

特约专栏

Applications of Intumescence for Reaction and Resistance to Fire of Materials

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Abstract: This paper will focus on how to use the intumescence phenomenon to make flame retarded polymeric materials (reaction to fire) and fire barrier on substrates (resistance to fire). The first part will define the intumescence and the second part will provide the reader a complete overview of the fundamentals of intumescence in terms of chemistry, dynamics and numerical modeling. The last part is devoted to the applications of intumescence through relevant examples.

Key words: flame retardant; intumescence; dynamics; numerical modeling

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膨胀作用在材料阻燃中的应用

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摘要: 文章第一部分定义了“膨胀”的概念和讲述了“膨胀”在聚合物阻燃方面的应用历史。第二部分从化学、动力学以及数值模拟的角度来阐述材料燃烧过程中形成“膨胀”的基本原理。最后一部分通过一些实例来体现“膨胀”在材料阻燃中的实际应用。利用膨胀现象来对聚合物材料阻燃以及基材防火是一种非常有效的方法;而基材表面形成膨胀炭层能够起到抑制火蔓延、隔绝热质传递从而保护基材的作用;因此,发展协效剂(特别是一些纳米颗粒)对膨胀阻燃体系的协效作用是今后阻燃的重要方向。文章旨在通过对“膨胀”形成机理的阐述并列出一些“膨胀”阻燃的实例,希望能够对利用膨胀阻燃来制备阻燃聚合物以及制备阻燃隔层来保护基材的阻燃科研者有所帮助。

关键词: 阻燃; 膨胀; 动力学; 数字模拟

1 Introduction

Fire is undoubtedly an emotive subject, especially when it comes to scenarios that we can imagine in a “closed system” (e. g. ship, aircraft or skyscrapers) where the possibilities to escape are restricted. The high fire hazards posed by polymeric materials both in historical times and to the present days are a consequence of their organic composition. Indeed the development of science and technology provides the availability of sophisticated products but concurrently, increases the use of combustible materials. Polymeric materials are commonly used in everyday day life increasing fire hazards and so, flame retardants are very often incorporated into them to limit their flammability. In this case, the contribution of the material to fire growth must be limited and it is defined as the “reaction to fire” of the material. The other aspect is the “resistance to fire” which is defined as the ability of ma-

terials to resist the passage of fire and/or gaseous products of combustion. The material is then designed to make a fire protection on substrate (e. g. construction materials such as steel and wood) and it acts as thermal barrier limiting heat transfer from the heat source to the substrate. One must also “block” fire and this latter must remain confined in a limited space. It can be achieved by intumescent materials which form an expanded multicellular material of low heat conductivity^[1-3].

This paper will focus on how to use the intumescence phenomenon to make flame retarded polymeric materials (reaction to fire) and fire barrier on substrates (resistance to fire). The first part will define the intumescence and the second part will provide the reader a complete overview of the fundamentals of intumescence in terms of chemistry, dynamics and numerical modeling. The last part is devoted to the applications of intumescence through relevant examples.

2 Intumescence: definition and history

The word “intumescence” comes from Latin “intumescere” which means “to swell up”. In French, the term “intumescence” (intumescence, an action denoting an object

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which swells (Litré, Dictionary of French Language)) has remained a literary expression for a long time. The verb, to intumesce, was used by the Elizabethan actor John Webster (1580 – 1624) with two meanings: “to grow or increase volume with heat” or “to present an upwards swelling by boiling”. Webster’s definition allows a totally exact description of the performance of a coating or an intumescent/swelling material which, heated beyond critical temperature, start to melt while boiling, then while swelling. The result of this process is the formation of a multicellular (alveolar) barrier, thick and non-flammable, which likely to protect the substrate or residual material from heat or flame action.

Intumescence was first reported by L. J. Gay-Lussac in 1821 in the case of the flame retardancy of textiles^[4]. The word “intumescence” was not mentioned but we can suspect an intumescent phenomenon since woven fabrics in hemp and flax were coated by a mixture of borate and ammonium phosphate (here there are the three ingredients of intumescence: the acid source, namely borate and phosphate, the char former, namely flax or hemp, and the blowing agent, namely the evolving ammonia from the phosphate). In 1934, a German patent (extended to the USA in 1938) claimed the flame retardancy of wood using a mixture of diammonium phosphate and formaldehyde^[5]. It reported the formation of a swollen char layer upon heating protecting wood but the word “intumescence” was not used in the text. The first comprehensive paper (it was applied on intumescent coating) was published in the early 70s by H. Vandersall and it gives the basics of intumescence^[6]. It was stated that the ingredients of intumescence were mainly composed of an inorganic acid or a material yielding acidic species upon heating (e. g. phosphate), of a char former (e. g. pentaerythritol) and of a component that decomposes at the right temperature and at the right time to enable the blowing of the system (e. g. melamine)^[2]. In the Vandersall’s paper, only coatings were considered and it was only in the 80s that G. Camino applied with success this concept to bulk polymers (mainly thermoplastics)^[7]. This basic work was useful for the development of products which were launched by different companies in the 90s.

3 Fundamentals of intumescence

The intumescence process results from a combination of charring and foaming at the surface of the substrate^[8–10]. So, the charred layer acts as a physical barrier which slows down heat and mass transfer between gas and condensed phase. The formation of an intumescent char is a complicated process involving several critical aspects: rheology (expansion phase, viscoelasticity of char), chemistry (charring) and thermophysics (limitation of heat and mass transfer).

3.1 Chemistry of intumescence and formulation

The usual chemistry of intumescence involves composition containing an inorganic acid or a material yielding acidic species at temperature between 100 °C and 250 °C, of a char former and of a component that decomposes to enable the blowing of the system. Typical examples of components used in intumescent systems are reported in Table 1.

Table 1 Examples of components of intumescent systems

(a) Inorganic acid source	(b) Polyhydric compounds
Phosphoric	Starch
Sulfuric	Dextrins
Boric	Sorbitol, mannitol
<i>Ammonium salts</i>	Pentaerythritol, monomer, dimer, trimer
Phosphates, polyphosphates	Phenol-formaldehyde resins
Borates, polyborates	Methylol melamine
Sulfates	Char former polymers (PA-6, PA-6/clay nanocomposite, PU, PC, ...)
Phosphates of amine or amide	(c) Blowing agents
Products of reaction of urea or Guanidyl urea with phosphoric acids	Urea
Melamine phosphate	Urea-formaldehyde resins
Product of reaction of ammonia with P ₂ O ₅	Dicyandiamide
<i>Organophosphorus compounds</i>	Melamine
Tricresyl phosphate	
Alkyl phosphates	
Haloalkyl phosphates	

The following sequences of events have been proposed to describe the development of the intumescent phenomenon:

- the inorganic acid is released between 150 and 215 °C depending on its source and other components;
- the acid esterifies the carbon rich components at temperatures slightly above the acid release temperature;
- the mixture of materials melt prior or during esterification;
- the ester decomposes via dehydration resulting in the formation of a carbon-inorganic residue;
- released gases from the above reactions and degradation products cause the carbonizing material to foam;
- as the reaction nears completion, gelation and finally solidification occurs. This solid is in the form of multicellular foam (Figure 1).

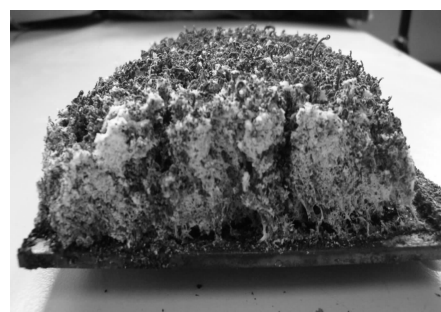


Fig. 1 Intumescent protective coating formed after fire testing

A typical example is the case of polypropylene (PP)-ammonium polyphosphate (APP)/pentaerythritol (PER) system^[11–12]. The reaction of the acidic species (APP and its degradation products into orthophosphates and phosphoric acid) with the char former agent (PER) takes place in a first stage ($T < 280$ °C) with formation of esters mixtures. The carbonisation process takes then place at about 280 °C (via the formation of double bonds followed by Diels Alder reaction and a free radical process increasing the size of the polyaromatic structure^[13]). In a second step, the blowing agent

decomposes to yield gaseous products (i. e., evolved ammonia from the decomposition of APP) which cause the char to swell ($280\text{ }^{\circ}\text{C} < T < 350\text{ }^{\circ}\text{C}$). The intumescent material decomposes then at higher temperatures and loses its foamed character at about $430\text{ }^{\circ}\text{C}$. Concurrently, the heat conductivity of the char decreases between $280\text{ }^{\circ}\text{C}$ and $430\text{ }^{\circ}\text{C}$ and the insulation of the substrate is enhanced^[14].

Incorporation of additional filler in an intumescent formulation can involve some unexpected “catalytic” effects. Performance is enhanced dramatically adding small amount of an additional compound which acts as a synergist^[15–17]. In the following, we will use the definition of synergy as “a synergistic effect occurs when the combined effects of two chemicals are much greater than the sum of the effects of each agent give alone”. Numerous synergists (micro- and nanofillers) have been used in conventional “three-based ingredients” intumescent formulations. It covers the boron compounds (zinc borates, B_2O_3 , borophosphate, borosiloxane)^[18–19], phosphorus compounds (phosphazene, ZrPO_4), silicon compounds (silica, silicone, silicalite)^[15, 20], aluminosilicate (mordenite, zeolite, montmorillonite)^[15, 21], rare earth oxides (La_2O_3 , Nd_2O_3)^[22], metal oxides (MnO_2 , ZnO , Ni_2O_3 , Bi_2O_3 , TiO_2 , ZrO_2 , Fe_2O_3)^[23–24] and others (carbon nanotubes, silsesquioxanes, layered double hydroxides, Cu, Pt, talc, sepiolite, zinc and nickel salts)^[25–27]. The presence of this additional filler can modify the chemical (reactivity of the filler versus the ingredients of the intumescent system)^[28] and physical (expansion, char strength and thermophysical properties)^[29] behavior of the intumescent char when undergoing flame or heat flux leading to enhanced performance. The probable mechanism involves the chemical reaction between the fillers and the acid source (mainly phosphate derivatives) yields to phospho-X compounds (e. g. phosphosilicate, zinc phosphate, borophosphate etc.) reinforcing the structure and/or the action of the fillers (or its reaction products) as nucleating agent. It permits the formation of a homogeneous foamed structure with appropriate thermophysical properties (lower heat conductivity, lower emissivity at the surface etc.).

3.2 Physics and dynamics of intumescence

The formation of an effective intumescent char occurs via a semi-liquid phase, which coincides with gas formation and expansion of the surface. Gases released from the degradation of the intumescent material, and in particular of the blowing agent, have to be trapped and to diffuse slowly in the highly viscous melt degraded material in order to create a layer with the appropriate morphological properties. The viscosity of the degraded matrix in the blowing phase is, as a consequence, a critical factor. Another significant aspect of intumescent formulations is the mechanical strength of the intumescent char. In the conditions of a fire, char destruction can proceed not only by means of ablation and heterogeneous surface burning but also by means of an external influence such as wind, mechanical action of the fire or convective air flows. The mechanical stability of the intumescent char depends both on the structure and porosity of the foamed intumescent material. If the structure of the char (morphology, distribution of voids inside the char) is appropriate, the thermal conductivity of intumescent chars can be very low and it limits ef-

ficiently heat transfer from the heat source to the substrate.

Rheological measurements using a rheometer in a parallel plate configuration have been done to measure viscosity and expansion of an epoxy-based intumescent coating as a function of temperature^[30]. It is clearly shown that expansion occurs when the viscosity is the lowest and when the temperature of charring is reached (about $250\text{ }^{\circ}\text{C}$) (Figure 2a). It is noteworthy that the viscosity must be high enough to accommodate internal stresses due to the internal pressure coming from the degradation gases (for comparison the viscosity at $250\text{ }^{\circ}\text{C}$ of the virgin epoxy is twice lower than that of the intumescent coating). Expansion is also measured in the rheometer (convective heating in a furnace) and it gives useful indications on which temperatures intumescence takes place. Another method can be used to follow the expansion “in situ” during cone calorimetry experiment (the heat source is a radiative heat flux). It is done using an infrared camera combined with image analysis and it provides the expansion as a function of time (Figure 2b). Those protocols have been applied to numerous intumescent coatings and the same trends were observed for each system evidencing the general behavior of intumescent material^[31–32].

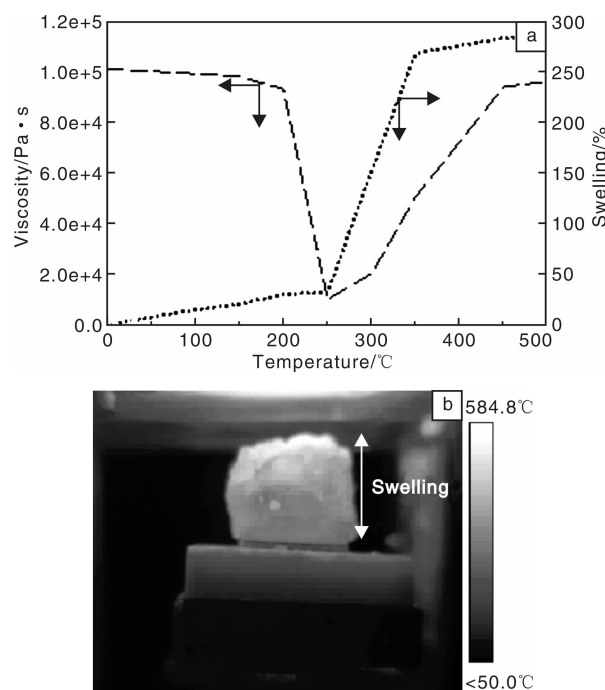


Fig. 2 (a) viscosity and swelling as a function of temperature of an epoxy-based intumescent coating and (b) formation of an intumescent char during cone calorimetry at the full expansion

The morphology of an intumescent coating is governed by the chemistry and the rheology of the system. It is crucial because it controls the thermal parameters of the insulative layer. It is necessary to form a charred foam exhibiting evenly dispersed small voids in its structure because it provides good mechanical properties (in particular char strength) and low heat conductivity. It is not easy to characterize such a structure but a powerful approach is to use 3D X-ray tomography to get the view of the internal structure of the char without destruction of it (e. g. microscopy requires piece or slice of char to be examined). Figure 3 shows an example of an intu-

mescent char analyzed by 3D X-ray tomography and it reveals in this particular case, the internal structure is not homogeneous with small and large voids.

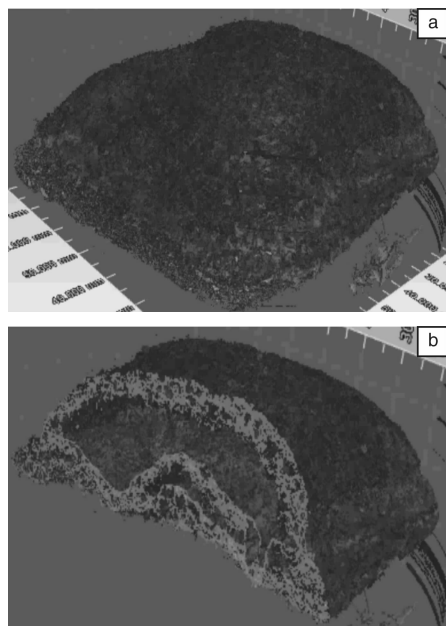


Fig. 3 Imaging of (a) complete and (b) slice of an intumescent char made by 3D X-ray tomography

Heat conductivity (k) is one of the most influencing parameter determining the efficiency of an intumescent barrier. As shown in the previous section and in a general way^[2], intumescent coating reacts around 250 °C forming char and starting to swell. At higher temperatures (up to 350 °C), the porosity of the intumescent char increases, and its volume increases. Finally between 400 and 600 °C, intumescent char degrades slowly and its expansion remains constant. Experimental results of k were determined with the hot disk method^[33] up to 800 °C for an epoxy-based intumescent material. At low temperature ($T < 200$ °C), k increases but when the material starts to react and to form a char k decreases dramatically (k drops from 0.45 to 0.1 W/m·K). It is attributed to the formation of an expanded foamed char. At higher temperatures ($T > 375$ °C), k increases considerably up to 500 °C due to the shrinkage and the partial destruction of the char. At $T > 500$ °C, k increases smoothly. From this experiment, it is then evidenced that intumescent coating exhibits low heat conductivity limiting heat transfer. This conclusion can be extended to other intumescent systems^[34].

3.3 Numerical simulation of intumescence

An intumescent material swells upon heating and it forms a porous low-density char, thereby reducing the heat transfer to the underlying virgin material^[35–37]. A mathematical formulation (in 2D) of this problem can be written considering that the intumescent coating (1 mm thick; $s(0)$) is applied onto a steel plate having a thickness of $e = 3$ mm and that the assembly undergoes a given radiative heat flux. It means we have a bi-layered setup: (i) the first layer is the underlying substrate (steel), whose boundaries remain constant throughout the process ($y \in]0, e[$) and (ii) the second layer is the original intumescent coating, and is then the

growing part, i. e., the upper boundary moves upwards while the lower boundary is the fixed interface steel/char ($y \in]e, s(t)[$). $s(t)$ describes the swelling of the intumescent coating in the y -direction and is time dependent. It is a typical problem of heat transfer including moving boundaries. The approach of this problem is to take into account the dynamics of the problem using the arbitrary Lagrangian-Eulerian (ALE) method coupled with heat transfer in the two layers described above^[38]. The relevant equations are the heat diffusion with a heat source, Q , to model the degradation of the intumescent layer (Equation 1) and without Q for the steel layer (Equation 2):

$$y \in]e, s(t)[, \rho c_p \frac{\partial T}{\partial t} = \nabla \cdot (\kappa \nabla T) \quad (1)$$

$$y \in]0, e[, \rho_{steel} c_{p,steel} \frac{\partial T}{\partial t} = \nabla \cdot (\kappa_{steel}) \quad (2)$$

where c_p is the heat capacity, ρ is the density, k is the thermal conductivity, T is the temperature and t is the time. Note that the subscript *steel* indicates the values are related to steel otherwise it is related to the intumescent coating. During the intumescence and the degradation of the material, it involves heterogeneous reactions (solid/gas) involving the destruction of the condensed phase with the evolution of gases and the formation of char. It corresponds to the source term, Q , which can be expressed as (Equation 3):

$$Q = \rho \cdot A \cdot \exp\left(-\frac{E}{RT}\right) \quad (3)$$

where A is the preexponential factor, E is the activation energy, R is the universal gas constant and L is the heat of decomposition.

The effective heat flux received by the material is (Equation 4):

$$q_{eff} = \alpha q_{rad} + h(T_{inf} - T) + \varepsilon \sigma (T_{amb}^4 - T^4) \quad (4)$$

where q_{eff} is the effective heat flux, q_{rad} is the heat flux, α is the absorptivity assuming to be 1, h is the convective coefficient (10 W/m²·K for a plate in an air flux), T_{inf} is the temperature of surrounding air (300 K), T_{amb} is the temperature of the surrounding (300 K), ε is the emissivity (0.9) and σ is the Stephan-Boltzmann constant.

The governing equations and the associated boundaries" conditions can be solved in 2D taking into account the dynamics of the problem using ALE method coupled with heat transfer using a finite element solver (e. g. Comsol Multiphysics). The expansion of the intumescent coating is expressed in the ALE frame and it is well captured by the model (Figure 4).

4 Applications of intumescence

4.1 Reaction to fire

Polymer nanocomposite exhibits low flammability in terms of cone calorimetry but it fails to other tests, in particular those with samples in vertical position (e. g. limiting oxygen index LOI, ASTM D2863; UL-94). The mechanism of protection involves the formation of char layer covering the entire sample surface acting as insulative barrier and reducing volatiles escaping to the flame. The formation of such a layer not forming cracks, when burning, is critical to obtain low

heat release rate (HRR) from nanocomposites^[39]. It is the reason why, nanoparticles have been combined with conventional flame retardants (in particular with intumescent ingredients) in order to create synergistic effect^[39–41].

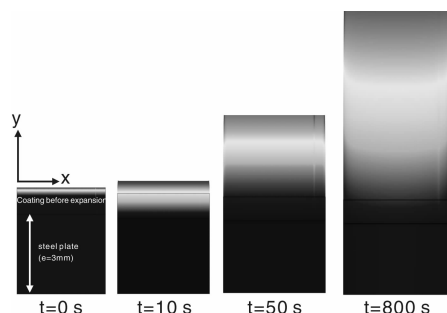


Fig. 4 Simulated heat gradient in an expanding intumescent coating as a function of time

The combination of APP with melamine (MEL) in an appropriate ratio (5 to 1 respectively) provides an efficient intumescent formulation for polylactide (PLA) at a loading as low as 10 % (mass fraction)^[42]. The incorporation of an additional nanofiller such as organomodified montmorillonite (C30B) or multiwall carbon nanotubes (MWNT) shows large effects on reaction to fire of the materials. A large synergistic effect is observed using C30B (Figure 5a) while it is antagonistic using MWNT (Figure 5b). It can be observed that the intumescent PLA combined with C30B does not burn and the small PHRR is only due at a very short ignition of the material. At 30 % (mass fraction) extremely high LOI values were measured (up to 52 %, volume fraction) and V-0 rating (3.2 mm) was achieved. This jump of performance was partially explained by the increase of the thermal stability of the formulation with C30B compared to that without. The explanation is that C30B could react with APP to form aluminosilicophosphate stabilizing the intumescent structure at high temperature. On the contrary, the incorporation of MWNT leads to an antagonistic effect. It is explained by the accumulation of MWNT in the intumescent char which increases a lot the apparent heat conductivity and hence, it does not permit the intumescent coating to play its role of heat barrier.

The intumescent PLA was also evaluated with a total loading of 10 % (mass fraction). This loading is still sufficient to get relatively high LOI (33 %, volume fraction) and a synergistic effect is observed with C30B (35 %, volume fraction) while LOI falls down when MWNT is incorporated in the formulation (24 %, volume fraction). It is noteworthy that V-0 at UL-94 is achieved for the formulations with and without C30B. As a conclusion, this kind of intumescent formulation offers an interesting way for designing flame retarded PLA.

4.2 Resistance to fire

The resistance to fire of intumescent coatings protecting a substrate (e.g. steel, composite or wood) is typically measured by a curve “temperature as a function of time” and the determination of a “time to failure” (time to reach a given temperature, temperature depending on the specifications)^[43]. The ultimate goal is to keep the integrity and the

functionality of the substrate as long as possible.

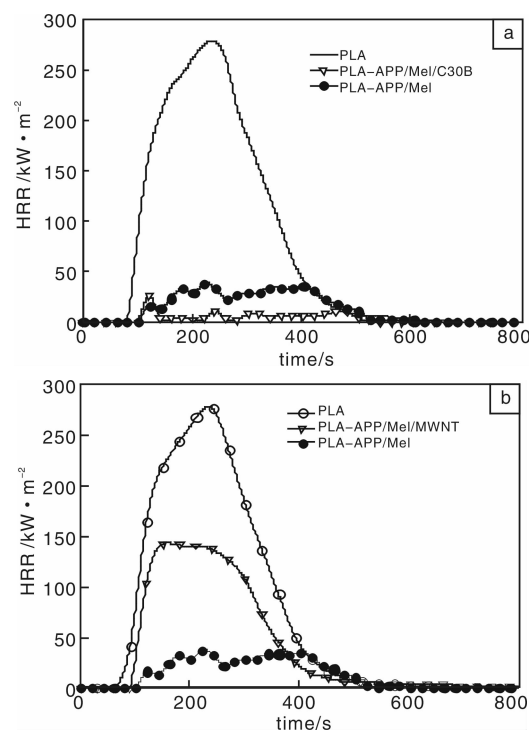


Fig. 5 Heat Release Rate (RHR) curves as a function of time of PLA/APP/Mel/Nanoparticles (C30B (a) or MWNT (b)) loaded at 30 % (mass fraction) compared to virgin PLA

Building codes and regulations require lower flame spread and low smoke generation for many materials. The Steiner Tunnel (ASTM E-84) is frequently referenced as a method to assess flame spread and smoke density and is a mandated test for many commercial building materials. The test consists of a 25' vented tunnel, lined with firebrick, with the test material mounted to the top of the chamber. At one end of the chamber, the sample is subjected to a high-energy flame for ten minutes. Flame spread is determined visually through windows built into the tunnel. An optical cell mounted at the tunnel exhaust measures smoke density. This test is very expensive and time consuming. It is the reason why we have developed a reliable, repeatable and fast small scale test permitting the fast screening of intumescent coatings. We have developed a mini Steiner tunnel for evaluating intumescent formulations. Temperatures as a function of time are measured during the test using 6 thermocouples (hereafter called T_x) at the interface coating/material, small windows permit also to follow flame spread and smoke is collected in the chimney to measure its opacity with a smoke density analyzer including a halogen light. Using the mini Steiner tunnel, we have investigated the potential benefit of using intumescent coatings for improving the resistance to fire of polyethylene terephthalate (PET) foam-based composite. The goal is to show if better performance in terms of fire retardancy and smoke emission can be obtained using an appropriate commercial intumescent coating for protecting the composite against fire. The composite to be tested is a polyethylene terephthalate (PET) foam block (ARMAform, Armacell Benelux SA) covered with glass woven fabrics (Gurit) impreg-

nated by an epoxy resin (Ampreg 21FR, Gurit). Different commercial intumescent coatings have been selected, including epoxy-based (Chartek 8 of International Paint, Firetex M93 of Leigh's paint and XE 2458/1 of Axson), polyester-based (Polycor 2330 BR, Cray Valley) and latex-based (Avicoat FS/DS of Arabian vermiculite, Firefree 88 of Fire-free coatings, Intuflamof Lurie and Pyroplast ST200 of Rutgers Organics) resins. A mass of 1 kg of wet paint per square meter has been applied.

The temperature/time curves (curves not shown) are very promising and allow us to discriminate the different coatings. Avicoat, Pyroplast ST200 and Intuflam give the best barrier properties. Visual observation of the residues indicates that not all the coatings have developed an intumescent structure. Avicoat and Intuflam do not swell but they provide the best performance forming a non-expanded char at the surface. In our conditions, thermal constraint is not high enough to make the material to expand. At the end of the test, we can observe that the PET foam is intact when protected with Avicoat which indicates that the efficiency of this coating is really high. Regarding the good results obtained with Avicoat in terms of fire barrier properties, a specimen coated with this reference has been tested under large scale ASTM E84 conditions. The Avicoat coating was about 700 μm thick and it exhibited good adhesion to the composite when carrying the ASTM D3359B test. The description of the specimen indicates that a charred aspect is observed on 85 % of the total length (Figure 6a). Then, a discoloration occurs. The picture of a section of the specimen however clearly shows that no intumescent phenomenon appeared during the test. The observation of the sample tested on the small scale tunnel also shows a charred aspect without intumescent phenomena; the coating is just distorted and cracked (Figure 6b). These results suggest that, on the one hand, the standard conditions are reproduced; the results of the small scale test can be extrapolated for the evaluation of the thermal barrier effect (time-temperature curves). On the other hand, the thermal constraints seem to influence the behavior of the coating as follows: the convective constraint (flame) and the conditions of the tunnel test lead to no intumescence, only to the formation of a crust.

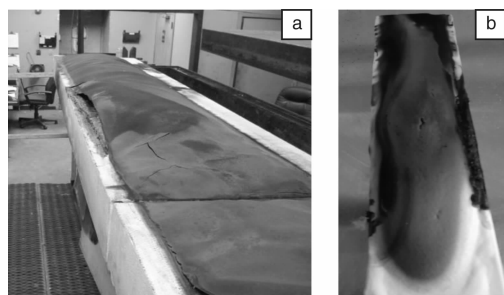


Fig. 6 (a) Avicoat coating protecting PET foam after the large scale Steiner tunnel and (b) after the mini Steiner tunnel test

5 Conclusion

This paper has shown that intumescence is a highly effi-

cient method for flame retarding polymers and for protecting substrates against fire. The use of synergist and in particular nanoparticles leads to synergistic effects with intumescent systems. Very promising developments in the synergy aspects are then expected and efforts should be made in this way. Intumescence also forms a fire barrier limiting heat and mass transfer which can protect substrates (steel, wood, composite ...) for long times; it can limit fire spread and it can prevent the collapse of structure. The use of intumescence is therefore a considerable advantage for the safety of people and of goods in case of fire.

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