# Flame-Retardant Systems Based on Alkoxysilanes for Wood Protection

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Additional information is available at the end of the chapter

**Abstract**

The aim of this study was to formulate, develop, and determine the performance of flame-retardant systems for wood protection. Flame-retardant systems involve wood impregnation and intumescent coating application. The impregnation was made in two retention levels using silanes of low and high hydrophobicity (methyltriethoxysilane and n-octyltriethoxysilane, respectively); these silanes were conducted to polymerize by sol-gel process in wood pores. The intumescent coatings were formulated with a polymeric binder (hydroxy-functional acrylic resin) modified with n-octadecyltriethoxysilane in two w/w ratios to combine the individual characteristics of each film-forming material. In this research, *Pinus radiata* panels were selected to study the performance of quoted flame-retardant systems. The results indicated excellent flame-retardant performance of some studied systems in two foot tunnel, in oxygen index cabin, and in horizontal-vertical chamber.

**Keywords:** wood, alkoxysilane, impregnation, intumescent coating, fire performance

## 1. Introduction

The use of wood in construction is often questioned by its natural combustibility and vulnerability in fires [1–3]. Nevertheless, the excellent resistance to fire penetration due to the low thermal conductivity and the ability to form a superficial char layer allow wood to maintain the physical-mechanical properties longer than metal or concrete [4–6].

The protection of wood against fire is limited to a retarding effect, since no chemical can transform wood in a noncombustible material within reasonable economic margins. Flame-retardants are applied to significantly reduce or delay the combustion of a material. Nevertheless, it is worth mentioning that the above-mentioned wood treatments only control small sources of energy (heat and/or fire) prolonging the beginning of conflagration and so providing the time to take the necessary actions [7–11].

Experiences and investigations on flame-retardant products show a wide range of substances that prove positive action, for example, on reducing the mass loss, the flame advance, and the permanence time of combustion and incandescence; these methods to improve fire performance of wood include chemical and/or physical modifications, as well as structural design considerations [12, 13].

High efficient flame-retardant systems for wood protection usually consist of impregnation and/or intumescent coating application. Several techniques have been studied for impregnations (chemicals in molecular dispersions and colloidal solutions) and for surface treatments (flame-retardant coatings), both of them with cutting-edge technologies (e.g., nanocomposites) [1]. The main problem of these flame-retardant treatments is the long-term performance in weather exposure where flame-retardant chemicals may leach out; while in indoor, the most important issue is the persistence of the aesthetic appearance that cannot always predict or ensure [12]. The use of intumescent coating is one of the most economical and efficient ways to protect materials against fire action without modifying their intrinsic properties [14–16] as the impregnation does [17, 18].

In previous papers, the authors studied the performance of various flame-retardant systems for wood protection; experiments on treated woods allowed to conclude that the performance of the impregnations depend on whether they give chemical or physical changes or both simultaneously [19–21] while that the efficiency of the intumescent coatings is strongly influenced by type (chemical composition) and content (pigment volume concentration, PVC) of functional pigments as well as by dry film thickness [22, 23].

Nowadays, many organosilicon compounds are chosen as environmental-friendly fire retardants to replace the traditional halogenated ones, for several materials protection including the wood; the most commonly used compounds include silanes, polysiloxanes, and polysilsesquioxanes, as well as structures containing heteroatoms in the main chain, such as polycarbosilane and polysilazanes [24, 25].

The aim of this research was to design highly efficient flame-retardants for the protection of *Pinus radiata* panels; the studied systems included an impregnation based on low and high hydrophobicity silanes (methyltriethoxysilane (MTES) and n-octyltriethoxysilane (OTES), respectively) polymerized inside wood pores by sol-gel process, and the subsequent application of a coating with intumescent properties formulated with a polymeric binder (hydroxy-functional acrylic resin) chemically modified with n-octadecyltriethoxysilane (ODTES) to improve the individual characteristics of each film-forming material.

## 2. Materials and Methods

### 2.1. Impregnation

The experiments included: (i) the preparation of wood panels; (ii) the choice of reactive impregnants; (iii) the selection of impregnation conditions; (iv) the setting of drying and curing conditions; and (v) the determination of impregnant retention.

*Preparation of wood panels*. *Pinus radiata* was selected because it is a macroporous and moderately penetrable wood. Boards from unseasoned trunks were provided by a sawmill; they were exposed in a chamber under controlled temperature and humidity conditions (20 ± 2°C and 60 ± 5% RH) until reaching the equilibrium moisture, according to the guidelines of ASTM D4933. Free-defect specimens were prepared, with the appropriate size for each test, using a power saw; then, the specimens were carefully sanded with fine sandpaper.

The cellulose was activated by immersion in a sodium hydroxide solution (pH 8.5); then, the specimens were washed with distilled water to remove the remaining alkali [26, 27]. Finally, the samples were again conditioned to reach the equilibrium moisture and sanded.

*Reactive impregnants*. Since silicon-derived monomers with low molecular weight react with the cellulose -OH groups present in the internal wall of wood pores [7], methyltriethoxysilane (MTES) and n-octyltriethoxysilane (OTES) were selected to obtain impregnants with different hydrophobicity (**Table 1**). For the impregnation, the silanes were solubilized in 1/1 v/v toluene/ethylenglycol (concentration, 12% v/v).

| Chemical name | Methyl triethoxysilane | n-octyl triethoxysilane | n-octadecyl triethoxysilane |
|---|---|---|---|
| **Chemical structure** | $(CH_3)$-Si-$(OC_2H_5)_3$ | $C_8H_{17}$-Si-$(OC_2H_5)_3$ | $C_{18}H_{37}$-Si-$(OC_2H_5)_3$ |
| **Empirical formula** | $C_7H_{18}O_3Si$ | $C_{14}H_{32}O_3Si$ | $C_{24}H_{52}O_3Si$ |
| **Abbreviation** | MTES | OTES | ODTES |
| **Aspect** | Colorless liquid | Colorless liquid | Colorless liquid |
| **Molecular weight** | 178.30 | 276.48 | 416.76 |
| **Density (25°C), g/cm³** | 0.895 | 0.880 | 0.875 |
| **Purity (gas chromatography), %** | 99.0 | 98.0 | 97.0 |

**Table 1.** Silanes properties.

*Impregnation conditions*. The impregnation was carried out under controlled operating conditions at 48–50°C in an autoclave equipped with vacuum pump and compressor. The autoclave was initially charged with the wood panels. Then, it was applied 500 mm Hg vacuum for 10 min to remove air and water vapor from pores to facilitate the penetration of chemical modifier; later, the solution of corresponding alkoxide was incorporated without decreasing the vacuum level. In all cases, the impregnating solution/wood ratio was 3/1 v/v to ensure that the panels were completely submerged during the entire process.

The operating conditions were adjusted to obtain two groups of panels with different retention levels of chemical modifier. To facilitate the penetration, the pressure was gradually increased from 1.5 to 6.5 kg/cm$^2$; this stage lasted between 15 and 60 min. Subsequently, a slight vacuum (about 200 mm Hg for 10 min) was applied to remove the excess of solution from panel surface.

*Drying and curing conditions*. After impregnation, wood samples were taken off from the autoclave, rinsed and exposed to controlled laboratory conditions (20 ± 2°C and 60 ± 5% RH) for 2 days to allow the complete drying (removal of organic solvent), the partial development of the curing reactions involved in the sol-gel process (hydrolysis, water absorption from the environment, and formation of water and ethylic alcohol by condensation), and, finally, the elimination of quoted products to the surrounding (aging). This process produces a chemical modification of wood, forming a polymer coating in the internal wall of the pores without sealing off [28–33].

*Impregnant retention*. It was gravimetrically measured and, as mentioned, two panel groups were selected: 45–50 and 85–90 kg/m$^3$. Finally, it was microscopically observed that the depth reached by the impregnants was complete (entire thickness of the panel) in the highest retention level and only partial in the other.

## 2.2. Hybrid intumescent coatings

The experimental part included: (i) the formulation; (ii) the manufacture; and finally (iii) the application.

*Formulation*. The intumescent hybrid coatings were based on a polymeric material chemically modified with a long chain silane (**Table 2**).

| Component | % v/v on dry film |
|---|---|
| **Ammonium polyphosphate** | 48.3 |
| **Pentaerythritol** | 17.7 |
| **Melamine** | 17.1 |
| **Titanium dioxide** | 6.9 |
| **Hydrated zinc borate** | 2.0 |
| **Alumina trihydrate** | 1.8 |
| **Additives** | 6.2 |
| **Film forming material (solids)** | 100.0 |
| **PVC = 65.0%** | |

**Table 2.** Intumescent coatings composition.

*Film-forming material*. A hydroxy-functional acrylic resin was used (**Table 3**). The hybrid binders included this resin and the n-octadecyltriethoxysilane (ODTES, **Table 1**). One of them was formulated with resin/ODTES in stoichiometric ratio (2.5/1.0 w/w): it was contemplated the three hydroxyl groups of silanol (generated by hydrolysis of triethoxysilane, 12.2% w/w) and the percentage of hydroxyl groups of the resin (4.9% w/w). The other was formulated with

an excess amount of ODTES with respect to stoichiometric ratio (1.0/1.0 w/w). In addition, a nonreactive (thermoplastic) acrylic resin based on methyl methacrylate diluted in xylene was selected as reference (**Table 4**).

| | |
|---|---|
| Solid content, % | 60.2 |
| Solvent | Xylene/ethylenglycol acetate, 2/1 v/v |
| Viscosity (25°C) | X-Z Gardner; 15.2 Stokes |
| Acid value, mg KOH/g | 6.1 |
| Density (25°C), g/cm³ | 0.972 |
| HO⁻ on solids, % | 4.9 |

**Table 3.** Properties of the hydroxy-functional acrylic resin.

| | |
|---|---|
| Solid content, % | 59.8 |
| Solvent | Xylene |
| Viscosity (25°C) | Z2-Z4 Gardner |
| Acid value, mg KOH/g | 4.0 |
| Density (25°C), g./cm³ | 0.825 |

**Table 4.** Properties of the nonreactive acrylic resin.

*Pigmentation.* The active pigments were the dipentaerythritol (water solubility at 20°C, 0.29 g/100 ml) as carbon source, an ammonium polyphosphate (white powder with 30.2% phosphorus and 14.5% nitrogen and low water solubility at 20°C, 0.18 g/100 ml) as acid catalyst, and, finally, a modified melamine (decomposition temperature about 130°C; water solubility at 20°C, 0.32 g/100 ml) as blowing agent [22, 34].

Complementary flame-retardant pigments were a hydrated zinc borate ($2ZnO.3B_2O_3.7.5H_2O$) and the alumina trihydrate ($Al_2O_3.3H_2O$) [30–32]. Rutile titanium dioxide ($TiO_2$) was used as opaque pigment (**Table 5**).

*Other components*. Rheological, dispersing, and stabilizing agents were selected as additives. The solvent mixture for film-forming materials was 2/1 v/v toluene/ethylenglycol acetate.

*Manufacture of intumescent coatings*. It was carried out in a high-speed disperser. In a first stage, the solvent mixture was added; subsequently, the rheological agent was gradually introduced (castor oil gel, 15% w/w) at high shear rate (1400 rpm), until reaching a system with the suitable viscosity for pigment dispersion (laminar flow, rolling-doughnut effect); the stirring was extended for about 10 min. Then, surfactants (dispersants and dispersion stabilizers) and pigments were incorporated under vigorous stirring for about 30 min to achieve adequate dispersion. Finally, at low shear rate (about 700 rpm), the hydroxy-functional acrylic resin was incorporated to achieve 65% pigment volume concentration (PVC). The corresponding silane solution (50% v/v) was placed in a second container in sufficient amount to achieve the 2.5/1.0

and 1.0/1.0 w/w ratios depending on the formulation considered (expressed in solids of acrylic resin/silane).

| | |
|---|---|
| **Alumina trihydrate** | Appearance, granular crystalline powder |
| | Density, 2.4 $g/cm^3$ |
| | Oil absorption, 53 g/100 g |
| | Particle diameter D (50/50), 0.65 μm |
| **Hydrated and stabilized zinc borate** | Appearance, white powder |
| | Density, 3.9 $g/cm^3$ |
| | Oil absorption, 28 g/100 g |
| | Particle diameter D (50/50), 5.20 μm |
| **Titanium dioxide (rutile)** | Appearance, white powder |
| | Density, 4.1 $g/cm^3$ |
| | Oil absorption, 39 g/100 g |
| | Particle diameter D (50/50), 0.25 μm |

**Table 5.** Characteristics of pigments.

In the case of reference coating, after finishing pigment dispersion, the nonreactive acrylic resin was incorporated in the same container (also 65% PVC).

*Application of intumescent coatings*. First, the content of the two packages was mixed in adequate amounts; in all samples the volume solids content, using the quoted solvent mixture, was adjusted to 50%. Subsequently, the impregnated panels (dried and partially cured) were coated with the intumescent products by brush (two layers, with an interval of 24 h).

In all cases, and to ensure the drying and curing of protective treatments, the panels were kept in controlled laboratory conditions (25 ± 2°C and 65 ± 5% RH) for 7 days. Dry film thickness ranged between 160 and 180 μm.

Visual and microscopic observations indicated the absence of checking and cracking, typical of the films based on only silanes as film-forming material. The identification of the panels is displayed in **Table 6**.

### 2.3. Fire performance

*Two foot tunnel*. Flame advance (AL) was determined by using equation AL = Ls − La, where Ls is the average of the three highest flame advances on the panels (consecutive readings measured at intervals of 15 s) and La is the average distance of flame reflection (55 mm) on a thin cement substrate selected as reference; panel consumption (PC) was also evaluated. Specimens were prepared with 6 × 100 × 605 mm size (radial × tangential × longitudinal); the tests were performed in triplicate according the guidelines of ASTM D3806. Then, the results were averaged.

*Oxygen index, OI*. This test determines the minimum oxygen concentration in mixture with nitrogen that can support the combustion of a material, under equilibrium conditions, as candle-like burning; the importance of OI determination lies in the high reproducibility of

results. The test was performed in triplicate under the guidelines of ASTM D2863, at 23 ± 2°C and with a 3.2 cm/s flow rate; test specimen dimensions were 150 mm length, 10 mm width, and 10 mm thickness (longitudinal, radial, and tangential, respectively).

*Resistance to intermittent flame of Bunsen burner, RIB.* For the first stage, the panels were exposed in a horizontal-vertical cabinet for 20 s to the action of the flame with 10 s rest: the number of cycles with self-extinguishing behavior was defined in 30 as maximum (it was assigned one point per cycle); for the second stage, the flame action was extended to 50 s with 10 s rest: the number of cycles with self-extinguishing behavior was defined in 35 as maximum (it was assigned two points per cycle), and, finally, when the system continued behaving as self-extinguishing, the flame was kept constantly for 30 min as maximum (it was assigned 5 points per minute). Lastly, the total score for each panel was calculated (the highest rating can reach 250 points). Test specimen dimensions were 150 mm length, 40 mm width, and 10 mm thickness (longitudinal, radial, and tangential, respectively).

| Impregnant | | Coating | Identification |
|---|---|---|---|
| Type | Retention, kg/m³ | | |
| – | – | Nonreactive acrylic | A.1 |
| | – | Acrylic/ODTES (2.5/1.0 w/w ratio) | A.2 |
| | – | Acrylic/ODTES (1.0/1.0 w/w ratio) | A.3 |
| MTES | 45–50 | Nonreactive acrylic | A.4 |
| | 45–50 | Acrylic/ODTES (2.5/1.0 w/w ratio) | A.5 |
| | 45–50 | Acrylic/ODTES (1.0/1.0 w/w ratio) | A.6 |
| | 85–90 | Nonreactive acrylic | A.7 |
| | 85–90 | Acrylic/ODTES (2.5/1.0 w/w ratio) | A.8 |
| | 85–90 | Acrylic/ODTES (1.0/1.0 w/w ratio) | A.9 |
| OTES | 45–50 | Nonreactive acrylic | A.10 |
| | 45–50 | Acrylic/ODTES (2.5/1.0 w/w ratio) | A.11 |
| | 45–50 | Acrylic/ODTES (1.0/1.0 w/w ratio) | A.12 |
| | 85–90 | Nonreactive acrylic | A.13 |
| | 85–90 | Acrylic/ODTES (2.5/1.0 w/w ratio) | A.14 |
| | 85–90 | Acrylic/ODTES (1.0/1.0 w/w ratio) | A.15 |
| Without impregnant | – | – | Reference |

**Table 6.** Panel identification.

## 3. Results

During experiences, visual and microscopic observations of treated panels allowed the description of the protective mechanism of flame-retardant systems: (i) when hybrid film is heated, the first resin layer is soften and the gases, produced by thermal decomposition of gas generator, are released allowing the film intumescence; (ii) then, the heat penetrates in the

adjacent deeper layer where the inorganic components melt or soften retarding the heat conduction, while organics degrade into smaller products that contribute to formation of the carbonaceous residue (char); (iii) the heat continues penetrating and reaches an even deeper layer, causing the degradation and forming products that are transferred to the combustion zone through the char: the kinetics of the process seems to decrease as the system forms a carbonaceous material with high inorganic content that accumulates in the interfaces during combustion, isolates the underlying material, and reduces the mass loss; (iv) when the heat finally reaches the impregnated substrate, in the first instance it forms a carbonaceous residue by degradation until reaching the phase conformed by siloxanes, which acts as flame-retardant due to their high thermal stability; and finally, (v) this process is repeated generating interfaces of carbonaceous material until siloxanes reappear and the process starts again, giving to wood self-extinguishing characteristics.

Regarding test results, they are shown in **Table 7**. With the purpose of establishing the efficiency against the fire action of each protective system, the values 0 and 10 were set for 16 and ≥45% in OI; for 555 and 0 mm in AL; for 7.38 and 0.00% in PC; and finally, for 0 and 250 points in RIB. In all the cases, intermediate values were proportionally calculated. Finally, the values were averaged for the interpretation of the results: the highest average value indicates the best performance (**Table 8**).

| Sample | Fire performance | | | |
|---|---|---|---|---|
| | AL, mm | PC, % | OI, % | RIB |
| A.1 | 165 | 2.22 | 31 | 175 |
| A.2 | 134 | 1.80 | 36 | 192 |
| A.3 | 138 | 1.89 | 33 | 188 |
| A.4 | 60 | 1.23 | 40 | 204 |
| A.5 | 49 | 1.11 | 45 | 214 |
| A.6 | 52 | 1.18 | 43 | 210 |
| A.7 | 38 | 0.52 | 42 | 228 |
| A.8 | 32 | 0.35 | 45 | 236 |
| A.9 | 33 | 0.41 | 44 | 230 |
| A.10 | 58 | 1.33 | 37 | 200 |
| A.11 | 52 | 1.20 | 40 | 210 |
| A.12 | 54 | 1.23 | 38 | 205 |
| A.13 | 40 | 0.58 | 40 | 220 |
| A.14 | 28 | 0.38 | 45 | 233 |
| A.15 | 35 | 0.44 | 43 | 225 |
| Reference | 555 | 7.38 | 16 | 2 |

**Table 7.** Test results.

| Sample | Individual value | Average value |
|--------|------------------|---------------|
| A.1 | 6.55 | 7.02 |
| A.2 | 7.43 | |
| A.3 | 7.08 | |
| A.4 | 8.42 | 8.75 |
| A.5 | 9.04 | |
| A.6 | 8.79 | |
| A.7 | 9.17 | 9.40 |
| A.8 | 9.60 | |
| A.9 | 9.43 | |
| A.10 | 8.10 | 8.30 |
| A.11 | 8.53 | |
| A.12 | 8.29 | |
| A.13 | 8.89 | 9.25 |
| A.14 | 9.58 | |
| A.15 | 9.27 | |
| Reference | 0.02 | 0.02 |

**Table 8.** Average flame-retardant performance of protective systems.

In relation to impregnant type, the analysis of the results indicates that MTES showed a higher performance than OTES (mean values, 9.08 and 8.78, respectively, **Figure 1**). This is based on that although MTES has a shorter hydrocarbon chain and therefore it is less able to generate the desired char, it forms siloxanes with higher silicon level (more percentage content of inorganic components) than OTES.
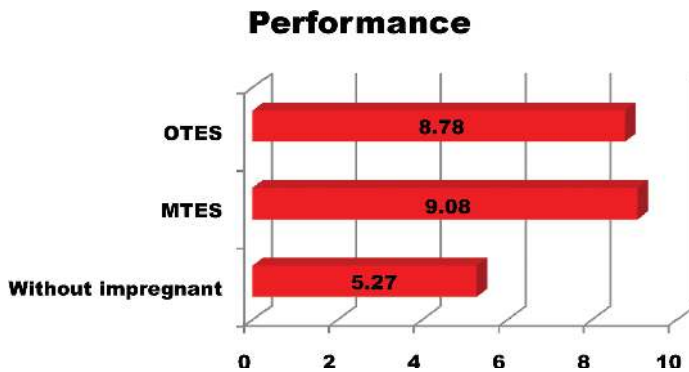


**Figure 1.** Flame-retardant performance according to the impregnant type.

With reference to retention level, flame-retardant efficiency improved as reactive impregnant level increased (mean values, 9.32 and 8.53 for 85–90 and 45–50 $kg/m^3$ respectively, **Figure 2**).
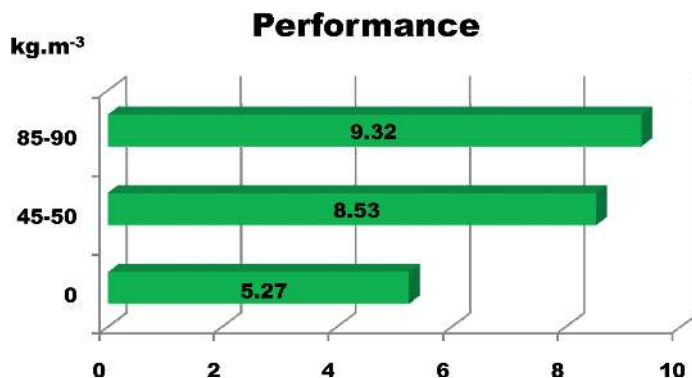
**Figure 2.** Flame-retardant performance according to the impregnant retention.

Finally, it is worth mentioning that panels treated with reactive impregnants displayed better performance with respect to those untreated (5.27). This would be supported by the chemical modification of wood produced by the formation of highly stable condensation products during the sol-gel process (≡Si-O-cellulose); the reactions involve the silanol groups generated by hydrolysis of the triethoxysilanes and the hydroxyl groups of wood cell wall.

In relation to wood panels also protected with hybrid intumescent coatings, it was observed that all impregnated samples displayed better performance against fire action than those without impregnation (**Table 8**). The above-mentioned is based on that chemical reactions in nonimpregnated panels would involve the hydroxyl groups of the film-forming materials and those of the wood cellulose, while in impregnated and partially cured panels, would react in addition to those groups that correspond to the impregnant. In the latter case, the highest thermal stability, attributable to the high quantity of strongly stable chemical bonds, complements the own performance of impregnants and of intumescent coatings.

Moreover, the tests allowed establishing that hybrid coatings were more efficient than those formulated with only one film-forming material and, in addition, that the hybrid coating formulated with hydroxy-functional acrylic resin/ODTES in the stoichiometric ratio showed the best performance (**Figure 3**).

SEM micrographs of chars corresponding to A.1, A.2, and A.3 panels are displayed in **Figure 4**. The analysis carried out on all panels indicates that: (i) the coating based on non-reactive acrylic resin had a moderately uniform distribution of cell size with some cracks; (ii) the coating modified with ODTES in the stoichiometric ratio generated a very uniform distribution of cell size without any crack; and finally, (iii) the coating modified with ODTES in excess led to a wide distribution of cell size with some cracks.

Above-mentioned indicates that the performance of treated panels depends strongly on the physical structure of the char formed by fire action. Correlating results of fire tests and SEM micrographs, it is observed that the best performance was achieved in panels with uniform chars free of cracks since they provide better insulation to the substrate.

In summary, the best flame-retardant system was that impregnated with MTES in the highest level of retention and superficially treated with the intumescent coating based on hydroxy-functional acrylic resin modified with ODTES in the stoichiometric ratio (**Table 8**; sample A. 8: average value, 9.60).
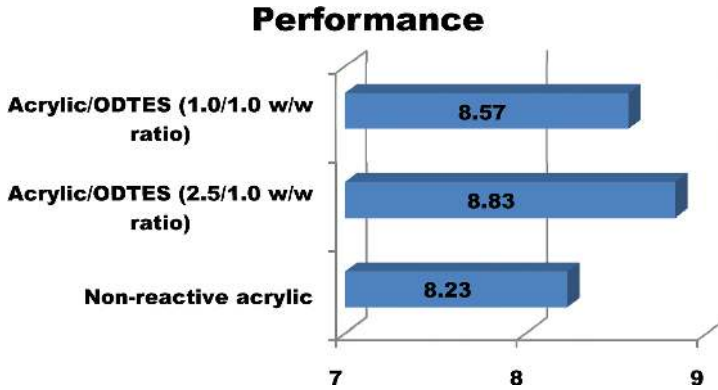


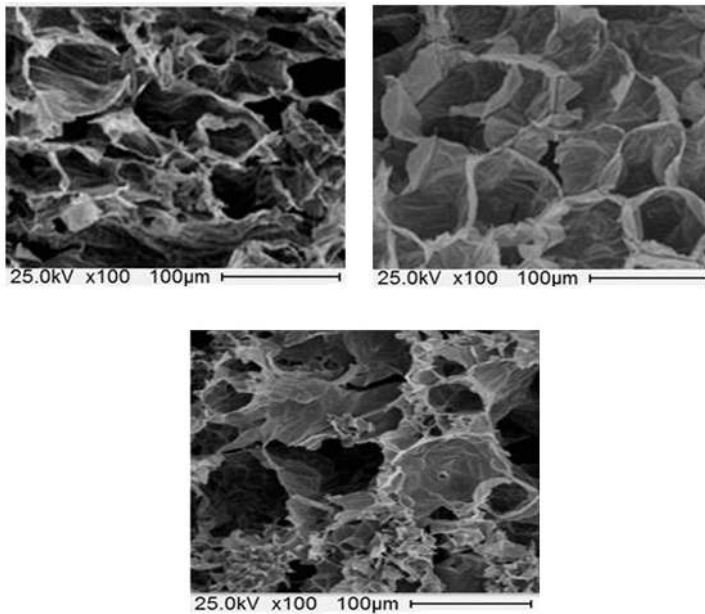**Figure 3.** Flame-retardant performance according to the intumescent coating.



**Figure 4.** Char SEM micrographs: left, non-reactive acrylic resin; right, hydroxy-functional acrylic resin modified with ODTES in 2.5/1.0 w/w ratio and down, hydroxy-functional acrylic resin modified with ODTES in 1.0/1.0 w/w ratio.

## Acknowledgements

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