Study Of The Thermal Stability Of Nano-Filament Of Polyamide 6 With Lignin C Obtained By The Electrospinning Method

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Abstract – This study focuses on the thermal stability of polyamide 6 with lignin, which is a flame retardant. In this study, we used the electrospinning method to produce nano-filament and to analyse the thermal stability of these filaments. The higher the voltage, the more difficult it will beto produce a bead-free spinning. This is done by varying the electric field and observing the presence or absence of "beads" on the non-woven. Figure 2 shows a SEM photo of polyamide 6 nano-filaments for the voltage value 14kV, the photo obtained corresponds to a spinningunder 14 kV. It can also be seen that decreasing the voltage to 9kV has the effect of creating polymer "beads" in the nonwoven structure, Figure 2 SEM photo a. The morphological structures and thermal properties of PA-6 were characterised by scanning electron microscopy (SEM), differential scanning calorimeter (DSC), thermogravimetric analysis (TGA). The thermal stability of PA6-LC nano-filaments was carried out by TGA, the TG and DTG curves of PA6 -LC nano-filament are presented in Figure 4. The decomposition of PA6-LC corresponds to an average of 404%, whatever the concentration of lignin C (2% LC up to 7.5% LC and 15%LC) and the maximum degradation rate of PA6-LC is on average 2.02% /°C.

Keywords – electrospinning; nano-filament; structure and morphology; thermal properties.

I. INTRODUCTION

Polyamides are technical materials used in an increasing variety of areas, such as the sports and leisure industry. Fibres are a particularly important application for polyamides because of their good mechanical properties. They are used in textiles. Spinning of polyamide 6 mixed with lignin occurs when the electrostatic forces at the surface of the liquid exceed its surface tension and cause the electrically charged polymer to be ejected and hit a target surface called the collector (fig.1). The charge repulsion in the polymer stretches the polymer to form nano-filaments that are deposited in fibrous webs (nonwovens) of less than 12 grams per m². Nano-filaments with diameters of less than600 nm, or even between 50 and 200 nm, are produced by these electrospinning processes. The lightness and extreme fineness of the fibres make it possible to envisage applications in the textile, medical and filtration fields [1]. Numerous parameters of both the polymer and the machine influence whether or not nano-filaments are obtained and the diameter of the nano-filaments:

-The nature of the polymer, its structure, molecular weight, mass distribution, concentration,conductivity and surface tension

-The distance between the needle and the collector, the applied voltage, the polymer extrusionrate and the ambient conditions of temperature and humidity [2,3].
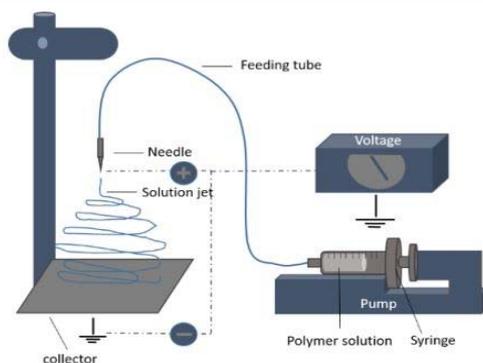
Figure 1: Vertical electrospinning device assembly [4].

II. MATERIALS

Polyamide 6 was supplied by BASF SE(Europe), formic acid by Prolabo, France as solvent andfinally lignin supplied by Sigma-Aldrich. The parameters, which were kept constant during all experiments, are presented in Table I below.

Polymer	Polyamide 6 (PA-6)
Flame retardant	Lignin C (L-C/LC)
Solvant	Formic acid (AF)
Flow	Flow rate (ml/h) : 0,1
Needle	Needle diameter (G) :45
Ambiant parameter	Température (°C) : 23
	Humidity : 21%
Spinning time	20minutes

The internal diameter of the needle or nozzle is also a necessary parameter to set before starting the electrospinning process

III. METHODS

a. Preparation of the electrospinning solution

Table 1. Description of polymer and solvent

	Polymer : PA-6
Molecular weight (g/mol)	10,000
Density (g / cm^3)	1.084
	Formic acid (AF)
Molar mass (g / mol)	46,02
Density (g / mL)	1,22
Pureté (%)	99
	Lignin
Density(g / cm^3)	1.3
Purity (%)	99

The mass of polyamide and lignin was measured using an analytical balance, dissolved in formic acid to obtain a homogeneous mixture. The

solution was stirred for 24 hours on a magnetic stirrer with a speed of 150 rpm, in a temperature of 80°C and then cooled and inserted into the syringe to be electro-filtered. The concentrations of the different solutions were presented in Table III. For the spinning to result in nano-filament, there is a critical concentration above which it is necessary to go [5,6].

The concentration of the polymer solution (PA6 - Lignin) plays an important role in the electrospinning process. It is the critical key in determining the diameter and morphology of the fibres.

Table 2. Concentrations of solutions

Tests	C (%) Polyamide-6	C(%) Lignin	C (%) Formic acid
1		2	83
2		3	82
3	15	5	80
4		7.5	77.5
5		10	75
6		15	70

Polymer concentration is one of the most important factors to be considered when electrospinning. The critical concentration above which the thinnest and most homogeneous fibres possible should be obtained is 15% PA -6 but varying the concentration of lignin C 2 to 15%.

IV. RESULTS AND DISCUSSION

b. Techniques for characterising solutions

Viscosity also plays an important role in the electrospinning process, particularly in determining the optimum concentration range from which nano-filaments can be produced. Generally, if the viscosity is low enough, the initial jet gradually takes on the shape of a string as the less viscous, solvent-rich regions form droplets instead of fibres due to the predominant surface tension [6,7].

Table 3: Electrochemical properties of solution

Solution	Viscosity (mPa)	Electrical conductivity (µS/cm)	Surface Tension (mNm)
PA/AF/L-C1 2%	322	1252,51	39,98
PA/AF/L-C2 3%	334	2100,77	40,13
PA/AF/L-C3 5%	346	3490,70	40,83
PA/AF/L-C4 7,5%	358	4053,74	40,94
PA/AF/L-C4 10%	370	5345,36	40,96
PA/AF/L-C5 15%	382	6234,35	40,97

The conductivity of the solution plays a less important role than the other parameters. Indeed, several researches have shown that highly conductive solutions cause jet instabilities in the presence of high electric fields leads to bending instabilities and causes a wide diameter distribution

of the resulting nonwoven [8,9]. Surface tension is the main force that opposes the repulsive force of charges on the surface of the jet. It is a characteristic that depends mainly on the solvent used (Formic Acid). This property of the solution plays an important role in the electrospinning process.

Indeed, a too high surface tension can cause the same consequences as a too low viscosity, i.e. it inhibits the electrospinning process by causing instabilities in the solution jet with the appearance ofpearled filaments.

c. **Electrostatic spinning**

Once the solution has been prepared, the parameters controlling the electrospinning process must be addressed. These are related to the set-up used. To ensure the electrospinning process, a high voltage is applied to create an electrically charged jet of polymer solution at the needle. The charges on the surface of the solution cause a force directly opposite to the surface voltage [10, 11], so as the electric field strength increases, the hemispherical surface of the solution at the tip of the needle becomes increasingly sharp, forming a so-called Taylor cone [12, 13].

Table 4. Properties of the spinning device

Tests	Voltage (kV)	Distance (cm)	Flow rate (ml/h)
1	9	7	0,1
2	10	10	0,1
3	14	13	0,1
4	18	16	0,1
5	22	19	0,1
6	26	22	0,1
7	30	23	0,1
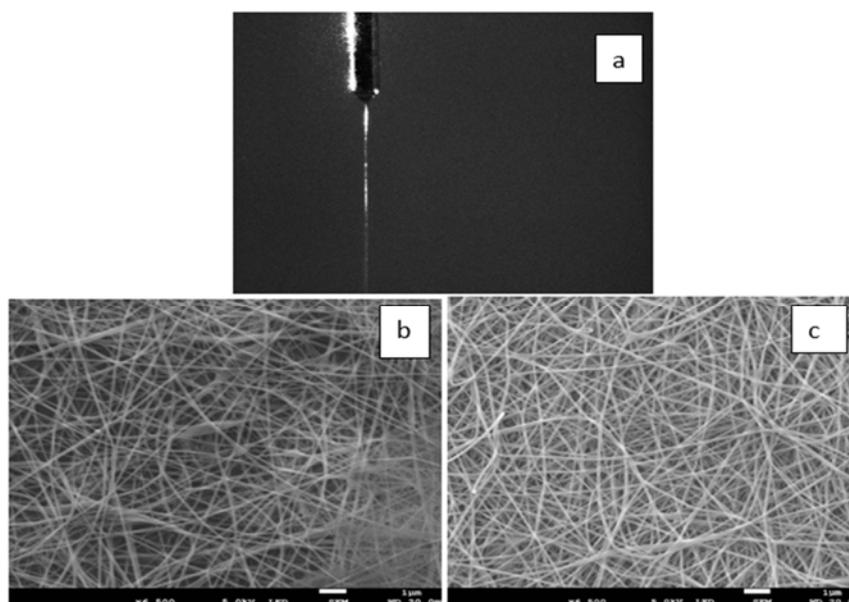
Figure 2. Taylor jet: a), PL-6/L-C filaments as a function of voltage and distance in solution: b) 9kV, 7cm; c) 14kV,13cm.

The previous figure shows that the formation of the "pearl" instabilities starts to appear with a voltage of 9kV, distance of 7cm, and that by increasing these two parameters, it causes a change in the morphology of the filaments obtained c).

V.THERMAL ANALYSIS

a. Differential scanning calorimetry (DSC) analysis

To carry out this analysis, 20 mg of the nano-filament films are introduced into the aluminium capsule. The capsule is then placed in an oven and undergoes the thermal cycle chosen according to the formulation. At the end of this cycle, the capsule is immediately immersed in liquid nitrogen in order to stop the cross-linking as quickly as possible. The sample thus prepared is then analysed by DSC under nitrogen at a rate of 10°C/min.

The following figures show the DSC thermograms recorded during the heating and cooling cycle of PA-6/L-C nanofibres at 10°C/min between 25°C and 300°C.
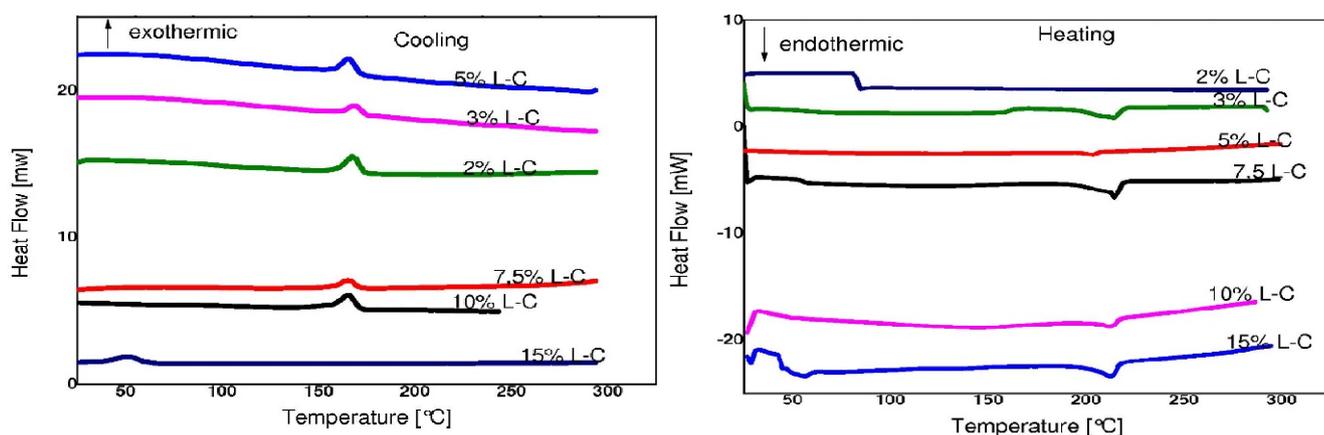
Figure 3: DSC thermograms of electrospun fibres

During the first temperature rise, the melting temperature T_f (85 to 215°C) and the enthalpy of fusion ΔH_f of the sample were measured. During the temperature decrease, the cooling crystallisation temperature T_c (52 to 167°C) and its enthalpy ΔH_c were also observed.

Table 5. Thermal properties of PA-6 and L-C nano-fibres

Material	Concentration(%) Lignin-C	T_c (°C)	T_f (°C)	T_g (°C)	ΔH_c (J/g)	ΔH_f (J/g)	X_c(%)
	2%	168	85	60	39,23	34,76	23,49
	3%	167	213	62	47,45	39,26	28,24
Polyamide-6 Lignin-C	5%	164	202	63	58,76	45,63	35,61
	7,5%	165	215	61	61,26	48,12	37,12
	10%	165	212	62	67,12	55,51	40,43
	15%	52	214	59	71,02	41,39	46,12

Thermal analysis is a technique that allows a quick estimate of the crystallinity rate from the enthalpy of fusion calculated during a heating cycle. However, it is necessary to know the enthalpy of fusion of the pure crystal as it is involved in the calculation [14,15].

A clear evolution in the thermograms can be seen by observing an increase in the melting temperature at 214°C with the increase in lignin C, with the increase in the crystallisation rate of 46.12%. From 2% Lignin, the crystallisation temperature increases progressively and decreases to 15% Lignin.

Increasing the lignin from 5 to 10% by weight in the polymer solution results in an increase in the enthalpy of fusion (and crystallisation) from 45 to 71 $J.^{g-1}$, corresponding to an increase in the crystallisation rate content from 35.61 to 46.12%. The weight of lignin has significant effects on thephase change temperature transition.

b. Thermogravimetric analysis (TGA)

Thermogravimetric analysis aims to characterise materials by direct measurement of mass loss as a function of temperature and/or time.

It measures the variation in mass of a sample when it is subjected to a temperature program, under controlled atmosphere. This variation can be a loss of mass (vapour emission) or a gain (gas fixation, oxidation). Experiments can be performed in an oxidising or inert atmosphere.
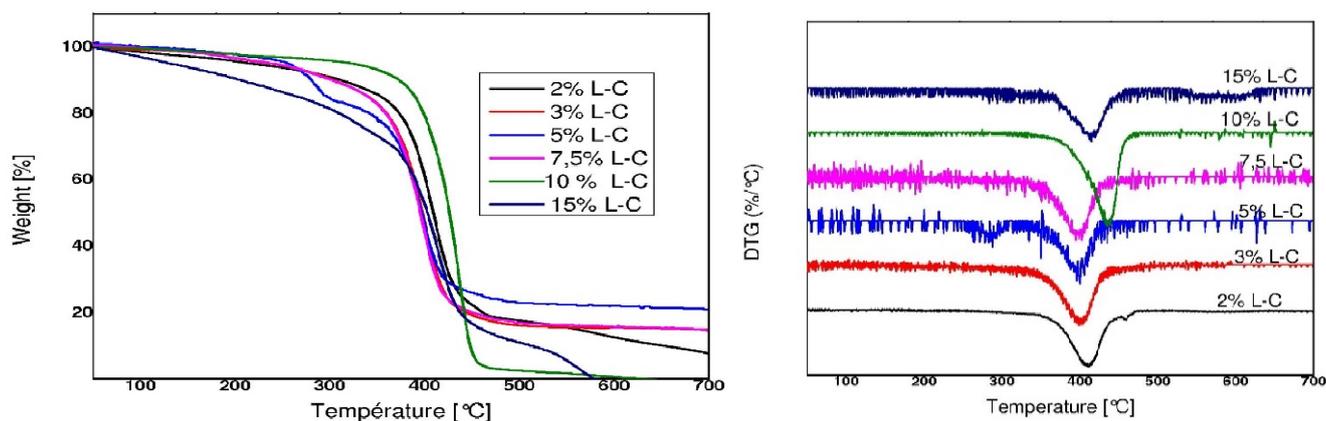
Figure 4: TG and DTG curves of nano-fibres

The thermo-microbalance used for thermogravimetric measurements of degradation in isothermal mode. It has a resolution of 0.1 µg. It operates between room temperature and 1000°C, with heatingrates freely adjustable between 0.001 and 100°C/min.

The degradation temperatures are higher according to the literature [16], the maximumdegradation temperatures in the first stage are significantly lower than the compound raw temperature. On the other hand, when the lignin weight is higher the maximum degradation temperature increases. The maximum degradation temperature with a lignin weight of 15% gives us a low residue content of 10.91%. In this region corresponds to a mass loss of 33.3% due to the departure of solvent molecules trapped in the pores of the compound.

Table 6. Thermal properties of PA-6 nano-fibres

Sample	Initial degradation temperature	Weight loss (287-500°C) (%)	Maximum degradation temperature (°C)	Maximum Degradation rat (%/°C)	Residue at 700 ° C (%)
2% L-C	388,33	72,70	411,70	2,1	12,86
3% L-C	385,56	69,02	400,50	2,1	14,09
5% L-C	384,76	56,78	398,60	1,9	16,74
7,5% L-C	383 ,23	52,17	397,30	1,9	15,22
10% L-C	393,69	80,69	438,80	3,2	11,97
15% L-C	381,64	51,23	412,10	2,1	10,91

VI. CONCLUSION

The study of the stability of PA-LC polyamide in the case of electrospinning has enabled progress to be made in understanding the interactions between the properties of this polymer and the processing conditions during electrospinning. The thermal stability of PA6-LC nanofilaments was analysed by ATG. The TG and DTG curves of PA6-LC nano-filaments are presented in the table "Thermal properties of PA-6 nano-fibres". The thermal behaviour of PA6-LC nano-filaments was influenced by the weight of the lignin and the solvent (formic acid) and shows a one-step degradation under N2 atmosphere. To study the stability of PA6-LC, we performed thermogravimetric tests.

In addition, the experimental protocol adopted in the DSC measurements is consistent and close to the theoretical values reported in the literature for the different thermodynamic properties measured [17].

PA6 -LC based nano-filaments show a maximum degradation in one step. This stage is between 398 and 412 °C and is attributed to the degradation of PA6 -LC. The presence of lignin C (LC) has no effect on the initial degradation temperature, which is around 381°C. During the maximum degradation a phenomenon occurs on the surface of the sample, the PA6-LC melts, and all nano-filament samples are in a liquid state.

Different experimental techniques have been used in our work for the physicochemical characterization of the studied nano-filaments: viscosity, electrical conductivity, surface tension, SEM, thermogravimetric analysis, differential scanning calorimetry analysis. However, some aspects on the analysis of PA6-LC need further analysis and interest in order to increase the realism of the application of these nano-filaments in the field of smart textiles.

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