



Aspects of the reduction of the coating fire resistance by the use of nanosized additives

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Abstract

As a new generation fire-resistant material, the intumescent coating has significant advantages over conventional fire protection materials. The applications of the intumescent coating have changed widely and have dominated the fire engineering market. In this study, intumescent coatings with different nanosized additives such as fumed silica, organo-montmorillonite, aluminum oxide and titanium dioxide were investigated. It was shown that organically modified montmorillonite and hydrophobized silica reduced fire resistance properties of intumescent coatings. The reason for such decrease is the shift of the expansion processes to higher temperatures. This phenomenon increases the time of direct heating of the substrate. Moreover, it was established that the minor concentrations of organically modified montmorillonite could significantly change the structure of coatings and increase the specific heat insulation properties of the carbon foams. Such an effect was also observed in the case of the use of hydrophobic silica, but to a lesser extent. It was shown that nanosized additives have effect on the expansion factor and the foam structure. It was suggested that this effect could be explained by the complex influence of the nanoparticles on the bubble growth processes through the melt viscosity modification.

Keywords Intumescent coating · Expansion factor · Heat insulation · Organically modified montmorillonite · Hydrophobic silica

Introduction

The protection of construction materials against fire is an important issue in the construction sector (Md Nasir et al. 2019; Yang et al. 2019). Steel structures have many advantages for architectural applications. But, steel has high thermal conductivity and can easily collapse when its temperature reaches 540 °C. Fire protection in steel structure

building is one of the basic requirements of building regulations in many countries. Many methods have been reported to protect the steel structure against fire (Puri and Khanna 2017). Among these, intumescent coatings are the best choice because of the advantage that steel does not alter its specific properties (e.g., mechanical properties). It is also easy and light to coat on the steel surface and has a good decorative effect which is very important for the appearance of buildings (Camino 1998).

Intumescent systems are conversion coatings that after being exposed to a certain flame's temperature transform into a layer of carbon foam, which is usually 10–60 times thicker than an original coating (Lv et al. 2019). Due to the reduced thermal conductivity of such foam, thermal insulation of the substrate is achieved, which allows increasing the response time to a destructive fire. The effectiveness of modern intumescent systems is estimated by the time the substrate reaches a certain temperature (450 °C according to ISO and 500 °C according to GB/T) under standard annealing conditions: the heat flow in the furnace is normalized. In some research cases, the achievement of temperature is

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evaluated by the final significant parameter, in particular via deflection of the steel beam under load.

Intumescent nanocomposites are based on acrylic, epoxy and polyurethane polymers (Rathod et al. 2017). The coating can be based on organic solutions or water dispersions of the mentioned polymers (Mariappan 2016). Most of these coatings contain three main components necessary for the formation of a protective layer: acid donor, carbon donor and blowing agent (Fan et al. 2013; Lv et al. 2019). The influence of the components of the ternary system is well understood (Horacek 2009), but other components might also influence the properties and, hence, the total fire insulation performance of the foam.

Hereby, we consider the most used type of intumescent systems based on the ternary mixture of ammonium polyphosphate, melamine and pentaerythritol. Such systems are usually loaded with white pigment—titanium dioxide TiO_2 , which can undergo the reaction with components of the triple system, especially with ammonium polyphosphate, and form thermally stable pyrophosphates (Duquesne et al. 2013; Puri and Khanna 2017). Titanium-containing products will form a residue at the substrate surface when the carbon is completely burned down. The addition of titanium dioxide might also affect the melt viscosity and influence such foam parameters as an expansion factor, cell size and its distribution.

Other inorganic fillers that could be used for the improvement of char strength (Kaur et al. 2017) or melt rheology (Bodzy et al. 2011) may affect expansion factor values as well as temperatures of onset of intumescence. In the paper (Vakhitova et al. 2016), the influence of organically modified clays on these factors was considered. It was stated that the use of such nanomaterials increases the temperature of expansion started by 50 °C.

The aim of this study is to determine the effectiveness of appended nanomaterials (organically modified montmorillonite and hydrophobic silica) on the thermal properties of intumescent systems. Titanium dioxide was used as the only reference.

Experimental

Materials

The triple intumescent system was used for intumescent coating recipe: ammonium polyphosphate Exolite AP 422 (Clariant), melamine—Melafine (OCI Nitrogen) and pentaerythritol—Chamor DP 40. All stated components were used in the pre-determined ratio 8:1:1, respectively, and here further is referred to as the intumescent system. Styrene—acrylic copolymer Neocryl 880 B (DSM Neoresins, Netherlands) was used as a binder and dissolved in xylene.

Solsperse 26000 (Lubrizol, USA) was used as a dispersion agent. Titanium dioxide (Kronos 2043), organically modified montmorillonite (O-MMT)—Claytone APA (BYK), hydrophobized silica—Aerosil R 972 (Evonik), alumina—MA88K F-60 (Saint-Gobain Ceramic Materials) were used in this research.

Experimental formulations were derived from the basic one (Table 1) by adding the determined quantity of the selected materials.

Preparation of intumescent coatings

Compositions for tests were prepared by mixing on a high-speed laboratory mixer (model GFS-RN, Qinhungdao Pengyi Chem-Industry machinery co., Ltd, China). First, the acrylic copolymer was added in small portions at a low speed (500 rpm) to the required amount of xylene. After completion of the polymer injection, the rotation speed was increased to 2000 rpm. The mixing process continued until a clear homogeneous solution was formed. The considered nanomaterials were added into this solution (marking of samples is given in Table 2) at the mixing speed of 350 rpm and further stirred at 2000 rpm for 5 min. Subsequently, titanium dioxide was added as a dispersant, which was further dispersed for 10 min at a speed of 3500 rpm. After completing dispersion, a low speed (300 rpm) was set up for degassing. The intumescent system was introduced gradually at a speed of 1200 rpm, after which the system was stirred for another 5 min until homogeneous.

Characterization and measurement

Thermogravimetric analysis was conducted using a PerkinElmer TGA 4000 system (SETARAM, France) to investigate the thermal degradation and determine the residual weight of the intumescent coatings.

To conduct a fire test, the composition was applied to steel plates with a thickness of 6 mm. The thickness of the resulting coatings was 1.6 mm. Applied coatings were dried in a fume hood at room temperature for 3 days, and then in a drying chamber for 24 h at a temperature of 80 °C. For a direct fire test, a steel plate with a protruded coating was mounted vertically on a tripod and was subjected to the

Table 1 Basic formulation of the coating

Component	Content, weight %
Xylene	24.9
Dispersion agent	1.5
Polymer	12.5
Intumescent system	53.5
Pigment	7.6

Table 2 Marking of samples

Sample name	Basic composition	Basic composition + 1.0 wt. % bentonite, g	Basic composition + 1.2 wt. % silica, g	Basic composition + 3 wt. % alumina, g	Basic composition + 4 wt. % TiO ₂ , g
Amount of additives to 100 g of basic composition	–	1	1.2	3	4

processing of a controlled flame of burning propane gas. The test setup consists of a sample holder, a propane canister and a thermocouple mounted on the uncoated steel plate side. The temperature was maintained at 1000 °C, with a distance of 150 mm from the nozzle to the test coating. The temperature of the substrate was measured by the thermocouple located at the center of steel plate from the opposite side from the fire direction. The measurement was conducted in automatic mode; therefore, data were transferred to a logger every 30 s. The resistance time was determined as the time of achievement of 500 °C by the substrate from the start of the test. The value of the expansion coefficient (*K*) is the ratio of the thickness of the initial coating (mm) to the thickness of the layer of coal foam (mm), which was obtained after a fire test. To account for the possible heterogeneity of the height of the foam, measurements were made at six points for each sample. As a result, the arithmetic mean value of the coefficient was calculated.

To obtain electron microscopy images, the carbon foam of the sample after the fire test was cut with a DB 80 microtome knife (Leica, Germany) into slices about 1 mm thick, which were fixed on a conductive adhesive to obtain an image. A Quanta SEM scanning electron microscope (Thermo Fisher Scientific, United States of America) was used. Electron microscopy images were processed using the ScopePhoto software (ScopeTec, China): bubble sizes and the wall thicknesses were determined for each sample (120–150 pcs.) The average values of these parameters were calculated. Due to the complex relief of the carbon layer, it was impossible to use the built-in program functions to count the number of particles.

Results and discussion

Thermal properties of the intumescent coating

As a whole, it was found that an increase in the content of fillers causes a shift in the characteristic temperatures of the processes toward higher temperatures. For example, with an increase in the content of titanium dioxide in the system by 4 mass. %, the decomposition points of an

acid donor (Lin et al. 2011) slightly increase from 258 to 262 °C (Figs. 1, 2). However, the pigment has the greatest influence on the temperature shift of the decomposition point of a blowing agent—melamine. In the original system, the maximum rate of weight loss is observed at 365 °C, and with an increase in the filler loading capacity 405 °C. Additionally, a peak for a composite with higher titanium dioxide content loses its symmetry due to the appearance of a shoulder with a maximum, occurring at 346 °C. The maximum reaction rate of the interaction of polyphosphoric acid with pentaerythritol (Bourbigot et al. 1995) increases from 410 to 425 °C. Moreover, the process proceeds more vigorously in the presence of an excess of titanium dioxide, as an increase in heat release rate by 60% is observed.

For composition with higher titanium dioxide content, the increase in the non-volatile residue is significantly varied from 33.6 to 37.2 mass. % after heating to 910 °C, as can be seen from the TGA curves (Fig. 3).

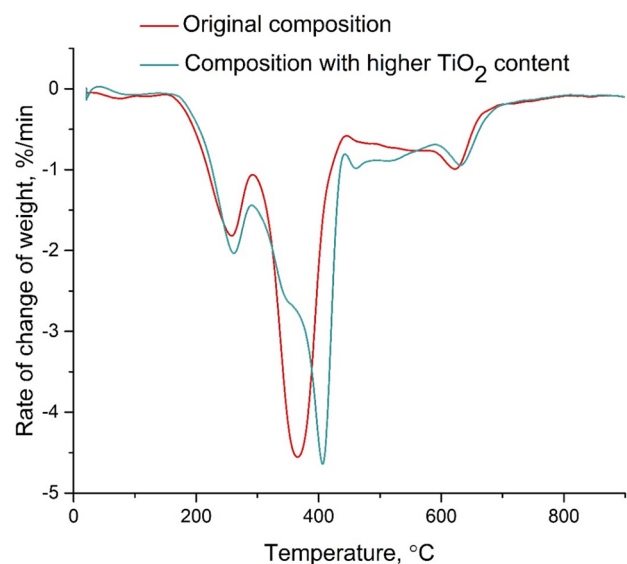


Fig. 1 DTG curves of the original composition and the composition with higher titanium dioxide content

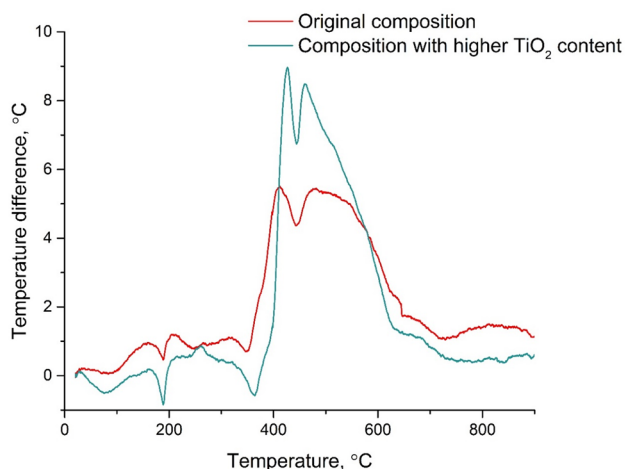


Fig. 2 DTA curves of the original composition and the composition with higher titanium dioxide content

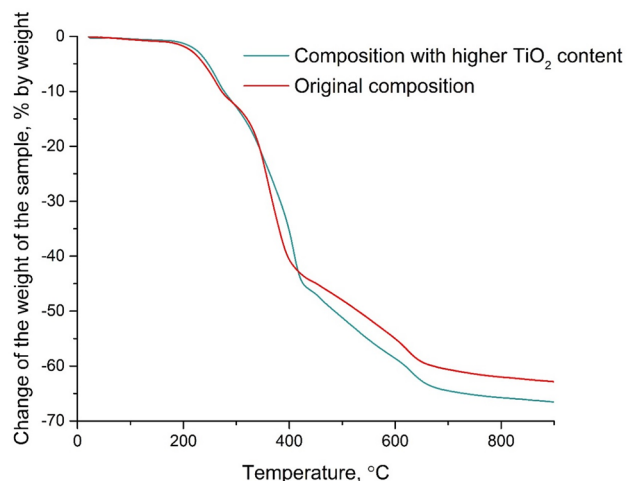


Fig. 3 Thermogravimetry of composites: the original composition and the composition with higher titanium dioxide content

In general, the presence of titanium dioxide increases the temperature of decomposition processes of the components of the composition. Other inorganic fillers behave similarly (Table 3).

Foam structure

An increase in frame temperatures for processes also affects the final performance of the system, namely, the expansion factor of the foam and, therefore, the common value of fire resistance. The reduction effect of the expansion coefficient was studied depending on the filler content of each of the considered species (Fig. 4). The greatest reduction effect of the coefficient is characterized by organically modified bentonite: up to 50% at a concentration of 0.5 mass. %. This is followed by Aerosil 33%, titanium dioxide 18% and alumina 14%.

Such expansion factor reduction correlates to some extent with the specific surface area of fillers. Specific surface areas are up to 0.8 m²/g, 60 m²/g, 120 m²/g, and 108 m²/g for alumina, titanium dioxide, o-MMT, and Aerosil, respectively.

However, this does not explain why o-MMT has such a strong effect on the foaming process. Probably, the decisive factor in this process is still the ability of the material to change the rheological properties of the melt, namely to increase its viscosity. It should be noted that this is one of the tools for regulating the structure of foams in other industries (Duquesne et al. 2005; Pimenta et al. 2016). Appending of fillers also causes a change in the structure of coal foam, namely an increase in the size of elementary bubbles and also an increase in wall thickness (Fig. 5).

Introduction of titanium dioxide causes a 2.5-fold increase in wall thickness (Fig. 5b), which can be explained by a decrease in the mobility of melt due to the expansion of the temperature gap between the decomposition of an acid donor and the decomposition of melamine. This is likely to be accompanied by an increase in melt viscosity.

In the case of o-MMT, along with the thickening of the walls, a significant decrease in the diameter of the bubbles is also observed, which can be explained by a significant increase in viscosity and the formation of a thixotropic structure of the melt.

Fire resistance properties

The fire resistance value of the formulation was determined as the time required for the steel substrate to reach 500 °C at the start of the test. Considering the possible deviations that

Table 3 Frame temperatures for processes depending on the presence of inorganic fillers in the system

Effect	Basic composition	Basic composition + 1.0 wt. % O-MMT	Basic composition + 1.2 wt. % silica	Basic composition + 3 wt. % alumina	Basic composition + 4 wt. % TiO ₂
Acid donor decomposition (DTG)	258	265	263	260	262
Melamine decomposition (DTG)	362	412	400	365	405
Carbonization (DTA)	410	427	418	412	425

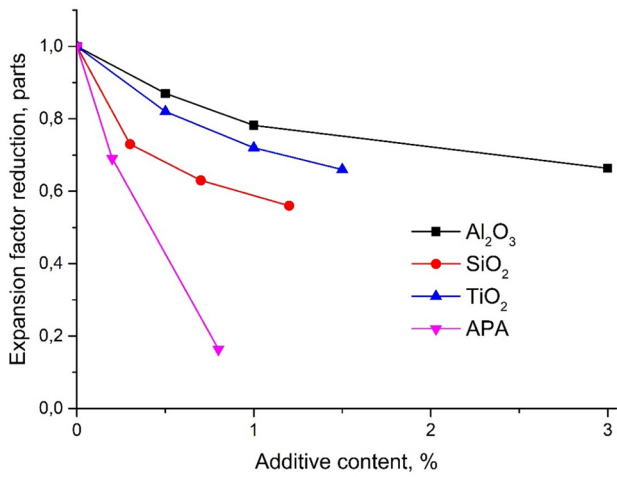


Fig. 4 Expansion factor reduction (in parts of the coefficient for the basic composition)

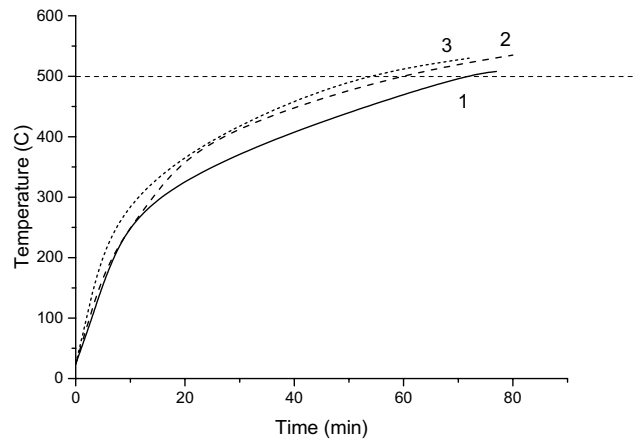


Fig. 6 Fire resistance properties of experimental coatings. 1. Base coating, 2. Filled with 0.25 wt. % of o-MMT, 3. Filled with additional 1.25 wt. % of silica

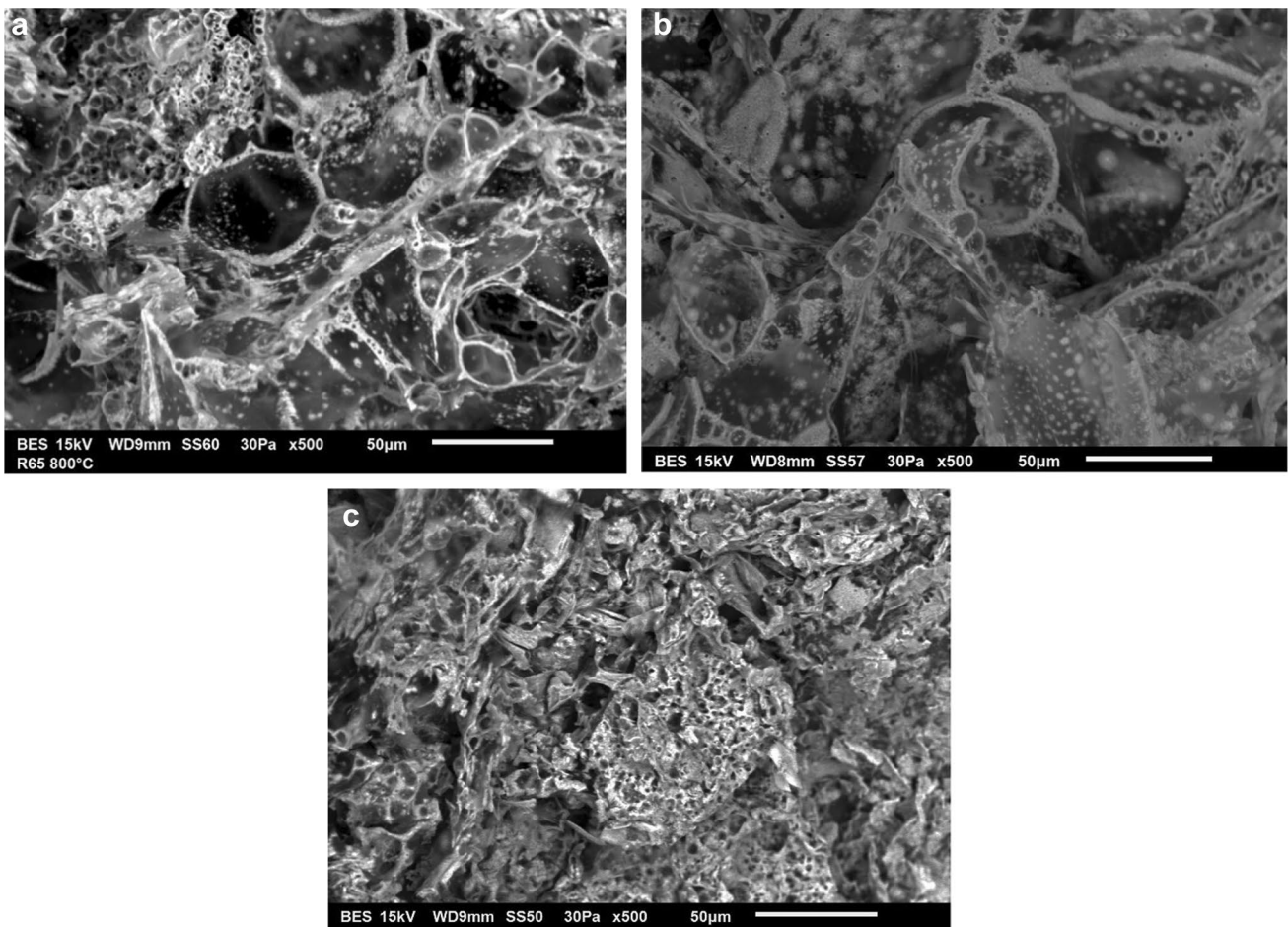


Fig. 5 SEM images of carbon foams: **a** Base composition, **b** composition filled with additional 1.5 wt. % TiO₂, **c** composition filled with 0.25 wt. % of o-MMT

Table 4 Fire resistance properties of intumescent coatings

Formulation	T500, min	Inflection point, °C/min	Section 2 slope, °C/min
Basic composition	71	328/12	2.92
Basic composition + 1.0 wt. % O-MMT	59	383/14	2.60
Basic composition + 1.2 wt. % silica	53	369/9	2.88
Basic composition + 3 wt. % alumina	70	330/11	2.91
Basic composition + 4 wt. % TiO ₂	62	345/13	3.26

may appear from the fire temperature changes, uniformity of the thickness of the coating, etc. The test was conducted five times for each formulation and the data were put to an average value for each testing time. It was noted (Fig. 6) that the character of the temperature rise in all cases is similar; the thermal curve has two main sections: from the start to the inflection point and from this point to the end. It may be suggested that the position of the inflection point and the slope of the first section are determined by the heat conductivity of non-expanded coating and the temperature of intumescence. The slope of the second section is completely determined by the heat conductivity of the resultant foam, namely the conductivity of the char layer obtained (not the specific resistance).

As can be seen from the comparison of curves 1 and 2 (Fig. 6), the slope of the second section of the line of o-MMT filled composition is less than the slope of the base composition line. It can be assumed that the addition of o-MMT to the base composition increases the thermal insulation ability (even considering the fact that the char layer thickness is lower due to the decrease of expansion factor). However, the position of the inflection point (Table 4) is by 57 °C higher, which can be explained by the delayed blowing agent decomposition stage (Table 3). The total fire resistance of the coating with o-MMT is 12 min lower than that of the basic formulation coating.

The general influence of additional load of inorganic fillers, including the nanosized additives (silica and o-MMT) delays the foam expansion process and, thus, decreases the total fire resistance ability of the coating. Nevertheless, the use of silica and o-MMT reduces the slope of the second segment of the thermal curve. This indicates the increase of heat insulation performance of such systems and further perspectives of their use in better balanced intumescent systems.

Conclusions

It was determined that in the particular case of basic composition used in this study, the nanosized additives—organically modified montmorillonite and hydrophobized silica—had reduced the fire resistance of the basic formulation. The

main reason for this reduction is the shifting of the intumescence processes to higher temperatures, thus increasing the time of direct substrate heating. However, it was also established that the minor concentrations of o-MMT (0.25 wt. %) can significantly change the structure and increase specific heat insulation property of the carbon foam. Such an effect can also be observed in the case of the use of hydrophobic silica, but to a lesser extent. In perspective, reducing the thermal insulation property of nanosized additives containing coatings can be overcome by using formulation solutions to help compensate for the reduction of the expansion factor and expansion temperature rise.

It was shown that nanosized additives have strong effect on the expansion factor and the foam structure. It was suggested that this influence can be explained by the complex influence of nanoparticles on the bubble growth processes through the melt viscosity modification.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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