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DEVELOPMENT OF A THERMOCOMPRESSION MANUFACTURING PROCESS ADAPTED TO FLAX-EPOXY LAMINATED COMPOSITES

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Abstract
This study focuses on the optimization of a manufacturing process adapted to flax fibers based composites in which the components are controlled. Twelve plies unidirectional composites samples were prepared by thermocompression using unidirectional flax fibers and fluid epoxy-amine resin. Temperature cycle was chosen to limit fibers degradation during fabrication. Different parameters have been studied to evaluate their influence on the mechanical properties of composites. 0° tensile specimens were tested at a 1mm/min crosshead speed. Measures were performed with a 50mm gauge length extensometer and a 100kN load cell. Furthermore, DSC analyses were performed to obtain information about cross-linking of the matrix. Properties are in accordance with the literature. Using 3bar pressure, fiber content was found to be around 46% (in volume). The density of the composite was measured using Archimedes' principle and was valued to 1.28 when the fibers' one was 1.45.

Keywords:
Composite; flax; process

1 INTRODUCTION

For decades, synthetic fibers have been developed and are used to craft laminated composites materials which are controlled and competitive in many areas. However the environmental footprint of this composites are not negligible. And in a context in which regulation encourages companies to reduce environmental impact of their materials supported by public opinion which is more and more sensitive to this issue, vegetal fibers can be a viable solution to replace synthetics ones. Indeed, the low density of vegetal fibers, such as flax (≈1.45), enables them to have comparable specific properties as glass fibers [Charlet, 2008] [Coroller, 2013]. This is why the idea of using this kind of vegetal fibers to replace glass fibers in some application, such as automotive or building, and lower environmental impact of laminated composite materials has emerged. The production of vegetal fibers adapted for this kind of application needs 60% less energy than glass fibers production [Brosius, 2006]. For some years, the flax industry is developing new production techniques to propose fibers with adapted properties and formats to manufactured composite materials. But the structure of flax fibers is complex and results of the association of multiple components (cellulose, hemicellulose, pectin, lignin, waxes…). This structure can already be seen as a composite in which the pectin plays the role of matrix, reinforced by cellulose fibers linked by hemicellulose. This leads to more complex behavior. And the use of this kind of fibers is challenging because they have some downsides that glass fibers do not, such as lower temperature degradability and hygrothermal sensibility. So manufacturing processes have to be adapted to match expected properties. The aim of this study is to develop a repeatable manufacturing process which enables the production of laminated composite plates with good properties, to be used as skin in sandwiches structures, in a reasonable range time.

2 MATERIAL AND METHODS

2.1 Non-woven flax fibers

The flax fibers used in this study are unidirectional fibers with no sewing string from Lineo (FlaxTape 110).

2.2 Matrix

The DGEBA matrix used in this study is produced by Sicomin and is composed of a prepolymer (SR 8500) and an amine hardener (SZ 8525).

2.3 Conditioning

A portion of flax fibers have been conditioned before processing at 23°C and 50% RH in a climatic chamber, Vötsch VC 7100.

2.4 Heated platen press

Laminated composites plates have been produced by thermocompression using a Fontijne Grotnes TPC 321 press. Temperatures (< 100°C) have been chosen to limit thermal degradation of the fibers during the process.

2.5 Cutting

Composites tensile test specimens (25x250mm) have been cut, from plates, using tile saw with water cooling. Edges and surfaces of all specimens have then been dried with paper.

2.6 Tensile tests

Tensile tests have been performed using a MTS Criterion Model 45, the force has been measured with a MTS 100 kN load cell (LPS.105) and the deformation with a MTS 50 mm gauge length extensometer (634.31F-24). Dimensions of the tensile test specimens are 25x250mm.

2.7 Modulated Differential Scanning Calorimetry (MDSC) analyses

MDSC analyses have been performed with a TA Instrument DSC 250 differential scanning calorimeter. Modulated differential scanning calorimetry has been preferred to classic DSC because it makes possible to separate reversible and non-reversible phenomenon and so enable to measure the glass transition temperature of the material despite the interferences of fibers. Two cycles have been carried out for each samples (from 25°C to 130°C for the first cycle then from 25°C to 150°C for the second with 1°C/min speed for both). The first cycle gives the glass temperature Tg1 and the second cycle Tg2. Comparison between Tg2 and Tg1 gives information about the state of crosslinking of the matrix.

2.8 Thermogravimetric analysis coupled with mass spectrometer (TAG-MS)

NETZSCH QMS 403 C and STA 449 F1 have been used to perform TGA-MS analyses from 25°C to 250°C on flax fibers to estimate their water content before manufacturing process.

2.9 Density measurements

The densities of composites and fibers have been measured using Archimedes' principle. To avoid solvent to be absorbed by fibers, dodecane has been used.

3 MANUFACTURING PROCESS

Separated fibers and matrix were preferred to pre-preg, to allow distinct analyses of components and especially to have a perfect control of the composites constituents. Considering the wide range of composites manufacturing processes in the literature for vegetal fibers, depending on fibers and matrixes, a specific manufacturing process has been developed to choose parameters that allow obtaining a composite material with adapted properties. Thermocompression processing has been preferred to vacuum in order to obtain a higher fiber content. Temperatures have been chosen to avoid thermal degradation of the flax fibers during processing. Selected temperatures are lower than 100°C to limit the evaporation of water and be lower than glass temperature of lignin (~90°C) [John, 2008]. Lignin is a hydrophobic component of natural fibers which allows them to regulate their moisture content. The first components to be affected by temperature are waxes and greases. Their fusion starts at 60 degrees. However, the influence of temperatures below 60°C has not been studied. Several parameters values have been tested to improve the mechanical properties of the final composite. The Young's modulus (initial slope) has been chosen as the determining parameter for a use as skins for sandwich structures. The aim was to obtain a material with E1 ≥ 30GPa.

A portion of flax fibers has been used as received and the rest has been disposed in a climatic chamber for one week at 23°C and 50%RH. 12 plies unidirectional composites plates were made by manual impregnation and draping. The mold had two closed and two free edges to allow the excess of matrix to be evacuated during the process. Different proportions of fibers and matrix have been tested. Resin was introduced in excess and evacuated by pressure. A ratio of 2:1 of matrix/fibers (in mass) has been chosen to allow a good repartition of the matrix and impregnation of fibers, under 3bar pressure.

Thermal cycle is composed of two steps and pressure is applied at the beginning of the first step as presented in the Fig. 1.

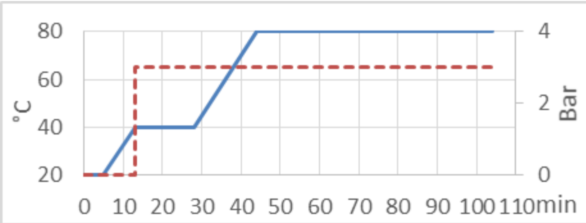

Fig.1: Thermocompression cycle (blue curve: temperature; red curve: pressure)

The influence of some parameters has been evaluated, such as the temperature of the second step, the cooling speed or the temperature at which the mold is extracted from the press. Some postcurings have been tested too in order to improve mechanical properties. Results are presented in the following section.

The plates have then been prepared in 0° tensile test specimens. Samples were cut from the plates with a tile saw and dried with paper. Edges of the samples were protected to limit ageing mechanisms by coating with the same matrix then were post-cured.

The following section presents the results of the characterization phase and the influence of some studied parameters in the manufacturing process improvement.

Fig. 2: Tensile specimen after tensile test

4 RESULTS

4.1 Young's modulus calculation

Tensile tests have been performed on 250x25mm composite samples at quasi-static speed of 1mm/min. A broken sample is presented in Fig. 2. Flax fibers usually exhibit a bilinear behavior in tensile and this behavior is observed in the composite. The first zone is attributed to an elastic deformation of cell walls and the second to the realignment of the cellulose micro-fibrils along the tensile axis with a visco-elasto-plastic comportment [Charlet, 2008]. The Young's modulus indicated by norms for composites does not seem relevant because the range of data used to calculate it (0.05% to 0.25% of deformation) includes the curve inflection point. In this study, E1 and E2 have been preferred to describe the behavior of specimens. Where E1 is the first slope of the strain/stress curve and E2 the slope just after the inflection point, both have been evaluated by linear regression as presented in Fig. 3.

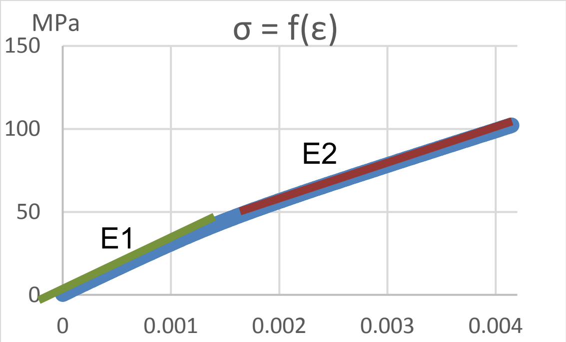

Fig. 3: tensile behavior of 0° sample

4.2 Density measurements

Densities of composites and flax fibers have been measured by weighing in air and in dodecane. Different samples (12 plies) manufactured by contact molding and thermocompression have been measured. The contact-molding-made composite density is 1.22 ± 0.01; thermocompression-made composites density is 1.28 ± 0.01, this is in accordance with higher fiber content, which has been found to be around 46% in volume. Flax fibers density has been measured to 1.45 ± 0.01 which is in accordance with the literature [Charlet, 2008].

4.3 Influence of processing parameters

The influences of processing parameters have been studied and some of them will be presented in this article. All the results will not be displayed here but the effects of fibers pre-conditioning and temperature of the second step of curing are presented in the next paragraphs.

Influence of fibers preconditioning on mechanical properties

The first parameter which has been studied is the fibers conditioning. Flax fibers are likely to exchange water with their environment. And it is known that moisture content plays a role in vegetal fibers mechanical properties. To evaluate the influence of moisture content, a fibers conditioning have been tested. For some plates, plies of fibers have been prepared and disposed in a climatic chamber at 23°C and 50% RH a few days before processing. The influence of these conditions on mechanical properties has been evaluated with 0° tensile test specimens from plates made with conditioned and non-conditioned fibers which have been tested and compared. A week conditioning at 23°C and 50%RH has been found to have no impact on failure stress (-4%) but a higher impact on Young's modulus. +12% for E1 and +25% for E2 as presented in Fig. 4. Temperature and hygrometry have been measured at 23°C and 30% in non-conditioned fibers storage room before manufacturing of composite plates. The difference in water content between non-conditioned fibers and one-week conditioned fibers has been evaluated to 2% in mass. Some studies have showed that completely drying flax fibers drastically reduces fiber's mechanical properties [Baley, 2012]. And these results are in accordance with the fact that, below an amount of moisture, mechanical properties of composites made with flax fibers are reduced.

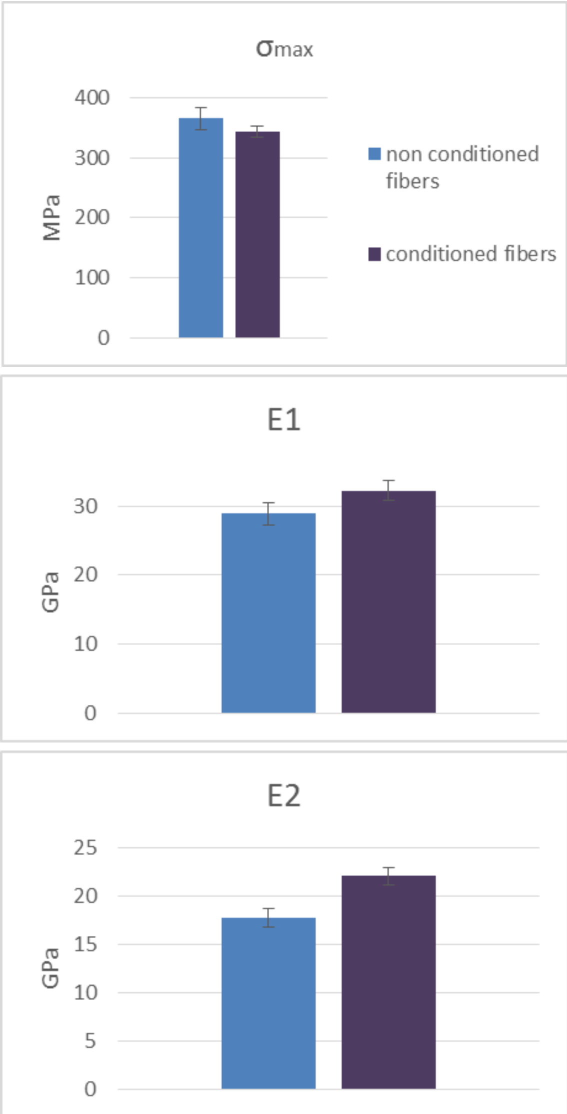

Fig. 4: mechanical properties of composites as a function of fibers conditioning

Influence of curing temperature on mechanical properties

Natural fibers are more sensitive to thermal degradation than classic fibers used in composites manufacturing such as glass and carbon. Temperature has been chosen below 100°C to limit water evaporation during the process. The fusion of waxes and greases present in flax fibers starts around 60°C and glass transition temperature of lignin is around 90°C. Two temperatures of curing have been chosen to reduce thermal degradation of flax fibers during the processing: 80°C and 60°C. Composites' samples made at the highest temperature exhibited better mechanical properties especially for failure stress (+11%) when differences are smaller for E1 (+6%) and E2 (+5%) as presented in Fig. 5. The curing at 60°C cannot induces more thermal degradation on the fibers. So matrix and/or interface are improved with the curing at 80°C. Matrix mechanical properties are poor compared to the fibers' one and cannot explain alone this rise. But it is in accordance with enhanced adhesion between fibers and matrix which is able to transferred more load from one fiber to another and thus improve its repartition between all fibers which leads to upper failure stress.

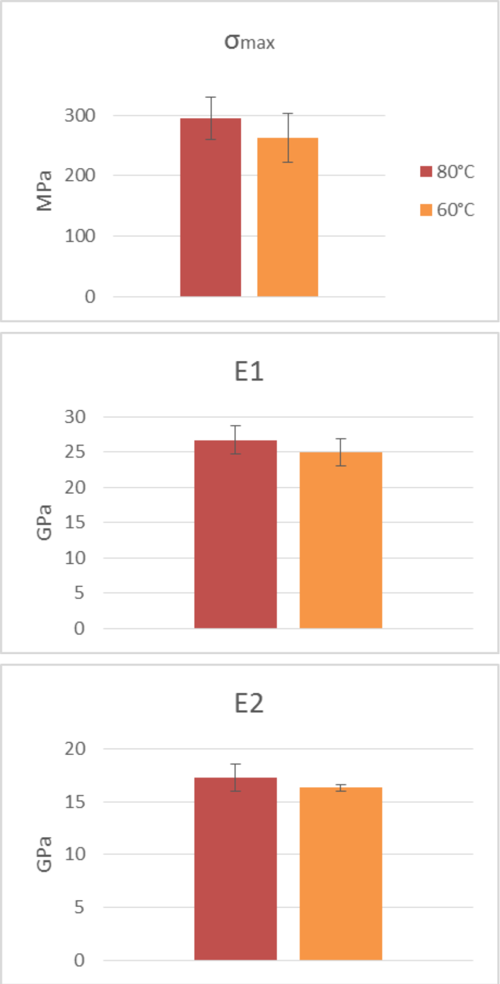

Fig. 5: mechanical properties of composites as a function of the curing temperature

Influence of fibers conditioning and curing temperature on glass transition temperature

For each combination of manufacturing parameters, glass transition temperature has been measured by DSC. In all cases, two temperature rises have been carried out, as shown in Fig.6. This allows comparing glass transition temperature of first and second cycle. In the case of 60°C, Tg1 is slightly lower than Tg2. Tg2 higher than Tg1 would indicate that crosslinking of the matrix was uncomplete and energy provided by the first cycle enables a better crosslinking of the matrix.

Thus, 60°C manufacturing process induces uncompleted crosslinking of the matrix. But, in the case of 80°C manufacturing process, Tg1 is higher than Tg2 for both conditioned and non-conditioned fibers. Tg1 higher than Tg2 can be attributed to a degradation of the composite after the first cycle (from 25°C to 130°C). So the matrix seems to be well crosslinked with this parameter.

Despite the chosen manufacturing cycle, composites exhibited higher glass transition temperatures than the one measured on the pure matrix. Such behavior can be observed in filled polymers and has been related to polymer-filler interaction energy [YIM, 1972].

4.4 Selection of manufacturing parameters

Manufacturing processes have been selected to elaborate composites with good properties in an acceptable timeframe. It included a fibers conditioning at 23°C-50%RH, curing at 80°C, controlled cooling and finally a post-curing. DSC analyses have been performed on 2 samples of 3 different composite plates elaborated with this manufacturing process and glass transition temperatures have been found to be stable at 111°C ±1°C. This tends to show that the process is controlled and repeatable.

Mechanical properties of the unidirectional (0°) tensile specimens have been determined from 5 samples and are the following:

- σ=314.7±6.2MPa
- E1=30.4±0.8GPa
- E2=21.3±0.4GPa

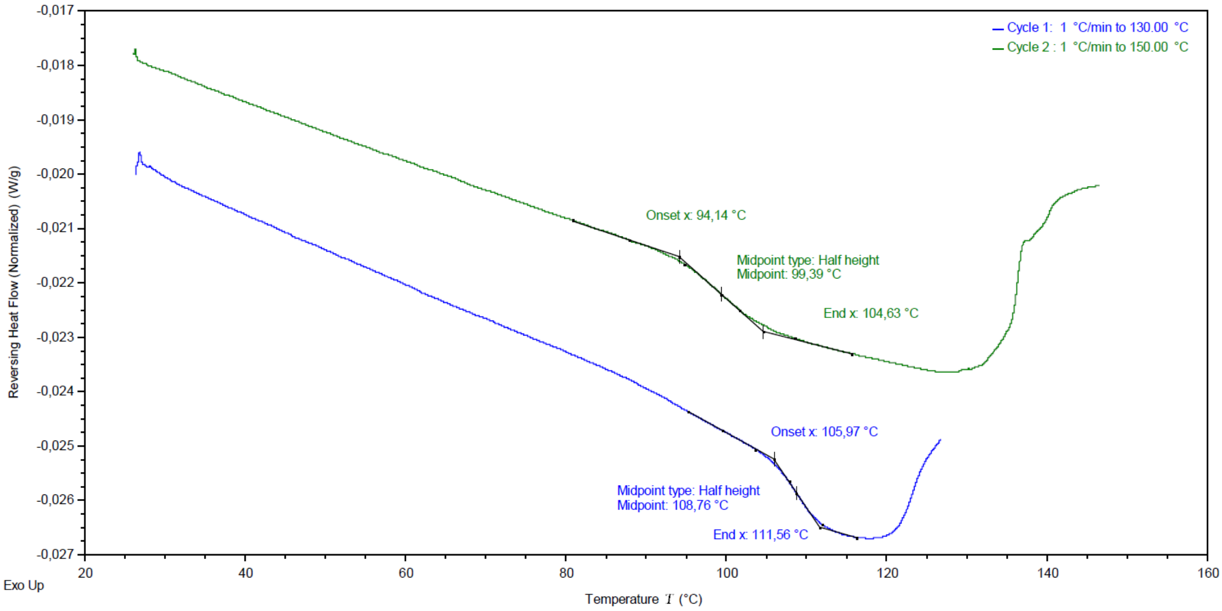

Fig. 6: DSC analysis. Reversing heat flow of composite plate with 80°C curing temperature

5 SUMMARY

The aim of this study was to propose a repeatable manufacturing process which enables the production of laminated composite plates with good properties in a reasonable range time. Termocompression method has been chosen to obtain a good fibers content in the material (≈46% in volume). The manufacturing process has been adapted for both natural fibers and epoxy resin and optimized to improve composite mechanical properties. Multi-scale analyses have been performed to evaluate properties of induced composites. The influence of several manufacturing parameters has been studied. Results about effects of preconditioning of fibers and the curing temperature have been exposed in this paper. It has been observed that preconditioning of fibers before manufacturing process has a beneficial influence on the modulus of composite. It increases E1 by about 10% and E2 by 25%. Moreover, it is not interesting to lower the manufacturing temperature too much to reduce thermal impact on fibers. The composite cured at 60°C exhibits lower mechanical properties than at 80°C. This is especially true for failure stress with a 10% drop. Finally, this manufacturing process enables to elaborate composites with stable properties and homogeneous glass transition temperature between plates.

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