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Structure-Properties relationships of moisturized sandwich composite materials under extreme temperature conditions (fire resistance)

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ABSTRACT

Thermo-mechanical properties of sandwich composite materials used in marine applications have been analyzed as a function of the burning duration with various moisture contents. Dry and wet coupons with glass reinforced polymer skins and balsa wood core (saturated with water) were submitted to fire. The mass loss kinetics and the post-combustion mechanical stiffness and strength were recorded. Facilities used are cone calorimeter following ISO 5660 standard, thermogravimetric analyzer (TGA) and 3-point bending mechanical test device. In addition, numerical simulations were adapted to predict the time and through-thickness dependences to the temperature and to the combustion advancing front $d_c(t)$. The importance of correlating experimental and simulated results was highlighted in order to accurately describe the structure-properties relationships induced during the decomposition of sandwich composite materials under extreme temperature conditions (fire resistance).

Keywords: Fire resistance, sandwich composite, durability, mechanical properties, moisture content, structure-properties relationships.

1. Introduction

For a long time, studying materials in extreme or exotic conditions have been play a key role in the understanding of the structure – properties relationships to predict and to improve materials behaviors. Analyses under extreme conditions make it possible to put a material in non-ambient conditions. The properties of that material are often drastically modified and new properties can then be studied. This

occurs when the material is subject to a severe low or high temperature environment, generally coupled to a second stress such as a light irradiation, a mechanical stress, a magnetic field or a high pressure [1-8]. Under such extreme conditions, the material undergoes important physical and/or chemical modifications, often leading to the appearance of metastable states or phase transitions [9-10]. It is then very interesting to understand the behavior of materials under extreme conditions in order to predict and to optimize their properties under standard pressure and temperature conditions, and thus allow their use for new applications. Measurements in extreme conditions are both a scientific challenge, to understand materials properties, and a technical challenge to study the material in specific and very severe environments. The field of composite materials with organic matrix does not escape this trend [11-13; 19-20].

The use of organic matrix composite materials has been continuously growing since the 1960s. This type of material nowadays has an impressive variety of applications in the aeronautics, aerospace, naval, ground transportation, civil infrastructures or various consumer products. The biggest disadvantage to the use of composite materials is their very low fire performance. When a composite material is exposed to high temperatures (typically 300-400°C), thermal degradation processes occur [15-19], the organic matrix decomposes under the effect of heat by emitting soot, as well as fumes and toxic volatile compounds. The composite loss its mechanical properties which can seriously compromise structural integrity and cause buckling and severe cracking, or even collapse of a supporting structures (wall, ceiling). After a fire, it is important to know the residual properties at room temperature of a burnt material in order to estimate its mechanical integrity and the damage suffered, especially from the safety point of view. It is for this reason that we are interested in the study of the post-combustion mechanical properties of composite sandwich materials with balsa core. These materials, when used in shipbuilding, generally consist of thin skins made of polymer (polyester, vinyl ester or epoxy) reinforced with fibers (glass, carbon or Kevlar) surrounding a core made of an ultra-light material (balsa or polyurethane foam). They are subject to strict regulation and it is necessary to know their thermo-mechanical properties before any application [20-22].

In this context, we propose an analysis of the thermo-mechanical properties of composite sandwich materials (E-glass fibers polyester skins and balsa core). As this is a naval application, we were interested in both the dry material and the aged one submitted to moisture. Several Authors studied the thermal degradation of composite materials [23-25] but very little by comparing a dry material with a hygroscopically aged material [26]. We can also note that some works focused more specifically on the mechanical properties of balsa at high temperature [27]. In this work, we analyzed, using a cone calorimeter, the fire resistance of these two materials (dry and wet) to determine their mass loss kinetics

under fire. Fire tests were performed with a heat flux of 50 kW/m² and for different pyrolysis times. This makes it possible to map materials during combustion in terms of structural variations (delamination, cracking, etc.) and changes in mechanical properties, particularly in bending.

2. Experimental

2.1. Materials

Present used materials are made from layered E-glass polyester skins, to which is added draining polyester felts which facilitate the use of resin infusion in a single process. To cover the needs of a ship, several stacking sequences are used to represent areas of a hull or deck structure subject to different mechanical loads. Sandwich composite specimens are made of glass/polyester skins directly infused on a balsa wood core. Fabrics are M450, Soric2, QX868 embedded in polyester resin. The M450 is a fiberglass chopped strand mat, Soric2 is a flow media for resin infusion and QX868 is a non-crimp quadriaxial E-glass fabric (0°/-45°/90°/+45°). The total fiber volume content is 21%. The upper and lower skins thicknesses are 2.5 mm and 2.0 mm respectively. The overall dimensions of the sandwich composite specimen are 110 x 40 x 18.5 mm^3. The used balsa panels have an average density of 126±30 $kg.m^{-3}$. During infusion, the balsa panel absorbs a significant amount of resin that fills voids left between the blocks of balsa.

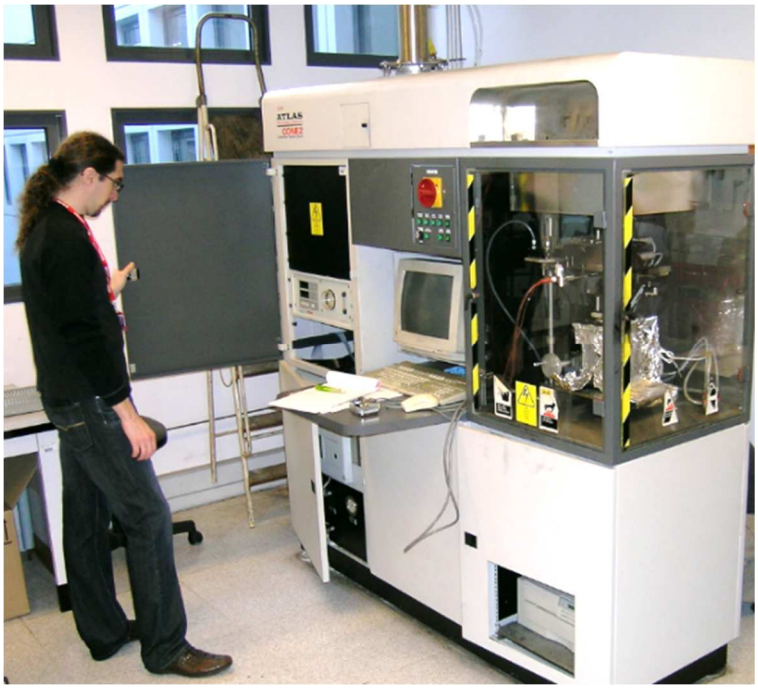

Figure 1. The ATLAS Cone2 cone calorimeter.

2.2. Thermal degradation measurement

Fire resistance tests are carried out on the cone calorimeter (ISO 5660 standard) which is a conical furnace (figure 1). The sandwich composite sample receives a radiative heat flux emitted by a cone constructed by winding an electrical resistance. The sample surface is positioned at a distance of 26 mm from the radiative source which provides a heat flux of 50 $kW.m^{-2}$ kept constant during all the measurement. Remember that the temperature of the flames during a fire is between 400 and 1200°C. The ignition of the material is here caused by a pilot spark. Gas fluxes are diluted with fresh air and drawn into a chimney. Our measurements are performed on an ATLAS Cone2 cone calorimeter. During a fire resistance measurement, the mass of the tested piece is recorded as a function of the burning time. In order to quickly stop its degradation, the sample and its holder are removed from the calorimeter cone and placed in a chamber under nitrogen atmosphere. After this step, post-fire mechanical tests can be conducted as detailed later.

2.3. Post-combustion mechanical response

Post-combustion properties characterization at room temperature enable to quantify the decrease of the residual mechanical properties of the material after a certain time of exposure to fire (degradation or combustion time). These properties are used to evaluate the residual mechanical integrity and safety of the structure where the material is used. It has be experimentally performed by 3-point bending flexural tests on both unaged and thermally aged samples, in order to be able to measure the maximum force reached before failure as well as the evolution of the flexural stiffness as a function of degradation time [28], for samples having undergone thermal degradation at different combustion times.

Based on a Zwick universal testing machine, a classical 3-point bending testing device with 15 mm radius supports is used with a displacement speed of 10 $mm.min^{-1}$. Both load and deflection are recorder. The test curve allows to identify bending stiffness and shear strength of the specimens. The bottom surface of the specimen (i.e. not in direct contact with the radiative source) remains at the bottom during bending tests. Dry and wet sandwich composite materials were analyzed (figure 2).

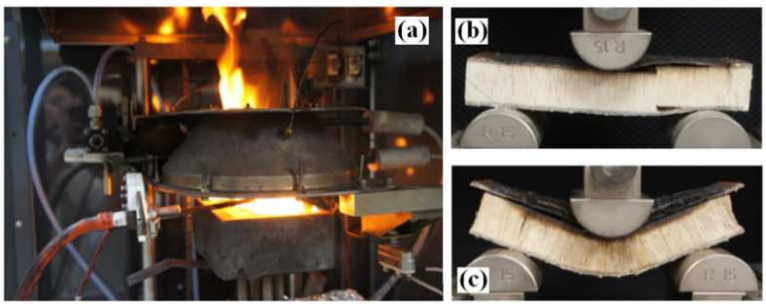

Figure 2. (a) Sandwich composite sample during fire testing on the ATLAS cone calorimeter. Post-fire 3-points bending measurements on (b) a dry and (c) a wet sandwich composite.

For numerical prediction of the standard flexural modulus, the thermally aged material can be represented by a two-layer model [20], used today in most studies of post-combustion mechanical properties in composite laminates, as shown in figure 3a for a laminate (i.e. one constituent – front skin, balsa core, or back skin – of the sandwich composite material) and a superposition of two-layer models as shown in figure 3b for the whole sandwich material. The first layer represents the region of the supposedly completely decomposed material (char material) after exposure to a heat flux, with weak mechanical properties, while the second one represents the region of the material which remains mechanically safe [29]. To appreciate the material properties variation, one must take the evolution of the boundary between the two regions (char and virgin materials) into account, which is called the *combustion advancing front*. This later is function of $d_c(t)$ the thickness of the carbonized layer (front skin, core or back skin), which also allow the determination of the flexural modulus of a constituent. Calculus of the flexural modulus of the whole sandwich composite material is adapted from the expression of the equivalent flexural modulus proposed by Theulen and Peijis [30].

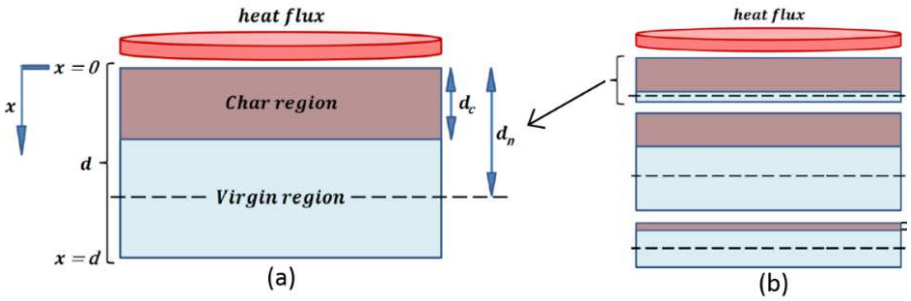

Figure 3. Scheme of the idealized two-layer model for studying the post-combustion mechanical properties (a) of one constituent of the sandwich composite material and (b) of the overall sandwich composite material.

3. Results and discussion

3.1. Fire resistance of sandwich composite materials

At first, we focused our attention on the dry material. This material consists of 3 distinct layers: front skin + core + back skin. In order to discuss the thermal properties of the sandwich composite, it is necessary to know beforehand the fire resistance properties of each separate element. For this, we made three

successive measures of fire resistance on 1) the front skin alone, 2) a bi-blade strip consisting of the balsa core and the lower skin and finally 3) the entire sandwich composite material. This separation is all the more important since we will compare the results obtained for the dry sample with those of a wet sample, which corresponds to the field of application in the naval industry. The skins, consisting mainly of resin and glass fibers, and the core, made of balsa impregnated with resin, have very different water-absorption behaviors, in particular, the skins are practically insensitive to water uptake whereas the diffusion of water in the core is very high, reaching more than 400% of the balsa weight (figure 4) [31]. It is thus expected a very different fire behavior between a dry and a wet sample.

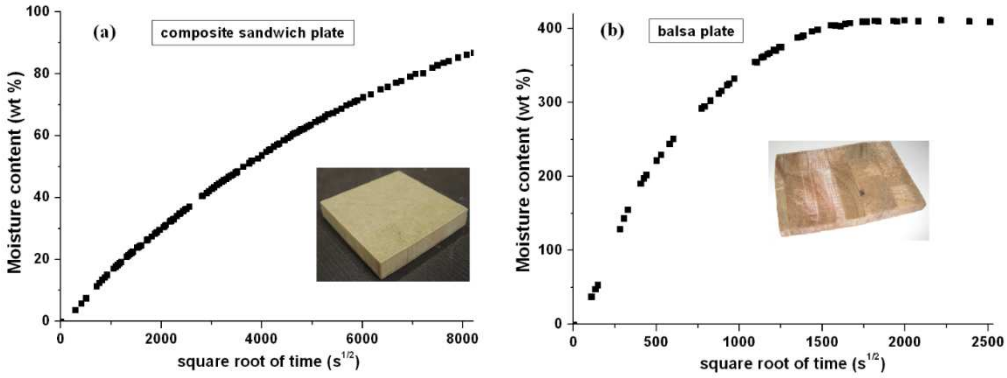

Figure 4. Kinetics of water diffusion at 40°C, in (a) a plate of sandwich composite material and in (b) a plate of balsa (alone without skins) infused with resin (plates size: 128 x 126 x 18a or 15b mm^3).

As said before, the front and back skins absorb a negligible amount of water. We can then consider that the fire behavior of a skin derived from a dry material and a skin from a hygroscopically aged material are similar in a first approximation. We therefore separated the front skin from a dry sandwich sample (size 110.52 x 40.95 x 2.04 mm^3) and measured its fire resistance under 50 $kW.m^{-2}$ heat flux. The corresponding combustion curve is shown in figure 5. The combustion of this component lasts about 200 s and causes a mass loss of 60.7% (initial mass = 10.99 g). It should be noted that more than 80% of the mass loss takes place during the first 104 s. It makes it possible to estimate the average burning rate of a skin to BR_{fs} = 0.072 $g.s^{-1}$. From the beginning of the combustion, this component burns by first emitting white smoke and quickly a thick black smoke. Small sparks, mainly on the edges of the specimen, are visible. At the end of combustion, the tested piece is charred, the resin has completely disappeared (pyrolysis into toxic volatile combustion products such as carbon monoxide CO, carbon dioxide CO_2, or aliphatic and aromatic hydrocarbons). Only fiberglass fabrics remain. Following these results, it could be considered for all the specimens that the degradation of the front and back skins is similar, inducing

systematically a mass loss of 6.67 g. This will allow to set the combustion limits between the constituents of the sandwich material. In addition, this mass loss for the skins will be considered identical between a dry material and a wet material.

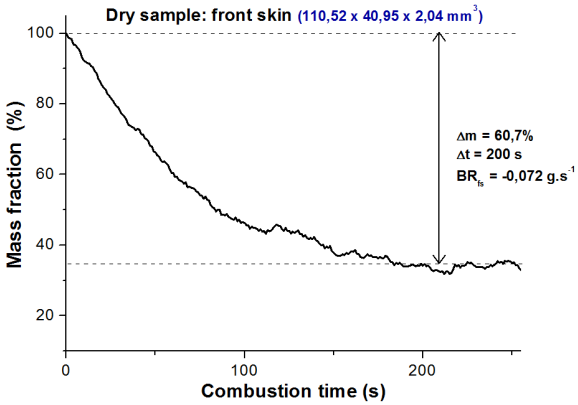

Figure 5. Dry sample: kinetics of combustion of the E-glass polyester skin alone.

We then analyzed the combustion of a sample without top skin (dimension 110.43 x 40.70 x 13.99 mm^3) consisting of a part of the balsa core impregnated with resin and the lower skin (figure 6). Knowing the mass loss associated to the back skin, i.e. 6.67 g, it is possible to separate the combustion characteristics of each component. Thus, the burning of balsa core lasts 335 s and causes a mass loss of 41.5% (mass loss = 8.95 g); the average burning rate of the balsa core is estimated to be BR_{balsa} = 0.025 $g.s^{-1}$. For the back skin, the combustion lasts 307 s for a mass loss of 31.0%, i.e. an average burning rate of BR_{bs} = 0.022 $g.s^{-1}$. It can be noticed that for the bi-blade strip, the burning rate of the back skin is lower than that of the front skin alone. This can easily be understood because the balsa, even pyrolyzed, plays the role of "retarder" to the combustion of the back skin which is not directly in contact with the incident radiative heat flux of the cone. Its combustion is therefore slowed down.

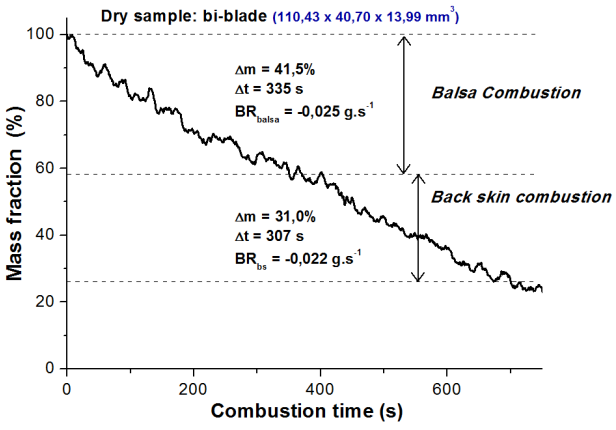

Figure 6. Dry sample: Burning kinetics of a specimen without top skin.

Let's now analyze the dry sandwich composite material as a whole (figure 7). We choose to separate the combustion in 3 successive steps: Step 1 = burning of the front skin, associated to a mass loss of 18.3% (i.e. 6.67 g) in 88 seconds. The burning rate is equal to -0.075 $g.s^{-1}$. Step 2 = burning of the balsa core, associated to a mass loss of 27.6% in 421 seconds. The burning rate is equal to -0.024 $g.s^{-1}$. Step 3 = burning of the back skin, associated to a mass loss of 18.3% (i.e. 6.67 g) in 383 seconds. The burning rate is equal to -0.017 $g.s^{-1}$. The mass of incombustible products is 13.01 g, or 35.7% of the initial mass of the sandwich composite material.

The results (time and burn rate) obtained for the constituents of the dry sandwich material as a whole are of the same order of magnitude as for each component studied separately. This separation in 3 steps just allows an estimate of combustion rates and a successive visualization of the combustion of the constituents in the hypothesis of a sandwich material combustion layer by layer. In fact, the burning of the skins and the core begins with a delay but not successively once the front skin is completely pyrolyzed. However, the mass loss data do not make it possible to determine when there is a superposition of the combustion of two or three constituents of the sandwich material.

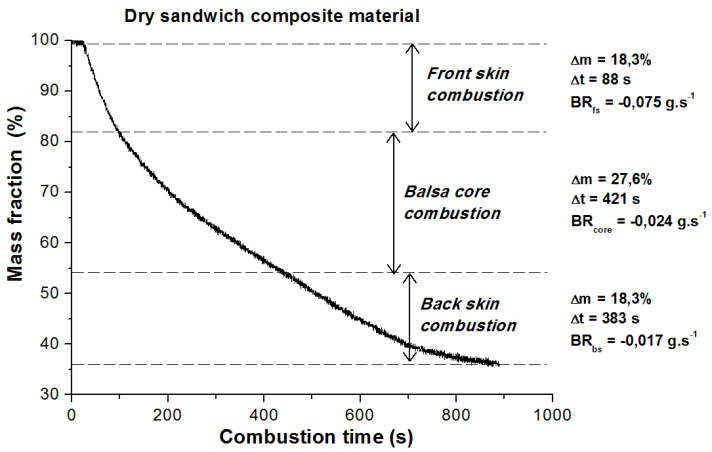

Figure 7. Dry sandwich sample: kinetics of combustion of the sandwich composite material.

In order to prepare mechanical testing, nine fire resistance measurements at burn times ranging from 40 s to 890 s (figure 8) were performed. These measurements will allow us to describe more accurately the degradation kinetics of the sandwich material. We observe that during the first 100 seconds, the front skin is completely degraded by the heat flux supply with a gradual delamination of the skin on the balsa core, but also a retraction of the skin (bulging aspect of the surface). The balsa also begins to degrade and a

combustion advancing front begins to be observed through the thickness. The skin resin filled with glass fibers burns with a thick black smoke, yellowish sparks are also visible on the surface. At the end of the degradation, the resin has completely disappeared into combustion products, especially gaseous, leaving only the apparent fiberglass fabric. Note that the pyrolysis temperature due to the chosen heat flux provides a maximum temperature of 750°C, which remains below the melting temperature of glass fibers (1065-1120°C) [32]. The skin-core delamination induces progressively an inflammation of the balsa on the edges of the specimen. The balsa then rapidly degrades, in particular, we noticed several major cracks between balsa blocks. The combustion front evolves rapidly and many secondary cracks appear. The main and secondary cracks are caused by the degradation of the resin which "evaporates" more and more as a function of time. Finally, the back skin is thermally degraded, which is clearly visible after 260 s (figure 8). We observe that at 380 s balsa curved and charred. This degradation remains beyond 380 s without any noticeable evolution which seems to indicate that the complete degradation of the back skin would be established before this characteristic duration, in particular in the range 260-380 s. The back skin from balsa delamination is much less pronounced, but a shrinkage of the back skin occurs, as shown in pictures taken at 382 s or 890 s in figure 8. All of this information match the results from measurements in figure 7. Thus, we can now conclude that, for the dry material, the front skin burns completely in the first 88 seconds of exposure to fire, the balsa core degrades from about 50 seconds and that the back skin begins to burn from 180 s (mid time values between 98 s and 260 s in figure 8) of exposure to a heat flux of 50 $kW.m^{-2}$. As a result, therefore, there is first a combustion of the front skin, then a superposition of two combustion advancing fronts for the front skin and the balsa core, then the combustion of the balsa alone, finally again a superposition of two combustion advancing fronts for the balsa and the back skin.

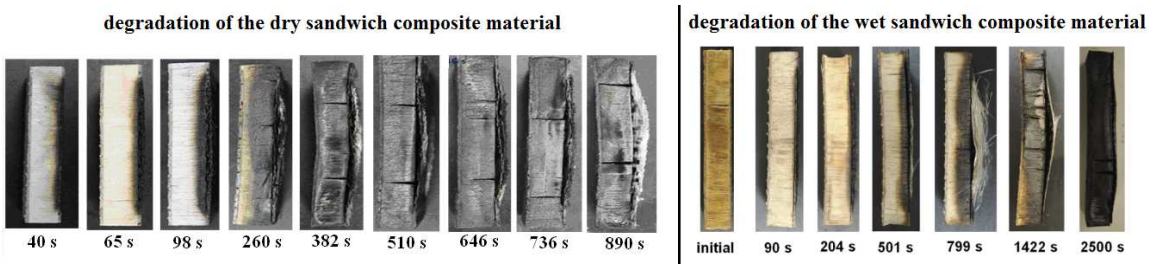

Figure 8. Degradation of the dry and wet sandwich materials after different burning times at 750°C.

In order to compare the thermal durability of our materials for naval application, the same measurements as above were made on wet materials (immersed in water at 40°C until saturation). We observe for the

wet sample a fire resistance behavior similar to the dry sample. Let's decompose the kinetics in 3 steps (figure 9): Step 1 = burning of the front skin, associated with a mass loss of 8.7% in 215 seconds (mass loss = 6.67 g). The burning rate is equal to -0.031 $g.s^{-1}$. Step 2 = burning of the balsa core, associated with a mass loss of 68.4% in 1641 seconds. The burning rate is equal to -0.032 $g.s^{-1}$. Step 3 = burning of the back skin, associated with a mass loss of 8.7% in 235 seconds. The burning rate is equal to -0.015 $g.s^{-1}$. The mass of incombustible products is 10.77 g, i.e. 14.1% of the initial mass of the sandwich composite material.

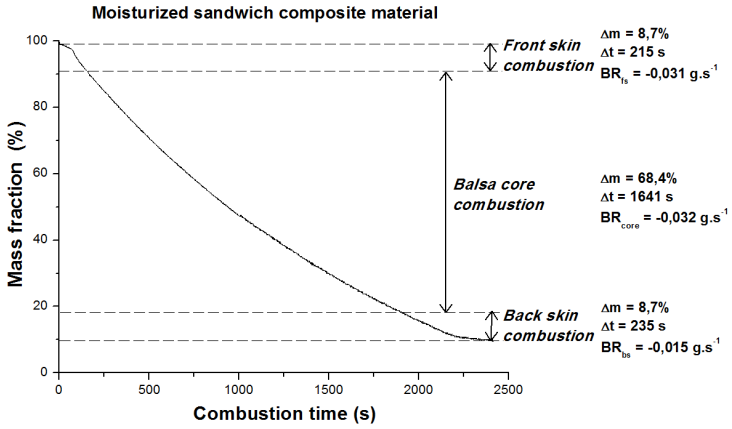

Figure 9. Wet sandwich sample: kinetics of combustion of the sandwich composite material.

Like the dry material, figure 8 shows also the evolution of the physical degradation of the wet sandwich material after different burning times. First, we observe the same degradation mechanism, but slowed down compared to the dry material since the complete fire deterioration of the wet sample lasts 2300 seconds. If the surface condition of the wet samples is observed more closely, it is found that the resin has completely disappeared as combustion products after about 210 s (215 s in figure 9 and 204 s in figure 8), and that the top surface fiberglass fabric is severely damaged: it looks like the thickness of the upper fabric E-glass layer increases as the burning time increases too. We also observe a much larger number of cracks in the core. On the dry samples, there are about 2 large cracks per sample, while on the wet samples there are 5 or more. To summarize the differences between dry and wet samples, we can conclude that in the wet sample delamination is much more important as is the number of cracks. In fact, during the pyrolysis, the water contained in the wet sample vaporizes which may significantly increase the internal pressure in the skins and especially in the balsa core which absorbed a large water quantity. For example, in a phenolic resin that has weight recovered 20-25% of water, the internal pressure close to the surface can increase by a factor of 10 [33], which suggests an even greater internal pressure in the

material volume. We made the same observation when numerically predicting the fire-resistance behavior of composite sandwich materials [14] with an improved fire model allowing the calculation of the internal pressure in the presence of diffused water in the sandwich material. In addition, Authors [34] measured the internal tensile stresses in polymer matrix composites having recovered up to 8% of water: for pyrolysis carried out at 300°C, the internal tensile stress was evaluated at 75 MPa, which is sufficient to induce delamination and significant matrix cracking. The water introduced into the many micro-cavities of the balsa can therefore weaken the material as a whole during its vaporization, creating cracks propagating from microcavities to microcavities [35]. The number, distribution and size of microcavities are therefore criteria to be considered in determining the mechanical behavior of fire resistance of wet samples and to understand the structural instabilities (cracking, delamination) that propagate throughout the material.

3.2. Post-combustion mechanical properties

Following fire resistance measurements, it is important to determine the mechanical properties of these thermally aged materials. Three-point bending measurements allow to analyze the thermo-mechanical behavior. For this purpose, 3-point bending measurements were performed using thermally aged specimens at different combustion times on dry and wet samples (figure 10). These analyzes are important when one knows that the limitations to the use of polymer matrix composite materials in the shipbuilding industry are the factors of *fire resistance* and *mechanical strength*. Thus, once these two factors are combined, the mechanical properties are strongly degraded. This thermo-mechanical degradation was studied by several authors [37-41], mainly on polymer matrix composite materials (including the three polymers used in the shipbuilding industry: polyester, vinyl ester and phenolic). These analyzes relate to an experimental description the mechanical degradation as a function of temperature and/or of the combustion time but also to a modeling prediction point of view the mechanical degradation kinetics [20-22; 42].

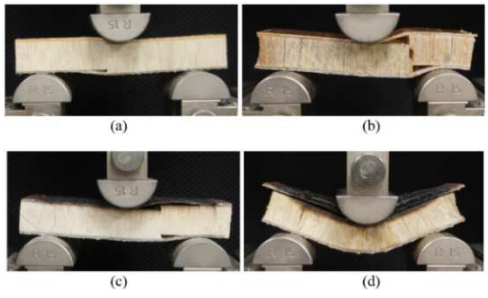

Figure 10. 3-point bending mechanical tests: (a) dry sample rupture without heat treatment; (b) wet sample rupture without heat treatment; (c) dry sample rupture with heat treatment of the front skin; (d) measurement of the wet sample with heat treatment of the front skin: sliding of the front skin (visible delamination on the sample edges) and appearance of cracks in the balsa core.

The performed mechanical measurements make it possible to plot the evolution of the flexural modulus (Figure 11) as a function of the combustion time for dry and wet samples. It is observed an exponential decrease as for other composite materials [20-22]. By comparing the normalized evolution the flexural stiffness of dry and wet samples, we notice that both follow the same thermo-mechanical exponential behavior law, with almost identical curves. This indicates that the mechanical behavior is mainly related to the degradation of the skins, in particular to the upper skin mechanical properties, and therefore doesn't depend on the moisture content in the balsa core but is strongly influenced by the duration of the heat treatment. These curves clearly show that wet and dry materials lost their mechanical properties beyond 250 s of exposure to fire. Recall that this characteristic time of 250 s corresponds to the complete degradation of the front skin and a very pronounced degradation of the back skin for the dry material. We can therefore confirm that the skins of the moisturized material degrade in the same time scale, i.e. in about 250 s. It should also be noted that the appearance of cracks during combustion further weakens the structure, so that the maximum force and the flexural modulus are strongly affected and rapidly exhibit very low values.

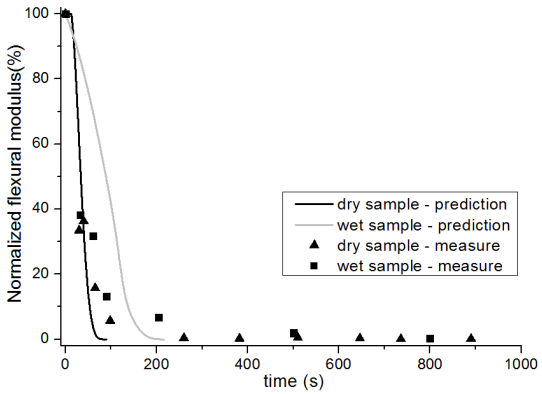

Figure 11. Time dependence of the post-combustion normalized flexural modulus of the dry and wet sandwich materials: measured by 3-point bending (■ and ▲), and the predicted curves (▬ and ▬) obtained by the evolution of the combustion advancing front $d_c(t)$ (E-glass/polyester/balsa sandwich composites at a heat flow of 50 $kW.m^{-2}$).

3.3. Structure-properties relationships and combustion advancing front

In this section, we will relate the experimental results obtained during cone calorimeter measurements, during thermogravimetric analyzes [36] and during 3-point bending mechanical tests with an important parameter: the *combustion advancing front*. This combustion advancing front delimits two layers in the constituent, having a total thickness d (figure 3). A first carbonized layer, of thickness d_c, is visible on the side where rises the incident heat flux; and a second layer, of thickness $(d - d_c)$, in which the material remains intact. As previously explained, for a composite sandwich material, three layers should be considered for the determination of the mechanical properties: the front skin, the balsa core and the back skin. However, in order to calculate the equivalent flexural modulus, only the front skin must be considered in the present case, because failure of sandwich composite is assumed to occur by unstable microbucking (kinking) of the front skin. The front skin is submitted to compression stress and has the highest degradation rate, which leads to failure. Then, balsa core and back skin are insufficient to carry the bending load initially ensured by the whole sandwich structure. The strength of the core is assumed to be much lower than the strength of the skins, so its contribution can be neglected. Thus, as the front skin degrades and finally collapses, the back skin receives the total load and fails also.

In order to predict the equivalent flexural modulus variation as a function of the burning time, the shape of the combustion advancing front $d_c(t)$ was calculated from the measured change in the mass loss of the upper skin, over a time of 88 s for the dry material (see figure 7) and a time of 215 s for the wet material (see figure 9). In a first approximation, we considered that the $d_c(t)$ function is inversely proportional to the masse loss function. Once $d_c(t)$ is estimated, the evolution of the normalized flexural modulus could be predict. Figure 16 shows the predicted normalized flexural modulus for the E-glass/polyester/balsa sandwich composite, for both the dry (black curve) and moisturized (grey curve) sample, taking only the contribution of the front skin into account. These numerical results are superimposed to the measured experimental data in order to analyze the influence of water content and also to validate the applied methodology.

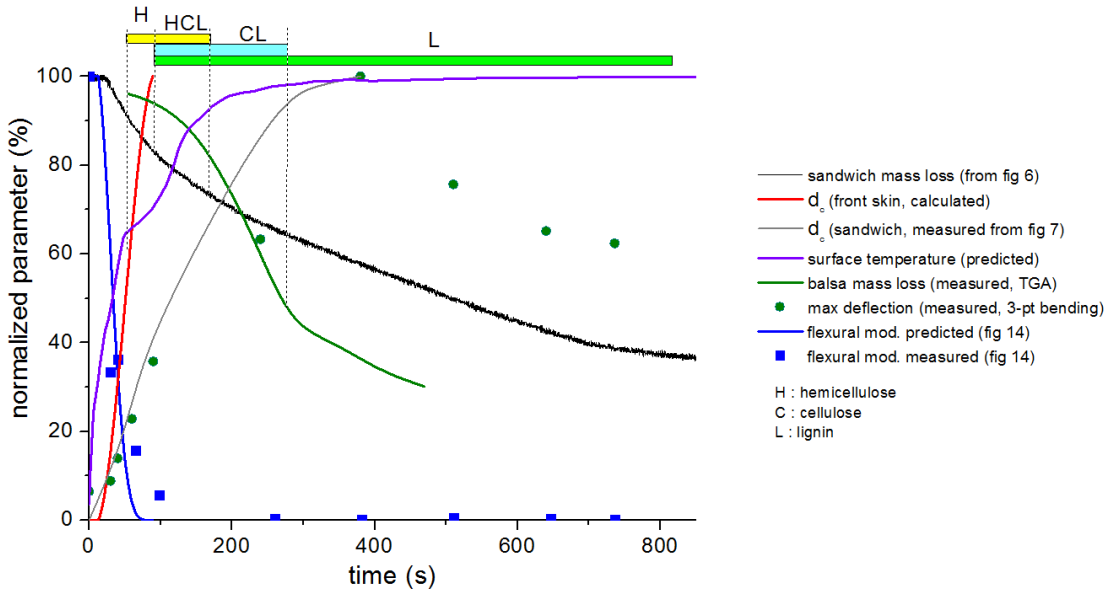

Figure 12. Structure-properties relationships of the E-glass/polyester/balsa sandwich composite material (dry material) during combustion: superposition of the evolution of the (1) normalized flexural modulus (■ experimental and ▬ predicted); (2) normalized combustion advancing front d_c of the front skin (▬) and of the sandwich material (▬); (3) normalized measured experimental mass loss m(t) from cone calorimeter data (▬) and from TGA data (▬, from [36]); (4) front skin surface temperature directly exposed to a 50 kW.m^{-2} heat flux (numerical simulation [14]) (▬); (5) normalized maximum deflection measured by 3-point bending tests (●); (6) thermal degradation intervals (from [36]) of hemicellulose ( ), cellulose ( ) and lignin ( ).

We observe that the two predicted curves for the evolution of the flexural modulus of a dry material or a wet material are in quite good agreement with the experimental data. The estimate of the loss of mechanical property is the best for the dry material. Concerning the wet material, the curve is slightly tilted towards larger durations but still averages over the measured points. For both materials, a very sharp and sudden decrease is observed as soon as the front skin begins to degrade with fire. The flexural modulus variation depends directly on the exposure time to fire. This last modifies the advancing combustion front location and consequently increases the carbonized layer thickness $d_c(t)$ which actually increases the contribution of the char material to the overall sandwich material mechanical properties (i.e. which makes the value of $\langle EI \rangle_{eq}$ tend to zero). One could observe that the equivalent flexural modulus in the case of the wet material is slightly offset in time respect to the curve calculated for the dry material. Indeed, thermal degradation could be influenced by the very low residual water content inside initial porosity of the front skin matrix, and by a larger part by the water vapor flow produced during the water evaporation inside the balsa core which might slightly cool the front surface down or modify heat

properties. This is why the two curves (dry and wet) are very close but still separated in time. The present proposed approach is very simple and only based on the evolution of the mass loss of the sample measured under the cone calorimeter. The obtained results do not use a complex thermal numerical model as in other studies [14] but lead to very similar results.

In conclusion, the results are very encouraging and the agreement with experimental data highly allows to validate the present approach to predict mechanical post-combustion properties of sandwich composites with polymer laminated skins and combustible core.

In order to analyze more finely the structure-properties relationships of the E-glass/polyester/balsa sandwich composite material (dry material) during combustion, figure 12 summarizes results by superimposing all experimental and numerical prediction data obtained from the present analysis, but also from previous work [14; 36]. In particular, Figure 12 includes the time dependence of the normalized mass loss obtained by thermogravimetric measurements (TGA) to an isolated balsa sample [36]. The TGA measurements make it possible to deconvolute the total degradation of the balsa sample in its three constituents. The TGA curve $-d\alpha/dT = -d\alpha/\beta dt$ (with α the decomposition rate and $\beta = dT/dt$ the experimental temperature rate) thus provides access to the temperatures (and therefore to the times) of the start and the end of hemicellulose, cellulose and lignin degradations. By plotting this information in figure 12, one could highlight a close relationship between results from cone calorimeter, ATG and 3-point bending tests.

At first ($t < 50$ s), only the front skin is degraded, inducing a significant loss of the mechanical properties of the sandwich material. In the same time interval, there is a sharp temperature increase up to 460°C at the surface (figure 13). Numerical simulations show that the temperature between the balsa layer and the front skin is around 210°C [14].

Then in the time interval [50; 88] s, the balsa core begins to degrade through the pyrolysis of hemicellulose. Indeed, the temperature of the balsa close to the interface is about 210°C after the sandwich material is exposed to a heat flux of 50 $kW.m^{-2}$ for 50 s (figure 13), which corresponds to the glass transition temperature of hemicellulose. During a heat supply, hemicellulose is broken down into various products and especially into acetic acid by an endothermic process. We then note a temperature decrease. Hemicellulose is the constituent binding the cellulose chains between each other, the balsa then loses its stiffness and its mechanical properties drop. If hemicellulose degrades, the bonds (covalent and weak) disappear and there is no more cohesion. The balsa temperature at the interface of the incident heat

flux side is approximately 250°C after 88 s of exposure. At the end of this time, the front skin has completely degraded and only the glass fiber fabric remains, which pyrolysis occurs at a very high temperature (> 1000°C) [32]. The surface temperature is then around 500°C (figure 13).

Over the time interval [88; 170] s, the temperature variation follows the same kinetics. Since hemicellulose degrades by producing acetic acid, the cellulose will progressively degrade by an endothermic process, acetic acid being a catalyst for the latter. Remember that the glass transition temperature of cellulose is about 250 to 270°C which corresponds to the temperature then reached by balsa at its upper surface. Lignin also begins to thermally degrade. The mass loss measured by TGA accelerates as the three constituents of balsa decompose at the same time. At time t = 170 s, hemicellulose is completely pyrolyzed. The mechanical properties are then extremely weak (close to 5% of the initial value) since the front skin is already completely pyrolyzed and the balsa has lost its cohesion. The mass loss of the sandwich material is approximately 25%, which is the expected value during the thermal decomposition of a wood at the end of the pyrolysis of the hemicellulose. Finally, it is interesting to point out that the combustion advancing front shifts from 88 s, induced by the nature of the constituents which decompose.

Over the time interval [170; 280] s, cellulose and lignin continue to degrade, but no more acetic acid from the decomposition of hemicellulose, the thermal degradation kinetics slows down, which is observed by a slight change in the slope of the mass loss curve. The mechanical properties of the sandwich now tend to zero. Temperature reaches a steady state around 590°C at the interface between the front skin and the core and about 180°C at the interface between the core and the back skin (figure 13). The surface temperature reaches about 700°C. Recall that the glass transition temperature of lignin is about 200°C. Until the time t = 280 s, the maximum deflection increases nearly linearly to its maximum, the rigidity of the front skin having been lost, the flexibility of the sandwich material is given by the flexibility of the remaining safe materials, flexibility which increases as the number of intra and inter-chain molecular bonds decreases in the core (the decrease in the number of molecular bonds increases the flexibility of the material).

Finally, after a fire exposure time greater than 280 s, only the lignin contained in the balsa continues to decompose, inducing a slow mass loss of about 25%. The temperature stabilizes and the maximum deflection reached exhibits decreasing values comprised in the range 60-80% since the structure of the sandwich material no longer has any cohesion apart from the few bonds that still contain the highly degraded lignin at this stage. The curve of the combustion advancing front of the sandwich material reaches almost its maximum value. It should be noted that the back skin degrades very slowly in relation to the temperature around 280-330°C, for t > 400 s, observed in this zone of thickness, its decomposition

probably taking place in the exposure time interval [170; 380] s according to figure 9. This final degradation time around 400 s for the back skin is also correlated with the beginning of fall of the maximum deflection value and with the temperature slow stabilization observed in figure 13.

Figure 12 clearly highlights the importance of correlating all the experimental data and numerically calculated results, obtained here completely independently, in order to accurately describe the structure-properties relationships induced during the decomposition of the sandwich composite material under extreme temperature conditions. These structure-properties relationships are strongly related to the combustion advancing front $d_c(t)$.

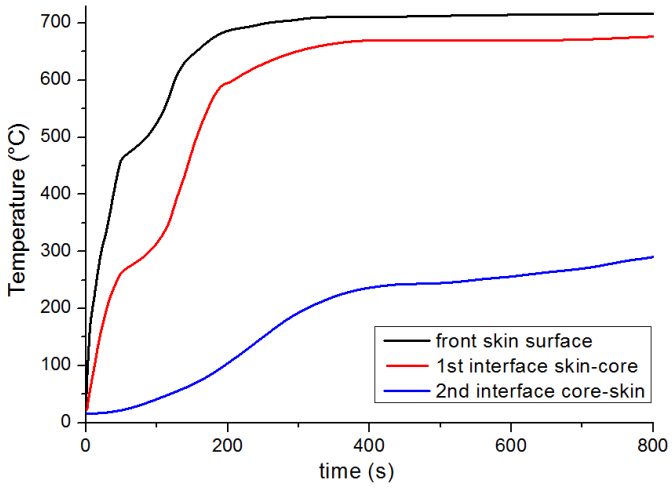

Figure 13. Time variation of the numerically predicted temperature for a E-glass/polyester/balsa sandwich composite material exposed to a 50 $kW.m^{-2}$ heat flux. Temperature curve represented for the front skin surface (in red), for the interface between front skin and balsa core (in black), for the interface between balsa core and back skin (in blue) [14].

4. Conclusion

The study of fire resistance properties of composite sandwich materials using the cone calorimetric allowed to compare the combustion of moisturized and dry materials. Thermal degradation rates under fire were identified for each component (skins and core) of sandwich specimens. These analyzes were combined to 3-point bending tests to analyze the post-combustion mechanical behavior of the dry and wet sandwich samples as a function of the combustion time under a heat flux of 50 $kW.m^{-2}$. This made it possible to highlight the various stages of degradation, in particular by studying the time evolution of the flexural modulus. The sandwich structure underwent a very rapid thermo-mechanical degradation during the first 88 s of heat treatment and that this degradation was strongly due to the degradation of the front

skin. The relative elasticity of the studied sandwich materials is independent of the hygroscopic treatment previously experienced by the material, but is strongly influenced by the duration of the heat treatment. Finally, the importance of correlating the set of experimental and simulated results was highlighted in order to accurately describe the structure-properties relationships induced during the decomposition of sandwich composite material under extreme temperature conditions (fire resistance). It is necessary, in parallel with the experimental measurements, to develop predictive models to simulate the thermal degradation of materials with the cone calorimeter. These numerical simulations give access to the temperature profile within the material as a function of exposure time to fire, as well as the mass variation as a combined function of time and temperature. In order to adequately reproduce the experimental results, the model used must include a large number of parameters while keeping a hierarchy in the importance of each one of them. To go further in the understanding of the structure-properties relationships of materials in extreme conditions, *in situ* thermo-mechanical measurements adapted to the cone calorimeter are envisaged using a specific instrumentation and new improved numerical model.

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Figure Captions

Figure 1. The ATLAS Cone2 cone calorimeter.

Figure 2. (a) Sandwich composite sample during fire testing on the ATLAS cone calorimeter. Post-fire 3-points bending measurements on (b) a dry and (c) a wet sandwich composite.

Figure 3. Scheme of the idealized two-layer model for studying the post-combustion mechanical properties (a) of one constituent of the sandwich composite material and (b) of the overall sandwich composite material.

Figure 4. Kinetics of water diffusion at 40°C, in (a) a plate of sandwich composite material and in (b) a plate of balsa (alone without skins) infused with resin (plates size: 128 x 126 x 18a or 15b mm^3).

Figure 5. Dry sample: kinetics of combustion of the E-glass polyester skin alone.

Figure 6. Dry sample: Burning kinetics of a specimen without top skin.

Figure 7. Dry sandwich sample: kinetics of combustion of the sandwich composite material.

Figure 8. Degradation of the dry and wet sandwich materials after different burning times at 750°C.

Figure 9. Wet sandwich sample: kinetics of combustion of the sandwich composite material.

Figure 10. 3-point bending mechanical tests: (a) dry sample rupture without heat treatment; (b) wet sample rupture without heat treatment; (c) dry sample rupture with heat treatment of the front skin; (d) measurement of the wet sample with heat treatment of the front skin: sliding of the front skin (visible delamination on the sample edges) and appearance of cracks in the balsa core.

Figure 11. Time dependence of the post-combustion normalized flexural modulus of the dry and wet sandwich materials: measured by 3-point bending (■ and ▲), and the predicted curves (— and —) obtained by the evolution of the combustion advancing front $d_c(t)$ (E-glass/polyester/balsa sandwich composites at a heat flow of 50 $kW.m^{-2}$).

Figure 12. Structure-properties relationships of the E-glass/polyester/balsa sandwich composite material (dry material) during combustion: superposition of the evolution of the (1) normalized flexural modulus (■ experimental and — predicted); (2) normalized combustion advancing front d_c of the front skin (—) and of the sandwich material (—); (3) normalized measured experimental mass loss m(t) from cone calorimeter data (—) and from TGA data (—, from [36]); (4) front skin surface temperature directly exposed to a 50 $kW.m^{-2}$ heat flux (numerical simulation [14]) (—); (5) normalized maximum deflection measured by 3-point bending tests (●); (6) thermal degradation intervals (from [36]) of hemicellulose (▭), cellulose (▭) and lignin (▭).

Figure 13. Time variation of the numerically predicted temperature for a E-glass/polyester/balsa sandwich composite material exposed to a 50 $kW.m^{-2}$ heat flux. Temperature curve represented for the front skin surface (in red), for the interface between front skin and balsa core (in black), for the interface between balsa core and back skin (in blue) [14].