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Study of autoclave process to manufacture thermoplastic composites constituted by PP/flax fibers

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Abstract. Autoclave processes are widely used from industries that produce thermoset polymer composite parts. However, these materials show sustainability issues as they are non-recyclable and produced by energy-intensive processes. The use of thermoplastic matrices reinforced with natural fibers can solve these problems; however the optimal use of this material is linked to the knowledge of the forming parameters. In this work, starting from semipreg sheets, the autoclave forming process for parts in flax woven and polypropylene is studied and developed: it represents a fundamental step to develop the use of these new eco-friendly materials starting from the well-established industrial knowledge, not only in terms of environmental sustainability, but also economic and social sustainability. First, working temperatures were determined by DSC and TGA; while optimal forming pressure were determined by ILSS tests.

Introduction

The use of fiber-reinforced polymers for structural and semi-structural applications has seen a strong growth in recent decades, especially in the aeronautical and automotive sectors. This trend is essentially due to the lightness and high specific resistance that these materials have, characteristics that allow to reduce consumption and CO_2 emissions of aircraft, boats, railway and road vehicles, etc. [1–3].

Nowadays, most of structural and semi-structural components are manufactured using prepregs cured by autoclave [4]. This technique allows to obtain high volumetric fractions of reinforcement, excellent mechanical performance and a very low presence of defects inside the parts. For these reasons, the autoclave is one of the main and most important equipment present in all those industries that nowadays deal with the production of polymer composite parts.

One of the problems faced by traditional fiber-reinforced polymer composites is their non-recyclability and their highly energy-consuming production process. In addition, they are mostly derived from synthetic petroleum products, which nowadays present environmental sustainability issues [5]. For these reasons, recently there is a growing interest in vegetal reinforcements, which have shown to have specific resistances similar to glass reinforcement, so they can be a valid substitute for the latter in the case of semi-structural parts. Specifically, flax, hemp and jute fibers have been the subject of numerous studies due to their excellent performance, superior in terms of specific resistance to E-glass [6].

Plant fibers have a lower permeability than glass, which is why making parts with these types of reinforcement through infusion or injection processes is quite complicated [7]. Moreover, they would only be recyclable if coupled with thermoplastic matrices, which have high viscosities. A solution to this problem can be given by the production of the composite part through film compression molding, in which the dry reinforcement is layered alternately with thermoplastic polymer films [8]. In this way, the path that the resin must make inside the reinforcement is limited in the direction of the thickness. However, the bio composites obtained with this technique generally have a high volumetric percentage of resin. Furthermore, they may have any internal defects due to the possible absorption of environmental moisture in the reinforcement. A solution to this problem can be given by the use of semipregs [9]. As well as traditional prepregs, semipreg are pre-impregnated reinforcements with the optimal amount of resin, in this case no longer thermosetting but thermoplastic. This aspect allows to greatly simplify the management and logistics of the material because the semipreg is chemically stable at room temperature and pressure. In addition, being the reinforcement protected from the external environment by the same thermoplastic resin, it is not necessary to store it in a controlled humidity environment and dry it just before the production of the component.

Generally, parts made of polymer composite material should be made by thermoforming [10]. In the case of thermoforming of structural or semi-structural polymer composites, the material is first layered and formed in hot-plate press in order to obtain a consolidated laminate with the nominal thickness provided by the project specification, then it is cooled and analyzed by non-destructive testing. If there are no inner defects, it is tensioned by means of tensioners and heated again by IR furnaces at the process temperature. Once this is achieved, the consolidated laminate is placed in the press and formed [11]. Being a totally different process from the traditional one in autoclave, most of the industrial companies that have developed their know-how on thermosetting composites should completely convert their departments in order to be able to produce components in bio thermoplastic composite material. In the authors' best knowledge, nowadays there are no scientific publications that study the process of thermoforming of bio composite materials in autoclave. This intermediate step, which consists in the manufacturing of bio composite parts through autoclave processes, would be fundamental to allow the production of bio-recyclable composite laminates with processes consolidated by many industrial realities. The adoption of natural fiber composites with thermoplastic matrix as a replacement, for example, of fiberglass would greatly reduce the environmental impact in terms of emitted CO_2, as, in addition to requiring energy-intensive processes, the production of the reinforcement itself would result in a negative CO_2 balance obtained by the plant photosynthesis process [12].

The aim of this work is to study the range of processability of this new type of materials in autoclave and, subsequently, investigate the effect of the obtained process parameters on the interlaminar shear strength, representative of the adhesion between the layers of the formed laminates. This study represents an intermediate but indispensable step for the development of this type of materials not only in terms of environmental sustainability, but also of economic and social sustainability [13]. Specifically, the main process parameters in autoclave for the production of polypropylene and woven flax fiber laminates were identified and the mechanical performance were evaluated.

Materials and Methods

The semipreg used in this work is produced by Bcomp and it consists of a 2x2 twill fabric reinforcement in flax fibers known as Amplitex 5040 and impregnated in a polypropylene matrix. It is a semipreg with an area density of 300 g/m^2 and a thickness of about 0.8 mm. Its tension strength is 224 MPa and it has a Young modulus of about 20 GPa.

Identification of process parameters

Since the temperature of workability of the material was not known, the first step of the analysis consisted in its definition. This range was determined by DSC (Differential Scanning Calorimetry) tests on semipreg samples with a mass of about 10 mg and using the DSC module Q20 V24, supplied by TA Instruments. The analyses were carried out according to EN 6032. Specifically, the samples were equilibrated to -60°C, therefore subject to a ramp of 10 ºC/min up to the target temperature of 250 ºC, at which they remained in isothermal conditions for 1 min, then cooled

Materials Research Proceedings 35 (2023) 385-392 https://doi.org/10.21741/9781644902714-46

with a cooling rate of -10 ºC/min until the room temperature was reached. By means of DSC analysis, it was possible to define the temperature range for thermoforming.

In order to evaluate if thermal degradation of the semipreg occurs at the temperatures of interest, TGA (Thermo Gravimetric Analysis) analyses were carried out both on dry reinforcement and on semipreg, using the TGA Q500 V20 module, also supplied by TA Instruments. In this case, the analysis was carried out on samples of about 10 mg but with a heating ramp of 3 ºC/min up to 250 °C. The TGA analysis made it possible to assess whether there was a degradation of the processed material in terms of mass loss in the range determined by the DSC tests. This analysis was carried out on both semipreg and dry woven in order to evaluate the barrier effect of the matrix against environmental moisture. Five replicas were made for both DSC and TGA analyses.

Once the working temperature range was determined, the range of pressures and optimal processing times were investigated by autoclave thermoforming of consolidated laminates. The consolidated laminates were made with 8 layers for a final thickness of about 5.4 mm. The layers were placed on the mold, so the bag was made and the vacuum applied. In this way the vacuum itself constrained the layers on the mold, preventing them from moving during the process. This approach, however, allows to stratify even more complex geometries, as the drapability of the individual ply at room temperature is always higher than that of the consolidated laminate, presenting the latter a much higher thickness (therefore a flexural stiffness which could cause the failure of the bag during the vacuum application). After compaction, the bag was placed in the autoclave and subject to the reference thermal cycle. The heating ramp adopted in this work was 3 C°/min, while the dwell time was obtained empirically. In particular, preliminary forming of flat laminates were carried out with type J thermocouples inside them in the position shown in Fig. 1. The dwell time was therefore defined as the time needed for the thermocouple to register a temperature within the formability range of the material obtained by DSC analysis.

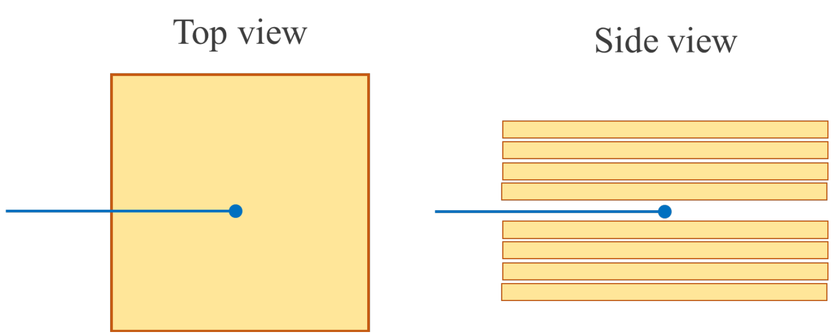


Fig. 1. Position of the control thermocouple.

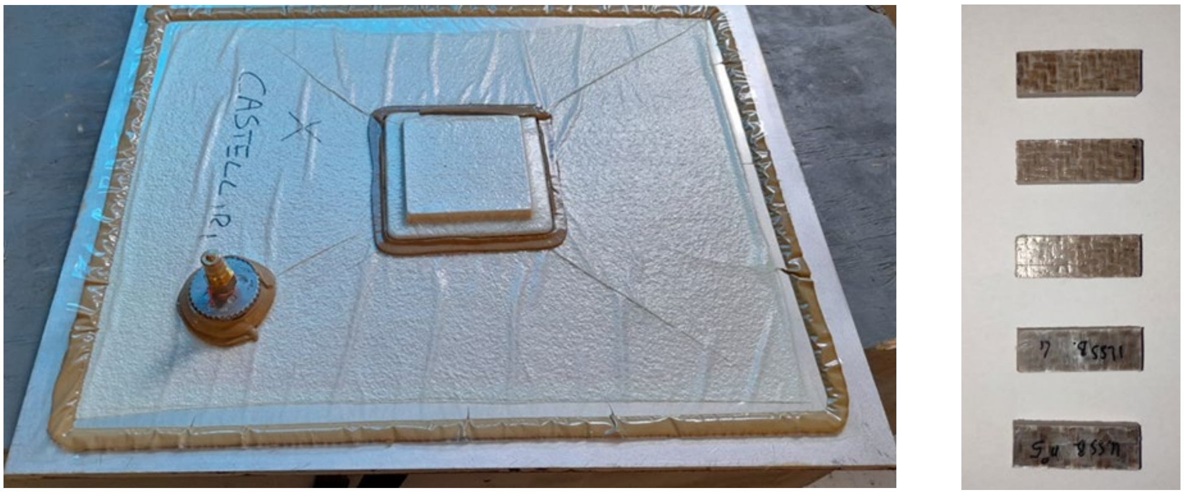
For completeness, the values in terms of temperature and pressure used for the production of the consolidated in autoclave were also reported in Table 1.

Table 1. Experimental plan for the manufacturing of consolidated thermoplastic laminates.

Factors	# Level	Levels
Temperature [°C]	3	160 – 170 – 180
Pressure [bar]	3	2 – 4 – 6
Repetitions	3	

Materials Research Proceedings 35 (2023) 385-392 https://doi.org/10.21741/9781644902714-46

Once consolidated, they were finished and cut to realize interlaminar shear strength specimens (ILSS, Fig. 2b), in order to evaluate their mechanical performance and adhesion between the layers. For each consolidated laminate, 5 specimens were made. ILSS tests were carried out according to ASTM D2344; in this case the dimensions were 40 mm x 12 mm x 5.4 mm, while the crosshead speed was 1 mm/min. All mechanical tests were carried out using a universal testing machine equipped with a 10 kN load cell.



a) b)

Fig. 2. Manufacturing of Flax/PP laminates: a) material compaction steps; b) ILSS specimens.

Results and Discussions

DSC results

The results of the DSC analyses showed a high repeatability and allowed the matrix melting temperature to be detected at 166.3 ºC with a standard measurement dispersion of about 0.3 ºC during heating. Moreover, recrystallization peaks between 130 and 120 ºC were observed during the cooling phase. It is possible to state that the thermoforming process will have to consider a thermal cycle that should have a process temperature around 166.3 ºC. An example of a DSC test result is reported in Fig. 3.

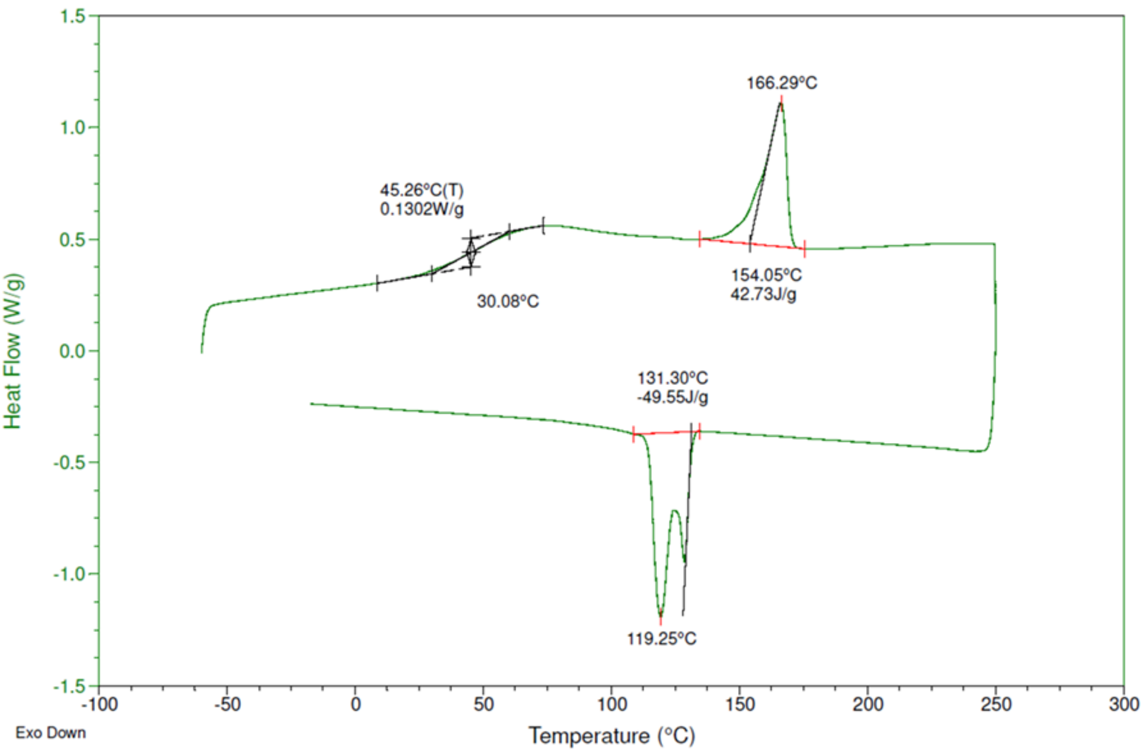


Fig. 3. Example of temperature /heat flow curve obtained from a DSC test on semipreg PP/flax fabric.

TGA results

While in the case of DSC tests it was possible to determine the range of the semipreg workability temperature, the TGA analyses allowed to evaluate the material degradation at the investigated process temperatures in terms of percentage of mass lost. Specifically, the specimens were subjected to a heating ramp of 3 ºC/min up to the temperature of 250 ºC. The results showed that the mass loss is always less than 3% on semipreg at the temperatures range obtained by DSC analysis, while the dry woven showed a strong variability, resulting in a mass variation between 7 and 9% near the processing temperature range (Fig. 4). This difference was mainly due to the presence of the PP matrix that provided a barrier effect on the reinforcement avoiding that the latter absorbs moisture from the environment. It is possible to state that the use of semipreg allowed an easier management of the forming process, as the storage conditions of the material will not lead to a moisture absorption that can deteriorate the reinforcement. Moreover, it will no longer be necessary to carry out the drying of the reinforcement itself as a processing step prior to stratification.

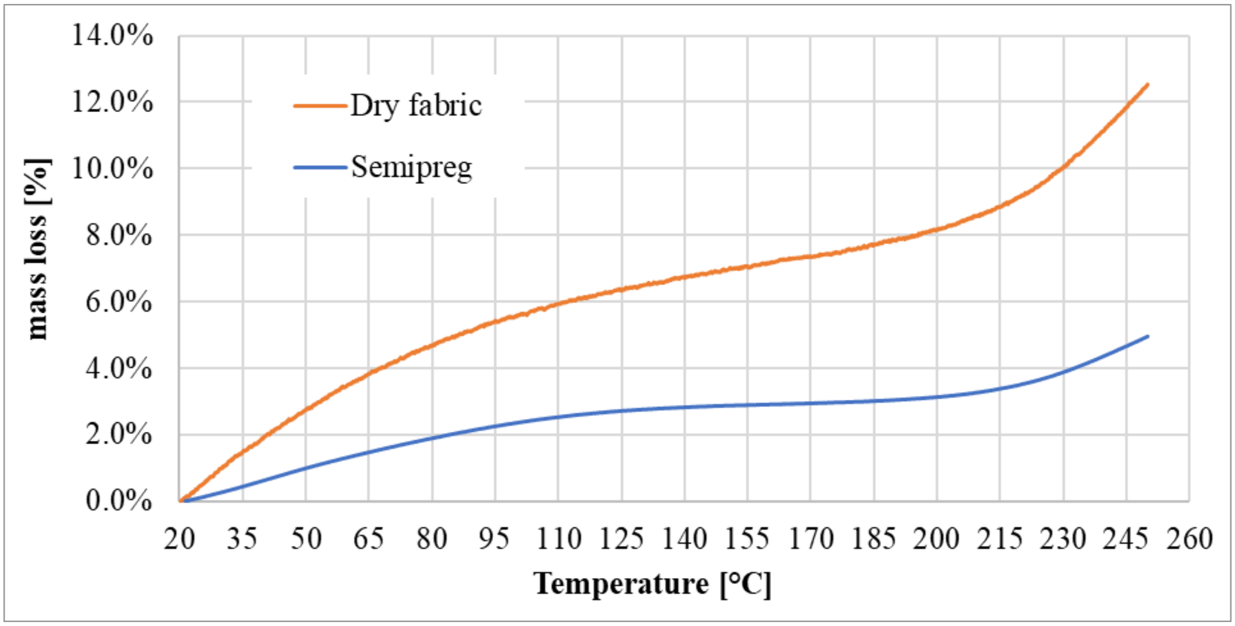


Fig. 4. Example of TGA results for dry flax fabric and PP/flax fabric semipreg.

ILSS test results

The results of the ILSS tests allowed the mechanical evaluation of adhesion between the layers as a function of the process parameters. The experimental results showed a strong variability in the range of the investigated process parameters, as shown in Fig. 3. In order to assess whether the effect of the individual process parameters on the interlaminar shear strength of the consolidated is significant or not, an ANOVA analysis of the results obtained was carried out. For this purpose, it has been hypothesized that the population investigated had a Gaussian distribution, was homoscedastic and that the observations made were independent. In addition, a significance level of 0.05 has been established for the analysis. The results obtained are reported in Table 2.

It is possible to say that the investigated process parameters, namely the forming temperature and pressure, had a not negligible effect on the interlaminar shear strength in the obtained laminates. Specifically, as shown in Fig. 5a, the most impacting factor was the processing temperature, with a contribution obtained of about 81%. This result was due to an increased energy available to allow the polymer to melt and subsequent solidification, resulting in an improvement in the adhesion between the layers. For this reason, the values obtained at 160 °C were found to be very low, while at 180 °C the maximum values were obtained. However, it has been observed that the pressure and the combination of temperature and pressure also had a not negligible effect, although with a lower contribution of about 8% and 10% respectively. In fact, observing Fig. 5 and Fig. 6b, it is possible to affirm that in the case of forming at 170 °C, the effect of the pressure on the interlaminar shear strength had led to a strong increase in performance as the compaction pressure increases, despite an increase in the dispersion of results.

Table 2. ANOVA table for ILSS results.

Source	DoF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
Temperature [°C]	2	1092.80	81.40%	1092.8	546.4	754.51	0.000
Pressure [bar]	2	105.03	7.82%	105.03	52.517	72.52	0.000
Temperature*Pressure [°C] [bar]	4	131.57	9.80%	131.57	32.892	45.42	0.000
Error	18	13.04	0.97%	13.04	0.724		
Total	26	1342.44	100.00%				

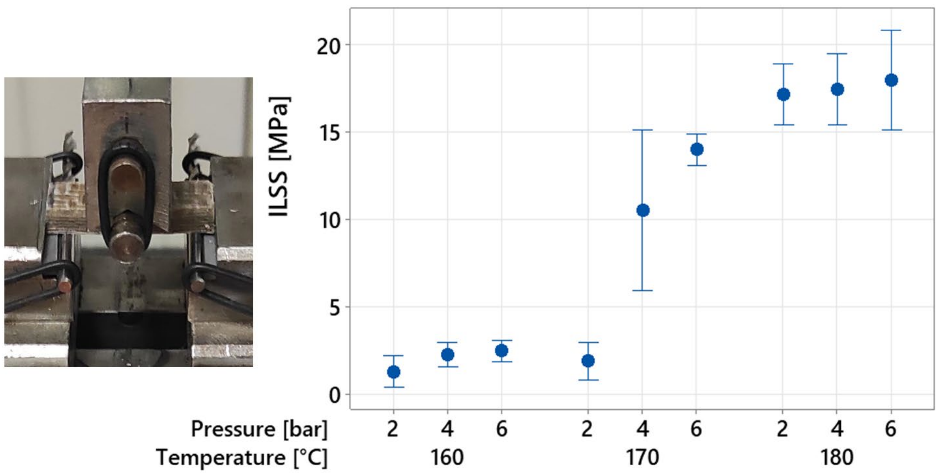


Fig. 5. Experimental results from ILSS tests.

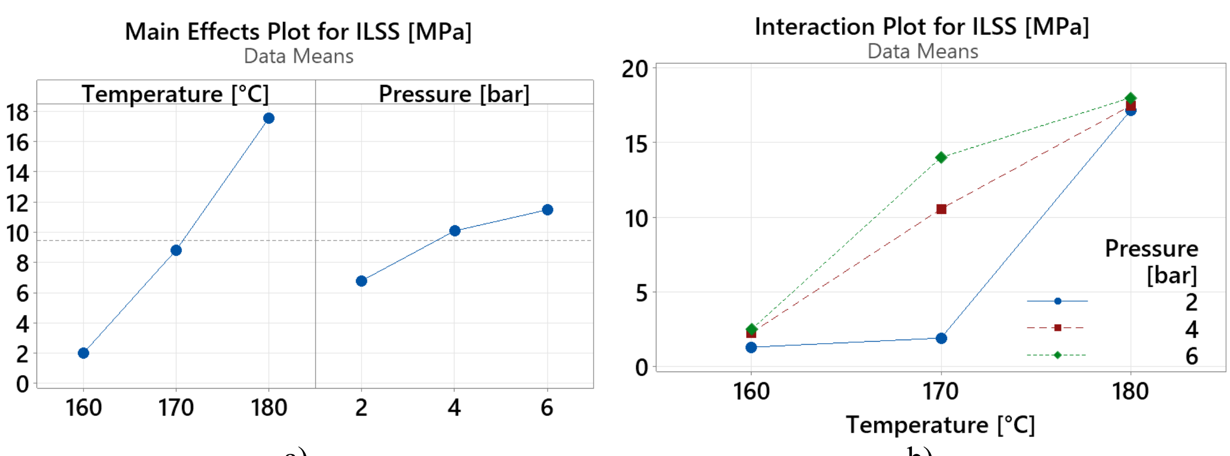


Fig. 6. ILSS experimental results: a) main effect plot; b) interaction plot.

Conclusions

In this work, starting from semipreg sheets, the study of autoclave process to manufacture thermoplastic composite laminates constituted by woven flax fibers and PP matrix was carried out. Specifically, process temperatures of the investigated material were identified between 160 and 180 °C by DSC and TGA tests. Subsequently, ILSS samples were produced with different pressures, in order to assess the good adhesion between the layers according to the process parameters. It was observed that the most impacting factor on performance was temperature, with a contribution of about 81%. In fact, average ILSS increased from about 2 MPa at 160 °C to about 18 Mpa at 180 °C. Finally, compaction pressure had an important effect especially at 170 ºC, which was the temperature closest to the melting of investigated material.

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