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Analysis Of Thermal Degradation Of Biofilms Made Of Cassava Starch Reinforced With Coconut Fibers

Doumbia Ahmed[1], Traore Seydou[2]

[1]Jean Lorougnon Guédé University, Earth Sciences Department, Faculty of Environment, Daloa, Ivory Coast, B.P. 150 Daloa

[2]Félix Houphouët-Boigny University, Physics, Electronic and Telecommunication System Department, Faculty of Sciences of structures of Materials and Technology, Abidjan, IvoryCcoast, 01 bpv 34 abidjan 01

Correspondence Author: Doumbia Ahmed, Jean Lorougnon Guédé University, Earth Sciences Department, Faculty of Environment, Box 150 Daloa, Ivory Coast
E-mail: Fackoly1@gmail.com
https://orcid.org/0009-0006-7507-6925

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ABSTRACT: Thermal degradation (or thermolysis) is explained by the breakdown of molecules under the effect of heat. The analysis of thermal degradation of polymer materials makes it possible to determine their stability conditions. It is therefore important, for the development of these materials, to know these conditions. The material subject of this study was developed during our thesis work. It is a biofilm made of starch and reinforced with coconut fibers. The previous article consisted of the analysis of its water behavior. The aim of this work is to analyze its thermal behavior. To do this, we carried out a thermogravimetric analysis followed by a differential calorimetric study. Regarding the first, the measurements were carried out with a TA/STD 2960 Series analyzer under an argon atmosphere in a temperature range from 100 °C to 950 °C with a sample mass equal to 10 mg. The differential calorimetric analysis was carried out with a Peklin Elmer Dimond DSC unit at atmosphere for a temperature varying from -100 to 250°C with a heating rate of 20 °C/min. The results obtained show, on the one hand, that the composite has stable thermal behavior in the temperature range of [-4°C, 40°C]. On the other hand, in this same range, there is no loss of mass. All this adds up to saying that we can use this biofilm under usual temperature conditions. In addition, this analysis confirms that the material developed is suitable for use in the field of packaging.

Keywords: *starch, cassava, coconut fibers, film, degradation*

INTRODUCTION

Thermal analysis of materials, particularly biopolymers, characterize their behavior when subjected to external thermal constraints. This makes it possible to anticipate performance or potential degradation in specific thermal conditions throughout their life cycle. This knowledge helps predict their thermal behavior (Thermoconcept Sarl, 2023). This is the case for starch-based composites, which have a very temperature-dependent state (Doumbia, 2020). When heated in the presence of water, the starch grain from a temperature of 60 oC passes successively through three states: swelling, gelatinization and solubilization. A physical gel forms during cooling; this is retrogradation (Bélibi, 2013; Sihem, 2015; Khatem, 2019). It is therefore important to control these phases and to know their effects on the degradation of the material. This work aims to analyze the effects of temperature variation on a biofilm made from cassava starch reinforced with coconut fibers. To do this, we will conduct a thermogravimetric analysis followed by a differential thermal analysis. OnOn one hand, it seems that the composite has thermal stability in the

temperature range [-4ºC, 40ºC]. On the other hand, we observe that there is no loss of mass for these same temperatures. We can, therefore use this biofilm under usual temperature conditions. Finally, this study confirms that the film can be used in packaging.

MATERIALS AND METHODS

Presentation of the composite film

The material subject of this study is a composite film based on cassava starch reinforced with coconut fibers. It was developed during our thesis work (Doumbia, 2020). Table 1 summarizes the proportions of different inputs used. The composite is shown in Figure 1.

Table 1: Final proportions of inputs retained for the formulation of the film

Inputs	Water/(water+starch)	Starch/(water+starch)	Glycerol/Starch	Fibers/Starch	Lime/water	Anti-foaming /(water+starch)
Mass rate (%)	90	10	45	3	0.32	4

Figure 1: Photo of the composite film

Thermogravimetric analysis (TGA)

Thermogravimetry measures the variation in the mass of a sample subjected to heat treatment. It is therefore a quantitative analysis. It makes it possible to highlight the chemical, physical or physicochemical phenomena which occur, under the effect of temperature, under a controlled atmosphere, from the variation in the mass of the sample investigated. modelA thermo balanceA thermo balance determines the variation in the mass of the sample determines the variation in the mass of the sample as a function of the temperature or the duration of the treatment under a controlled atmosphere (Nitrogen or Argon or Helium inert gas) for tests at high temperature or, under a dioxygen oxidizing atmosphere. Thermogravimetry is therefore the work of four actors: the sample, the mass, the duration, the environment.

The objective is to characterize the materials by directly measuring their mass variation by interpreting the thermogram which corresponds to the degradation of the material, here the polymer, and therefore to the phase release. It also makes it possible to determine kinetic parameters such as the activation energy (Assanvo, 2015). The testing temperature range is 100ºC to 950ºC and each sample has a mass equal to 10 mg (Fig. 2).

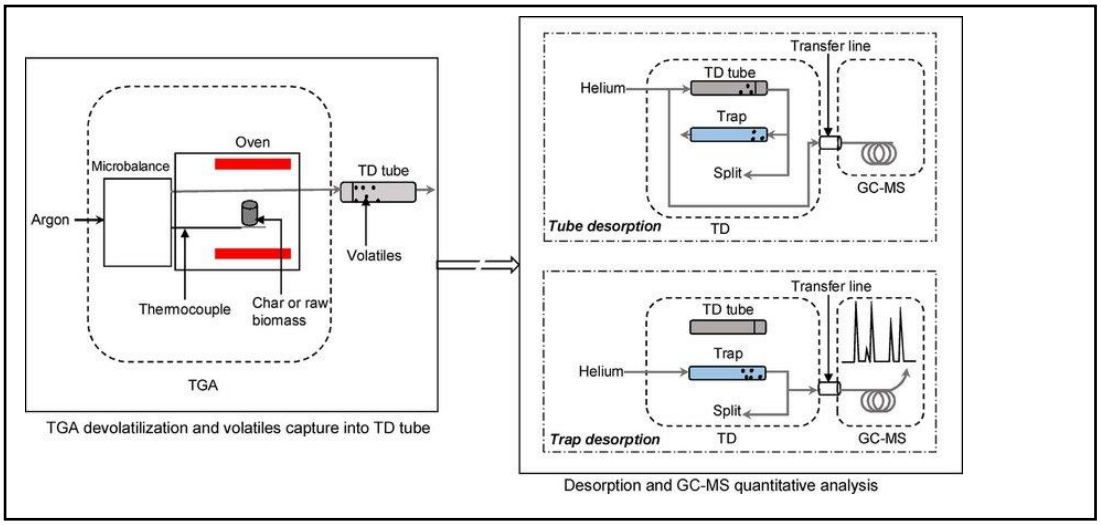

Figure 2 : Schematic diagram of thermogravimetric analysis

Generally speaking, the degradation of solid polymers can be translated by:

$$A_{solid} \rightarrow B_{solid} + C_{gaz} \quad (1)$$

with A, the starting material, B the material after the loss of function or molecules and C the gas released following heat treatment. The measurements were carried out with TA/Series STD 2960 analyzer under an argon atmosphere.

Differential scanning calorimetry (DSC)

DSC makes it possible to study the thermal transitions of materials to determine their particularities such as the glass transition (T_g), the crystallization temperature (T_c) or the melting temperature T_f. Figure 3 gives its principle diagram.

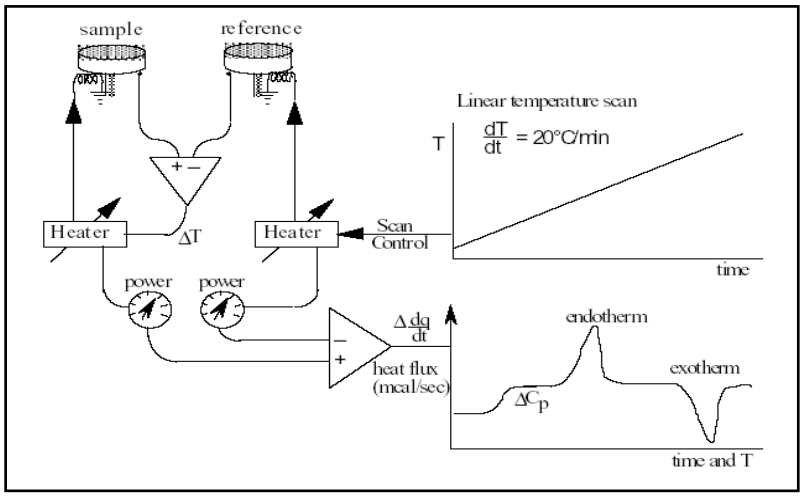

Figure 3 : Schematic diagram of an analysis DSC (Perken Elmer DSC)

In addition to verifying the purity of a polymer, DSC is also used to measure its degree of crystallinity. This property is important because it directly affects physical characteristics such as permeability, density or melting temperature. Additionally, DSC can provide insight into the degradation of a polymer, which usually results in a drop in its melting temperature. This involves measuring the energy required to heat a sample as a function of temperature, relative to a reference. We also speak of measuring enthalpy (or heat flow) as a function of temperature. The device therefore adjusts the quantity of energy transmitted to the sample so that its temperature remains identical to that of reference. A DSC analysis is in principle carried out under inert gas (nitrogen or argon) to avoid a reaction of the sample with the air in the chamber. Analysis was performed using a Perkin Elmer DIMOND DSC unit. The measurements are carried out in the atmosphere on 2 to 5 g of the polymer sample weighed in aluminum trays subjected to a heating rate of 20°Cmin^{-1} over the temperature range from -100 to 250°C.

RESULTS

Thermogravimetric analysis

Figures 4. give the curves of the thermogravimetric analysis TGA (a) and its derivative (DTG) of films based on cassava starch plasticized with glycerol at a heating rate of 20°Cmin^{-1}. The TGA curve (Figure 4.a) shows a rapid decrease until near the mass percentage equal to 23%, which admits a horizontal asymptote.

The DTG curve (Figure 4.b) indicates four main stages of material decomposition. The first stage is from 25 to 100°C, the second from 100 to 200°C, the third from 200 to 360°C and the last from 360 to 600°C.

At the first stage, the low mass loss is due to the presence of residual water in the film, considering the exposure humidity. As the temperature rises in the composite in the next phase, the evaporation of water and the breakdown of polymer bonds promote greater loss than before. This increase becomes more remarkable from 200°C to a maximum reached at 292.51°C. After this peak, the proportion of remaining composite is considerably reduced; which results in a progressive reduction in mass loss up to 600°C.

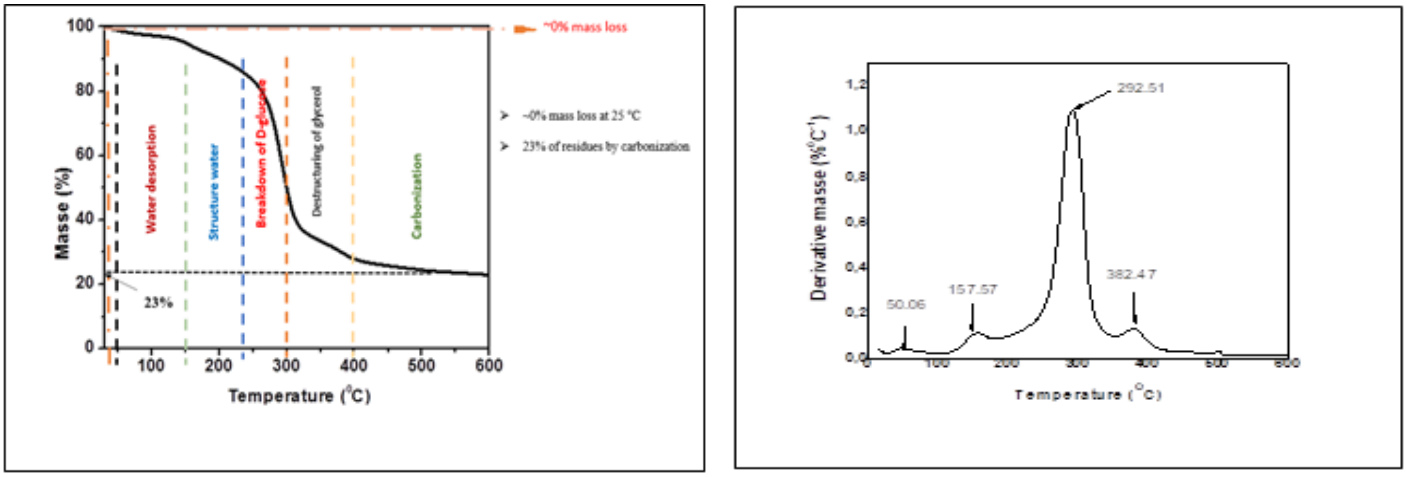

Figure 4 : Curves (a) TGA at the heating rate of 20oC.min-1 (b): DTG curve at the heating rate of

Differential scanning calorimetry

Figure 5 shows the DSC thermograms as a function of the relative humidity of cassava starch plasticized with glycerol and reinforced with the coconut microfibers. The thermodynamic values found are given in Table 2.

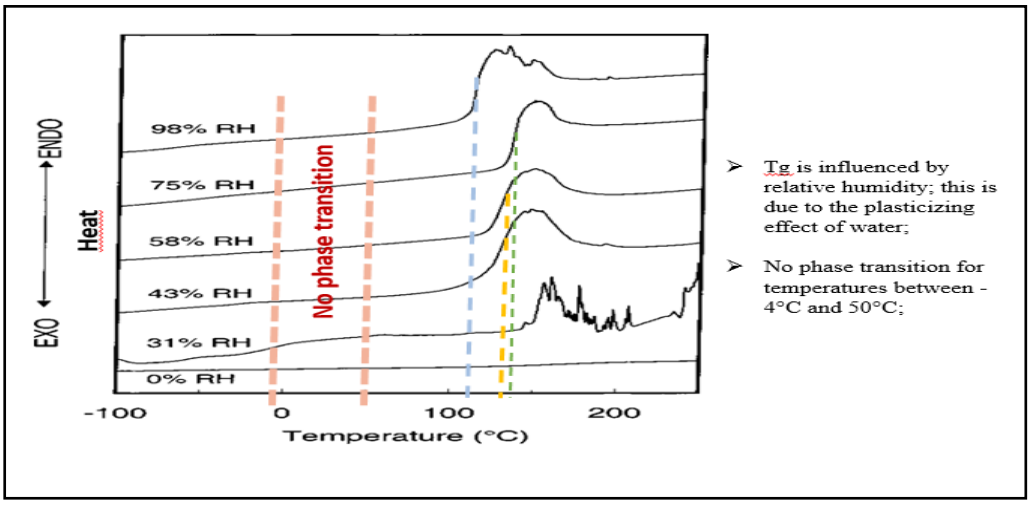

Figure 5 : Thermo-grams and Influence of the relative humidity of cassava starch plasticized by glycerol and reinforced by coconut

The analysis is carried out by exposure under six atmospheres of different relative humidity (98%; 75%; 58%; 43%; 31% and 0%) to take into account the water's effect on the material's thermodynamic characteristics. We observe a decrease in T_g when humidity (and therefore water content) increases. We note a flattened shape of the thermogram for a relative humidity of 0%. The thermogram presents a succession of narrow, line-shaped peaks. When the relative humidity increases from 31% to 43%, the melting temperature T_f decreases from 146.2°C to 137.4°C. The highest values of the heat of fusion are above a relative humidity of 31%. However, it stabilizes from 75%. Furthermore, for a relative humidity around 53%, the water content is estimated at 20.1% with a T_g approximately equal to 37.2°C.

Table 2: Impacts of relative humidity on thermal transitions determined from DSC curves.

RH (%)	Water content (%)	T_g (°C)	ΔC_p ($J.g^{-1}.K^{-1}$)	T_m (°C)	ΔH_m ($J.g^{-1}$)
0	3.7	11.1	0.42	----	---
31	14.6	6.7	0.34	146.2	132
43	19.6	-33.8	0.43	137.4	879
58	23.3	-38.3	0.65	131.8	987
75	26.2	-59.4	0.73	126.6	852
98	32.1	-63.2	0.52	125.4	876

RH : relative rumidity; Tg : glass transition temperature; ΔC_p : massic heat; T_m : melting temperature; ΔH_m : mass enthalpy

DISCUSSION

Thermogravimetric analysis

The greatest decomposition appears at the third stage (from 200 to 360 °C). The first stage (25 to 100 °C) of decomposition corresponds to the evaporation of the water contained in the sample. The second stage (from 100 to 200 °C) indicates the decomposition of the cross-linked polymer,and the third is due to the decomposition of the more stable cross-linked polymer formed in the second stage. The last step (360 to 600 °C) shows the residual volatilization of the remains of the unreacted sample (Avérous et al., 2000; Konwar et al., 2015). Thus, under ambient conditions, the material does not decompose. Decomposition heat's influence is because decomposition occurs at temperatures much higher than ordinary temperatures. Along with this, Garcia et al. (2009a) showed the ATG spectrum of cassava starch that had been softened with glycerol but not reinforced. This work's spectrum shows a higher residual mass rate for the composite, at 223%, compared to that of the unreinforced matrix, which is about 9% (Garcia et al., 2009a; Garcia et al., 2009b). The report by Garcia et al. (2009b) confirms this increase, which finds a rate of around 17% of mass residues with corn nano-crystals as reinforcements. This residue level is due to the presence of coconut fibers and, therefore, the reinforcements' nature, which have good heat resistance and a low degradation rate (Van et al., 1994).

Differential scanning calorimetry

The decrease in T_g when humidity (and therefore water content) in the environment increases is due to the plasticizing effect which causes film softening (Trommsdorff et al., 1995; Mathew et al., 2002; FAO, 2023). Indeed, during storage, if the sample receives heat δq, to therefore keep its internal energy state U, it will provide work δW such that:

$$dU = \delta q + \delta W \quad (2)$$

It is this work which will lead to the rearrangement of the amorphous starch chains, and lead to the formation of crystalline domains by the amylopectin chains. This decrease in T_g when the humidity level increases, for glycerol-plasticized and reinforced cassava starch-based films, remains valid for unreinforced films by the reports Assanvo (2015) and Garcia et al. (1996). During this process the glycerol can be expelled from the crystalline zones; increasing the plasticizer ratio in the amorphous parts.

Following plasticization, the amorphous regions increase and consequently the Tg decreases. Conversely, during this reduction, the amylopectin chains become more mobile leading to increased crystallinity during storage. The crystalline domains function as cross-links and slow down the relaxation of the amorphous parts of amylopectin, promoting an increase in the glass transition temperature T_g.

The flattened shape of the thermogram at 0% RH indicates an amorphous structure of plasticized cassava starch (Anglès et al., 2000). Also, unlike virgin films (Assanvo, 2015), at a relative humidity of 30% and high temperatures, the present thermogram presents a succession of narrow, line-shaped peaks indicating the presence of fibers which create thermal heterogeneity within the film. material. The lower values of the melting temperature T_f, when the water content increases, are linked to two phenomena which coexist: the reorganization and crystallization of molecules due to the effect. Indeed, when the relative humidity increases from 31.4% to 41.7% for unreinforced films, the melting temperature drops from 131°C to 116°C (Assanvo, 2015). For the reinforced films in the present study, when the relative humidity increases from 31% to 43%, this temperature T_f decreases from 146.2°C to 137.4°C. For approximately equal relative humidity values, melting occurs for reinforced films than virgin films.

Thus, the very high mobility of the amorphous chains causes large crystalline zones to appear for higher melting temperatures, which decrease when relative humidity increases. With increasing crystalline areas, amorphous chains become less mobile. This leads to strengthening the network by forming physical cross-links and stabilizing the retrogradation phenomenon. This decrease is due to increased plasticization at high relative humidity.

The appearance of the highest values of the heat of fusion above 31%RH is explained by the formation of crystalline domains with increased water content and increased water content and more mobile amorphous chains. However, it stabilizes from 75% RH showing a decrease in the mobility of amorphous zones in favor of crystalline regions. For unreinforced films, two transitions are observed from a relative humidity equal to RH = 14.6% (Assanvo, 2015) this is the same for the present work thermograms. This phenomenon occurs for the present work's thermograms, but only at 31 %RH.

These observations can be explained by brown coconut fibers with good heat resistance and a low degradation rate (FAO, 2023). With the values of the T_f determined (Table 2.), we see that under ordinary conditions of use temperatures, the material cannot reach a melting state whatever the relative humidity.

In addition, for a relative humidity of around 53% RH, the water content is estimated at 20.1% with a T_g approximately equal to 37.2°C. This relative humidity value is conducive to the material's use conditions relating to water content and temperature.

CONCLUSION

Thermal analysis is of capital importance because it makes predicting damage to manufactured materials possible. The material studied was a composite film based on cassava starch reinforced with coconut fibers. For this study, we conducted a thermogravimetric analysis and a differential calorimetric analysis of the composite. The results revealed convincing behavior of

the material. There is thermal stability of the film between -4°C and 40°C. In addition, the mass loss in this temperature range is almost zero. We can therefore use this composite under usual temperature conditions. Finally, this study confirms that the film can be used in packaging. The next article will focus on the analytical and numerical study of the damage of this composite.

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Conflict Of Interest:
The authors declare no conflict of interest.

Author's Contribution : Doumbia Ahmed : writing manuscript, data collection, data analysis, and interpretation; Traoré Seydou : data collection, reviewing and editing of the manuscript.

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