ASSESSING THE STRENGTH OF SHIPBUILDING WOOD IN WET ENVIRONMENT AND HIGH TEMPERATURE

ĐÁNH GIÁ SỨC BỀN CỦA GỖ ĐÓNG TÀU TRONG MÔI TRƯỜNG ẨM ƯỚT VÀ NHIỆT ĐỘ CAO

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Abstract - Optimizing the spending energy in the naval structures is to decrease their weight. Thus, balsa wood plates are frequently used instead of solid plates because of their high stiffness-to-weight ratio. The mechanical properties of these materials can be significantly reduced by presence of moisture inside them when they are exposed to a wet environment and high temperature. Thermogravimetric analyses under air atmosphere were performed on balsa wood to investigate the thermal degradation process of two types of samples aged differently: a dry balsa specimen and a hygroscopically aged material. The thermogravimetric method was used to determinate the kinetic parameters as the activation energy, the pre-exponnential factor and the order of reaction. The three constituents of balsa (i.e. hemicellulose, cellulose and lignin) were well identified and the decomposition temperature region well characterized. The presence of a large quantity of water affects the thermal decomposition behaviour of wood inducing notably a maximal degradation temperature.

Key words - composite materials; diffusion; naval structures; strength; balsa wood

Tóm tắt - Để tối ưu năng lượng tiêu thụ cho tàu thủy cần phải giảm trọng lượng của nó. Do đó, những tấm gỗ nhẹ balsa thường sử dụng để thay các tấm thép truyền thống. Tuy nhiên, sức bền của gỗ có thể giảm do ảnh hưởng của môi trường ẩm ướt và nhiệt độ cao. Để đánh giá sức bền của gỗ dưới tác động của môi trường ẩm ướt và nhiệt độ cao, sự phân tích nhiệt động được thực hiện trên loại gỗ balsa thường dùng để đóng tàu. Thực nghiệm đã tiến hành trên hai loại mẫu gỗ: nhóm mẫu gỗ khô, nhóm gỗ khác đã ngâm nước đến bão hòa rồi tiến hành phân tích. Phương pháp phân tích nhiệt động được sử dụng để xác định các tham số phá hủy nhiệt động. Giới hạn nhiệt độ gây phá hỏng gỗ cũng đã chỉ ra. Ngoài ra, ảnh hưởng của môi trường ẩm ướt đến sức bền của gỗ cũng được nghiên cứu. Kết quả nghiên cứu đã chỉ ra nồng độ nước thấm trong gỗ có ảnh hưởng rất lớn đến các tham số phá hủy nhiệt động.

Từ khóa - vật liệu composite; khuếch tán; kết cấu tàu thủy; sức bền; gỗ balsa

1. Introduction

One of the main objectives of the naval industries is the optimization of structures in terms of lightening and strength. This may be achieved by substituting metallic materials commonly used with lighter and cheaper materials such as composites. Nowadays, the balsa material is a hardwood used mostly in the form of large building plate formed of smaller plates glued together by resin. As a biomass material, balsa consists of cellulose, hemicellulose and lignin components which decompose more or less rapidly depending on the type of degradation. Many studies have already been conducted to understand and predict the aging of wood subjected to a wet environment, deformed by a mechanical action or thermally degraded. Knowledge of variations of the physical, chemical and mechanical properties obtained in these later studies [Di Blasi, 2008; Popescu *et al.*, 2011] allowed significant optimization of wood manufacturing processes. At present, researches are directed towards a better understanding of the thermal decomposition process of natural fibres as biomass materials are often subject to thermal degradation in relation to composite processing but also degrade very quickly during a fire. This last point is precisely a restriction on the extensive use of composites made of wood or natural fibres in naval and aerospace applications.

The present study deals into this thematic by providing knowledge about the thermal decomposition process of balsa, in an air atmosphere to reflect the real services conditions. The measurements were performed by thermogravimetric analysis in particular to determine the activation energy. Since marine environment corresponds to a wet surroundings, we compared results obtained on two samples, a dry one and the other aged hygroscopically until water saturation. This comparison establishes the originality of the study because usually, the analyzed thermal degradations are performed under ambient conditions of humidity and do not take into account the possible changes of external conditions that can be extreme, as is the case in the aeronautic and naval areas.

2. Experimental section

Samples were separate in two distinct sets. Set 1 is composed of balsa core specimen without any aging process thus the moisture content of these samples was around 5% depending the laboratory atmospheric conditions. Set 2 is constituted of balsa core specimen immersed in distilled water maintained at 40°C; continuous monitoring of the moisture uptake was performed over several months until the full water saturation of the specimens.

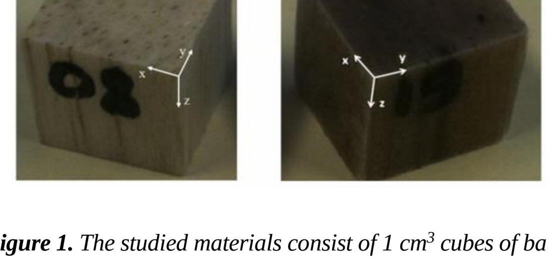

Figure 1. *The studied materials consist of 1 cm^3 cubes of balsa wood. Dry materials (a) and saturated moisturized materials (b)*

Experimental measurements were performed using a Mettler Toledo TGA/DSC STAR^e System thermogravimetric analyzer. Thermal decomposition was measured in terms of global mass loss. The TGA system detects mass variations of 0.1 µg as a function of temperature. For both testing specimens (dry and moisture saturated), the thermal decomposition was measured at 5 different linear heating rates 5, 10, 15, 20 and 25 °C.min^{-1} over the range 35-700°C.

3. Theoretical section

Using TG measurement it is possible to derive the kinetic parameters of the thermal decomposition of solid materials thanks to the following expression:

$$\frac{d\alpha}{dt} = k(T)(1-\alpha)^n \qquad (1)$$

where α is the fraction of solid material decomposed at time t, n is the reaction order. The conversion rate parameter α can be expressed according to the measured weight loss at the various reaction times such as:

$$\alpha = \frac{W_0 - W_t}{W_0 - W_f} \qquad (2)$$

where W_0, W_f and W_t are respectively the initial weight, final weight and weight at time t of the testing specimen.

The constant rate k(T) is given by the Arrhenius equation:

$$k(T) = k_0 \exp\left(-\frac{E_a}{RT}\right) \qquad (3)$$

where k_0 is the pre-exponential factor (time^{-1}), E_a is the activation energy (kJ.mol^{-1}), T is the Kelvin temperature and R = 8.314 (J.K^{-1}.mol^{-1}) is the universal gas constant. The constants k_0 and E_a are intrinsic properties of the material. The constant Ea represents the energy barrier opposing the reaction. The k_0 factor points out the reactional probability of a molecule having the energy E_a. Substitution of Eq. (3) into Eq. (1) gives the following expression:

$$\frac{d\alpha}{dt} = k_0 \exp\left(-\frac{E_a}{RT}\right)(1-\alpha)^n \qquad (4)$$

In the case of non-isothermal experiments with a linear heating rate $\beta = dT/dt$, Eq. (4) can be re-written as:

$$\frac{d\alpha}{dT} = \frac{k_0}{\beta} \exp\left(-\frac{E_a}{RT}\right)(1-\alpha)^n \qquad (5)$$

4. Results and discussion

4.1. Moisture content

Figure 2 shows the measured moisture content and the fitted curves as a function of exposure time for the different specimens. Experimental results confirm the Fickian properties of the material beforehand assumed for indentifying.

4.2. Moisture expansion

The moisture expansion can be explained that the moisture is first absorbed by diffusion to the boundary of specimen and begins to absorb to the volume of specimen. Thus, the moisture absorption period to the boundary induced an important strain. This called free expansion state, (figure 5). To obtain swelling characteristic of balsa core, we used the slope of the linear ranges of the moisture-induced strain curves. This linear range corresponds to an actual final state of balsa.

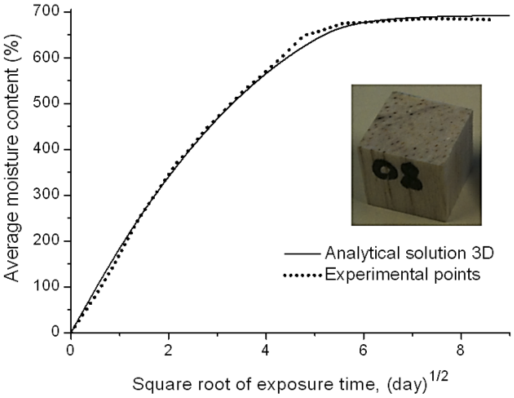

***Figure 2**. Moisture diffusion kinetics at 40°C in a balsa wood cube. The measured experimental data (●) and the analytical Fickian 3D solution (▬) are plotted*

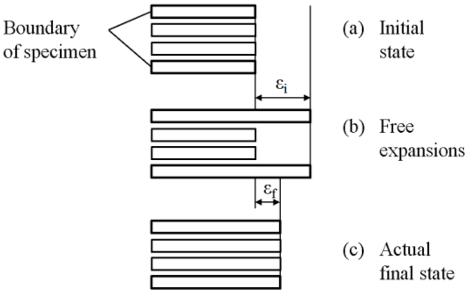

***Figure 3.** Definition of the different hygroscopic strains of balsa, (ε_i – free expansion, ε_f – final expansion)*

4.3. Characteristics of wood thermal degradation

Due to the presence of three constituents, the analysis of the thermal degradation of wood is not trivial and the global result is the overlapping of each individual decomposition. Figure 4 shows a classical example of wood thermal degradation with the first derivative $-d\alpha/dT$ of the mass fraction α as a function of temperature. Commonly, hemicellulose, first component to degrade, appears on the $-d\alpha/dT$ curve as a shoulder rather than a clear defined peak because it is hidden with the cellulose decomposition peak. Cellulose being the main component of wood fibers, the analysis was focused on this item. The peak temperature T_m, discussed in previous theoretical section, will be taken as the maximum temperature of the degradation of cellulose. These two components (hemicellulose and cellulose) then form a strong peak that can be or not followed by a much less intense second peak corresponding to the decomposition of lignin. Lignin damages on a very large temperature interval, this last peak may be not present but be diffuse on the corresponding temperature range. The $-d\alpha/dT$ curve is deconvoluted into each of its constituents, performed considering gaussian multi-peak fittings. The scheme illustrates wood structure with its three principal components.

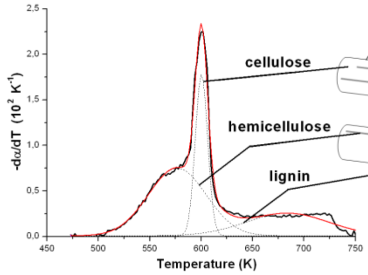

Figure 4. *Typical example of first temperature derivative of the mass fraction as a function of temperature for a wood species*

To well characterize the thermal behavior of balsa wood, the first time $-d\alpha/dt$ or temperature $-d\alpha/dT$ derivatives must be analyzed. Figure 5 shows the variation of $-d\alpha/dt$ as a function of temperature for the two analysed balsa wood samples for TGA at a heating rate of 10°C.min^{-1}. For each sample, the global degradation variation of the $-d\alpha/dt$ curve was deconvoluted into each of its constituents between 175 and 550°C. The deconvolution of the kinetic reaction well demonstrates the individual influence of the three wood components in the degradation process and the predominant mechanism at a particular temperature. Deconvolutions in figure 5 were performed considering gaussian multi-peak fittings leading to R^2 correlation coefficients of 0.991 and 0.992 for the dry and wet samples respectively; the temperature of each maximum is indicated.

we can observe that the shoulder induced by the hemicellulose decomposition is less distinct for the dry sample. The second comment concerns the maximum temperature values for hemicellulose, cellulose and lignin decomposition. These maxima are higher in the case of the wet sample. If, for the wet sample, the maximum decomposition temperature is higher by 43°C for cellulose (wood is composed with about 50% of cellulose) and by 42°C for lignin, the difference reaches 71°C for hemicellulose. However, as noticed in figure 5, thermal decomposition of balsa material starts about at the same temperature for both samples, around 215°C. Thus, it induced a more pronounced shoulder in the $-d\alpha/dt$ curve if the sample is initially moisturized. Deconvolution curve in figure 5 well illustrate the role of hemicellulose constituant in the degradation process of balsa wood. The associated peak is considerably larger for the wet sample in relation to the dry one. This means that water diffusion has a real effect on the thermal degradation of balsa since the beginning of the thermal kinetic reaction. At this point, we have to consider two types of water molecules: hydration or composition water molecules. To quantify the moisture diffusion kinetics in balsa wood, we immersed 13.0 x 13.0 x 13.0 mm^3 samples in distilled water at 40°C during 3 months. Figure 2 resumes the obtained results showing that moisture content reaches nearly 700% in full saturated 2 cm^3 balsa sample.

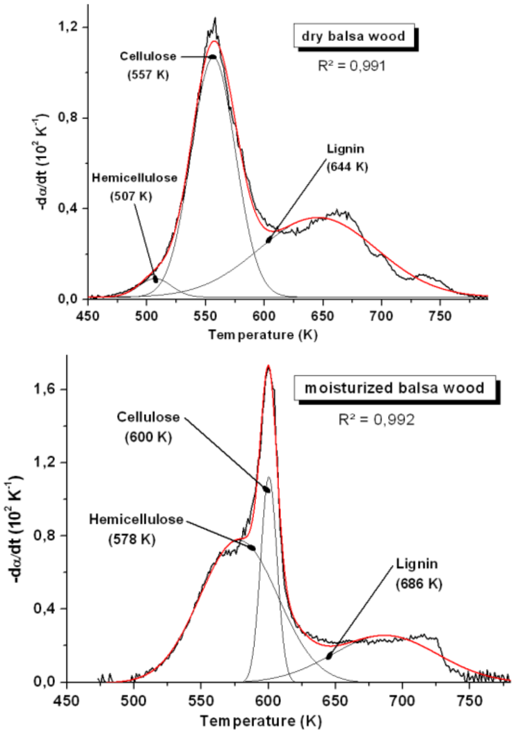

Figure 5. *Thermal degradation of balsa wood at an heating rate of 10°C.min^{-1}: first time derivative of the weight loss as a function of temperature for a dry and a moisturized specimen. Deconvoluted curves as well as the maximum degradation temperature values are showed for the three wood components*

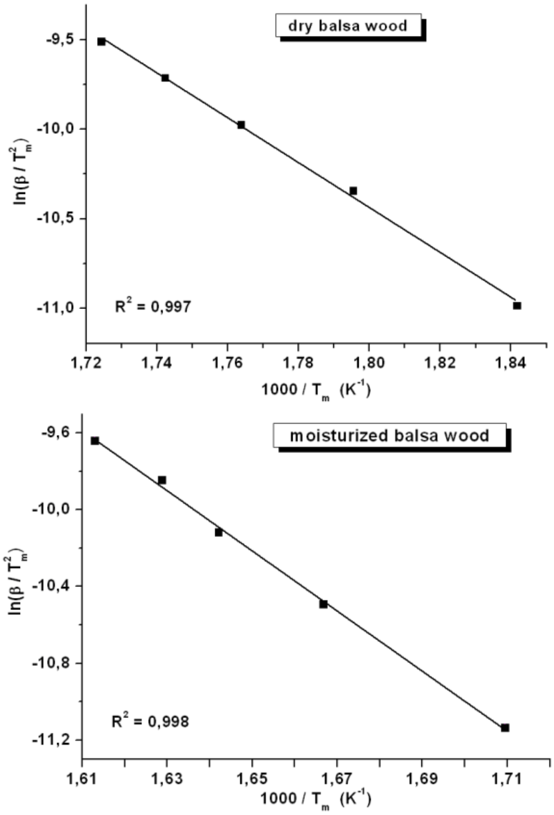

Figure 6. *Iso-conversional plot $\ln(\beta/T_m^2) = f(1/T_m)$ of Kissinger method for dry and moisturized balsa woods*

The results obtained during the TGA measurements allow to estimate the kinetic parameters using the Kissinger method. The activation energy E_a and the pre-exponential factor k_0 were determined for the dry and moisturized balsa woods from the curve $\ln\left(\beta/T_m^2\right) = f\left(1/T_m\right)$ (figure 6). Experimental data were fitted by a linear least square refinement as the slope and the exponential of the y-axis intercept are proportional to E_a and k_0 respectively. The reaction order n was derived from equation (5) (Table 1 and 2). The results are the following: E_a = 104(2) $kJ.mol^{-1}$, k_0 = 4.1(1) 10^7 s^{-1} and n = 1.13(6) for the dry balsa sample and E_a = 130(3) $kJ.mol^{-1}$, k_0 = 3.2(4) 10^9 s^{-1} and n = 1.9(1) for the moisturized balsa sample. For both materials, the calculated values are in the order of magnitude expected for biomass materials [Jiang *et al.*, 2010; Shi *et al.*, 2013]. The dry sample has a reaction order close to 1 as expected for woods. Concerning the moisturized balsa wood, the value of the reaction order is higher as its activation energy in relation to the dry sample. This is consistent with the information discussed above particularly in connection with the molecular structure. The hygroscopically aged material having a hydrogen bonds network more developed than the dry material, it must provide more energy to induced degradation, its activation energy is thus larger. The high value of the reaction order also indicates that factors influencing the thermal degradation kinetics of wet balsa are more numerous.

5. Conclusions

Moisture diffusion and hygroscopic aging in the balsa wood and their constituents were investigated in this research. The thermal decomposition of two types of infused balsa wood was investigated by thermogravimetry: dry wood and water saturated aged wood. Qualitatively, both types of wood, moisturized or not, present similar general features in the weight loss process when temperature increases and the three decomposition regions (water evaporation below 150°C, active and passive pyrolysis regions) are well marked. Quantitatively, these two different aged woods present large variations in the values of the characteristic parameters due to the moisture diffusion.

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(The Board of Editors received the paper on 11/05/2014, its review was completed on 11/06/2014)