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A physical approach in the understanding of the phenomena accompanying the thermal treatment of lignin

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Abstract

In this work, a mechanical approach is associated with the thermal behavior of lignin. Samples of lignin are submitted to a thermal treatment accomplished at different final temperatures of pyrolysis. The dimensional variations which occurred during the degradation of lignin are quantified by the Jacobian of the transformation. The increase of the Jacobian in the interval 180 to 260°C signifies the formation and the development of a plastic phase by crazing as is indicated by scanning electron microscope micrographs of lignin residues. The apparition and the evolution of the plastic phase are not a new fact in fracture mechanics, but the characterisation of this phase and the mechanics of its formation and its fracture allow us to explain some aspects until now unknown in the thermal decomposition of lignin. The importance of this work relies on the analogy made between the thermal behaviour of lignin and the mechanical behaviour of polymers. This analogy permits us to make some interpretations and, for the first time, to explain the weak weight loss and the exothermic effect of the thermal degradation of lignin. © 1997 Elsevier Science B.V.

Keywords: Crazing; Fracture; Lignin; Mechanical stress; Plastic phase; Thermal stress

1. Introduction

In most of the literature devoted to the thermal treatment of the principal components of wood, the interpretations given about the mechanisms of thermal degradation of lignin are not satisfactory. This is partly due, in our opinion, to the methodology used in the approach to these mechanisms. Indeed, in the case of cellulose, the studies based on the mass loss measurements, on the qualitative and quantitative analysis of pyrolysis products and on the comparative survey of the thermal treatment of cellulose and carbohydrates, permitted an appropriate approach to the mechanism of cellulose thermal decomposition. In adopting the same procedure, the mechanism of lignin degradation is only partially explained. These studies, oriented rather towards the chemical aspects of pyrolysis, do not seem to interpret appropriately the phenomenon of the thermal degradation of lignin, since it is an amorphous, three-dimensional polymer of very complex structure compared to cellulose. As we will show in this work, under the temperature effect, lignin under-

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goes important physical changes that are necessary to associate it with the chemical aspects of lignin pyrolysis. That is why we use the concepts of fracture mechanics to understand the physical changes that lignin undergoes under thermal stress; these changes are comparable to those of polymers when submitted to a mechanical stress. The originality of this work therefore resides in the bringing together of the thermal effects in the case of pyrolysis, and the mechanical effects in the case of fracture mechanics. This approach allowed us to draw some interpretations of the physical and energizing aspects which accompany lignin pyrolysis. The explanations given in this work have never appeared in the literature up to now.

2. Experimental part

Gunpowder lignin, commercialised by Aldrich (France), is offered by Professor A. Zoulalian of The Nancy 1 University, France. Weight loss measurements and differential thermal analysis are made on TA Instruments 2000 Thermal Analysis by Professor J. Arauzo of Saragosse University, Spain. The description of this equipment and the characteristics of lignin are given in a previous paper [1]. The weight of the sample is 5 mg, the heat rate is 10°C/min and the nitrogen flow is 15 $\mathrm{cm}^3/\mathrm{min}$.

The dimensional variations of lignin during its pyrolysis are made on cylindrical tablets of 1 mm diameter and 3 mm height. The tablets are prepared from the gunpowder and the dimensional variations are evaluated by the Jacobian of the transformation of lignin. The tablets are measured before and after pyrolysis achieved in an oven in identical operational conditions to those used in a thermobalance.

The micrographs of pyrolysed samples are held on the scanning electron microscope, GEOL JSM T-330.

3. Theory

In this work, dimensional variations of the treated samples are estimated by the Jacobian of their geometrical transformation. The Jacobian, representing the ratio of present volume (V) to initial volume (V_0) of the sample, is defined by the following expression:

$$J = V/V_0$$

$$J = 1 + \operatorname{div}\vec{u} = 1 + u_{i,i}$$

where $\vec{u}$ is the displacement vector.

The detail of demonstrations of the expression of J is given in reference [2].

4. Results and discussions

The tracings of weight loss, differential weight loss and differential thermal analysis are given in Figs. 1 and 2, respectively. The Jacobian evolution with temperature is given in Fig. 3.

The results show that the mass loss of lignin pyrolysis is accompanied by the release of heat. The literature indicates that the mass loss and the rate of mass loss of lignin pyrolysis are much weaker than

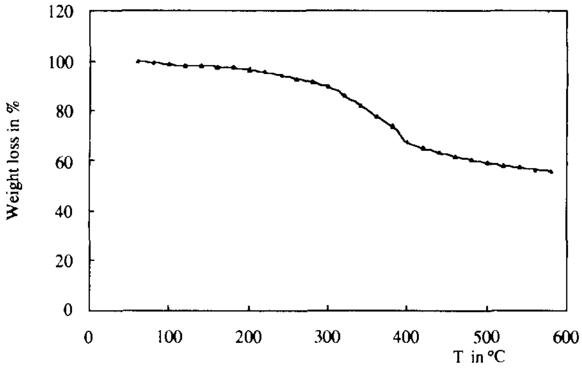

Fig. 1. Lignin weight loss versus temperature.

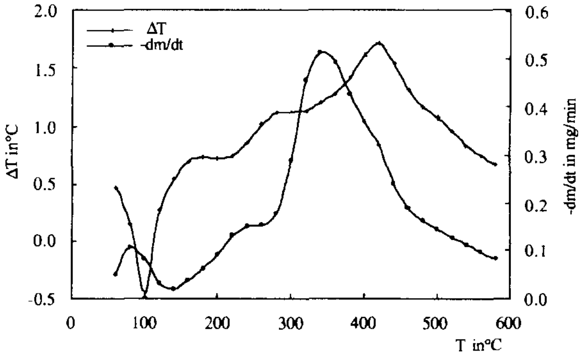

Fig. 2. Lignin differential weight loss and differential thermal analysis versus temperature.

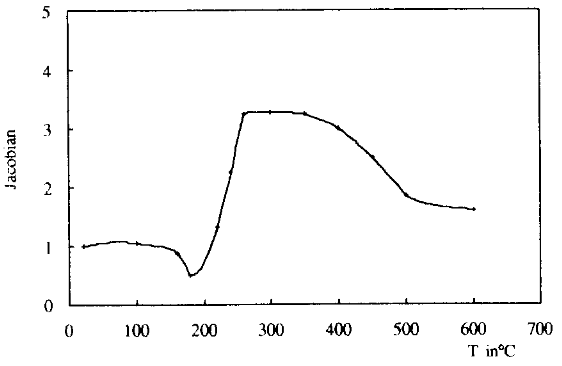

Fig. 3. Evolution of the Jacobian of lignin deformation with temperature.

those of cellulose [3–7] and that, in opposition to lignin, cellulose decomposition is endothermic [6–9]. The endothermic effect of cellulose consists of depolymerisation reactions and the volatilisation of products [3,10], but no interpretation is given for the exothermic effect of the decomposition of lignin in the literature. The difference which exists between the temperature corresponding to the maximum value in the differential thermal analysis and the rate of weight loss curves (Fig. 3) was also noticed by Capart [11] but he offered no interpretation for this. We think that this difference would be linked to the viscosity due to the inner frictions in the structure. On the other hand, Tang and Bacon [12] studied the dimensional variations of a cellulose fibre and showed that this substance contracts under the effect of temperature. In the case of lignin, an inflation is noted [13] but not quantified.

The Jacobian evolution with temperature (Fig. 3) clearly indicates four deformation zones. The first one, in the interval of 140 to 180°C, indicates a shrinkage; the second, in the interval of 180 to 260°C, shows a dilation that reaches a maximum value at 260°C. Beyond this temperature and up to 350°C, the Jacobian retains an almost constant value. In the last step, between 350 and 600°C, the Jacobian decreases, leading to a corresponding shrinkage.

In order to explain the inflation occurring between 180 and 260°C, we use the concepts of fracture mechanics. According to Friedrich [14], polymers which undergo volumic dilatation when submitted to mechanical or thermal stress, undergo plastic deformation by crazing.

Since the volume of lignin increases under the temperature effect, only a microscopic characterisation of pyrolysis residues allows us to understand the mechanisms which produce an increase in the volume of this substance. So, micrographs of lignin residues obtained at 300 and 400°C (Figs. 4 and 5) are held on a scanning electron microscope. The micrographs were interpreted by A. Kifani [15] who confirmed the formation of a plastic phase by crazing. Even though the existence of this phase has already been signalled [13], no indication has been formulated on the mechanism of its formation, or on its degradation, or on the link between the formation of this phase, the weak mass loss and the exothermic effect accompanying the reaction.

In order for the plastic phase to take place, the structure of the polymer must present some defects or heterogeneities around which crazing occurs. Its development requires a continual energy contribution [16–20], which is stored in the structure above its fracture. After that, all accumulated energy is released [16–19].

The structure of the polymer necessarily presents some heterogeneities inherent in their elaboration. In the case of lignin, the gaseous disengagement taking place at low temperatures found expression in the decrease in the Jacobian (Fig. 3). The gaseous disengagement acts as the source of microcavities or micropores in the structure of lignin, the development of which leads to the plastic phase by crazing under the effect of temperature. The heterogeneities in the case of fracture mechanics are equivalent to micropores resulting from gaseous disengagement in the case of thermal treatment. Mechanical and thermal stress concentrations take place around these defects leading to the development of microcavities.

This structure, formed of micropores surrounded by matter, requires a continual contribution of energy used for the development of the micropores and for the straining of the matter. When the strain of the fibrils surrounding the micropores reaches a critical value, some fibrils break, leading to microcracks and releasing of energy used for their formation. This stage could be the origin of the first exothermic peak between 200 and 280°C in the differential thermal analysis curve (Fig. 2), since the thermal energy stored in the lignin during its pyrolysis is freed in

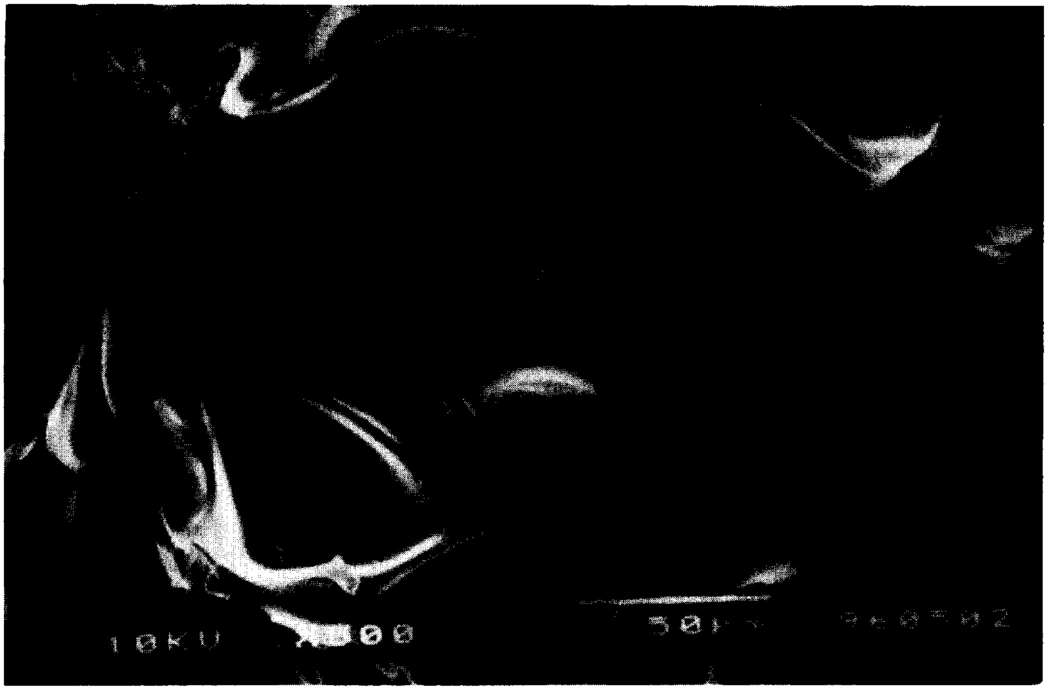

Fig. 4. SEM micrograph of lignin sample pyrolysed until 300°C.

Fig. 5. SEM micrograph of lignin sample pyrolysed until 400°C.

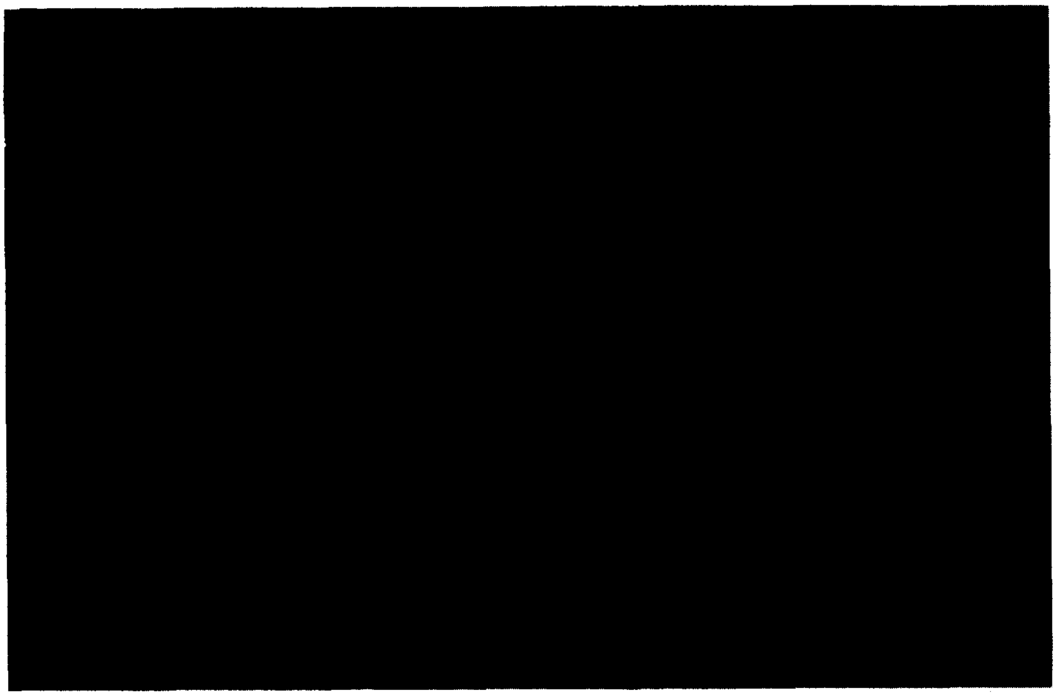

Fig. 6. SEM micrograph of lignin sample pyrolysed until 450°C.

Fig. 7. SEM micrograph of lignin sample pyrolysed until 450°C.

the form of heat alongside the formation of microcracks.

The microcracks are not produced at the same time in the structure because of the anisotropic heat propagation, probably due to the polymerisation of the matter. During the propagation of stable microcracks, the Jacobian keeps a constant value. When the crack length reaches a critical value, the fracture of the structure occurs. The scanning electron microscope micrograph of the lignin sample pyrolysed until 450°C (Figs. 6 and 7) clearly shows the apparition of cracks which indicate the fracture of the plastic phase. With the fracture of this phase, the heat accumulated during its formation and development is completely released, explaining the exothermic effect accompanying the thermal degradation of lignin and corresponding to the second peak after 320°C in the differential thermal analysis curve (Fig. 2).

Once the plastic phase is broken, the Jacobian decreases (Fig. 3). This may be explained by stress relaxation and therefore by the contraction of microvoids and fibrils in other zones of the structure, following fast crack propagation.

5. Conclusion

In this work, we explain the exothermic effect of the pyrolysis of lignin by the formation of plastic phase by crazing, which releases, during its damage, all the heat necessary to its formation and to its development.

The weak mass loss is due to the plastic phase which conserves the matter. The Jacobian evolution indicates the different phases of the pyrolysis of lignin. A good correlation is found between the geometrical deformations and the results of differential thermal analysis.

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