

# Hybrid Intumescent Coatings for Wood Protection against Fire Action

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**ABSTRACT:** Hybrid intumescent coatings for wood protection against fire were developed. Several resins were chosen as film-forming materials. Similar active and complementary pigments were used. To improve the efficiency, coatings were formulated by using reinforcing fibers. The performance of hybrid coatings was determined on panels of *Araucaria angustifolia*; some coatings showed an excellent performance in thermal conductivity test, two-foot tunnel, OI cabin, UL 94 horizontal–vertical chamber, and TGA trials. The best performance was achieved with chlorinated rubber, followed by phenolic resin, and finally by epoxy resin. With respect to fibers, hybrid formulations had a superior performance in relation to the respective reference samples; in addition, coatings displayed the best behavior with alumina, carbon, aramid, and glass fibers in their composition, in that order. An elevated synergistic effect was observed; the mentioned synergistic effect could be based on that the nature of the interface in a composite would affect its combustibility.

## 1. INTRODUCTION

Fire is an energy manifestation that constantly squires human activity, so the emerging risk must be assumed. Fire develops highly exothermic chemical reactions, beginning when oxidizer and fuel are in a sufficient energy state (activation energy).

The fuel includes substances that are not in their maximum state of oxidation; in general, any material that contains carbon and/or hydrogen can be oxidized, and consequently it behaves as a combustible material. The most important oxidizing is air, which is composed by about the fifth part of oxygen; during the combustion, the other components remain unchanged (except at very high temperatures), and they are part of the combustion fumes.

Part of the energy released in the reaction is dissipated by generating an increase in temperature of the medium, and the remainder is transferred to the reaction products contributing to the activation energy for the continuation of the process; if this is not enough, the burning stops.

Taking into account the current technology in the field of coatings, it is important to mention the generic concept of “passive fire protection”, which presents efficiency independent of human activity. Research and development studies are significant to reduce the flammability of materials and propagation speed of the flame front as well as to maintain during the conflagration the mechanical properties of structures based on combustible and noncombustible materials. The building design and the material selection also play a highly important role.

Efforts to reduce the flammability of materials and wood in particular began in ancient times. However, the knowledge of the physic-chemistry of combustion has allowed only in the last decades the development of products and effective means of defense to prevent unwanted conflagration to which combustible materials tend spontaneously. In addition, this increase in scientific and technological level has allowed drafting standards and specifications related to flammability control.

The results before-quoted allowed the development of composites. A composite material is a heterogeneous mixture of two or more homogeneous phases, which have been bonded

together. Usually, all matrix materials used for coating formulations are highly flammable, so they can burn vigorously with evolution of heat and loss of their physical and mechanical properties; fibers are the dominant constituents of the most composite systems as they act as ideal reinforcing elements providing composites with improved several properties. These properties depend upon the methods used to combine these components into one material.

The composite fire-resistance to the typical flame temperatures in no wished conflagrations is defined by that of the organic matrix, and, in addition, by that of the fibers, so the selection of the last ones is fundamental to formulate efficient flame-retardant composites. Flame retardancy of these materials is a major issue in these days because, depending on applications, they must pass some types of regulatory fire tests to ensure public safety.

For this reason, in this Article, it is pretended to understand how individual components (i.e., film-forming materials and fibers) and their possible interaction between them influence the end-product efficiency and, finally, how is the best way to formulate new hybrid intumescent coatings to make them more flame-resistant.

On the basis of the cited above, the design of hybrid intumescent coatings to give a satisfactory performance to the wood against fire action was defined as the fundamental objective of this research.<sup>1–10</sup>

## 2. MATERIALS, FORMULATION, AND MANUFACTURE OF THE HYBRID COATINGS

**2.1. Main Components.** *2.1.1. Active and Complementary Pigments.* Pentaerythritol was selected as supplier of carbon (water solubility at 20 °C, 4.05 g/100 mL), ammonium polyphosphate as

**Received:** January 4, 2011

**Accepted:** September 21, 2011

**Revised:** September 5, 2011

**Published:** September 21, 2011

catalyst (white powder; 30.2% phosphorus and 14.5% nitrogen; water solubility at 20 °C, 0.18 g/100 mL), and melamine sulfate as blowing agent (water solubility at 20 °C, 0.32 g/100 mL).

Concerning the thermal degradation of melamine sulfate·H<sub>2</sub>O, the pathway consists of step 1, 100–230 °C, anhydrous melamine sulfate and water vapor; step 2, 300–400 °C, melam pyrosulphate and volatile products (about 15% melamine, NH<sub>3</sub>, and H<sub>2</sub>O); step 3, 450–520 °C, melon and volatile products (NH<sub>3</sub>, H<sub>2</sub>O, SO<sub>3</sub>, etc.); and step 4, >520 °C, melon decomposition.<sup>11</sup>

Trihydrated alumina (granulated crystalline powder; average diameter, 0.65 μm) and magnesium hydroxide (MgO content, 97.5%; average diameter 78 nm) were used as flame-retardant pigments. Both inorganic compounds contain a high percentage of hydration water.

The flame-retardant action of trihydrated alumina (aluminum hydroxide) is attributable in part to the absorption of thermal energy produced by the dehydroxylation and in addition to the dilution of combustible gases with water vapor formed during the conflagration. When degraded by the effect of temperature to more than 240 °C, the aluminum hydroxide forms the alumina that acts as a surface barrier that prevents the flame spreading.

On the other hand, magnesium hydroxide acts the same way as trihydrated alumina, but its thermal decomposition does not occur until it reaches approximately 325 °C. For this reason, a combination of magnesium hydroxide and trihydrated alumina in 1.0/1.0 ratio v/v was used in this study.

**2.1.2. Opaque Pigment.** Rutile titanium dioxide (fine white powder; average diameter, 0.25 μm) was used as opaque pigment. This improves the coverage power of the film, and it shows also significant activity by dividing the binder in “isolated” parts by occupation of pores and amorphous regions; besides, it requires a high amount of heat for reaching the pyrolysis temperature.

**2.1.3. Film-Forming Materials.** Film-forming materials are polymers, and they can be of thermoplastic or thermoset nature. In the present experience, chlorinated rubber was selected as thermoplastic resin, while phenolic and epoxy were selected as thermoset ones because they are the most common matrix materials used for formulating heavy-duty coatings.

The thermoplastic resins have the advantage that they can be formed by the physical processes. Reversibility of this process generates composites having a thermoplastic property and, hence, poor physical resistance to heat and to solvents. Chlorinated rubber resins are formed by the reaction of rubber with chlorine; in general, they are white powders with about 65% chlorine in weight. In this case, grade 20 was used (it means it has a viscosity between 18 and 22 cP in a solution at 20% w/w in pure toluene, measured in a Ostwald U-tube viscometer at 25 °C). Chlorinated rubber needs to be plasticized to obtain good properties of film; in general, the resin–plasticizer ratio varies between 60/40 and 70/30 w/w. In this experiment, 54% chlorinated paraffin in 65/35 w/w ratio was used.

The second type of polymers is manufactured from the respective resin and the curing agent; in these materials, solidification from the liquid phase takes place by the action of an irreversible chemical cross-linking reaction, which produces a tightly bond three-dimensional network of polymer chain. The level of cross-linking between functional groups depends on the degree of curing, and this usually involves application of heat, although some resins cure at room temperature.

Phenolic resins are of synthetic nature, highly resistant to heat and water; resoles are formed by condensation of phenol and

formaldehyde in excess. In this study, a resol-type resin of high reactivity (10.5% w/w methylol groups), partially esterified with pentaerythritol to improve the hardness and increase the melting point of the system, was used. The quoted esterified phenolic resin maintains a high reactivity (8.0% w/w methylol groups).

For curing at room temperature, phenol sulfonic acid was used; resin/acid mixture was mechanically mixed. Free methylol groups of phenolic resin chemically react with hydrogen ions liberated from phenol sulfonic acid protonating the oxygen of the methylol. This intermediate reacts with the free methylol liberating water and forming dimethylene ether links (–CH<sub>2</sub>–O–CH<sub>2</sub>–).

When the pH of the system is very low, reaction rate is slow due to the repulsion between two positively charged groups (protonated oxygens). Consequently, the pH of the system defines the dehydration rate. In this experience, a 22.6/100.0 w/w phenol sulfonic acid/phenolic resin ratio was used.

Epoxy resins are widely used in coatings technology. In this Article, a commercial brominated bisphenol-F epoxy resin was used because it has shown good ability as flame retardant; in addition, it generates less toxic gases and smokes than other halogenated compounds (i.e., chlorinated alkyd resins).

Diethylenetriamine in stoichiometric amount was used as curing agent at room temperature; because its equivalent weight is 20.6 (MW, 103.0; amount of H<sup>+</sup>, 5), to polymerize 100.0 g of epoxy resin of WPE (weight per epoxyde) equal to 500, 4.1 g of curing agent (20.6 × 100/500) is required.

The three resins were characterized by laboratory tests.

**2.1.4. Reinforcing Fibrous Materials.** A composite (FRP, fiber-reinforced polymer) was formulated and developed to obtain a unique combination of properties; the incorporation of reinforcing fibers to coatings forms a hybrid structure.<sup>12,13</sup>

Fiber is defined as any material that has a minimum 10/1 length/average transverse dimension ratio; in addition, the transverse dimension should not exceed 250 μm.

These hybrid systems were developed and produced with reinforcing fibers of different physical and chemical characteristics. The formulations included fibers of alumina, carbon, glass, and aramid in their composition in a level of 3% v/v on dry film. The first three are synthetic and have inorganic characteristics, while the last one is also synthetic but of organic nature.

Alumina fibers exhibit significant rigidity (high modulus of elasticity), low tensile strength, and reduced elongation specifically in the zone of elastic behavior. As a disadvantage, they have a relatively high density.<sup>14</sup> In this work, alumina fibers with average values of 1150 and 95 μm, respectively, for the length and transverse dimension were used.

Carbon fibers exhibit high modulus of elasticity, tensile strength, and specific elongation; they have a relatively low density.<sup>15</sup> In this work, carbon in fibers form was selected with average values of 1020 and 82 μm, respectively, for the length and transverse dimension.

Aramid fibers are based on an aromatic polyamide in which at least 85% of the functional groups are connected directly to an aromatic group. The aramid fibers used have a high modulus of elasticity, tensile strength, and specific elongation; their density is low.<sup>16</sup> In the formulated coatings, aramid fibers with average values of 1180–100 μm, respectively, for the length and transverse dimension were used.

Glass fibers selected in this work are based on 65% SiO<sub>2</sub>, 25% Al<sub>2</sub>O<sub>3</sub>, and 10% MgO. The most important properties of these fibers are high modulus of elasticity in relation to a film-forming

material properly plasticized but significantly lower than other fibers, high tensile strength, and elevated specific elongation; they have an intermediate density.<sup>17</sup> In this work, glass fibers with average values of 955 and 86  $\mu\text{m}$ , respectively, for the length and transverse dimension were used.

The four reinforcing fibers were characterized by laboratory tests.

**2.2. Coating Formulation and Manufacture.** For this experience, the intumescent coatings were formulated with 62% PVC, which implies a slightly lower value than the corresponding CPVC; this is because the level of intumescence is directly proportional to the percentage of pigment in the dry film according to conclusions reached in previous works.

In this case, CPVC values were estimated by the method of Gardner;<sup>18</sup> in all of the vehicles, the surface tension was fit previously to the dispersion of the pigment to 38 dina  $\text{cm}^{-1}$  to obtain similar CPVC (between 64% and 68%).

The standard components in formulation of intumescent coatings, expressed in v/v on solids, were: (i) pigmentation and additives, ammonium polyphosphate (44.2%), pentaerythritol (16.8%), melamine (15.0%), rutile titanium dioxide (6.8%), nanopowder magnesium hydroxide (3.7%), micronized-powder trihydrated alumina (3.7%), dispersants and rheological additives (6.8% v/v), and reinforcement fibers (3%); and (ii) solids of film-forming material (100.0%).

The adding of reinforcing fibers in the vehicle was made by ultrasonic dispersion at 40 °C for about 30 min. The efficiency of the fiber dispersion in the polymeric matrix was rheological monitored (viscosity of the system, measured at  $10^{-3} \text{ s}^{-1}$ ); it decreased during the sonification process until reaching a stationary value. In addition, dispersion degree was microscopically verified by SEM: a satisfactory wetting (adhesion, penetration, and propagation of the vehicle in the fiber set), a correct fiber separation in a multidirectional form under the action of a shear stress, and a suitable stabilization (no fiber association in the package for at least 6 months) were noted in all cases.

Finally, coating manufacture (dispersion of active and complementary pigments) was conducted in a high-speed disperser, according to the rules of art in this field.

### 3. PERFORMANCE AGAINST FIRE ACTION

**3.1. Preparation of Panels.** Wood panels were selected without flaws; they were stationed in a laboratory environment for 6 months to reach equilibrium moisture content and then sanded to standardize the absorption of products applied.

Next, the intumescent products were applied by brushing reaching approximately 280–300  $\mu\text{m}$  dry film thickness (three layers, 48 h interval between them).

In all cases, and to ensure the curing of the films for testing, the specimens were kept in controlled laboratory conditions ( $25 \pm 2$  °C and  $65 \pm 5\%$  relative humidity) for 10 days.

**3.2. Laboratory Tests.** The analysis of the current regulations in the world indicates the existence of a large number of trials of different features to determine the performance of materials against fire action.

A variety of procedures to assess similar features is usually selected; they provide a comparative indication and can vary according to the applied test. The variables considered include the size and position of the specimen, the type of initiating source, the test duration, and the indices measured. For this reason, the following tests to achieve a result more representative

of the overall performance of hybrids intumescent coatings were carried out.

**3.2.1. Thermal Conductivity, CT.** The determination was carried out by using Fourier's law. This law states that the heat flux  $H$  (in terms of energy per unit time) is directly proportional to the area transverse to the flow direction  $S$  and to the temperature gradient  $\Delta T$  between both sides of the system under study (degrees Celsius per unit length  $L$  traveled by the energy).

The constant of proportionality is the thermal conductivity  $K$ . For systems with multiple overlapping plates or sheets, Fourier's law is expressed as  $H = S\Delta T + \Sigma(L/K)$ .

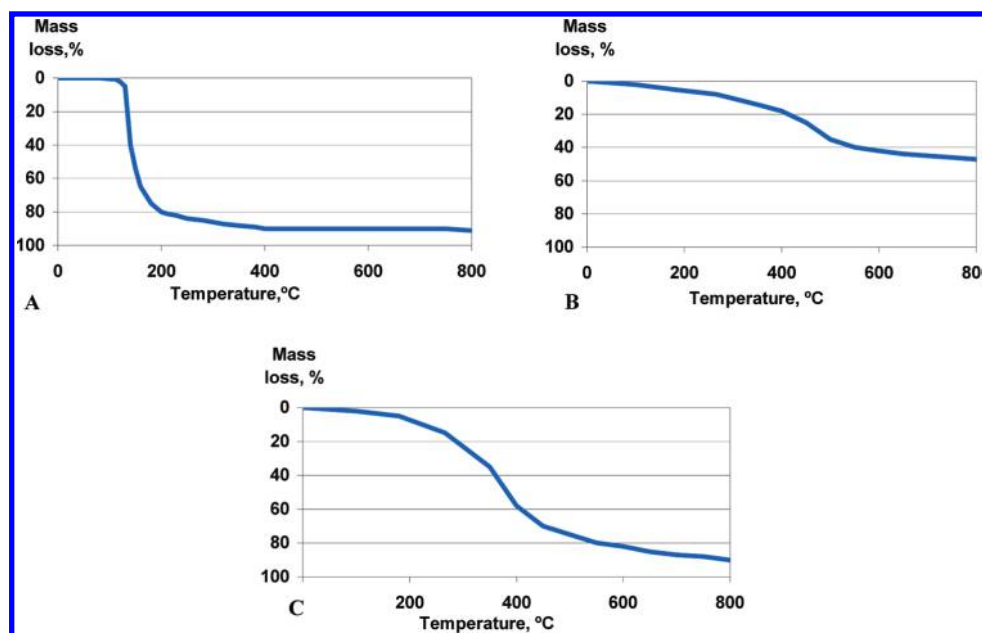
Coated wood panels were first intumesced by the flame action and then exposed at room temperature (22–25 °C) before beginning the test. Temperature of the side of the panels protected with the coatings under study was fixed at 100 °C (boiling point of water at normal atmospheric pressure) and at 56.2 °C (temperature at which acetone distillates; it was placed in a glass container fitted with a condenser). The amount of condensed acetone in mass terms was calculated starting from the volume distilled and the density ( $0.791 \text{ g cm}^{-3}$ ); the mass was multiplied by the latent heat of boiling ( $524 \times 10^3 \text{ J kg}^{-1}$ ) and divided by the elapsed time allowed to calculate the heat flux  $H$ .

The area of flow considered was of 4  $\text{cm}^2$  on both sides; the edges were insulated to prevent lateral dissipation of heat. Starting from the calculated  $H$  and the values corresponding to section  $S$ , the temperature difference  $\Delta T$ , the time of experience, and the thickness of each material that formed the system studied, the thermal conductivity  $K$  of the intumesced coating films was calculated with the expression previously mentioned. The determination of the CT was done in triplicate.

**3.2.2. Flame Advance, AL.** This test was carried out in a two-foot tunnel, according to the guidelines of ASTM D 3806. The top of the apparatus was a 600 mm  $\times$  100 mm section constructed of angle iron and inclined 28° from the horizontal. The 610  $\times$  100  $\times$  10 mm test panels of *Araucaria angustifolia* were prepared and placed in the opening. A 215 mm high, 40 mm diameter natural gas burner was inserted in the enclosed space below the specimen to provide the fire exposure for 4 min. On the basis of measurements taken every 15 s in the first 4 min, the average of the three highest consecutive readings of the flame advance in millimeters was calculated. An asbestos–cement board (zero flame-spread) was also tested. For this study, the AL of the panels was computed using the equation  $AL = L_s - L_a$ , where  $L_s$  is the average of the three flame-advance readings for the test specimen and  $L_a$  is the average of three flame-advance readings for the zero flame spread board. The determination of AL was done in triplicate.

**3.2.3. Oxygen Index, OI.** This testing determines the minimum oxygen concentration that just supports combustion of a material under equilibrium conditions as candle-like burning, according to ASTM D 2863. It is one of the favorite tests in the assessment of the flame-retardant treatments of polymeric materials because it gives reproducible numerical results. The OI chamber consists of a glass tube with a perforated plate and glass beads at the bottom that facilitates the mixing of the oxygen and the nitrogen, a clip to support the sample of test panel, devices for controlling and measuring the gases (filters, gauges, microvalves, flow meters, etc.), and a propane flame ignition system.

A 150  $\times$  10  $\times$  10 mm specimen of *Araucaria angustifolia* was clamped vertically on the approximate centerline of the column



**Figure 1.** Thermogravimetric analysis (TGA) of film-forming materials: plasticized chlorinated rubber resin, (A); modified, resol-type phenolic resin, (B); and epoxy-polyamine resin (C).

with the upper edge of the sample at least 100 mm below the top of the open glass column. Next, the flow valves were set so that the desired concentration of oxygen flows through the glass column. The total flow rate was  $3.2 \text{ cm s}^{-1}$ . After the system was purged with the oxygen–nitrogen flow for 30 s, the top of the specimen was ignited with the propane flame so that the top of the test specimen was well alight. If the specimen continued to burn after the igniter flame was removed, a new specimen was inserted, and the oxygen concentration was adjusted to a lower level. If the specimen did not continue to burn, the oxygen concentration was increased to an intermediate value for the subsequent specimen. Testing continued until the minimum oxygen concentration was established. The determination of the OI was done in triplicate.

**3.2.4. Resistance to the Intermittent Flame of a Bunsen Burner, RIB.** The testing wood panels of *Araucaria angustifolia* ( $200 \times 100 \times 3 \text{ mm}$ ) were arranged in a flame cabinet according to UL 94 (Underwriters Laboratories Standard). The longitudinal axes of the coated panels were set with an inclination of  $45^\circ$  with respect to the supporting level, while their transversal axes were in a parallel position. The test done in triplicate consisted of submitting the front bottom part of the test panel to the intermittent flame of a Bunsen burner vertically disposed. Flame was adjusted to reach 10 mm height of blue cone. The exit hole of the burner was arranged at 25 mm of the testing surface.

The panel, in the above-mentioned position, was submitted to flame action for 20 s, with resting periods of 10 s (first stage). When the number of cycles of extinguishable behavior reached the value 30, the action of the flame lasted for 50 s with resting periods of 10 s (second stage). The exposure fire/resting cycle was repeated in both stages until the flame did not extinguish within 5 s or the carbonized zone did not exceed  $8 \text{ cm}^2$  after that burner flame was shut off.

Finally, if panels continued to be extinguishable after 35 cycles in the mentioned second stage, the flame stayed constant during 30 min as maximum (third stage); in this case, the test was finished when the carbonized zone exceeded  $8 \text{ cm}^2$ .

The number of cycles with extinguishable behavior was determined; the quantification of the first two stages was carried out with one and two points, respectively, while the third one was made with five points by every minute. The total amount of points for each panel and the average of the three panels were then calculated. The qualification and classification of panels were done, respectively, according to: 200–250, approved, Class A; 150–199, approved, Class B; 100–149, nonapproved, Class C; and 99 or less, nonapproved, Class D.

**3.2.5. Thermogravimetric Analysis, TGA.** This assay allows the quantitative determination of weight loss as a function of temperature, at controlled heating rate. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change.

The analyzer usually consists of a high-precision balance with a pan (generally platinum) loaded with the sample. A different process using a quartz crystal microbalance has been devised for measuring smaller samples on the order of a microgram (versus milligram with conventional TGA). The sample is placed in a small electrically heated oven with a thermocouple to accurately measure the temperature. The atmosphere may be purged with an inert gas to prevent oxidation or other undesired reactions. A computer is used to control the instrument.

Analysis is carried out by raising the temperature of the sample gradually and plotting weight (percentage) against temperature; the temperature in many testing methods routinely reaches  $800 \text{ }^\circ\text{C}$  or greater.

The different materials considered in this experience, film-forming materials, reinforcement fibers, resin/fiber composites, and hybrid intumescent coatings, were tested.

## 4. RESULTS AND DISCUSSION

**4.1. Film-Forming Materials.** By analyzing the TGA curve of plasticized chlorinated rubber (detector Shimadzu TGA-50 H,  $10 \text{ }^\circ\text{C}/\text{min}$  in argon atmosphere), it is inferred that it is suitable for continuous service up to  $80 \text{ }^\circ\text{C}$  (there is virtually no mass

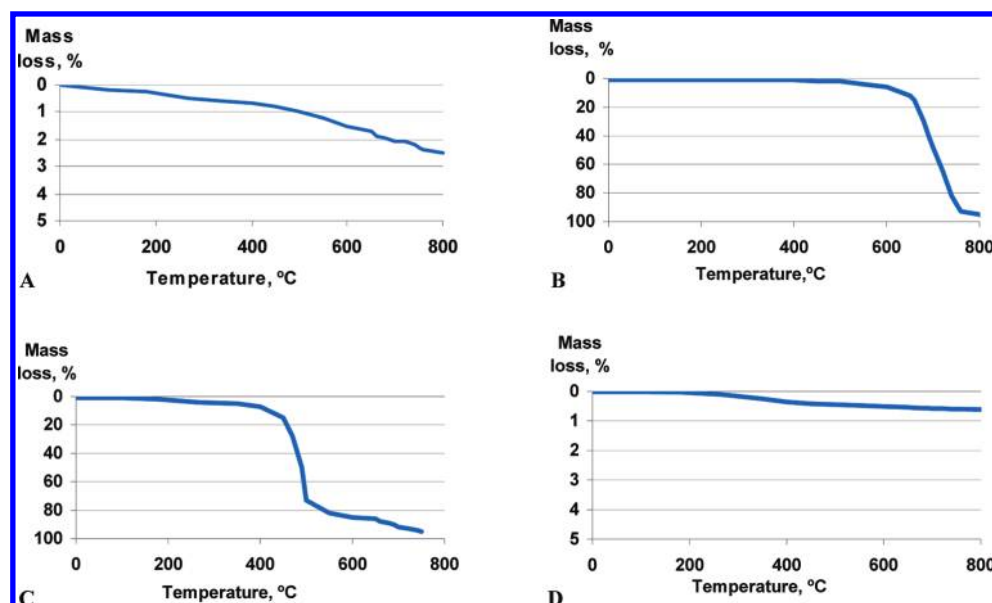


Figure 2. Thermogravimetric analysis (TGA) of reinforcement fibers: alumina (A), carbon (B), aramid (C), and glass (D).

loss); in addition, it decomposes significantly above 130–135 °C, Figure 1A. At higher temperatures, the resin is completely broken and charred without melting at around 200–220 °C (the mass loss at 800 °C reaches approximately 82%). On the other hand, this film-forming material presents a low value of OI (22%) applied on wood panels at approximately  $100 \pm 5 \mu\text{m}$  dry film thickness, which implies that chlorinated rubber-based films showed a reduced flame resistance.

Concerning the modified, resol-type phenolic resin, it was possible to conclude that it showed a better flame-retardant efficiency than the plasticized chlorinated rubber resin probably due to its higher thermal stability. In addition, phenolic resin has as relative advantage a difficult ignition and a high tendency to form char during thermal decomposition. This last feature was determined by interpretation of the TGA curve, Figure 1B. Thus, up to 350 °C, the mass loss was only 12%; from that temperature, the decrease was abrupt up to 600 °C (residual mass was 58%), and finally from 600 to 800 °C the decline was gradual reaching a final value of 53%. In addition, the phenolic resin applied on wood panels at approximately  $100 \pm 5 \mu\text{m}$  dry film thickness presented a relatively higher value of OI (26%), which allows classifying it as self-extinguishing. On the other hand, because the curing reactions involve the generation of water, this may remain trapped in the composite and during the action of the flame be removed as a vapor; the sensible and latent heat consumed by evaporation would diminish the temperature increasing of the system.

Finally, the epoxy-polyamine resin used in this experience is characterized by its low tendency to form char during thermal decomposition, Figure 1C. The TGA curve showed an initial decline gradually up to 150 °C (in this range, the mass loss was approximately 5%). Between 150 and 450 °C, the decomposition of this film-forming material led to a mass decrease of 70%; from 450 °C to about 800 °C, the loss was gradual again, reaching approximately 90% (10% remaining solids). The epoxy resin showed also a low value of OI (22%) applied on wood panels at approximately  $100 \pm 5 \mu\text{m}$  dry film thickness (it indicates that it is flammable when exposed to the atmosphere in the presence of enough activation energy).

It is well-known that for char-forming polymers, flame-retardants acting in the condensed phase are very successful. These flame-retardants enhance the formation of polymer char at the expense of combustible volatiles; in other words, there is a direct relationship between the flammability of a polymer and its char yield.

The analysis of results indicates that the inherent fire-retardant behavior of the phenolic would be due to the char-forming tendency of the cross-linked chemical structure. Because of the large proportion of aromatic structures in the cross-linked cured state, phenolic resins carbonize in a fire and hence extinguish once the source of fire is removed: they may encapsulate themselves in char.

On the other hand, epoxy resins carbonize less than phenolic ones and continue to burn in a fire; in addition, visual observations indicate that structures based on these components produce more smoke than phenolic resins, which could also be attributable to their lower level of aromatic structures.

Finally, due to the above-mentioned structural reasons, plasticized chlorinated rubber displays lower char formation.

Therefore, for use in load-bearing structures, although epoxies do not display very good flame-retardant properties due to their very high mechanical strength, they are the more popular choice. Concerning phenolic resins, despite that they have inherent flame retardant properties, their mechanical properties are inferior to epoxies and consequently are less favorable. For the above-mentioned reason, plasticized chlorinated rubber must be not selected as film-forming material when coating films are exposed at strength mechanical requirements.

**4.2. Reinforcement Fibers.** The alumina fibers have  $3.410 \text{ g cm}^{-3}$  density; in this case, they are composed of 85%  $\text{Al}_2\text{O}_3$  and 15%  $\text{SiO}_2$  by weight. They are heat-resistant because they exhibited reduced mass loss in the TGA trial (detector Shimadzu TGA-50 H,  $10 \text{ }^\circ\text{C}/\text{min}$  in oxidizing atmosphere); this was about only 2.5%, Figure 2A. This feature is correlated with the high temperature that can operate in service (around 1000 °C) without a significant decrease of their properties.

The carbon fibers have  $1.756 \text{ g cm}^{-3}$  density; they display high reactivity in oxidizing atmosphere when they exceed 600–650 °C,

Table 1. Results of Laboratory Tests<sup>a</sup>

coating type		laboratory tests				
fiber	film-forming material	10 <sup>3</sup> CT, W m <sup>-1</sup> K <sup>-1</sup> (*)	AL, mm (*)	OI, % (*)	RIB (*)	char yield, % (**)
without	chlorinated rubber resin	33	154	38	165	50
	phenolic resin	26	98	44	210	56
	epoxy resin	28	154	37	182	51
carbon	chlorinated rubber resin	22	72	49	245	63
	phenolic resin	30	102	46	230	58
	epoxy resin	28	127	44	220	54
glass	chlorinated rubber resin	22	60	>50	250	50
	phenolic resin	29	85	48	240	52
	epoxy resin	27	167	34	155	51
aramid	chlorinated rubber resin	20	83	47	235	61
	phenolic resin	27	88	48	235	57
	epoxy resin	26	138	37	190	53
alumina	chlorinated rubber resin	32	55	>50	250	65
	phenolic resin	33	59	>50	250	60
	epoxy resin	38	94	45	235	56

<sup>a</sup> Tests carried out: (\*) on coated panels; (\*\*) on dry coatings at 800 °C.

registering a significant reduction of mass until 750 °C; then, the loss is more gradual, arriving at 800 °C with a residual weight of only 5% (almost complete combustion), Figure 2B. It is possible to conclude that the above characteristics provide good nonflammable properties in the presence of abundant oxygen but in more limited temperature ranges than the alumina fibers. The OI value is 57%, and the maximum temperature in service is about 400–450 °C.

The aramid fibers have 1.440 g cm<sup>-3</sup> density; they display thermal stability, which extends until around 300–400 °C, Figure 2C; then, an abrupt reduction is registered until the 600–650 °C to finally display a low final residue in the highly oxidizing atmosphere. It is noted that because they are an organic material of high molecular weight, require a high level of oxygen for combustion, and contribute to the char formation. The OI value is 30%, and the maximum temperature in service is about 300–350 °C.

Finally, the glass fibers have 2.491 g. cm<sup>-3</sup> density; they support up to 250 °C without practically losing mass, although they soften slightly from that temperature (maximum temperature in service); then, a slight decrease was only observed up to 800 °C (final residue was 99.4%), Figure 2D.

In summary, some of inorganic fibers selected (alumina and carbon) display elevated thermal stability while the other one was considered (glass) soft or melts at low temperature; in addition, they do not act as insulators (property less favorable). On the other hand, the organic fiber studied (aramid) degrades into smaller products to form a fibrous char (characteristic positive because it could slow the burning).

**4.3. Resin/Reinforcement Fiber Composites.** Composites just based on plasticized chlorinated rubber and fibers were also considered; these composites were formulated with a level of fibers significantly higher than those included in intumescent coatings formulation to study clearly the influence of their incorporation (30% v/v).

The results achieved in the curves of TGA, by using the above-quoted detector Shimadzu, indicate a char yield at 800 °C between 57% and 92% (the highest value corresponded to the

alumina, followed by carbon, aramid, and glass, in that order). It is important to mention that this range of values is superior to those obtained with composites based on phenolic and epoxy resins.

In addition, the OI of the plasticized chlorinated rubber-fiber composites obtained by their application on wood panels (also about 100 ± 5 μm dry film thickness) increased depending on the nature of the reinforcing fiber to 41% as minimum (in some cases exceeded 46%). Those features explain its greater efficiency as film-forming material for intumescent coatings than epoxy-polyamine resin and modified, resol-type phenolic resin.

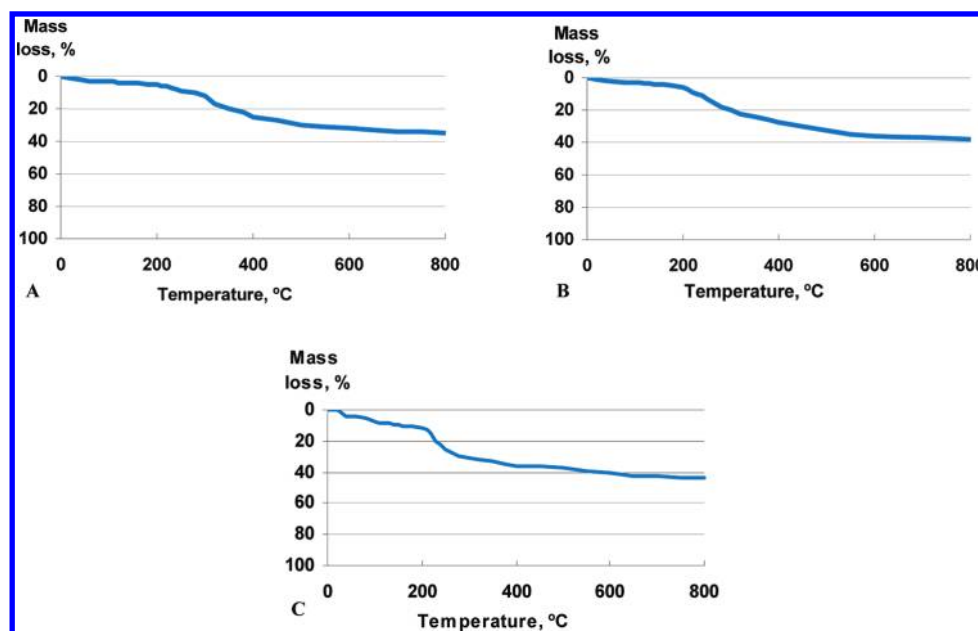
It is also worth mentioning that the composite consisting of phenolic resin and the different fibers was also studied at 30% v/v. The results achieved by the curves of TGA obtained in the quoted detector Shimadzu indicated a char yield at 800 °C, which ranged between 45% and 89% depending on the type of fiber (in the order cited in the case of chlorinated rubber resin).

In addition, the OI of the composite applied on wood panels, also about 100 ± 5 μm dry film thickness, increased from 41% to 46% depending on the fiber under consideration (behavior self-extinguishing in all cases). The above properties explain the excellent performance during the testing of intumescent coatings made with modified, resol-type phenolic resin.

Furthermore, the composite consisting of epoxy-polyamine resin and different fibers at level of 30% v/v was also studied. The results achieved by the curves of TGA obtained in the mentioned detector Shimadzu indicated a char at 800 °C that varied for different fibers between 26% and 71% (values significantly lower than for the other resins considered and with the same efficiency sequence as in the two previous cases).

In addition, the OI of this composite applied on wood panels, also about 100 ± 5 μm dry film thickness, oscillated between 34% and 41% for different fibers studied, the lowest range of all studied composites. The above-mentioned characteristics would justify the lower performance of intumescent coatings based on epoxy-polyamine resin.

In summary, results obtained in laboratory tests display that the best performance was reached by composites based on



**Figure 3.** Thermogravimetric analysis (TGA) of intumescent coatings based on alumina as reinforcement fiber: plasticized chlorinated rubber resin (A), modified resol-type phenolic resin (B), and epoxy-polyamine resin (C).

plasticized chlorinated rubber resin, modified resol-type phenolic resin, and epoxy-polyamine resin, in that order.

The analysis of results obtained with composites displays a synergistic effect.<sup>19,20</sup> It was manifested by a “synergism” in char production (there was a strong increase in char, beyond the char amounts predicted on the basis of the additive effect of their components) as well as in a significant raise in OI values (in a general way, composites practically duplicated the mentioned values in relation with those of the three film-forming materials without reinforcing fibers).

The mentioned synergistic effect could be based on the nature of the interface in the composite, which would affect its combustibility. In the case of plasticized chlorinated rubber, the interface formed with fibers would be very strong, which means that the heat could not penetrate further, not reach the underlying resin causing its degradation, and, in addition, any product formed could not move to the burning zone. On the other hand, in epoxy-polyamine resin, the interface formed with fibers would be weak, so the composite could divide in two well differentiated phases (polymer and fiber), and, consequently, it could burn in additive form as each one in an individual way does. Concerning the modified, resol-type phenolic resin, the interaction in the interface would have an intermediate value between those corresponding to plasticized chlorinated rubber and epoxy-polyamine resin.

**4.4. Hybrid Intumescent Coatings.** *4.4.1. Laboratory Tests.* The results obtained in the different assays are included in Table 1. It is important to mention that the nonuniformity of test panels (both in the wood and in the coating), variations in the fuel supply and rate, and operator are the chief sources of error in operation of the thermal conductivity test CT, flame tunnel, cabin OI, and UL 94 horizontal–vertical chamber. Concerning the precision of experimental tests, in standard deviation terms, it was  $1 \times 10^{-3}$ , 2, 1, and 4, respectively.

Results indicate that flame-retardant, hybrid intumescent coatings applied on wood panels showed an excellent performance in thermal conductivity test CT, in two-foot tunnel

(flame advance, AL), in cabin OI (oxygen index), and in UL 94 horizontal–vertical chamber (resistance to intermittent flame of a bunsen burner, RIB). The whole of them displayed a significantly better performance than untreated wood panels (CT,  $0.123 \text{ W m}^{-1} \text{ K}^{-1}$ ; AL, 555 mm; OI, 16%; and RIB, 15).

Particularly noteworthy is that the thermal conductivity CT of the wood used as substrate was significantly reduced in all cases due to the intumesced insulating layer. This feature achieves significance as it allows one to control the heat transference in buildings and industrial facilities through doors, walls, etc.; so, it is possible to prevent the formation of the fire triangle through the contribution of the activation energy generated in a conflagration in an area adjacent or contiguous. Results show that the influence of each fiber on the conductivity CT was markedly different in coatings formulated with several film-forming materials. This indicates that if this property is only considered, the selection of fiber for each formulation is very specific. The results display that, in general, coatings with inorganic fibers did not act efficiently as insulators because they would not have reflected the radiant heat back toward the heat source; therefore, they could not control adequately the increase of the temperature on the reverse side of wood panels. Thus, hybrid coatings with alumina as reinforcing fiber showed the highest average CT value ( $0.034 \text{ W m}^{-1} \text{ K}^{-1}$ ), while those with aramid in their composition showed the lowest one ( $0.024 \text{ W m}^{-1} \text{ K}^{-1}$ ). On the other hand, the influence of film-forming material on CT values was less significant (from  $0.026$  to  $0.029 \text{ W m}^{-1} \text{ K}^{-1}$ ).

Continuing with the analysis of the results obtained with coatings applied on wood (Table 1), although trials in two-foot tunnel, in cabin OI, and UL 94 horizontal–vertical chamber evaluate different properties, it is possible to conclude that the best average performance was reached with alumina, carbon, aramid, and glass as reinforcement fiber and with plasticized chlorinated rubber, modified resol-type phenolic resin, and finally epoxy-polyamine resin as film-forming material, in all cases in the mentioned order.

Table 2. Statistical Results<sup>a</sup>

hybrid coatings		average
reinforcement fiber	alumina	8.8
	carbon	8.5
	aramid	8.3
	glass	8.1
	without	7.4
film-forming material	chlorinated rubber resin	8.6
	phenolic resin	8.5
	epoxy resin	7.5
coatings without fibers		average
film-forming material	phenolic resin	8.2
	epoxy resin	7.2
	chlorinated rubber resin	7.0

<sup>a</sup>The test values were averaged to obtain an overall result of intumescent coating performance against fire action.

Concerning TGA analysis carried out on solids of the hybrid intumescent coatings (Table 1), results show values of char yield at 800 °C, which range between 50% and 65%. Average values allow corroborating the sequence of the efficiency reached in determinations of CT, AL, OI, and RIB for both the reinforcing fibers and the film-forming materials. Figure 3 displays the thermogravimetric analysis (TGA) of intumescent coatings based on alumina as reinforcement fiber.

To analyze the global performance of hybrid intumescent coatings simultaneously in all laboratory tests, numerical values were set. Thus, 0 and 10 were assigned respectively to 0.123 and 0.020 W m<sup>-1</sup> K<sup>-1</sup> in the thermal conductivity test, 555 and 0 mm for net flame advance in two-foot tunnel (on a bare cement-asbestos panel selected as reference, the distance due to the reflection of the flame was 55 mm), 16% and ≥50% for oxygen index in the OI cabin, 15 and 250 for RIB in the UL 94 chamber, and finally 0% and 100% for residual weight in TGA analysis at 800 °C. In all cases, intermediate values were considered.

Finally, average values were calculated for each of the tests. In a final stage of the statistical interpretation, the values of all trials were averaged to obtain, as mentioned, an overall result of coating performance; these results are included in Table 2.

To support the results of Table 2, the analysis for each variable studied and their possible interaction between film-forming material/fiber was carried out in a separated way.

**4.4.2. Film-Forming Materials.** The statistical results indicate that intumescent coatings without reinforcing fibers showed a decreasing performance with phenolic resin (average value 8.2), epoxy resin (7.2), and chlorinated rubber resin (7.0); the whole of them displayed a significantly worse performance than the corresponding hybrid products. The last ones, formulated with the plasticized chlorinated rubber and modified, resol-type phenolic resin, exhibited higher performance (similar average values of 8.6 and 8.5, respectively) than those based on epoxy resin (average value of 7.5). The synergistic effect demonstrated in film-forming material/reinforcing fiber composites was corroborated in the corresponding hybrid intumescent coatings.

**4.4.3. Reinforcing Fibers.** All hybrid systems showed better performance than the reference ones (without reinforcement fibers; average value of 7.4). In general, decreasing performance was shown by the intumescent coatings with alumina (8.8), carbon

(8.5), aramid (8.3), and finally glass (8.1) as reinforcing fibers in their composition, in that order.

## 5. GENERAL CONCLUSIONS

The suitable adhesion between the two phases (reinforcement fibers and film-forming material) is essential to optimize the behavior of the composite: the interface is an important region and requires that a stable link be generated, whether physical or chemical. A strong interface would display a favorable synergistic effect as seen in the present investigation, while if the fiber-matrix interface is weak the flammability of the composite could be increased.

This synergistic effect would be based on widely different modes of action, particularly embracing the principles of the condensed phase mechanism and intumescence. The degree of interaction of components in a composite is physicochemical in nature, and therefore it would be considered as a kinetic process controlled by both the temperature and the time. We are carrying out some studies by pyrolysis–gas chromatography to elucidate the mechanism and the variables controlling the synergistic effect in film-forming material/reinforcing fiber composites.

According to the above-mentioned, it is possible to conclude that the choice of resin and of reinforcing fibers is of extreme importance: the results indicate the meaning of knowing in advance the characteristics of the individual components in study to estimate the performance against fire action of composite, without excluding potential synergistic and antagonistic effects.

Microscopic observations of the studied hybrid systems allowed reaching the following complementary conclusions: (i) when the composite is heated, the resin of the first layer is degraded and ignites to form combustible products; (ii) then the heat penetrates into the layer of adjacent fibers: their thermal stability and the characteristics of interface define the kinetic of heat penetration in the deepest layers and consequently the flammability of the composite.

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## ACKNOWLEDGMENT

We thank CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas), UTN (Universidad Tecnológica Nacional), and CIC (Comisión de Investigaciones Científicas de la Provincia de Buenos Aires) from Argentina for their sponsorship of this research.

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