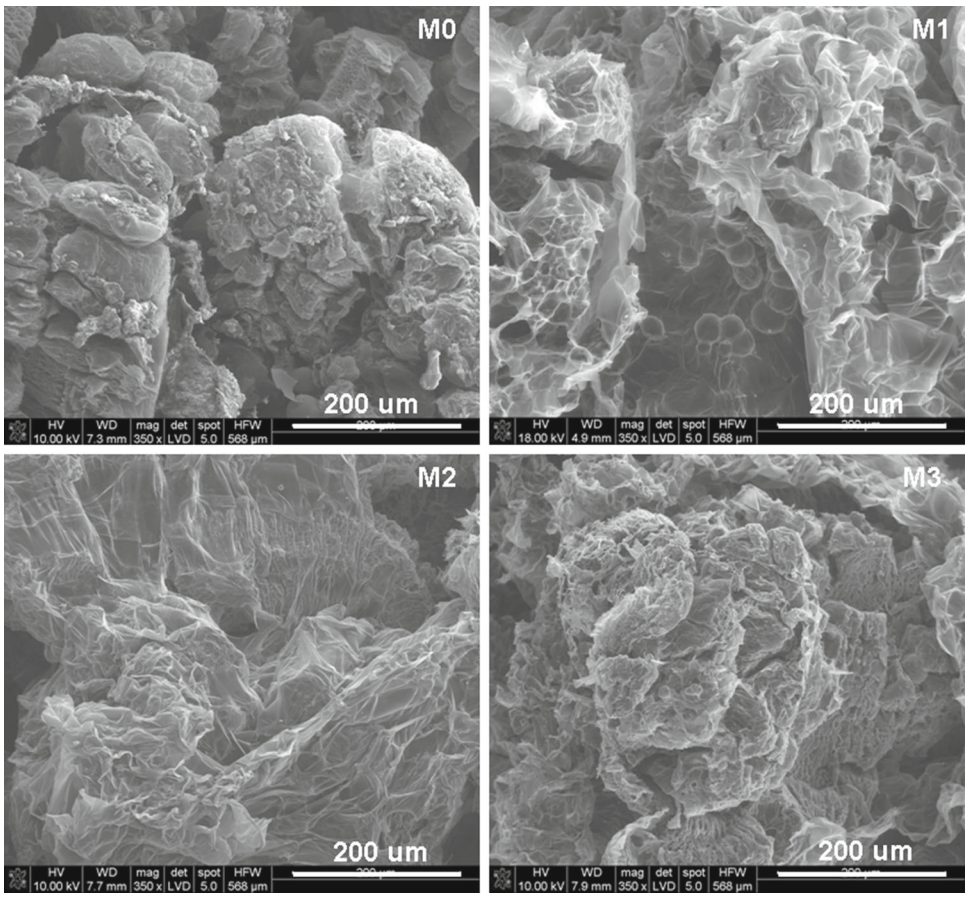


**Fig. 3** The SEM microphotograph of the intumescent coatings with pure halloysite (**M0**) and its modified versions (**M1**- APP and aceton, **M2**- sulfuric acid, **M3**- ammonium persulfate and sulfuric acid)

**Table 2** The TG/DSC analysis of the intumescent coatings

| | M0 | | | M1 | | | M2 | | | M3 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mass loss [wt%] | Temp. [°C] | Effect | Mass loss [wt%] | Temp. [°C] | Effect | Mass loss [wt%] | Temp. [°C] | Effect | Mass loss [wt%] | Temp. [°C] | Effect |
| I | − 19.28 | 127/175 | Endo | − 11.44 | 187 | Endo | − 14.70 | 131/174 | Endo | − 11.60 | 186 | Endo |
| II | − 19.50 | 261 | Endo | − 39.95 | 315 | Endo | | – | – | | 264 | Exo |
| III | − 21.30 | 336/366 | Exo | | 390 | Exo | − 25.97 | 380 | Exo | − 36.61 | 318/369 | Endo/exo |
| IV | − 11.37 | 500 | Exo | − 18.37 | – | – | − 17.88 | 604 | Exo | − 9.58 | 580 | Exo |
| Total mass loss [wt%] | − 71.45 | | | − 69.76 | | | − 58.55 | | | − 57.79 | | |

peak, visible in all of the curves, associated with the transformation of epoxy resin, i.e. its first stage of thermosetting (174–187 °C). However, it should be remembered that in this temperature range it may overlap with the crystal transformation of the pentaerythritol [17, 43–47]. At about 260 °C, the DSC curve of sample M0 shows an endothermic peak, while the DSC curve of sample M3 shows an exothermic peak in this range. It is related to the decomposition of melamine and first step of ammonium polyphosphate decomposition (release of gases and polyphosphoric acid)/graphite expansion, respectively. In the DSC curves of M1 and M3 samples, at a temperature of about 315 °C, a slight endothermic peak related to the release of melamine stable condensates (melam, melem and melom) is observed. The remaining peaks towards higher temperatures in all the curves are already exothermic. Up to a 400 °C, the exothermic peaks related to the graphite transformation, i.e. its expansion and decomposition, peaks related to the transformation of epoxy

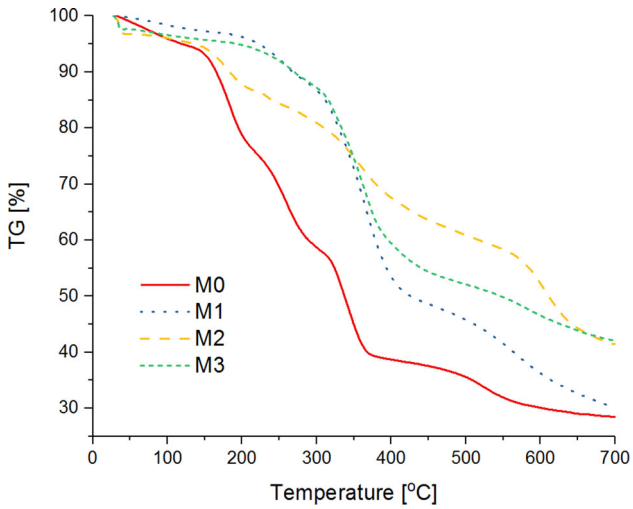


**Fig. 4** The TG thermogram of the intumescent coatings with pure halloysite (M0) and its modified versions (M1- APP and aceton, M2- sulfuric acid, M3- ammonium persulfate and sulfuric acid)

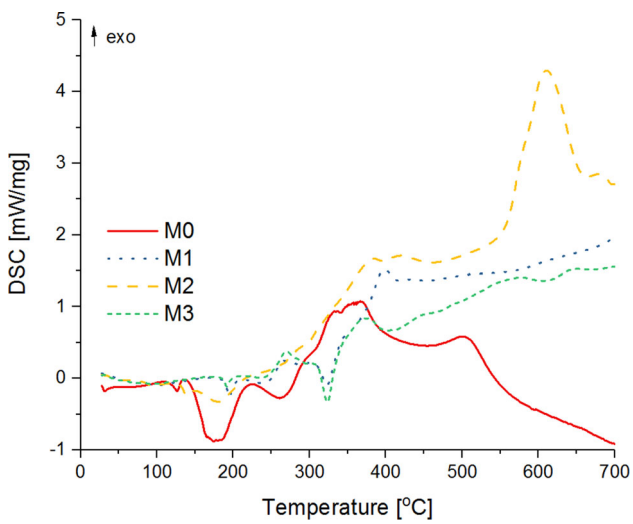


**Fig. 5** The DSC thermogram of the intumescent coatings with pure halloysite (M0) and its modified versions (M1- APP and aceton, M2- sulfuric acid, M3- ammonium persulfate and sulfuric acid)

resin, i.e. its polymerization and cross-linking, and peaks related to the further decomposition of the polyphosphoric acid and pentaerythritol overlap with each other [2, 3, 3, 5, 11, 18, 23, 43, 48–54].

In the temperature range of 500–600 °C, exothermic peaks associated with the final decomposition of the epoxy resin and pentaerythritol are visible. It is interesting that in all of the DSC curves, the peaks characteristic for the temperature transformations of halloysite were covered by the remaining peaks, previously described. This could be due to the fact that the halloysite content was low, only 7 wt%. Only the exothermic peak in the DSC curve of the M0 sample at 500 °C can be attributed to the conversion of halloysite to metakaolin, resulting from the loss of the structural water [36, 55]. Similarly with regard to the differences in the TG and DSC curves of the analyzed intumescent coatings samples. They result from the fact that each composition contained a differently modified halloysite.

## 4 Conclusions

The article presented various ways of modifying halloysite, including an implementation of the method used for graphite expansion. The aim was to test whether halloysite could be modified using the same methods as for graphite and whether this would have a significant impact on the subsequent expansion of the intumescent coating used for the protection of steel. In comparison with our previous work [39], where kaolin/ expandable graphite configuration was used with ammonium polyphosphate/ pentaerythritol/ melamine system, intumescent properties have improved. Multiplication for the initial coating thickness of 1 mm has increased up to 30 times, from 20-fold to even 50-fold. The obtained results confirmed that the modified halloysite can be successfully used as a filler in the intumescent paints, next to the expandable graphite. It successfully works as a substance that decreases rate of the combustion of the intumescent film, also strengthening its structure during the thermal expansion. This information may contribute to the development of the new auxiliary ceramic agents for the fire protection coating systems based on the modified minerals of the tubular-plate structure as halloysite. It was additionally checked whether a higher amount of ammonium polyphosphate, which is a well known fire retardant, can be introduced into the intumescent system without deteriorating the physicochemical properties of the coating. In each of the analyzed cases, intumescence of the coating after the temperature test was at least doubled, compared to the addition of pure halloysite (15-fold multiplication),: APP and aceton- 30-fold multiplication, sulfuric acid- 50-fold multiplication, ammonium persulfate and sulfuric acid- 30-fold multiplication. There were also noticeable differences in the appearance of the charred intumescent layers, as well as in their microstructure. Similarly, there were differences in the TG and DSC curves of the analyzed intumescent coatings. They differed significantly from one another due to the fact that each composition contained differently modified halloysite. The best results with regard to use as a intumescent protective paint for steel were shown by the sample with sulfuric acid-modified halloysite, what confirmed the other literature data. Apart from 50-fold multiplication, the structure of the resulting pumice was uniform, with a smooth surface and no open pores, while its microstructure was also homogeneous with few internal pores. However, this does not mean that the other modifications were insufficient. They can be

used for other applications of halloysite, but more research should be done in this direction. In addition, anticorrosion tests and spectroscopic analysis are planned to provide more detailed information on the physicochemical characteristics of the developed fire-resistant paints with a modified halloysite/expandable graphite system.

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## Declalarions

**Conflict of interest** Manuscript is original, unpublished and is not being consider for publication elsewhere and there is no scientific or financial conflict of interest.



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