Development of low-density particleboards bonded with starch-based adhesive

Sandra Cristina Costa Monteiro

Dissertation presented for the degree of
Doctor of Philosophy in Chemical and Biological Engineering

by
Chemical Engineering Department - Faculty of Engineering of University of Porto

Supervisors:
Fernão Domingos de Montenegro Baptista Malheiro de Magalhães
(Faculty of Engineering of the University of Porto)

Luísa Maria Hora de Carvalho
(Polytechnic Institute of Viseu and Faculty of Engineering of the University of Porto)

Porto, June 2020

To Nelson and Tiago

ACKNOWLEDGEMENTS

I would like to thank the financial support of PDEQB - Doctoral Programme in Chemical and Biological Engineering for this work. This work was financially supported by: Base Funding - UIDB/00511/2020 of the Laboratory for Process Engineering, Environment, Biotechnology and Energy – LEPABE - funded by national funds through the FCT/MCTES (PIDDAC); project NORTE-01-0145-FEDER-000005 – LEPABE-2-ECO-INNOVATION, supported by North Portugal Regional Operational Program (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF).

My heartfelt thanks to my supervisors Professor Fernão de Magalhães and Professor Luísa Carvalho for all the given support, shared knowledge and guidance. Your contribution was absolutely essential to give this work a scientific robustness.

A special thanks to Professor Jorge Martins for his hands-on approach, helping me with the laboratorial work and also for his permanent support and supervision.

Thanks to João Pereira and Margarida Almeida for the support and enormous help in the laboratory work.

A truly heartfelt thanks to my dears Ana Gomes e Inês Camoiana for all good moments and friendship.

My profound gratitude to Ângela, Ana Antunes, Ana Henriques, Eva and Carolina for all the friendship and the laughs and tears that we shared.

For their unconditional love and never-ending support, my deepest gratitude to lovely family, my parents Avelina and João, my siblings Andreia and Pedro and my brother-in-law Roberto, and not forgetting, because they are also part of the family, my friends Marta and Hugo Martins many thanks for your love and support.

Finally, a special thanks to my love Nelson. Thank you for your patience and for showing me that there is always a solution for each problem. Thank you for all your love, for your support, for believing. Thank you for everything. “Just the two of us building castles in the sky”.

ABSTRACT

Nowadays, low-density materials assume a great importance in several industries, such as aerospace, building and furniture. The low-density is desirable for economic (materials and transportations cost) and environmental (resources, eco-efficiency) reasons. In this way, the lightweight particleboard plays an important role in furniture industry.

This product is traditionally produced using amino resins as particle binder. These particles can be wood, wood residues, recycled wood or any other lignocellulosic materials. However, international regulations for the reduction of formaldehyde emissions have forced industry to look for sustainable alternatives with less environmental impact.

The first goal of this work was to produce low-density particleboards using a binder based on cassava starch, taking advantage of its adhesive and self-expansion properties. The physico-mechanical characterization (density, internal bond strength, thickness swelling and moisture content) of the produced panels was carried out according to the European standards. The particleboards produced showed densities between 207 $\mathrm{kg \cdot m^{-3}}$ e 407 $\mathrm{kg \cdot m^{-3}}$. The best performance corresponds to panels with a density of 318 $\mathrm{kg \cdot m^{-3}}$, internal bond strength of 0.47 $\mathrm{N \cdot mm^{-2}}$ and thickness swelling of 8.7%. It was observed that a heat post-treatment (24 h, 80 °C) led to worse performance in terms of internal bond strength, but lower thickness swelling was observed.

The preliminary studies described above have shown that this composite could not be produced using the conventional pressing method of the particleboards. Therefore, the next step of this work was to determine the proper conditions for the production process of the panels. The pressing methodology which was developed involves two steps: in the first, the panels were pressed at a specific thickness during a certain period of time, called pressing time. In the second one, the top platen of the press is raised to allow for panel expansion during a certain

period of time, designated as hold time. The parameters studied were the pressing time (10 to 150 s), the hold time (290 to 890 s) and the top platen temperature (80 to 190 °C). The panels were characterized in terms of density, internal bond strength, thickness swelling and moisture content. The panels with best performance (density of 405 $kg \cdot m^{-3}$ and internal bond strength of 0.44 $N \cdot mm^{-2}$) were produced at 190 °C, with a pressing time of 60 s and a hold time of 540 s.

After establishing the process conditions for particleboards production, the next step was to optimise the adhesive formulation. It was necessary to understand the role of each component present in the starting formulation, and also the optimum amounts to be used. Two important changes were introduced at this stage, as a consequence of existing circumstances. The first one was to replace the cassava starch with a national starch (potato starch). The second alteration was the substitution of the recycled wood particles by cardoon particles, which are a by-product of the national cheese industry with no commercial value.

In this way, different ratios starch/cardoon (0.6; 0.8; 1 and 1.2) were studied. In the two ratios most promising (0.6 and 0.8), we evaluated the effect of different bio-based additives (chitosan, wood fibre and glycerol) on the performance of the adhesive system. The results showed that the addition of chitosan improves significantly the internal bond strength of the produced particleboards. On the other hand, the introduction of wood fibre impairs the mechanical performance of the panels. Concerning glycerol, the addition of this plasticiser did not have a significant effect on the mechanical properties of particleboards. So, the panels with the best physico-mechanical performance (density of 323 $kg \cdot m^{-3}$, internal bond of 0.35 $N \cdot mm^{-2}$ and thickness swelling of 15.2%) were produced with a starch/cardoon ratio of 0.8, chitosan/starch of 0.05 and water/starch of 1.75.

Finally, the developed composite was used in the production of pieces with non-flat geometries using a moulding process.

SUMÁRIO

Hoje em dia, os materiais leves assumem grande importância nas mais diversas indústrias, nomeadamente na indústria aerospacial, construção e mobiliário. A baixa densidade é desejável pelas vantagens que traz em termos económicos (custos de materiais e transporte) e ambientais (recursos e ecoeficiência). Desta forma, o painel de aglomerado de partículas de baixa densidade desempenha um papel importante na indústria do mobiliário.

Este produto, é produzido tradicionalmente utilizando resinas amino-formaldeído como aglutinante de partículas. Estas partículas podem ser de madeira, resíduos de madeira, madeira reciclada ou qualquer outro material lenhocelulósico. Contudo, a legislação internacional para as reduções de emissão de formaldeído tem obrigado a indústria a procurar alternativas sustentáveis com menor impacte ambiental.

O primeiro objetivo deste trabalho foi produzir painéis de aglomerado de partícula de baixa densidade utilizando como ligante amido de mandioca, tirando partido do seu comportamento auto-expansível e das suas propriedades adesiva. A caraterização físico-mecânica (densidade, resistência interna, inchamento em espessura e teor de água) dos painéis produzidos foi efetuada de acordo com as normas europeias. Os painéis produzidos apresentaram massas volúmicas entre os 207 $kg \cdot m^{-3}$ e 407 $kg \cdot m^{-3}$. O melhor desempenho corresponde aos painéis com massa volúmica de 318 $kg \cdot m^{-3}$, com uma resistência interna de 0,47 $N \cdot mm^{-2}$ e inchamento em espessura de 8,7%. Nesta fase do trabalho os painéis foram sujeitos a um tratamento térmico (24 h, 80 °C) apresentando estes painéis um pior desempenho em termos de resistência interna. Contudo, apresentaram uma diminuição do inchamento em espessura.

Os estudos preliminares descritos acima mostraram que este compósito não poderia ser produzido utilizando o método convencional de prensagem de painéis aglomerados de partícula. Desta forma, a fase seguinte deste trabalho consistiu em determinar as condições mais adequadas para a produção dos painéis. O método de prensagem desenvolvido envolve duas etapas: a primeira, uma prensagem a uma espessura específica durante um período de tempo, ao qual designamos por tempo de prensagem. A segunda, o prato superior da prensa é levantado durante um determinado tempo, designado por tempo de espera, de forma a permitir que o painel expanda. Os parâmetros estudados foram o tempo de prensagem (10 a 150 s), o tempo de espera (290 a 890 s) e a temperatura do prato superior da prensa (80 a 190 °C). Os painéis foram caracterizados em termos de densidade, resistência interna, inchamento em espessura e teor em água. Os painéis com melhor desempenho (massa volúmica de 405 $kg{\cdot}m^{-3}$ e resistência interna de 0,44 $N{\cdot}mm^{-2}$) foram produzidos à temperatura de 190 °C com tempo de prensagem de 60 s e um tempo de espera de 540 s.

Após estabelecido o processo de produção dos painéis e determinadas as condições de prensagem, o trabalho seguinte foi otimizar a formulação do adesivo. Era necessário compreender o papel de cada componente presente na formulação inicial, assim como as quantidades ótimas a serem usadas. Nesta etapa do trabalho duas alterações importantes fizeram sentido antes de se iniciar o estudo da formulação. A primeira foi a substituição do amido de mandioca, o principal componente do sistema adesivo, por um amido nacional (amido de batata). A segunda, passou por substituir as partículas de madeira por partículas de cardo, um subproduto da indústria nacional de queijo que não tem qualquer valor comercial. Deste modo estudaram-se diferentes razões amido/cardo (0,6; 0,8; 1 e 1,2). Nas duas razões mais promissoras (0,6 e 0,8), avaliou-se o efeito de diferentes aditivos de base natural (quitosano, fibra e glicerol) no desempenho do sistema adesivo. Os resultados mostraram que, a adição de quitosano contribui para um aumento significativo da resistência internas dos painéis produzidos. Por outro lado, a introdução de fibra prejudica o desempenho mecânico dos painéis.

No que se refere ao glicerol, a adição deste plastificante não tem efeito significativo nas propriedades mecânicas dos painéis produzidos. Assim, os painéis que apresentaram melhor desempenho físico-mecânico (massa volúmica de 323 $kg{\cdot}m^{-3}$, resistência interna de 0,35 $N{\cdot}mm^{-2}$ e inchamento em espessura de

15,2%), foram produzidos com uma razão amido/cardo de 0,8, razão quitosano/amido de 0,05 e razão água/amido de 1,75.

Por fim, o compósito desenvolvido foi utilizado na produção de peças com geometria não-plana utilizando o processo de moldagem.

RÉSUMÉ

Actuellement, les matériaux à faible densité sont très important pour plusieurs industries, telles que l'aérospatiale, le bâtiment et l’ameublement. La faible densité est souhaitable pour des raisons économiques (coût des matériaux et des transports) et environnementales (ressources, éco-efficience). De cette façon, le panneau de particules léger joue un rôle important dans l'industrie de l’ameublement.

Ce produit est traditionnellement fabriqué en utilisant des résines aminoplastes comme liant des particules. Ces particules peuvent être du bois, des résidus de bois, du bois recyclé ou d’autres matériaux lignocellulosiques. Cependant, les réglementations internationales pour la réduction des émissions de formaldéhyde ont conduit l'industrie à rechercher des alternatives durables avec moins d'impact sur l'environnement.

Le premier but de ce travail a été de produire des panneaux de particules légers à l'aide d'un liant à base d'amidon de manioc, en profitant de ses propriétés adhésives et auto-expansibles. La caractérisation physico-mécanique (masse volumique, cohésion interne, gonflement en épaisseur et teneur en humidité) des panneaux produits a été réalisée selon les normes européennes. Les panneaux de particules produits ont eu des masses volumiques comprises entre 207 $kg \cdot m^{-3}$ et 407 $kg \cdot m^{-3}$. Les meilleures performances correspondent à des panneaux avec une masse volumique de 318 $kg \cdot m^{-3}$, une cohésion interne de 0,47 $N \cdot mm^{-2}$ et un gonflement en épaisseur de 8,7%. Il a été observé qu'un post-traitement thermique (24 h, 80 °C) conduisait à une plus basse performance au niveau de la cohésion interne. Cependant, ils ont présenté un gonflement en épaisseur plus faible.

Les études préliminaires décrites ci-dessus ont montré que ce composite ne pouvait pas être produit en utilisant la méthode de pressage conventionnelle des panneaux de particules. De cette façon, la prochaine étape de ce travail a été de déterminer les conditions appropriées pour le processus de production des panneaux. La méthodologie de pressage qui a été développée comprend deux

étapes: dans la première, les panneaux ont été pressés à une épaisseur spécifique pendant une certaine période de temps, appelée temps de pressage. Dans la deuxième, le plateau supérieur de la presse est relevé pour permettre l'expansion du panneau pendant une certaine période de temps, désignée comme temps d'attente. Les paramètres étudiés sont le temps de pressage (10 à 150 s), le temps d’attente (290 à 890 s) et la température du plateau supérieur (80 à 190 °C). Les panneaux ont été caractérisés au niveau de la masse volumique, de la cohésion interne, du gonflement en épaisseur et du teneur en humidité. Les panneaux les plus performants (masse volumique de 405 $kg{\cdot}m^{-3}$ et cohésion interne de 0,44 $N{\cdot}mm^{-2}$) ont été produits à 190 °C, avec un temps de pressage de 60 s et un temps d’attente de 540 s.

Après avoir établi les conditions du processus de production des panneaux de particules, l'étape suivante consistait à optimiser la formulation de l'adhésif. Il était nécessaire de comprendre le rôle de chaque composant présent dans la formulation de départ, ainsi que les quantités optimales à utiliser. À ce stade, deux changements importants ont été introduits. Le premier consistait à remplacer l'amidon de manioc par un amidon national (fécule de pomme de terre). La deuxième modification a été la substitution des particules de bois recyclées par des particules de chardon, qui sont un sous-produit de l'industrie nationale du fromage sans valeur commerciale.

De cette manière, différents rapports amidon/chardon (0,6; 0,8; 1 et 1,2) ont été étudiés. Dans les deux rapports les plus prometteurs (0,6 et 0,8), nous avons évalué l'effet de différents additifs biosourcés (chitosane, fibre de bois et glycérol) sur les performances du système adhésif. Les résultats ont montré que l'ajout de chitosane améliore considérablement la cohésion interne des panneaux de particules. Par contre, l'introduction de la fibre de bois change les performances mécaniques des panneaux. Concernant le glycérol, l'ajout de ce plastifiant n'a pas eu d'effet significatif sur les propriétés mécaniques des panneaux de particules. Donc, les panneaux avec les meilleures performances physico-mécaniques (masse volumique de 323 $kg{\cdot}m^{-3}$, cohésion interne de

0,35 N·mm^{-2} et gonflement en épaisseur de 15,2%) ont été produits avec un rapport amidon/chardon de 0,8, chitosane/amidon de 0,05 et eau/amidon de 1,75. Finalement, le composite développé a été utilisé dans la production de pièces à géométrie non plane à l'aide d'un procédé de moulage.

LIST OF ABBREVIATIONS

cs	Chitosan
D	Density
EPS	Expanded Polystyrene Foam
FTIR	Fourier Transform Infrared Spectroscopy
Gly	Glycerol
HDF	High Density Fibreboard
HPT	Heat Post-Treatment
IARC	International Agency for Research on Cancer
IB	Internal Bond Strength
JIS	Japanese Industrial Standards
L-MDF	Light Medium Density Fibreboard
LVDT	Linear Variable Differential Transformer
MC	Moisture Content
MDF	Medium Density Fibreboard
MDI	Methylene Diphenyl Diisocyanate
MOE	Modulus of Elasticity
MOR	Modulus of Rupture
MS	Expandable Microspheres

MUF	Melamine-Urea-Formaldehyde
OSB	Oriented Strand Board
PB	Particleboard
PF	Phenol-Formaldehyde
PMDI	Polymeric Methylene Diphenyl Diisocyanate
PW	Plywood
SEM	Scanning Electron Microscopy
Tg	Glass Transition Temperature
TMP	Thermo-Mechanical Pulping
TS	Thickness Swelling
UF	Urea-Formaldehyde
UL1-MDF	Ultra-Light Medium Density Fibreboard Type 1
UL2-MDF	Ultra-Light Medium Density Fibreboard Type 2
UL-MDF	Ultra-Light Medium Density Fibreboard
VOCs	Volatile Organic Compounds
WBPs	Wood-Based Panels
WPC	Wood Plastic Composite

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

Introduction

1. Introduction

1.1. Thesis motivation and outline

Wood-based panels (WBPs) is a generic term for a diversity of board products, being one of them particleboards (PB). In the last decades, the demand for light wood-based panels has increased, especially for use in furniture and wall coverings. The reduction of weight is desirable for economical reasons (material and transportation costs) and environmental reasons (resources, eco-efficiency). The trends in the furniture market have a huge impact on the demand for lightweight furniture. Consumers prefer products that can be easily handled and that are available at the time of purchase. In addition, there is a trend in furniture design to use high-thickness components, whereby low-density is a fundamental requirement. Panels with a density below 600 $kg \cdot m^{-3}$ are defined as lightweight particleboard according to European Technical Specification CEN/TS 16368. There are several ways to reduce the weight of panels, such as incorporation of low-density particles in the core layer, the use of foam as a core layer and the use of low-density wood species. However, the reduction of weight leads to decrease in mechanical performance (flexural strength, internal bond strength and resistance to axial withdrawal of screws), in the quality of finishing (coating, edge lamination) and in machinability.

Synthetic formaldehyde-based resins are normally used in the production of particleboards due to their low cost, high reactivity and good bonding properties. However, the main disadvantage is the formaldehyde emission during the production and lifetime of the panels. In this way, the interest in the development of bio-sourced adhesives increases, not only to give an answer to government regulations but also to the people concerns with environmental issues. Nature-sourced alternatives have been tested for production of wood-based panels, such as adhesives based on tannins, lignin, soy protein and starch. Starch is one of the most abundant natural polymers, and is widely used as binder due to its excellent affinity towards polar materials such as cellulose, thanks to the abundance of hydroxyl groups in its structure, forming strong adhesive interactions. For this reason, starch is a good candidate for a natural adhesive system for wood-based panels, substituting the traditional synthetic resins and therefore producing panels with lower environmental impact. In this way, the development and optimization of the adhesive system and its impact on the physico-mechanical properties of the panels becomes a crucial task. The process of panels production is also a challenge because it is important to determine the impact of key parameters (temperatures and times) in the pressing process on the final properties of the panels, and in this way establish a methodology that assures the quality of the final product.

The main goal of this work is the production of low-density particleboards using as binder a starch-based adhesive, without compromising the physico-mechanical properties of the final panel. To achieve this goal, different approaches were followed. This thesis is divided into five chapters, described below.

Chapter 1, titled “Lightweight Wood Composites: Challenges, Production and Performance”, is an introduction to the thesis, outlining the main goal and an overview of the state of the art of the work. In this chapter is given a special attention to bio-based adhesives used in the production of lignocellulosic composites and literature review of lightweight composites, which includes the production process of particleboards.

Chapter 2, “Low-density wood-based particleboards bonded with foamable sour cassava starch – preliminary studies”, describes a starting formulation of an adhesive based on sour cassava starch. It was intended to understand whether it was possible to produce low-density particleboards, taking advantage of the adhesive and foam expansion properties of sour cassava starch, without compromising the good mechanical performance of the particleboards.

Chapter 3, “Low-density wood particleboards bonded with starch foam – study of production process conditions”, studies the particleboard production process using the adhesive system developed in the preliminary studies. The impact of press parameters (temperature, pressing time and hold time) on the final properties of particleboards was analysed.

Chapter 4, “Low-density cardoon (*Cynara cardunculus*) particleboards bound with potato starch-based adhesive”, looks into a different type of particles for particleboard production. The recycled wood particles used in the previous chapters were replaced by cardoon particles. This came as a consequence of the work team having identified cardoon as a by-product from the national cheese industry, with no added value. The main component on the adhesive system was also replaced: cassava starch was substituted by national potato starch. This chapter discusses the effect of the components of the adhesive system formulation for this new type of particleboard.

Chapter 5 summarizes the main conclusions and outlines some suggestions for future work.

The proof of concept is presented in Appendix A, here it is shown that starch/cardoon composite can be moulded into flat and non-flat geometries, which is one potential advantage of this product when compared to particleboards produced from thermosetting resins.

1.2. Bio-based adhesives

The industry of wood-based panels (WBPs) uses predominantly synthetic thermosetting adhesives, such as urea-formaldehyde (UF), phenol-formaldehyde (PF) and melamine-urea-formaldehyde (MUF) [1]. Other type of adhesive also used in the manufacture of WBPs is polymeric methylene diphenyl diisocyanate (pMDI).

UF resins are usually used as adhesive in the production of particleboards (PB) and medium density fibreboard (MDF), in fact the manufacturing of theses panels consumes 68% of UF resins produced in the world [2]. Their extensive use its due to their high reactivity, good binding strength and low price. The panels show lower performance when compared with a MUF resin, for this reason they are adequate for less demanding purposes in indoor use.

PF resins have excellent stability and good resistance to moisture combined with high mechanical strength. These characteristics make them a good binder for the production of exterior grade panels. Commonly, PF are used in the production of oriented strand board (OSB) and plywood (PW), however the high price constraints their broad application.

Panels produced with pMDI exhibit better stiffness and high-water resistance. pMDI requires a shorter curing time than MUF or PF, and a small amount of resin is needed to prepare the panels. These adhesives provide non-formaldehyde emitting solutions for panel manufacturers, nevertheless the higher price (3 or 4 times higher than UF adhesive) combined with problems that may result during the industrial process related with press-sticking, in particular in cases of face-layer applications limits its application [1,3]. Another issue is the toxicity associated with the diphenylmethane diisocyanate monomeric (MDI) residue, which is known as a powerful irritant for the respiratory system [4]. Table 1.1 show overall summary of the advantages and disadvantages of the synthetic adhesives used in the production of wood-based panels.

Table 1.1. Advantages and disadvantages of different types of adhesives used in the production of wood-based panels. (adapted from [2])

	Adhesives			
Properties	**UF**	**MUF**	**PF**	**pMDI**
Price	L	M/H	M	H
Cure Temperature	L	M	H	M
Press Time	S	M	M/l	Short
Affinity for wood species	H	M	L	H
Efficiency	L	M/H	M/H	H
Compatibility with bio-based raw-materials	M	M	M/H	H
Handling	Easy	Easy	Easy	Difficult
Hydrolysis resistance	No	M/H	H	H
Use in wet conditions	No	Partially yes	Yes	Yes
Formaldehyde emission	*E1 (≤0.1 ppm) *CARB I (0.18 ppm)	E1 (≤0.1 ppm) CARB II (0.09 ppm)	Very low	No

L-low; M-medium; H-high, S-short and l-long

*Class E1 according to EN 13986+A1

*CARB- California Air Resources Board

Currently, the use of formaldehyde-based adhesives raises different issues that panel's industry needs to face. These problems are related to 1) the sustainability of raw material and the final products, 2) price fluctuations of fossil resources, 3) applicable legislation to synthetic adhesives is increasingly stringent and 4) formaldehyde emissions (especially in indoor applications).

Formaldehyde is a chemical compound toxic by ingestion, inhalation and skin absorption [5]. The International Agency for Research on Cancer (IARC) classified formaldehyde as carcinogenic and toxic for humans [1,6]. Different strategies were adopted from wood-based panels industry to produce boards with very low formaldehyde emission, such as reducing formaldehyde to urea (or amine groups) ratios, the use of appropriate formaldehyde scavengers in the adhesive, and the development of (synthetic or bio-based) formaldehyde-free adhesives [7,8].

The development of bio-based adhesives has aroused the interest of wood adhesives producers in order to find economically and eco-friendly options taking account the availability, cost and the energy of natural resources. Several options have been studied such as lignin, tannins, proteins (soy) and carbohydrates (starch).

Lignin is a natural polymer produced by plants, being a natural binder of cellulose microfibrils. It is the main component of pulping liquors from the paper industry. Due to the complexity of its chemical structure, low level of reactive sites and chemical variability, the use of lignin as an adhesive itself is limited [9]. Therefore, lignin is usually combined with synthetic resins, mainly phenol formaldehyde due to its phenolic structure [10].

Tannins are natural polyphenolic compounds that can be divided in two classes: hydrolysable and condensed. Tannins-based adhesives can be obtained by polycondensation with formaldehyde, hexamine and precondensates of urea-formaldehyde with the use of sodium hydroxide as a catalyst [11]. In these conditions the tannins and formaldehyde react to form products with high molecular weight and highly branched, with low susceptibility to hydrolysis and low formaldehyde emission.

The use of adhesives based on soy protein has increased in the wood industry due to its low price, availability and ease of handling [12]. The chemical properties of proteins are influenced by their complex structure. The presence of amino acids (constituted by amino and carboxyl as functional groups) is responsible for its amphoteric behaviour, in other words they can behave as acid or base depending of the pH value of the medium. To use the protein as an adhesive it is necessary its denaturation to expose more polar groups and allow their solubilisation and formation of hydrogen bond with the substrate. Adhesives based on proteins are susceptible to biological degradation, have high viscosities, fast cure and lower moisture resistance when compared to synthetic adhesives. For these reasons they are used for indoor applications [13,12].

Carbohydrates are an abundant and low-cost raw material and are, in general, non-toxic, biodegradable, and come from renewable resources. The polymeric carbohydrates existing in large scale are cellulose, starch, sugars and gums.

Starch is one of most abundant natural polymers (Figure 1.1), available in abundance in nature and it is manly extracted from roots (cassava), tubers (potato) and cereal grains (corn and wheat). These are some of the commercial sources of starch for industrial exploitation [14]. Starch can form strong adhesive bond with cellulose, due to the presence of the hydroxyl groups in its structure [15]. During the centuries starch was used as binder for paper and wood and as gum for the textile industry [16].

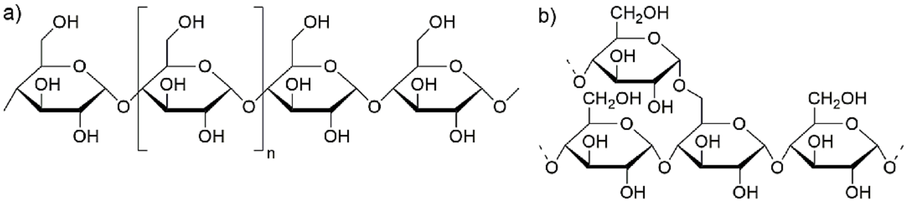


Figure 1.1. Molecular structure of a) amylose and b) amylopectin.

The morphological features of starch vary with the botanical source and the content of amylose, amylopectin and with the presence of lipids, proteins and inorganic compounds. Table 1.2 presents different features from different types of starches such as their granules shape, size and amylose content.

Table 1.2. Different features from different types of starches (adapted from [16]).

Source	Diameter (µm)	Amylose content (%)	Shape
Maize	5-25	28	Polyhedric
Cassava	5-35	16	Semi-spherical
Potato	15-100	20	Ellipsoidal
Wheat	20-22	30	Lenticular, polyhedric

Starch consists of two major molecular components, amylose and amylopectin which can be differentiated by their chemical structure. The linear α-(1→4) linked glucan is called amylose while an α-(1→4) linked glucan with (4.2–5.9)% α-(1→6) branch linkages is amylopectin [14].

Inside a starch granule, there are two different regions: one crystalline, constituted by amylopectin chains, and another amorphous, constituted by amylose, where part of it forms a helical complex with lipids. Amylose is located next to or intertwined with amylopectin, keeping the integrity of the granule [14].

Starch presents different polymorphic crystal forms, called A-, B- and C-type. A and B types are usually present in native starch, being that the first is associated to cereal starches and the second to root starches, however B-type also occurs in maize starches. The crystalline forms A and B are very similar; however, the molecular packing of crystalline form A is higher than for form B. The C-type is a mixture of both A and B forms, and it is present in pea and bean starches. The V-type form (Verkleisterung) is a result of amylose being complexed with other substances (for example lipids). Types A and B differ in the packed arrangement, being type A more compacted and less hydrated when compared with type B [17].

When heated in water or other solvent that allows the formation of hydrogen bonding, starch granules become hydrated and swell, thus occurring the disruption of the granules. This phenomenon is called gelatinization. This occurs above a characteristic temperature, designated by gelatinization temperature.

During this process amylose is leached from the granule and dissolves in water, resulting in an increase in solution viscosity [14].

The starch/water ratio influences the melting temperature. The gelatinization process is influenced by the molecular structure of amylopectin (chain length, extension of branching, molecular weight), starch composition (ratio amylose/amylopectin) and granule architecture (proportion of crystalline and amorphous regions). Usually, high transition temperatures are associated with high degree of crystallinity, which makes the granules more stable and resistant to gelatinization (Figure 1.2) [18].

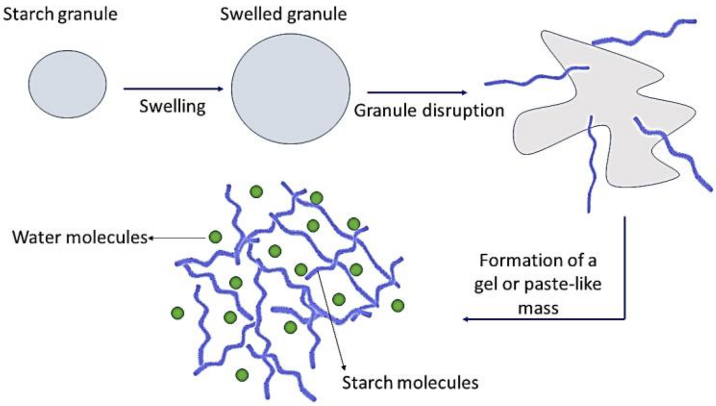


Figure 1.2. Process of starch gelatinization.

The heating of starch in presence of water, followed by cooling, leads to gradual reorganization of the disrupted amylose and amylopectin chains into a different ordered structure, in a process known as retrogradation. The retrogradation process is affected by the type and amount of starch, the ratio between amylose and amylopectin, the storage temperature, pH and the presence of other components [19,20].

In the literature there are some studies that report the use of starch-based adhesives in the production of particleboards. Moubarik *et al*. [21] reported that the incorporation of a small amount of cornflour (7 wt%) in UF resins contributes to improve the physico-mechanical properties of the produced particleboards (0.57 $N \cdot mm^{-2}$ of internal bond strength (IB)) and the reduction of formaldehyde emissions. Amini *et al.* [22] used modified corn starch with 25% glutaraldehyde hardener solution as a binder for rubberwood particleboards. Particleboards were produced with three different densities: 600 $kg \cdot m^{-3}$, 700 $kg \cdot m^{-3}$ and 800 $kg \cdot m^{-3}$.The modulus of rupture (MOR) and the IB obtained were acceptable. However, to improve water resistance it was necessary to add water repellent agents. In another study, oil palm starch was firstly crosslinked by phosphoryl chloride ($POCl_3$) and then reacted with sodium chloroacetate ($C_2H_2ClNaO_2$) to form a carboxymethylated starch to produce particleboards. The modulus of elasticity (MOE) and IB of the particleboards produced met the requirements of the Japanese Industrial Standards (JIS), except for the MOR [23]. In order to achieve the minimum values specified by the JIS for MOR, addition of 2% of UF to the carboxymethylated starch adhesive could be an option.

Starch adhesives had low water resistance due to their highly hydrophilic character. The high viscosity is a limitation for industrial uses. These types of adhesives have a poor storage stability and low bonding strength [24].

1.3. Lightweight wood composites: challenges, production and performance[1]

Abstract

Wood composites are materials made by bonding together wood and adhesives into a large material that can be used for different purposes. Nowadays, lightweight materials play an important role in several industries: aerospace, building and furniture. The reduction of weight is desirable for economic reasons (materials and transportation costs) and environmental reasons (resources, eco-efficiency). Once wood composites are employed in these industries, low-density is a desired property. There are several options in the market to reduce the weight of composites, such as the use of low-density wood species, lower compaction of the wooden mat, incorporation of light fillers in the core layer of the panel, or use of sandwich panels with honeycomb core. All these strategies have challenges with respect to manufacture, machinability (connections and lamination of the edges) and performance (physico-mechanical properties).

---

[1] Monteiro, S.; Martins, J.; Magalhães, F.D.; Carvalho, L. Lightweight wood composites: challenges, production and performance. In *Lignocellulosic Composite Materials*, 1st ed.; Springer International Publishing:Cham, Switzerland, 2018; volume 1, pp. 293–322.

1.3.1. Introduction to lightweight wood-based composites

Wood composites are materials made by bonding together wood with different shapes and sizes and adhesives, forming a large material which can be used for a variety of products with the required physico-mechanical properties: furniture, flooring, roofing, palettes, decking, structural beams, marine applications, aircraft materials, etc.

The advantages of using wood-based composites, in relation to solid wood, are 1) use of small diameter trees, 2) use of waste wood from industrial processing and agriculture residues, 3) products with uniform and defect-free appearance, 4) better strength than solid wood, 5) products with unique shapes and dimensions, and 6) products with special properties such as low thermal conductivity, fire resistance, and better biological durability [25].

Several factors have a huge impact on the mechanical properties of wood-based composites such as: wood species, forest management regimes (naturally regenerated, intensively managed), kind of adhesive used, shape (fibres, flakes, strands, particles, veneer, lumber) and the arrangement of wood elements in composite and the final composite density. The performance of wood composites can be characterized according to several engineering properties. Structural and non-structural applications are defined by the mechanical properties of the composite.

Static elasticity and strength are the key properties used to choose the materials or set up the design and the specifications [26].

Nowadays, the use of lightweight materials becomes a topical issue in many developed industrial countries. The trend concerning lightweight materials is notorious in many industries and the furniture and wood-based panels industries do not miss out. The increase of the mobility of people demands that materials should be lightweight and also have proper physico-mechanical properties.

Generally, a lightweight material brings many advantages for producers, designers and consumers: 1) lower costs in consequence of mass reduction and transportation, 2) possibility of obtaining thick elements, answering current design trends, 3) more rational use of wood, when its price is high or availability is scarce, 4) ease of transportation by producer and final costumer, with lower environmental impacts [27]. According to CEN/TS 16368, panels with density below 600 kg·m^{-3} are classified as lightweight materials. Materials such as tubular board, honeycomb panel and panels with foam core are included in this group. Figure 1.3 shows the different ranges of density for wood based-materials, emphasizing those considered as lightweight.

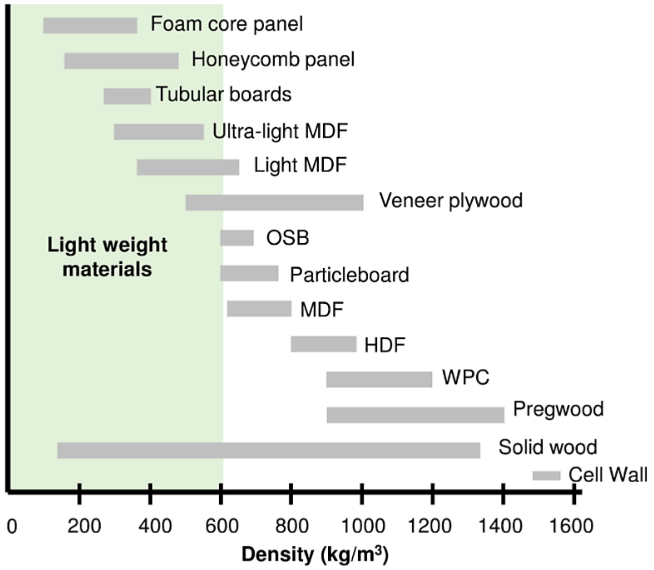


Figure 1.3. Density of wood-based materials and for cell wall: foam core panel, honeycomb panel, tubular boards, ultra-light and light MDF(medium density fibreboard), veneer plywood, oriented strand board (OSB), particleboard, medium density fibreboard (MDF), high density fibreboard (HDF), wood plastic composites (WPC), pregwood and solid wood (adapted from [28]).

The different strategies available for obtaining the lightweight wood composites already available in the market are summarized in Figure 1.4 [29–31].

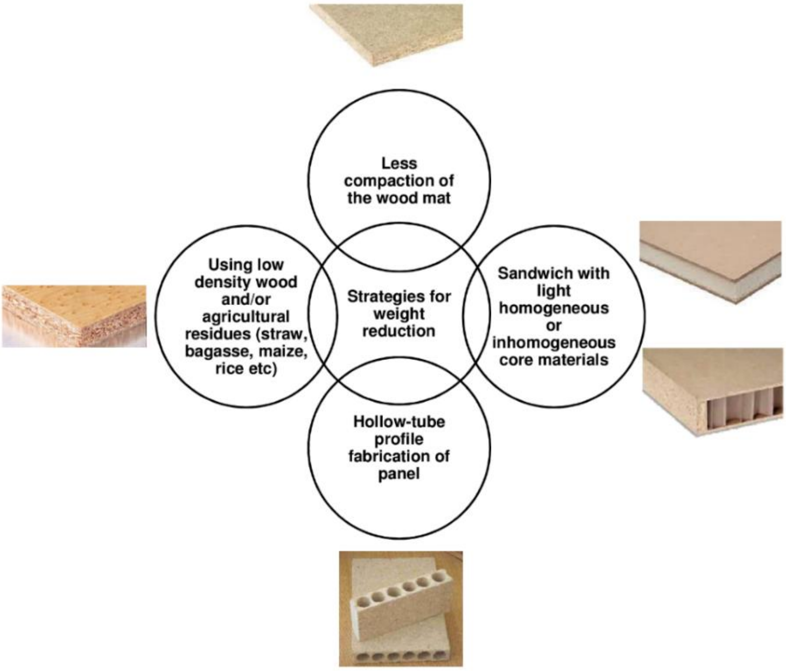


Figure 1.4. Strategies for panel weight reduction.

Panels such as MDF and particleboards with low-density are produced by using lower compaction of the wood mat. Another strategy is using very light wood species like *Ochroma* spp. (50 to 300 kg·m^{-3}) or *Ceiba* spp. (300 kg.m^{-3}) from North America and South America respectively. *Populus* spp. (450 kg·m^{-3}) from Europe is another type of light wood also used in the production of lightweight particleboards [32]. Extruded tubular boards are frequently used and the density achieved with this method may vary between 250 to 400 kg·m^{-3}. Sandwich panels with foam core (made of polyurethane or polystyrene foam) or paper-based honeycomb structures are a major trend in the industry, achieving densities from 100 to 350 kg·m^{-3}. However, lightweight panels have certain restrictions, which constitute a challenge to be overcome:

- Reduction of mechanical properties, which disallows the use of panels in applications requiring load bearing capacity,
- The use of agricultural residues requires higher amount of resin,
- Difficult storage of non-wood bio-based materials such as agriculture crops,
- Limitations in terms of surface finishing and post-forming,
- Increase of production cost associated to the need of new additives due to lower bonding strength of the new raw materials [27,33].

1.3.2. Fibreboard

Fibreboard is a wood-based panel with a nominal thickness of 1.5 mm or greater, manufactured from lignocellulosic fibres with application of heat and/ or pressure (EN 316). The bond is derived from either the felting of the fibres and their inherent adhesive properties or from a synthetic binder added to the fibres. Other additives can be included (EN 622-5).

The most commonly used lignocellulosic fibres are wood, but other plant fibres can be used such as bagasse and cereal straws. Thermo-mechanical pulping (TMP) is the process commonly used to make fibreboards. This process consists in breaking the bonds between the wood cells by combining action of heat and mechanical energy. The lignin present in the wood have the ability to absorb small amounts of water, therefore its softening temperature is dependent of moisture content. The TPM process uses high temperature (170-195 °C) and humidity (60-120%) that increase the probability of breaking the wood cells, when subjected to a mechanical energy during the refining process [35,36].

The methods of wood-based fibreboard manufacture are generally divided into wet and dry process. The definitions of fibreboards are formulated in the

European standard (EN 316). Fibreboards are classified by their production process as follows:

- Wet process fibreboards (fibre distribution in water),
- Dry process fibreboards (fibre distribution in air).

Wet process boards are fibreboards having fibre moisture content of more than 20% at the stage of forming. Additionally, wet process boards are classified according to density, as follows:

Hardboards (HB)	Boards with density $\geq 900\ \mathrm{kg \cdot m^{-3}}$
Medium boards (MD)	Boards with density $\geq 400\ \mathrm{kg \cdot m^{-3}}$ to $\pm\ 900\ \mathrm{kg \cdot m^{-3}}$
Softboards (SB)	Boards with density $< 400\ \mathrm{kg \cdot m^{-3}}$

Dry process fibreboards are fibreboards having a fibre moisture content of less than 20% at the stage of forming and having a density $\geq 450\ \mathrm{kg \cdot m^{-3}}$. Medium density fibreboard (MDF) is one of the most rapidly growing composite panel products in forest products market.

Raw materials namely wood, binders and other additives and the production parameters are the factors that have major effect on physico-mechanical properties of MDF [37]. When wood is considered as a raw material, wood fibre properties such as fibre structure and strength, anatomical and chemical properties of fibre, and fibre composition (percentages of whole and broken fibres and fines) are considered to be basic characteristics influencing fibreboard properties, since they occupy a large portion of the total panel volume. For marketing purposes, MDF of specific density range can be given different denominations. For example, the following density-related marketing terms for MDF have become established:

High Density Fibreboard (HDF)	MDF with density ≥ 800 kg·m^{-3}
Light MDF (L-MDF)	MDF with density ≤ 650 kg·m^{-3}
Ultra-light MDF (UL-MDF)	MDF with density ≤ 550 kg·m^{-3}

1.3.2.1. Wet process fibreboards: softboard

Softboards are usually used in the interior of walls and floors, and as underlays in roofs, in order to provide heat insulation properties. The low-density leads to a more energy efficiency caused by the many air voids in the panel [38,39].

Softboards can be produced via a wet process (Figure 1.5), which is really an extension of paper manufacturing technology.

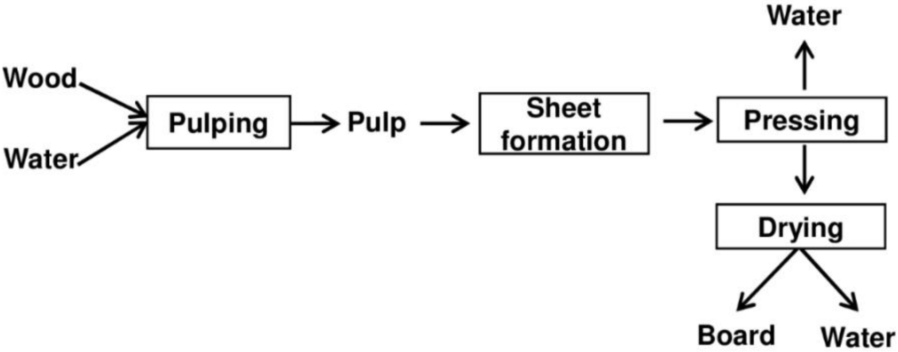


Figure 1.5. Wet process manufacture (adapted from [40]).

Wood enters a chipper to be reduced in size (with sizes of approximately 25 and 5 mm thick). The chips are screened to remove undersized (< 2 mm) and oversized (> 50 mm) particles. The chips are washed to remove contaminants and to facilitate defibration, and then fed into the pre-heater or digester, where they are heated with overheated steam at 6-10 bar and at a temperature of 175-195 °C for 3-7 minutes. The steam treatment softens the lignin, which binds the fibres together allowing their separation in a pressurized discs' refiner under saturated steam at 8-10 bar. Here, the steamed chips are transformed into fibres. Some wet-process boards are made without additional binders. If the lignocellulosic materials contain sufficient lignin, this compound can serve as binder, as long as it is retained during the refining operation. Under heat and pressure, lignin will flow and act as a thermosetting adhesive, enhancing the naturally occurring hydrogen bonds. The fibres are discharged from the defibrator and then water is added to form a slurry (water is used as the dispersion medium for forming the fibres into a mat, this is the reason why the process is called wet-process). This slurry is introduced into a wire mesh conveyer belt to form the board, losing its water prior to drying. The boards are lightly compressed and dried in an oven. The voids created after the evaporation provide the board its good thermal properties.

Contrary to other wood-based boards, fibre-based insulation materials are not required to display high strength. Surface appearance, internal bond, and bending strength are also not of primary importance for softboards. The typical properties of these boards are presented in Table 1.3.

Table 1.3. Typical properties of softboards [39].

Property	**Values**
Density	170-280 $kg{\cdot}m^{-3}$
Flexural strength	1.0-2.7 MPa
Modulus of elasticity	80-400 MPa
Maximum thickness swelling	12-20%
Sound absorption of acoustical board (522 Hz)	50-85%

There are several insulation products available in the market. The board properties vary with production technologies, final application and specific requirements. Table 1.4 gathers examples of few commercial softboards and their properties.

Table 1.4. Comparison of properties of different softboards available in market [41].

Product/ Producer	**Application area**	**Thickness (mm)**	**Density ($kg\cdot m^{-3}$) EN 1602**	**Heat conductivity [W/(m K)]**	**Materials and Additives**
HolzFlex®/ Homatherm	Intermediate rafter framework	40-200	40	0.038	-Wood fibres -Polyolefin fibres -Ammonium polyphosphate
Steico-Flex/ Steico	Intermediate rafter framework	40-200	50	0.038	-Wood fibres -Polyolefin fibres -Ammonium sulphate
Agepan THD N+F 230/ Glunz	Over rafter	40/60/80	230	0.047	-Wood fibres -Polyurethane resin
Thermosafe Homogen/ Gutex	Universal insulating board	20-240	< 110	0.037	-Wood fibres -diphenylmethane di-isocyanate (pMDI)

The major benefit of this production process is the low volatile organic compounds (VOCs) emission level caused by the low amount of resin used and the drying time that is longer. The density (> 150 $kg\cdot m^{-3}$) and the board thickness (< 40 mm) are the two mainly restrictions in the wet process. Panels with higher thickness need a longer drying time which causes an increase of production costs [41,42].

1.3.2.2. Dry process fibreboards: light MDF and ultra-light MDF

Light MDF and ultralight MDF are widely used in the manufacture of furniture, doors and walls due to many excellent properties such as low density, low thermal conductivity and good sound absorption [43]. These types of panels are manufactured by using what is called a dry process (Figure 1.6).

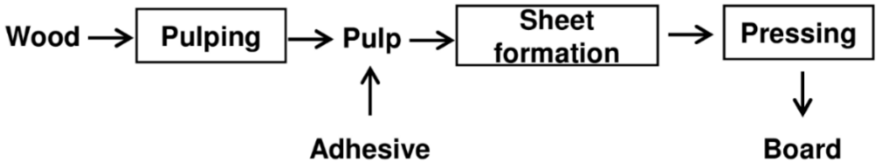


Figure 1.6. Dry process manufacture (adapted from [40]).

In this process, the fibres are produced in the same way as the wet process. After the defibration process, wood fibres are discharged into a pressurized blowline, a tube with 80 to 120 mm of diameter, which transports wet fibres to the dryer. In the blowline, when the fibre is blended under high pressure, the resin is more easily distributed due to the steam expansion that causes the separation of fibres [36].

Resins like polymeric diphenylmethane di-isocyanate, urea-formaldehyde and phenol-formaldehyde are used as adhesives [44]. The adhesive, as well as other additives, are injected into the blowline through a 3-5 mm nozzle at high pressure (12-14 bar). The adhesive load is usually between 8 and 15% (resin solids/oven dry wood). The wet resinated fibres are then blown through a flash tube dryer (with around 100 m long and 1-3 m in diameter) at around 30 $m \cdot s^{-1}$. At the end of the tube, cyclones separate the dried fibre from steam. After drying, fibres have approximately 8-12% moisture content. The dry fibre is conducted to mat formers. These are made with the purpose of distributing an even layer of fibres onto a continuously moving belt. Here, the panel thickness is controlled by monitoring the speed belt. The forming head spread fibre mattress homogenously. In the case of an 18 mm thick MDF board, the mat is around 680 mm high and has a bulk density of 23 $kg \cdot m^{-3}$. After passing a continuous prepress to reduce its height, the mat is then pressed in a continuous hot-press with temperature in the range of 180-210 °C and pressure between 0.5 and 5.0 MPa [36]. The pressing stage can be used to manipulate panel properties by changing the panel density profile. This operation has a major effect on the balance of properties of the resulting panel: a rigorous control of all processing variables is necessary to achieve appropriate product quality and to minimize pressing time [45]. Immediately after pressing the panels are fed into a star shape cooler where boards are stood on their edges to expose their faces to ambient air to facilitate rapid cooling. Finally, boards are subjected to finishing operations, which includes trimming, sanding and cut to size. Nowadays manufacturer also includes several surface treatments such as laminating, profiling and painting.

Light and ultra-light MDF are produced in the same way as MDF, but lower pressing pressure is used to attain lower density MDF. The main advantage of this process is the decrease of the density to 50 $kg \cdot m^{-3}$and an extensive range of thicknesses (< 200 mm). A disadvantage of the dry technology is the high level amount of resins that is needed to strengthen the fibre bonds [41].

Light MDF is used in situations where weight reduction is required in the range of 15-20% and where the machinability performance is not a limiting factor.

In the manufacturing of MDF, several important factors have direct effects on mechanical properties and stability of the panel, namely the resin system, moisture content, hot-pressing conditions, and wood fibre characteristics. The structure and morphology of fibres have more influence than their mechanical characteristics on the board properties. Fibres with different morphologies have different specific surface areas [46]. Short fibres need higher amount of resin when compared with longer fibres, which generally results in better mechanical properties for the panels. When the resin content of the panels increases from 6 to 12%, an increase in mechanical properties (internal bonding, modulus of rupture and modulus of elasticity) is observed, while thickness swelling and water absorption decrease. In the thermo-mechanical pulping process, usually used to refine fibres, refining pressure and time are two important features that affect the final properties of the board. With the exception of water absorption, refining pressure has great influence in overall panel properties. On the other hand, refining time does not alter the properties of fibre and board [47]. The effect of moisture content change on panel flatness is difficult to predict because of the characteristic variation of the density level throughout the thickness, or vertical density profile.

The panel properties depend of the compaction ratio of each layer that forms the panel. Generally, the difference between the layers is defined by the compaction ratio, since that no differences exist in geometry fibre and resin amount in the whole panel [48].

The requirements for light MDF are different depending on its use in dry or humid conditions. Panels in humid conditions have to withstand the presence of water vapour in the surrounding air and casual contact with water on surface. Table 1.5 specifies the requirements for light MDF boards for use in dry and humid conditions, particularly interior fitments including furniture.

Table 1.5. Requirements for light MDF boards for use in dry and humid conditions (type L-MDF and type L.MDF.H) (EN 622-5).

Property	**Conditions**	**Test method**	**unit**	**Ranges of nominal thickness (mm)**					
				>6-9	>9-12	>12-19	>19-30	>12-19	>45
Swelling in thickness 24 h	Dry	EN 317	%	20	16	14	12	11	11
	Humid			18	16	13	12	11	10
Internal Bond	Dry	EN 319	$N \cdot mm^{-2}$	0.45	0.45	0.45	0.45	0.40	0.40
	Humid								
Bending strength	Dry	EN 310	$N \cdot mm^{-2}$	20	20	18	15	14	14
	Humid			20	20	18	16	16	14
Modulus of elasticity in bending	Dry	EN 310	$N \cdot mm^{-2}$	1700	1700	1600	1500	1400	1200
	Humid								

Concerning ultra-light MDF, the requirements are different from light MDF. In this case, panels are divided in two groups:

- Ultra-light MDF Type 1 (UL1-MDF), these boards are typically used as insulation panels providing limited mechanical stiffness;

- Ultra-light MDF Type 2 (UL2-MDF), these boards are typically used as panels with stiffening function; they also can be used with fasteners. These panels have insulating properties. The next table specifies the requirements for these two types of panels under dry conditions (Table 1.6).

Table 1.6. Requirements for ultra-light MDF boards for use in dry conditions (type UL1-MDF and type UL2-MDF) (EN 622-5).

Property	**Conditions**	**Test method**	**unit**	**Ranges of nominal thickness (mm)**				
				>9-12	>12-19	>19-30	>30-45	>45
Swelling in thickness 24 h	UL1-MDF	EN 317	%	18	14	13	12	12
	UL2-MDF							
Internal Bond	UL1-MDF	EN 319	N·mm^{-2}	0.15	0.15	0.15	0.13	0.13
	UL2-MDF			0.35	0.35	0.35	0.30	0.30
Bending strength	UL1-MDF	EN 310	N·mm^{-2}	7.7	6.9	6	5.1	5.1
	UL2-MDF			18	16	14	12	12
Modulus of elasticity in bending	UL1-MDF	EN 310	N·mm^{-2}	600	560	510	470	470
	UL2-MDF			1400	1300	1200	1100	1100

The most important feature of low-density MDF is its homogeneous density profile along the thickness, which allows turning and edge profiling operations. The possibility of surface and edges finishing is one of main advantages of this material over other wood composites.

There are several options of traditional light and ultra-light MDF in the market, in Table 1.7 are presented some examples.

Table 1.7. Mechanical properties of some light and ultra-light MDF available in the market for dry conditions. Information taken from the products' datasheets.

Product	**Application area**	**Thickness (mm)**	**Internal Bond ($N\cdot mm^{-2}$)**	**Swelling in thickness, 24 hr (%)**	**Bending strength ($N\cdot mm^{-2}$)**
Kronospan	Building material for a substitute for timber in non-load bearing walls, ceilings, partitions	15-18	≥0.80	12	45
Fibrapan	Loudspeaker boxes for sound equipments, doors, decorative mouldings	6-45	0.50-0.55	9-18	15-20
Caberwood	General purpose joinery	12-25	0.45	12	20
Medite ultra-light	Furniture Ceilings Picture frames Mobile home components	12-18	0.35	10-15	15
Fibrapan ultra-light	Used in the construction industry and in the setting-up of exhibitions and fairs	9-28	0.50	13-17	14-18
Caberwood Ultra-light	Theatre scenery Film sets and exhibitions	12-25	0.35	13-18	14-18

There is a new technology to produce low-density fibreboards different from traditional manufacturing. Dascanova® developed a unique mat modification technology that alters the compressibility of selected particles before pressing the final board. This allows redistribution of the density inside the board. Unlike conventional fibreboards that have homogeneous density in the core and higher density on the surfaces, Dascanova fibreboard has a vertical density profile that changes along the entire board (Figure 1.7).

The ideal construction form is the triangular or wave structure. In comparison to standard technology, up to 30% less raw materials (including resin and other chemical components) are needed for producing Dascanova Fibreboard. The mechanical properties are similar to standard fibreboard, while internal bond strength is improved due to this special internal structure. The panels produced have average density of 428 kg·m^{-3} with a bending strength and modulus of elasticity of 9.2 N·mm^{-2} and 2.097 N·mm^{-2} respectively [49].

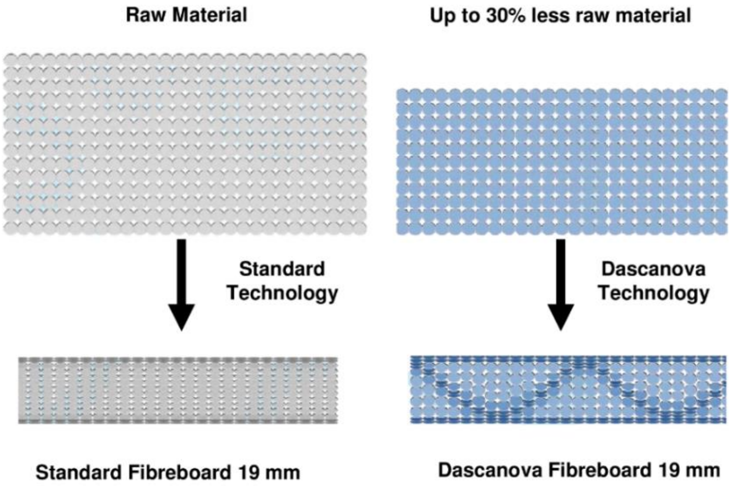


Figure 1.7. Scheme of the comparison between the standard technology of fibreboard production and the developed Dascanova technology (adapted from (www.wbpionline.com)).

1.3.3. Particleboard

As defined in European Standard EN 309, particleboard is a "*wood-based panel manufactured under pressure and heat from particles of wood (wood flakes, chips, shaving, sawdust and similar) and/or other lignocellulosic material in particle form (flax shives, hemp shives, bagasse fragments and similar) with the addition of an adhesive*". As said before, particleboards with density below 600 kg·m^{-3} are defined as lightweight particleboard (European technical specification CEN/TS 16368). These panels are commonly used in furniture, being overlaid with different materials for decorative purposes. Particleboard can also be employed in flooring systems, in houses constructions, for stair treads and as underlayment [51]. These applications require high mechanical strength and good dimensional stability, once the panels are exposed to bending stress, static and impact forces. Besides that, particleboards must be resistant to water absorption [52]. Particleboard is the most popular wood-based panel in the market due to its lower cost, which results from the use of recycled wood, and to its intrinsic relatively low density compared with other boards.

1.3.3.1. Particleboard manufacture

The raw materials used in particleboard manufacture consist of wood residues from sawmills, recycled cellulosic materials and plant residues such as wheat straw and bagasse. The initial step in particleboard production is the reduction of the wood into smaller sizes. For this, large particles are chipped in the Breakdown Machines, using hammer mills and flakers. The shape and integrity of the wood particles have a huge influence in the final properties of particleboard. The use of homogeneous raw material is very important to produce panels with good strength, smooth surfaces and similar swelling. After the particles are cut to the desired size, they are sent to dryer in order to obtain the intended moisture content, usually in the range of 2-8%, depending on the resin chosen to produce the board. Higher values of moisture content can generate a large amount of water vapour during pressing, causing the lamination of the panel. The adhesive system must be prepared according to the formulation. Different amounts of adhesive are used in the surface and core layers. The adhesive content is calculated on a solid adhesive to oven-dry wood basis. Normally, particleboards have three layers, a core layer with coarser particles and a lower density and two surface layers with finer particles and higher densities [52]. The smaller particles contribute to improve the surface quality and the larger one provides better mechanical properties like bending.

After being mixed with the resin, the particles are formed into a mat and then transferred to the hot press for the panel curing process. This step is critical and requires carefully controlled temperature, pressure and timing. The press time and temperature are very important, since it is necessary to get a high enough temperature in the core to cure the adhesive, at the same time as the temperature at the surface should not be too high to avoid thermal degradation. Typical pressures are 2-4 MPa and temperatures 200-220 °C. After pressing the boards are cut, sanded and finally the edges are trimmed. Boards may also be subjected to different finishing. They can be veneered or overlaid with other materials, like impregnated paper laminates. Paint and lacquer can also be used in the board finishing [53]. A schematic example of particleboard production can be seen in Figure 1.8.

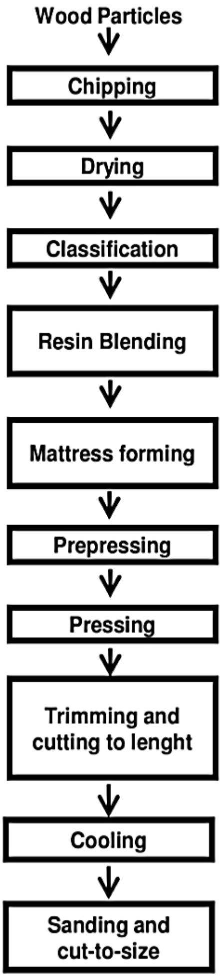


Figure 1.8. Particleboard manufacture.

The resins most commonly used in particleboard production are urea-formaldehyde (UF), melamine formaldehyde (MF) and phenol formaldehyde (PF), the last one being used to a much lesser extent. Other types can be used such as isocyanate resin (methylene diphenyl diisocyanate – MDI and polymeric diphenylmethane di-isocyante – pMDI) [54,55]. The advantage of UF resins when compared with the other ones is their high reactivity, fast curing, good adhesion to wood and low cost [55].

Usually, physico-mechanical properties are evaluated according to European standards. The mechanical properties specifications for general purpose lightweight boards (type one-LP1) and for use in dry conditions (type two-LP2) are presented in Table 1.8.

Table 1.8. General purpose lightweight boards LP1 and LP2 for use in dry conditions (CEN/TS 16368).

Type	**Property**	**Test method**	**unit**	**Ranges of nominal thickness (mm)**					
				>6-13	>13-20	>20-25	>25-32	>32-40	>40
LP1	Bending strength	EN 310	N·mm^{-2}	4.0	3.5	3.0	2.5	2.0	2.0
LP2				8.0	7.0	6.0	5.0	4.5	4.0
LP1	Modulus of elasticity in bending	EN 310	N·mm^{-2}	550	500	475	450	400	375
LP2				1000	950	900	850	750	650
LP1	Internal bond	EN 319	N·mm^{-2}	0.28	0.24	0.20	0.17	0.14	0.14
LP2				0.35	0.30	0.25	0.20	0.17	0.17

1.3.3.2. Particleboards made from light wood species

One of the interesting strategies used by the lightweight wood-based panel industry to achieve the density reduction of particleboard is the use of light available wood species. With this strategy it is possible to achieve maximum reduction of one third of the initial density. However, to maintain the mechanical properties such as internal bond and bending strength at acceptable values, producers had to increase the amount of used resin and optimize the board’s density profile. On the other hand, the use of light wood species is strongly dependent on the availability and seasonality of wood, the global resources are limited and they are not sufficient to meet market needs. The production cost caused by the increasing of resin in the manufacture of boards also is a huge concern to the producers. Usually, the material costs related with this type of product are more than half of the production costs [57].

In literature there are a few examples of particleboards produced with wood light species such as poplar (*Populus spp.)* [58] Seraya (*Shorea spp*.) [59], paulownia (*Paulownia tomentosa)* [60], kelempayan *(Neolamarckia cadamba)* [61]. Figure 1.9 shows the internal section of particleboard made from *Populus* spp. wood.

Figure 1.9. Internal section of particleboard made from *Populus* spp. wood.

Particleboards produced with these light wood species have a range of density between 300 and 600 kg·m^{-3}. In these studies, an isocyanate adhesive is usually used as the binder, due of its ability to form covalent bonds with the hydroxyl groups on the wood surface. This high reactivity allows faster cure rates, when compared with the amino and phenolic resins, and lower adhesive loads. In general terms, the properties of particleboards are significantly affected by the density of the raw materials; panels produced with light wood species may lead to panels with higher strength when compared with higher density species. This occurs because light species have higher compaction ratio, which allows a greater contact area between the wood particles during the pressing operation obtaining a good bonding. To obtain maximum bonding a certain amount of pressure is needed; the adequate pressure depends on the ratio between the board density and the wood species density. To produce particleboards with medium density, the required ratio is commonly higher than 1.3 (typically ratio in boards produced with amino resins). Boards produced with high density species with admissible properties for use in most applications have high density. It is possible to obtain a reduction of density by mixing high and low-density species. On the other hand, the use of raw materials with different density can cause problems in some steps of manufacturing process such as:

- milling operation - particles with different densities are milled differently;
- drying operation - loss of moisture content is affected by density;
- pressing operation - particle compressibility depends on density.

The amount of resin to be used can also be affected by the different characteristics of the wood material [51,62].

Boruszewski *et al.* studied the effect of technological parameters on mat compression during the producing of lightweight particleboards (500 kg·m^{-3}) made of two low-density species (*Populus* spp. *and Pinus* spp.). Three series of panels were produced: one made with only pine, other made with only poplar, and the last one with a mixture of the two wood species. The results showed that the characteristics of the species used, such as heat transfer coefficients, and moisture content affect significantly the compression process. Lower density species require higher pressing times or higher heat transfer in the panel core layer. With regard to mechanical properties, the modulus of rupture (MOR) and the modulus of elasticity (MOE) had higher values for panels made with poplar wood. This is related to the low density of poplar wood, which leads to higher compaction. However, boards produced with mixed poplar-pine revealed the best performance in terms of internal bond (IB). This result is explained by the density different of the two wood species used, which requires the use of higher resin amount. Another reason is the higher extent of compaction of poplar face layers in the mixed boards, due to the lower density of this wood furnish [58].

Studies carried out by Kalaycioglu *et al.* showed that particleboards produced with paulownia with density of 550 kg·m^{-3} had MOE and MOR strength values that meet the requirements for general uses and interior fitments established in EN standards. As expected the panels with density of 650 kg·m^{-3} presented better mechanical properties [60].

Another trend of lightweight wood-based panel industry is the use of alternative raw materials such as agriculture residues and annual/perennial plants to produce particleboards Dziurka *et al.* studied particleboards made from wood and rape straw particles to produce particleboards with density in the range of 350-550 kg·m^{-3}. The results revealed that, as established, the reduction of density in both series of produced panels (wood and rape straw) lead to a reduction of bending strength and modulus of elasticity. Panels manufactured with rape straw showed a reduction of strength of 32% when the density of the boards is reduced from 550 to 350 kg·m^{-3}. For the same density variation, strength reduction was 18% for particleboards produced from wood. The modulus of elasticity showed the same trend. The use of veneer on panels surface improves significantly the bending strength. All produced boards meet with the requirements of boards for interior decoration and furniture applications (lightweight boards LP2) [31].

1.3.3.3. Particleboards with light fillers

In recent years, the competition for wood has been increasing, particularly due to the extensive use of this resource in the construction and furniture sectors. Therefore, the use of non-wood raw materials to reduce the weight of particleboards is an interesting approach. Materials like expanded polymeric particles, starch granulates or even popcorn [63] have been mixed with wood in the core layer of panels. In low-density particleboards, the light fillers fill the voids between wood particles, allowing for improved machinability of panel edges [64].

BASF Company developed Kaurit Light, with core made from a mix of expanded polystyrene foam (EPS) and wood particles (Figure 1.10), with 30% lower weight than a conventional particleboard, while maintaining the same strength as standard [65]. The size range of the EPS particles used is 0.3-0.8 mm.

Figure 1.10. Internal section of particleboard produced with expanded polystyrene foam (EPS) mixed with wood particles in core layer.

To produce expanded polystyrene foam, deionized water, styrene and the mixture initiator are added to the reactor under agitation at ambient temperature. Then the stabilizer is added to the reactor. The stabilizer consists of insoluble inorganic salts such as magnesium carbonate, which prevent the monomer droplets from coalescing. It is during the heat cycle that occurs the development of droplet size.

After polymerization, when the spherical particles are formed, the mixture is cooled and centrifuged to separate the water from the polymer beads and then the beads are dried. The beads and the water are added to the impregnation reactor. During heating, the reactor is pressurized with blowing agent, usually n-pentane, at 5-7% w/w with respect to polymer. During this step the blowing agent diffuses into the beads. At the end of this stage the system is cooled down and the excess of stabilizer is removed from the particle surface in a washer tank. The separation of polymer beads from water is made by centrifugation. Then the particles are dried. In the final processing, the EPS beads are heated, usually with steam that causes the beads to expand by foaming and their volume to increase [66].

Another type of expanded material usually used in core layer of particleboards is expandable microspheres (MS). This filler is commercially available under the name of Expancel and is produced by AkzoNobel company. The microspheres consist of a polymer shell (typically acrylonitrile or vinylidene chloride copolymerized with methyl methacrylate or methyl acrylate) encapsulating a gas (isobutene) [67]. Increasing temperature above 85 °C causes the polymer shell to soften, which, in combination with increased pressure of the encapsulated gas, results in sphere expansion. The particle size of MS is approximately 15 μm before expansion [68] and 40 μm after expansion.

The main difference between MS and EPS is that the first are added to the core layer in the unexpanded state, having micrometric sizes. EPS particles are already expanded, having sizes of few millimetre. For this reason, MS can be more difficult to scatter in the core layer. Another important difference is the glass transition temperature (Tg): EPS particles have a higher Tg (103 °C) compared to MS (85 °C). This property affects the processing conditions of the panel. The inflammability of the blowing agents used in both fillers is a main limitation; this implies restrictions in some applications [27].

In the studies carried out by Shalbafan *et al.*, the mechanical properties of multi–layered lightweight panels produced with MS core layer with different surface thickness (3, 4 and 5 mm) were evaluated. The target density of particleboards varied from 300 to 500 kg·m^{-3}. The study revealed that the IB of the panels with MS in the core layer increased when the face layer thickness is raised. The same applies to bending strength. This is explained by the increase of density in the board core (120-180 kg·m^{-3}), which promotes a better interaction between wood particles and MS. However, when compared with conventional panels, only particleboards with MS with higher density (500 kg·m^{-3}) had IB higher than 0.24 N·mm^{-2} (IB requirement for lightweight particles boards' type 1) [68].

In another study developed by Shalbafan *et al.*, different amounts of expanded polystyrene particles (5, 10 and 15% based on the dry mass of wooden particles) were used to produce particleboards with two different densities (450 and 500 kg·m^{-3}). The research showed that the use of these fillers affects the physical and mechanical properties of the particleboards. Fillers absorb lower amounts of resin when compared with wood particles, which improved the efficiency of the adhesive. As expected, panels with higher density had better flexural properties. Panels with density of 500 kg·m^{-3} had higher IB when compared with conventional particleboards, due, according to the authors, to a bonding reinforcement effect caused by the fillers in panel core layer. Concerning physical properties, low-density particleboards had lower thickness swelling compared to conventional particleboards, mostly due to the presence of a hydrophobic filler. The same trend was observed for water absorption [64].

1.3.4. Extruded particleboards

Extruded boards, also called tubular boards, are a type of particleboard produced by extrusion (Kreibaum process), while the conventional particleboards are manufactured by flat-pressing (Fahrni process) [69]. In the extrusion process, wood residues and vegetable waste can be used if they are reduced to short particles. Glued wood particles are introduced in hot press, compressed using a piston driven by an eccentric flywheel, and extruded through the hot section of the press, forming a board. Different types of hollows tubes are formed, depending on the diameters of the heated rods used (Figure 1.11) [70].

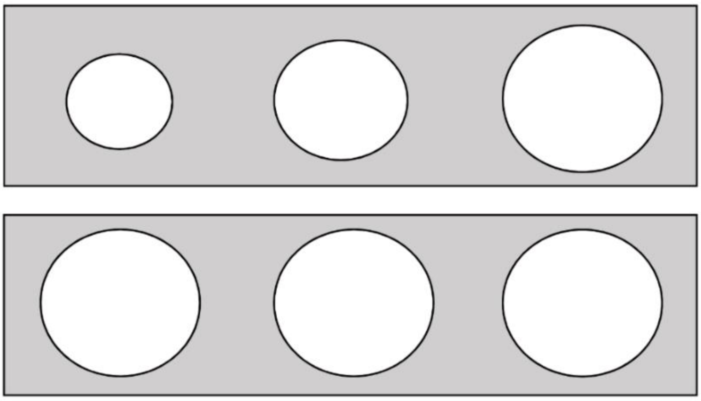


Figure 1.11. Scheme of cross section of tubular boards with identical (top) and different (bottom) diameters of hollow tubes.

Extruded boards are used in the production of furniture components such as low-density core for doors, table tops, and wall boards. They can also be employed in the production of prefabricated houses. Tubular boards have low strength in the longitudinal direction, higher linear swelling and lower perpendicular swelling when compared to the flat pressed boards. Usually this type of boards is reinforced by using surface veneers [39,71].

1.3.5. Sandwich panel

Sandwich panels are multilayer structures with two thin facings adhesively bonded to a thick core produced from lightweight material (Figure 1.12). This type of arrangement leads to an increase of the strength and stiffness without much increase of the weight [72,73].

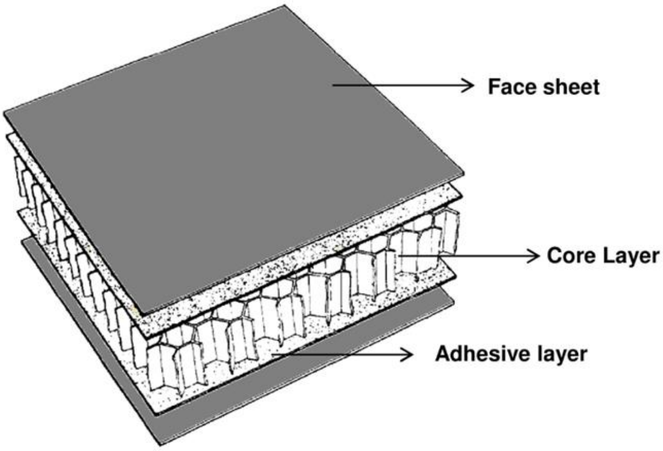


Figure 1.12. Schema of sandwich structure (adapted from [73]).

This type of panel has several applications in fields where high performance (higher strength, damage tolerance and thermal resistance) and low weight are required, such as aerospace and marine industries, furniture and automotive constructions [74,75].

The appropriate selection of facing and core material enable obtaining a product with the desired characteristics. A waterproof facing can be used in several houses' panels, a facing with abrasion resistance can be applied to floors. In addition, for decorative purposes plastic facings could be applied in walls, doors and furnishings. The type of material used in the core can be selected to confer thermal insulation, fire and degradation resistance to the panel [39].

1.3.5.1. Sandwich assembly

The crucial step in the assembly of the sandwich composite is gluing the faces to the core of the panel. This process could be carried out in a hot or cold press, in a continuous press or by moulding. Low pressures must be used to avoid crushing the core. In addition, the press plates must be precisely parallel, otherwise the core can crush gradually.

Timber-based boards can be used as facing materials. However, this disallows use in continuous foaming lines and commonly the board's lengths are lower than 3.5 m. This type of facing is more suitable to the mould foaming and bonding methods. It is necessary to use appropriate joints to produce long panels. Wood-based chipboard or plywood can be applied for low humidity environments, however if the panel is subject to long-term loading, core and face deformation may occur. Plywood is made from thin layers of wood veneers, designated plies, that are glued and pressed to form the panel [25]. The usual thickness is in the range of 4-27 mm and the density varies between 550 and 700 $kg \cdot m^{-3}$. Chipboard is produced from wood chips with thickness between 0.2 and 0.4 mm that are bonded together employing temperature and high pressure. The thickness is usually in the range of 2-25 mm with a density between 600 and 750 $kg \cdot m^{-3}$ [76].

The preparation of cores in sandwich structures commonly involves cutting to adequate thickness, and expanding honeycomb cores to obtain the intended cell size, if the core was acquired in the unexpanded form. Foams cores may be pre-formed into a block or foamed *in situ*, between the faces [77]. An adhesive is used to bond the faces to the core. A low viscosity adhesive can be applied by spraying, in successive coats, while an adhesive with higher viscosity can be applied with a brush or hand roller [39].

1.3.5.2. Types of sandwich core materials

Usually, the core of the panel is produced with low strength materials. However, the high thickness provides higher bending stiffness to the sandwich construction. Structurally, the core has two functions: 1) separate the faces and prevent deformation in the direction perpendicular to the face plane and 2) confer some degree of shear rigidity along the planes that are perpendicular to the face. Table 1.9 shows some properties of different materials that can be used as core in sandwich construction.

Table 1.9. Properties of different core materials [39].

Core material	**Density ($kg\cdot m^{-3}$)**	**Elastic Modulus (MPa)**	**Shear Modulus (MPa)**		**Shear Strength (MPa)**	
			TL*	**TW***	**TL**	**TW**
Balsa wood	80	1530	68	84	1.1	1.0
	112		103	145	1.6	1.4
	144		138	205	2.1	1.8
	176		174	264	2.6	2.2
Paper honeycomb	27	-	-	17	-	0.21
	32	-	-	-	-	-
	50	-	-	53	-	0.76
Polystyrene foam	28	8	8	-	0.22	-
	48	14	12	-	0.39	-
	72	21	18	-	0.39	-
Polyurethane foam	96	28	12	12	0.83	0.76
	144	83	25	28	0.65	0.69
	160	62	24	19	1.6	1.4

*TL-parallel to the core ribbon direction.

*TW-perpendicular to the core ribbon direction.

In the design of sandwich panels it is necessary to take into account the following factors: 1) the specific characteristics of the core, which can vary depending on the material used; 2) the effect of shear flexibility of the core; 3) the effect of the core on the buckling of the faces; 4) the effect of temperature in causing stresses and deflections and 5) the deformation behaviour [78]. Non-structural features like thermal conductivity, permeability, weight and moisture sorption should be considered in the design of the panel [39].

It is possible to distinguish two types of core layer in sandwich panels: homogeneous and non-homogeneous [79]. The first group includes cores made from hardwood strips (*Ochroma* spp., *Populus* spp., low-density *Pinus* spp.). Thermosetting or thermoplastic foams with open or closed cells are also used to produce a sandwich panel with homogeneous core. The foams are produced from polymers like polyurethane, polystyrene and polyvinyl chloride [80–82]. The group of non-homogenous cores includes textile, corrugated and honeycomb cores (Figure 1.13). Honeycomb cores can be made of metal, plastic or paper.

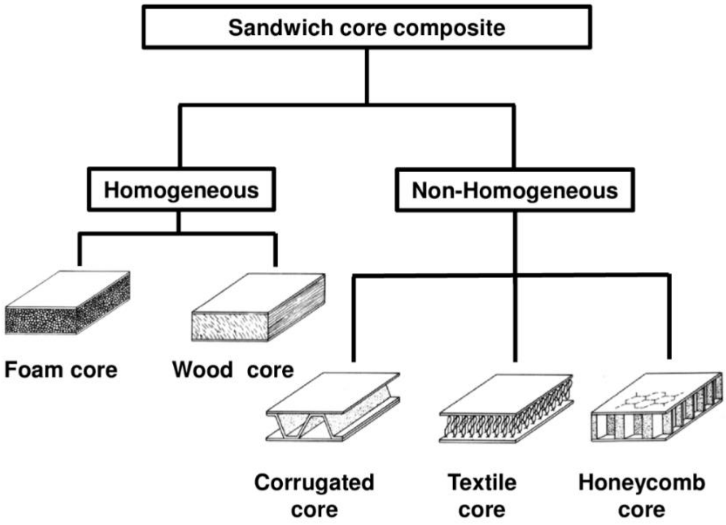


Figure 1.13. Scheme of varies types of sandwich cores (adapted from [83]).

Foamed core panels

Figure 1.14 shows a board with a foam core. There are several methods for manufacturing a sandwich panel with foam core.

Figure 1.14. Sandwich panel with a polystyrene foam core and wood-based particleboard in the facings.

In the batch process, the prefabricated layers are assembled together with the adhesive and the stack is pressed under temperature and pressure needed to cure the adhesive and form the final sandwich panel [77]. The high production costs necessary for this manufacture process and the limited sizes countervail the weight reduction achieved with this method [57]. Another process is mould forming. In this case, an exact amount of foam is directly introduced in the cavity between two faces to fill the mould. It is a discontinuous process where the board is produced in a closed mould whose dimensions are the same as the final panel. The upper face is supported by spacers in order to maintain it in position. If edge profiles are required, these must be placed at this stage. The mould structure must be rigid enough to withstand the high pressures reached during foam formation. After the introduction of foam in the mould, the panel is left in the mould for a defined period of time and then is removed. The main advantage of this method is allowing the production of panels with complex shapes. However, this is a relatively slow process that can cause void spaces within the panel, due to the non-uniformity of foam flow [76].

For the mass production of foam sandwich panel, a continuous process can be used. The face material run through the roll formers into coils, that creates the surface and edge profiles. In this process foils or impregnated paper are used for prefabricated facings and the core is usually foamed between the faces. Depending of the properties of the foam, an additional adhesive layer may be need. For example, if the core layer is a polyurethane foam, the additional layer of adhesive is not used. The foam liquid is introduced by injection in the panel line. The foam expands and then the panel is cooled down and cut to the desired length (Figure 1.15).

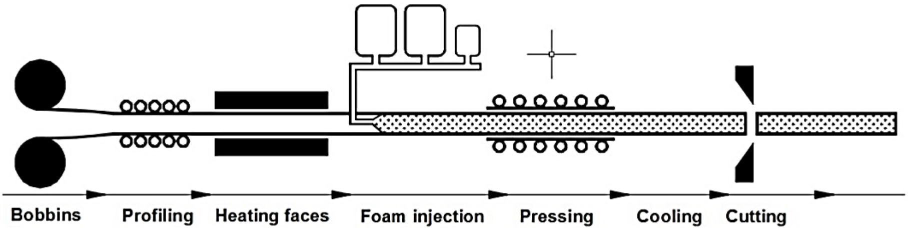


Figure 1.15. Continuous line of foam production (adapted from [76]).

The main advantage of this process is to have less production steps, compared to the other process describe above, which leads to a higher efficiency in time, material and human resources. This aspect had huge effect on the final panel cost [27].

Honeycomb core panels

A honeycomb panel is constituted by a honeycomb-type core (typically with hexagonal cells) bonded to the surfaces [84]. Hexagonal cells are the most usual configuration; but there are others, such as the square, rectangular, corrugated, flex-core and reinforced cells shown in Figure 1.16.

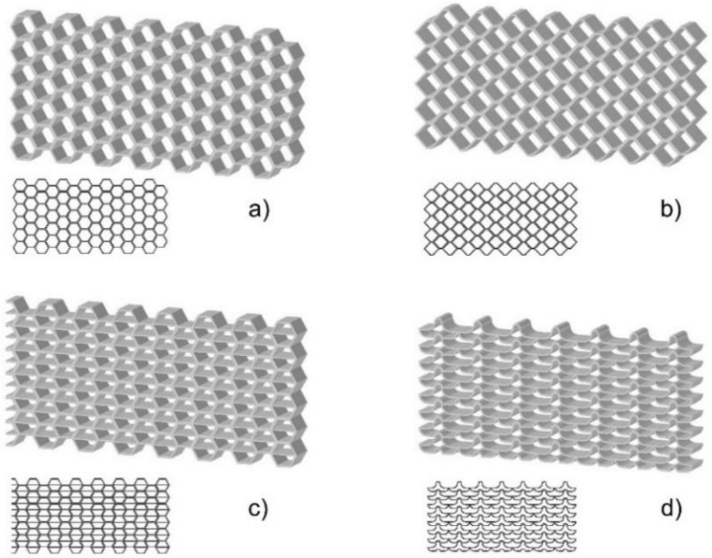


Figure 1.16. Different honeycomb cells configurations: a) hexagon, b) square cell, c) reinforced hexagon and d) flex-core (adapted from [85]).

The type of surfaces chosen for a particular application is determined by functional requirements such as strength, stiffness, damage tolerance and appearance at minimum overall cost. In this kind of composite, the bending loads (compression and tension) are supported by the faces and the shear loads are supported by the core [84]. As said before, the core materials can be plastic, metallic or paper. Paper honeycomb panels (Figure 1.17) have been widely used for the production of door leaves not only in the construction or furniture, but also in aerospace and automobile sectors.

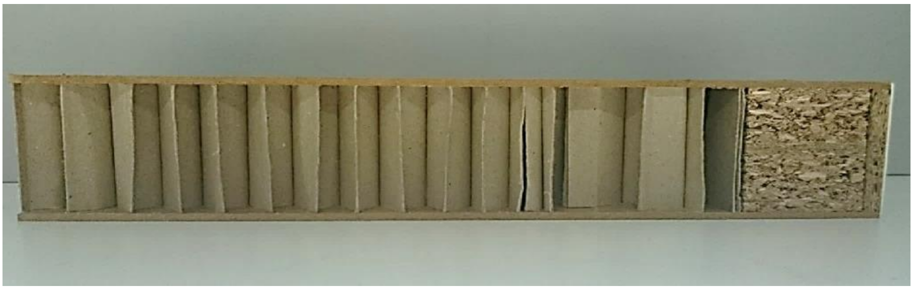


Figure 1.17. Sandwich panel with paper honeycomb core.

In general, any type of wood-based panel can be used for the faces, but the most common are particleboards and MDF, due to their low cost [86]. Paper honeycomb can be produced by two different processes: expansion manufacturing and corrugation manufacturing (Figure 1.18).

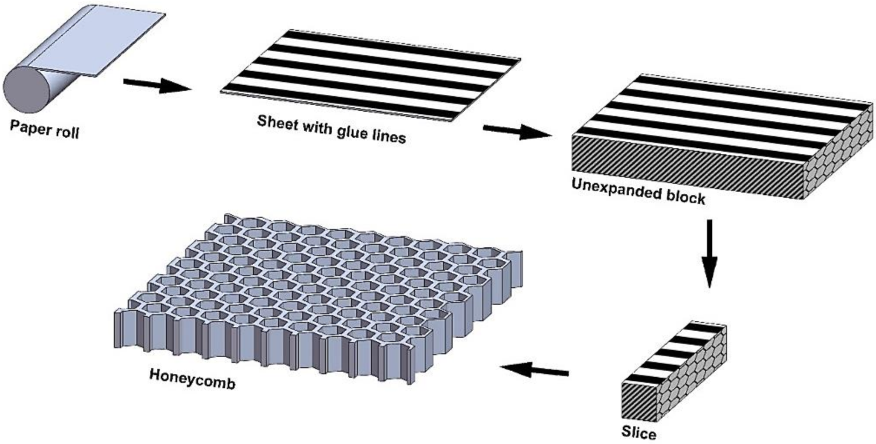


Figure 1.18. Manufacture process by expansion of honeycomb (adapted from [85]).

This process begins with cutting flat sheets of paper from a roll fixed on a rotating drum. As the sheets are stacked, alternating lines of glue are printed on each sheet. After the sheets are stacked the adhesive is cured. Slices of the unexpanded bock are cut with the required thickness (typically above 10 mm) and the sheets are pulled apart, causing the expansion of the hexagonal honeycomb core. After expansion, the residual stress is reduced by the controlled application of heat and moisture.

The corrugation process is another way to produce honeycombs (Figure 1.19). Here the material is corrugated or folded into a certain shape and then the shaped layers are glued into a honeycomb block. The block can be then sliced into pieces of the required size [83].

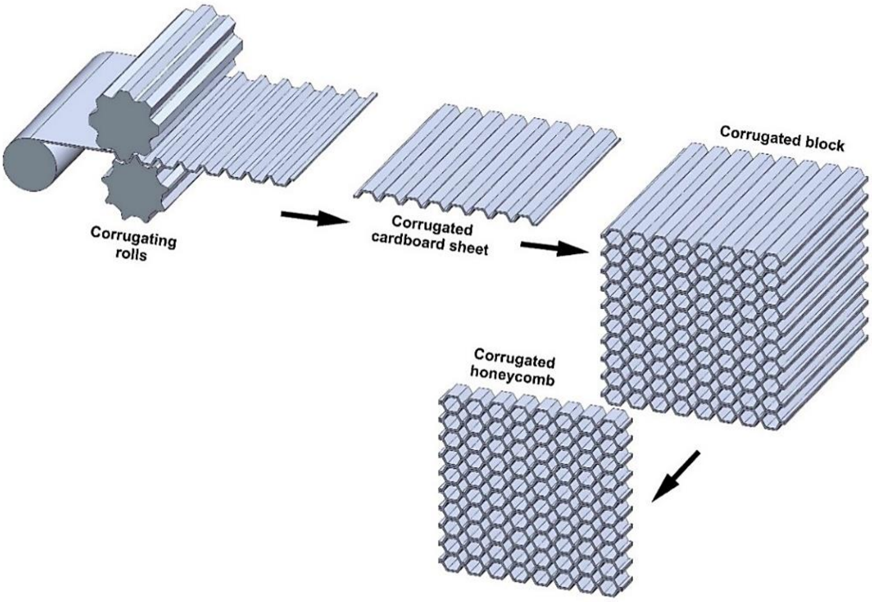


Figure 1.19. Scheme of corrugated production process (adapted from [85]).

Honeycomb panels present good load-bearing behaviour, despite the weight reduction. However, they have some limitations:

- mechanical properties of the structure without the frame are usually lower than for particleboards;
- it is necessary to develop specific fittings and edge connections to improve the mechanical integrity of the structure;
- edges lamination is very difficult;
- low resistance to parallel loads;

- low moisture resistance of the core;
- the board shows low resistance to highly localized external loads, as in case of impact;
- shear properties have different values if the tests are made along the length or across the face width [28,87,86].

1.3.6. Conclusion and future perspectives

Lightweight wood composites are in high demand for many different industries. A lightweight material can bring many advantages that appeal to manufacturers, designers and consumers. These include: lower raw-material and transportation costs; new design possibilities, involving thicker elements; more rational use of wood, providing alternatives in case of wood shortages or high cost; easier transportation of the final product.

Different approaches have been adopted in the last decades to produce lightweight wood composites with varying density ranges and properties. The most commonly used products are lightweight fibreboards, particleboards and sandwich panels.

The biggest challenges faced by the manufacturers of these composites involve the reduction of mechanical performance that results from lowered density, the difficulties in edges connection/lamination, and the low machinability. Further developments should provide strategies to overcome these limitations.

1.3.7. References

1. Ferdosian, F.; Pan, Z.; Guchuhan, G.; Zhao, B. Bio-Based Adhesives and Evaluation for Wood Composites Application. *Polymers (Basel).* 2017, 9, 70.

2. Hemmilä, V.; Adamopoulos, S.; Karlsson, O.; Kumar, A. Development of sustainable bio-adhesives for engineered wood panels – A Review. *RSC Adv.* 2017, 7, 38604–38630.
3. Gonçalves, C.; Martins, J.; Magalhães, F.; Carvalho, L.; Paiva, N.T.; Ferra, J.M.; Barros-Timmons, A. Utilization and characterization of amino resins for the production of wood-based panels with emphasis on particleboards (PB) and medium density fibreboards (MDF). A review. *Holzforschung* 2018, 72, 653–671.
4. Ferreira, H.E.; Condeço, J.A.D.; Fernandes, I.O.; Duarte, D.E.; Bordado, J.C.M. HPLC-UV and HPLC-ESI $^+$ -MS/MS analysis of free monomeric methylene diphenyl diisocyanate in polyurethane foams and prepolymers after stabilization with NBMA a new derivatizating agent. *Anal. Methods* 2014, 6, 9242–9257.
5. Athanassiadou, E.; Ohlmeyer, M. Emissions of Formaldehyde and VOC from Wood-based Panels in Performance in Use and New Products of Wood Based Composites. In Proceedings of the COST Action WG3 (E49) Performance in use and new products of wood based composites.; Brunel University Press: London,United Kingdom, 2009.
6. Solt, P.; Konnerth, J.; Gindl-Altmutter, W.; Kantner, W.; Moser, J.; Mitter, R.; van Herwijnen, H.W.G. Technological performance of formaldehyde-free adhesive alternatives for particleboard industry. *Int. J. Adhes. Adhes.* 2019, 94, 99–131.
7. Costa, N.; Pereira, J.; Martins, J.; Ferra, J.; Cruz, P.; Magalhães, F.; Mendes, A.; Carvalho, L. Alternative to latent catalysts for curing UF resins used in the production of low formaldehyde emission wood-based panels. *Int. J. Adhes. Adhes.* 2012, 33, 56–60.
8. Dongbin, F.; Jianzhang, L.; An, M. Curing Characteristics of Low Molar Ratio Urea-Formaldehyde Resins. *J. Adhes. Interface* 2006, 7, 45–52.

9. Hemmilä, V.; Trischler, J.; Sandberg, D. Lignin-an adhesive raw material of the future or waste of research energy. In Proceedings of the Proc. 9th Meeting of the Northern European Network for Wood Science and Engineering (WSE); Brischke, C., Meyer, L., Eds.; Hannove, Germanyr, 2013; pp. 98–103.

10. Zhang, W.; Ma, Y.; Wang, C.; Li, S.; Zhang, M.; Chu, F. Preparation and properties of lignin–phenol–formaldehyde resins based on different biorefinery residues of agricultural biomass. *Ind. Crops Prod.* 2013, 43, 326–333.

11. Bertaud, F.; Tapin-lingua, S.; Pizzi, A.; Navarrete, P.; Petit-Conil, M. Development of green adhesives for fibreboard manufacturing , using tannins and lignin from pulp mill residues. *Cellul. Chem. Technol.* 2012, 46, 449–455.

12. Wescott, J.M.; Frihart, C.R.; Traska, A.E. High-soy-containing water-durable adhesives. *J. Adhes. Sci. Technol.* 2006, 20, 859–873.

13. Liu, Y.; Li, K. Chemical modification of soy protein for wood adhesives. *Macromol. Rapid Commun.* 2002, 23, 739–742.

14. Singh, N.; Singh, J.; Kaur, L.; Sodhi, N.S.; Gill, B.S. Morphological , thermal and rheological properties of starches from different botanical sources. *Food Chem.* 2003, 81, 219–231.

15. Amini, M.H.M.; Hashim, R.; Hiziroglu, S.; Sulaiman, N.S.; Sulaiman, O. Properties of particleboard made from rubberwood using modified starch as binder. *Compos. Part B Eng.* 2013, 50, 259–264.

16. Belgacem, M.; Gandini, A. *Monomers, Polymers and Composites from Renewable Resources,* 1st ed.; Elsevier: Oxford, United Kingdom, 2008, 321-342.

17. Lund, D.; Lorenz, K.J. Influence of time, temperature, moisture,

ingredients, and processing conditions on starch gelatinization. *C R C Crit. Rev. Food Sci. Nutr.* 1984, 20, 249–273.

18. Sulaiman, N.S.; Hashim, R.; Amini, M.H.M.; Sulaiman, O.; Hiziroglu, S. Evaluation of the properties of particleboard made using oil palm starch modified with epichlorohydrin. *BioResources* 2013, 8, 283–301

19. Appelqvist, I.A.; Debet, M.R.Starch-biopolymer interactions—a review. *Food Rev. Int.* 2009, 13, 163–224.

20. Tharanathan, R.N. Starch – value addition by modification. *Crit. Rev. Food Sci. Nutr.* 2005, 45, 371–384.

21. Jouppilaav, K.; Kansikasb, J.; Roosa, Y.H. Factors affecting crystallization and crystallization kinetics in amorphous corn starch. *Carbohydr. Polym.* 1998, 36, 143–149.

22. Soykeabkaew, N.; Thanomsilp, C.; Suwantong, O. A review: Starch-based composite foams. *Compos. Part A Appl. Sci. Manuf.* 2015, 78, 246–263.

23. Selamat, M.E.; Sulaiman, O.; Hashim, R.; Hiziroglu, S.; Noor, W.; Wan, A.; Syuhada, N.; Zulhairie, M. Measurement of some particleboard properties bonded with modified carboxymethyl starch of oil palm trunk. *Measurement* 2014, 53, 251–259.

24. Ribba, L.; Garcia, N.L.; D'Accorso, N.; Goyanes, S. Disadvantages of Starch-Based Materials, Feasible Alternatives in Order to Overcome These Limitations. *Starch-Based Mater. Food Packag.* 2017, 37–76.

25. Matuana, L.; Heiden, P.Wood Composites. *In Encycl. Polym. Sci. Technol.* 4th ed.; 2004, 12, 521–546.

26. Cai, Z. Wood-Based Composite Board. *In Wiley Encycl. Compos.* 2 nd ed.; 2012, 1–11.

27. Shalbafan, A. Investigation of foam materials to be used in lightweight wood-based composites,Ph.D. Thesis, University of Hamburg, Hamburg 2013.

28. Thoemen, H. Lightweight panels for the furniture industry: Some recent developments. In *Lightweight wood–based Composites Production, Properties and Usage*, Proceedings of COST Action E49 Processes and Performance of Wood–Based Panels; Ljubljana, Slovenia, 2008;1-14.

29. Shalbafan, A.; Welling, J.; Luedtke, J. Effect of processing parameters on mechanical properties of lightweight foam core sandwich panels. *Wood Mater. Sci. Eng.* 2016, 7, 69–75.

30. Wang, D. Impact behavior and energy absorption of paper honeycomb sandwich panels. *Int. J. Impact Eng.* 2009, 36, 110–114.

31. Dziurka, D.; Mirski, R. Lightweight boards from wood and rape straw particles. *Drewno* 2013, 56, 19–31.

32. Trischler, J.; Sandberg, D.; Thörnqvist, T. Evaluating the competition of lignocellulose raw materials for their use in particleboard production, thermal energy recovery, and pulp- and papermaking. *BioResources* 2014, 9, 6591–6613.

33. Balducci, F.; Harper, C.; Meinlschmidt, P.; Dix, B.; Sanasi, A. Development of innovative particleboard panels. *Drv. Ind.* 2008, 59, 131–136.

34. EN 622-5, Fibreboards- Specifications-Part: 5 Requirements for dry process boards (MDF).

35. Donaldson, L.A.; Lomax, T.. D. Adhesive/fibre interaction in medium density fibreboard. *Wood Sci. Technol.* 1989, 23, 371–380.

36. Thoemen, H.; Irle, M.; Milan, S. *Wood-based panels an introduction for specialists*; 1 st ed. Brunel University Press: London, England, 2010.

37. Akbulut, T.; Ayrilmis, N. Influence of compression wood on physical and mechanical properties of medium density fiberboard. *Wood Res.* 2004, 49, 17–24.

38. Rowell, R.M.; Kawai, S.; Inoue, M. Dimensionally stabilized, very low density fiberboard. *Wood Fiber Sci.* 1995, 27, 428–436.

39. Kollmann, F.F.P.; Kuenzi, E.W.; Stamm, A.J. *Principles of Wood Science and Technology II Wood Based Materials*; 1 st ed. Springer-Verlag Berlin Heidelberg: New York, United States of America, 1975.

40. Suchsland, O.; Woodson, G.E. *Fiberboard manufacturing Practices In the United States*; USDA Forest Service Agriculture Handbook: Virgina,United States of America, 1986.

41. Barbu, M.C.; Pieper, O. Light Fibreboards for Insulation Purposes. In *Lightweight wood–based Composites Production, Properties and Usage,* Proceedings of COST Action E49 Processes and Performance of Wood–Based Panels; Ljubljana, Slovenia, 2008; 34–51.

42. Porter, B. *Carpentry and joinery*; 3rd ed.; Routledge Taylor & Francis Group: New York, United States of America, 2012.

43. Chen, T.; Liu, J.; Wu, Z.; Wang, W.; Niu, M.; Xie, Y. Evaluating the effectiveness of complex fire-retardants on the fire properties of ultra-low density fiberboard. *Bioresources* 2016, 11, 1796–1807.

44. Suhaily, S.S.; Jawaid, M.; Abdul Khalil, H.P.S.; Mohamed, A.R.; Ibrahim, F. A review of oil palm biocomposites for furniture design and applications: potential and challenges. *Bioresources* 2012, *7*, 4400–4423.

45. Carvalho, L.H.; Costa, C.A.V. Modeling and simulation of the hot-pressing process in the production of medium density fiberboards (MDF). *Chem. Eng. Commun.* 1998, 170, 1–21.

46. Xing, C.; Riedl, B.; Cloutier, A. Measurement of urea-formaldehyde resin

distribution as a function of MDF fiber size by laser scanning microscopy. *Wood Sci. Technol.* 2004, 37, 495–507.

47. Nayeri, M.D.; Tahir, P.M.; Mohammad, J.; Ashaari, Z.; Abdullah, L.C.; Bakar, E.S.; Namvar, F. Medium density fibreboard made from Kenaf (Hibiscus cannabinus L.) stem: effect of thermo-mechanical refining and resin content. *Bioresources* 2014, 9, 2372–2381.

48. Ganev, S.; Gendron, G.; Cloutier, A.; Beauregard, R. Mechanical properties of MDF as a function of density and moiture content. *Wood Fiber Sci.* 2005, 37, 314–326.

49. Denesi, M. Method for producing a particle-based element .US Patent 2012/032539 A1, 2012.

50. http://www.wbpionline.com. Accessed 20 Sep 2016.

51. Maloney T.M. *Modern particleboard & Dry-process Fiberboard Manufacturing*; 3rd ed.; Miller Freeman Publications: San Francisco, United States of America,1989.

52. Nemli, G.; Demirel, S. Relationship between the density profile and the technological properties of the particleboard composite. *J. Compos. Mater.* 2007, 41, 1793–1802.

53. Nemli, G.; Demirel, S. Relationship between the density profile and the technological properties of the particleboard composite. *J. Compos. Mater.* 2007, 41, 1793–1802.

54. Dunky, M. Urea-formaldehyde (UF) adhesive resins for wood. *Int. J. Adhes. Adhes.* 1998, 18, 95–107.

55. Stoeckel, F.; Konnerth, J.; Gindl-Altmutter, W. Mechanical properties of adhesives for bonding wood -A review. *Int. J. Adhes. Adhes.* 2013, 45, 32–41.

56. CEN/TS 16368 Lightweight Particleboards - Specifications.

57. Barbu, M.C.; Ludtke, J.; Thomen, H.; Welling, J. Innovative production of wood-based lightweight panels. In Proceedings of the Processing Technologies for the Forest and Biobased Products Industries; Kuchl, Austria, 2010; 115–122.

58. Boruszewski, P.; Borysiuk, P.; Mamiński, M.; Czechowska, J. Mat Compression Measurements During Low-Density Particleboard Manufacturing. *BioResources* 2016, 11, 6909–6919.

59. Kawai, S.; Sasaki, H.; Nakaji, M.; Makiyama, S.; Morita, S. Physical properties of low-density. *Wood Res.* 1986, 72, 27–36.

60. Kalaycioglu, H.; Deniz, I.; Hiziroglu, S. Some of the properties of particleboard made from paulownia. *J. Wood Sci.* 2005, 51, 410–414.

61. Lias, H.; Kasim, J.; Johari, N.A.N.; Mokhtar, I.L.M. Influence of board density and particle sizes on the homogenous particleboard properties from kelempayan (*Neolamarckia cadamba*). *Int. J. Latest Res. Sci. Technol.* 2014, 3, 173–176.

62. Xu, J.; Sugawara, R.; Widyorini, R. Manufacture and properties of low-density binderless particleboard from kenaf core. *J. Wood Sci.* 2004, 50, 62–67.

63. Kharazipour, A.; Bohn, C. Use of popcorn for timber and composite materials.US Patent 8,168,303 B2, 2012.

64. Shalbafan, A.; Tackmann, O.; Welling, J. Using of expandable fillers to produce low density particleboard. *Eur. J. Wood Wood Prod.* 2016, 74, 15–22.

65. Peretolchin, M. Kaurit Light-the solution for lightweight furniture. In Proceedings of the International Panel Products Symposium; Nantes, France, 2009; 139–143.

66. Kannan, P.; Biernacki, J.J.; Jr, D.P.V. A review of physical and kinetic models of thermal degradation of expanded polystyrene foam and their application to the lost foam casting process. *J. Anal. Appl. Pyrolysis* 2007, 78, 162–171.

67. Magnus, J. Thermally expandable microspheres prepared via suspension polymerization- synthesis, characterization and application, Technical University of Denmark, 2010.

68. Shalbafan, A.; Luedtke, J.; Welling, J.; Thoemen, H. Comparison of foam core materials in innovative lightweight wood-based panels. *Eur. J. Wood Wood Prod.* 2012, 70, 287–292.

69. Zhang, H.; Lu, X. Elastic properties of the extruded tubular particleboard. *Wood Mater. Sci. Eng.* 2015, 10, 185–188.

70. Wittmann, O.; Wolf, F. Wood-Based Materials. *In Ullmann´s Encycl. Ind. Chem.* 1 st ed.; 2014, 1–39.

71. Borgin, K. Development of the particle board industry in europe. *J. South African For. Assoc.* 1958, 32, 56–71.

72. Alessandro, V.D.; Petrone, G.; Franco, F.; Rosa, S. De A review of the vibroacoustics of sandwich panels : models and experiments. *J. Sandw. Struct. Mater.* 2013, 15, 541–582.

73. Petras, A.; Sutcliffe, M.P.F. Failure mode maps for honeycomb sandwich panels. *Compos. Struct.* 1999, 44, 237–252.

74. Schubel, P.M.; Luo, J.; Daniel, I.M. Low velocity impact behavior of composite sandwich panels. *Compos. Part A Appl. Sci. Manuf.* 2005, 36, 1389–1396.

75. Meraghni, F.; Desrumaux, F.; Benzeggagh, M.L. Mechanical behaviour of cellular core for structural sandwich panels. *Compos. - Part A Appl. Sci. Manuf.* 1999, 30, 767–779.

76. Davies, J.M. *Lightweight Sandwich Construction,* 1 st ed.*;*Blackwell Science Ldt, London, United Kingdom, 2008.

77. Karlsson, K.F.; TomasÅström, B. Manufacturing and applications of structural sandwich components. *Compos. Part A Appl. Sci. Manuf.* 1997, 28, 97–111.

78. Davies, J.M. Sandwich panels. *Thin-Walled Struct.* 1993, 16, 179–198.

79. Wang, X.; Wang, Y. Static analysis of sandwich panels with non-homogeneous soft-cores by novel weak form quadrature element method. *Compos. Struct.* 2016, 146, 207–220.

80. Pishan, S.; Ghofrani, M.; Kermanian, H. Study on mechanical properties of lightweight panels made of honeycomb and polyurethane cores. *Lignocellulose* 2014, 3, 59–68.

81. Karagiozova, D.; Nurick, G.N.; Langdon, G.S.; Yuen, S.C.K.; Chi, Y.; Bartle, S. Response of flexible sandwich-type panels to blast loading. *Compos. Sci. Technol.* 2009, 69, 754–763.

82. Bull, P.H.; Edgren, F. Compressive strength after impact of CFRP-foam core sandwich panels in marine applications. *Compos. Part B Eng.* 2004, 35, 535–541.

83. Pflug, J.; Xinyu, F.; Vangrimde, B.; Verpoest, I. Development of a sandwich material with polypropylene/natural fibre skins and paper honeycomb core. In Proceedings of the 10 th European Conference on Composites Materials; Brugge, Belgium, 2002.

84. Nilsson, E.; Nilsson, A.C. Prediction and measurement of some dynamic properties of sandwich structures with Honeycomb and foam cores. *J. Sound Vib.* 2002, 251, 409–430.

85. Bitzer, T. *Honeycomb Techniology*; 1 st ed.; Springer, Netherlands, 1997.

86. Barboutis, I.; Vassiliou, V. Strength properties of lightweight paper honeycomb panels for the furniture. In Proceedings of the Proceedings of International Scientific Conference 10th Anniversary of Engineering Design (Interior and Furniture Design); Sofia, Bulgarian, 2005; 1-6.

87. Aktay, L.; Johnson, A.F.; Kroplin, B.-H. Numerical modelling of honeycomb core crush behaviour. *Eng. Fract. Mech.* 2008, 75, 2616–2630.

CHAPTER 2

Low-density wood-based particleboards bonded with foamable sour cassava starch: preliminary studies

2. Low-density wood-based particleboards bonded with foamable sour cassava starch: preliminary studies[2]

Abstract: This work investigates the feasibility of producing low-density particleboards using an adhesive system based on sour cassava starch, taking advantage of its adhesive and self-expansion properties. Relevant properties of the produced particleboards were evaluated according to European Standards including: density, internal bond, moisture content and thickness swelling. Low-density particleboards were produced with densities between 207 kg·m^{-3} and 407 kg·m^{-3}. The best performance corresponded to particleboard with a density of 318 kg·m^{-3}, an internal bond strength of 0.67 N·mm^{-2}, and a thickness swelling of 8.7%. These values meet the standard requirements of general purpose lightweight boards for use in dry conditions. Heat post-treatment (24 h at 80 °C) led to lower internal bond strength, due to retrogradation (recrystallization of amylose and amylopectin chains upon cooling) causing higher rigidity of the starch binder. However, it showed to have a significant effect on decreasing the thickness swelling.

---

[2] Monteiro, S.; Martins, J.; Magalhães, F.D.; Carvalho, L. Low-density wood-based particleboards bonded with foamable sour cassava starch: preliminary studies. *Polymers*. 2016, 8, 354.

2.1. Introduction

According to Mohanty, “sustainability, industrial ecology, eco-efficiency, and green chemistry are guiding the development of the next generation of materials, products, and processes.” There is a vital need for development of innovative bio-based products and technologies that are not dependent on fossil fuel [1]. Biomaterials, obtained partially or entirely from biomass sources, play a relevant role in this context [2]. European standard EN 309 defines particleboard as a “panel material manufactured under pressure and heat from particles of wood (wood flakes, chips, shavings, saw-dust and similar) and/or other lignocellulosic material in particle form (flax shives, hemp shives, bagasse fragments and similar), with the addition of an adhesive” [3]. Lately, special attention has been given to lightweight particleboards, in an effort to facilitate handling and transportation. Furthermore, there is a current trend in furniture design to use high-thickness components, further increasing the demand for materials with reduced weight. Panels with a density below 600 $kg \cdot m^{-3}$ are defined as lightweight particleboard (CEN/TS 16368) [4]. One way to decrease the weight of panels is by incorporating low-density particles in the core layer [5]. However, this comes along with decreases in mechanical performance (flexural strength, internal bond strength, and resistance to axial withdrawal of screws), in the quality of the finish (coating, edge lamination), and in machinability.

Synthetic formaldehyde-based resins are currently used to produce wood-based particleboards, due to their low cost and good binder performance. Natural-based alternatives have been reported, such as adhesives based on tannins, lignin and their combinations [6–8], soy protein [9–12] and starch [13,14]. Unlike tannins, the other natural adhesives must be combined with a synthetic compound, such as phenol-formaldehyde resin or PMDI (polymeric isocyanate), in order to satisfy the requirements of relevant standards [15].

Starch is one of the most abundant natural polymers and is relatively inexpensive. Cereal grains (such as corn and wheat), tubers (such as potato), and roots (such as cassava) are some of the commercial sources of starch for industrial exploitation. Starch consists of two major molecular components, amylose and amylopectin (Figure 2.1), which can be differentiated by their chemical structure. The linear α-(1→4) linked glucan is called amylase while an α-(1→4) linked glucan with 4.2 – 5.9% α-(1→6) branch linkages is amylopectin.

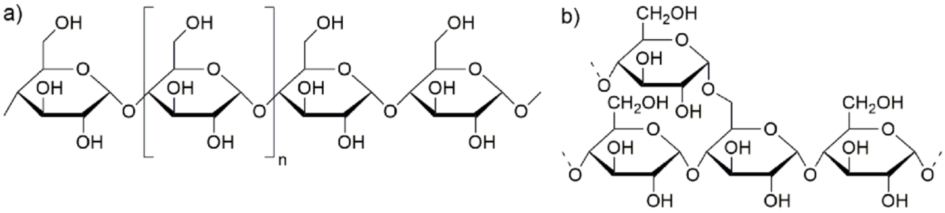


Figure 2.1. Molecular structure of (a) amylose and (b) amylopectin.

Starch has excellent affinity towards polar materials such as cellulose, because of the many hydroxyl groups, forming strong adhesive bonds [16]. It is extensively used in the form of binders, sizing materials, glues, and pastes [17]. Its current use in particleboard production involves a combination with synthetic adhesives, such as isocyanates and urea-formaldehyde resins [18].

Cassava sour starch is a traditional food ingredient made by fermentation and sun drying of native cassava starch. It shows good expansion upon heating, which makes it widely used in baking. Expansion occurs after starch gelatinization, as a consequence of water vaporization combined with appropriate paste fluidity, swelling and solubilization. Presence of carboxylate functional groups, formed during fermentation/sun drying, has been correlated with expansion performance [19]. Some authors studied the production of biodegradable foam trays based on cassava starch blended with chitosan and Kraft fibre [20] or with sunflower protein and cellulose fibre [21]. Cassava starch, in combination with a small percentage of urea-formaldehyde resin, has been used as a binder in wood-based particleboards with densities of 650 and 750 kg·m^{-3} [22].

The world´s largest producers of cassava are Africa with 57% and Asia with 31%. Latin America and the Caribbean provide 12% of the world's supply [23]. Approximately 60% of the production is used for human consumption, about 33% for animal feed and 7% for different industries such as textile, paper, food and adhesives [24]. The uses of cassava vary depending on the continent. While in Asia it is used mostly in industry, in Africa its main purpose is human consumption. Even though the cassava world trade grows about 36% per year, its price has remained stable and can actually be considered low when compared to other crops. It can be argued that cassava can be used on a large scale as a raw material for different products without compromising its consumption as food or the local ecosystems. An important factor that contributes to this observation is that cassava can be produced in low fertility soils and where the drainage is insufficient [25], unlike corn or potato. This allows taking advantage of currently deteriorated and unused land for cassava production [23]. In addition, cassava can be stored for long periods of time [26]. According to the report of the United Nations, in some African countries there is a political interest in making cassava a driving force of local economic growth [27]. Agriculture must be viewed not only as a means of subsistence but also as a foundation for the integrated and sustainable industrial production of food, energy and biosourced materials [23,28]. The present work studies the feasibility of producing low-density particleboards using sour cassava starch as the main binder, taking advantage of its adhesive and expansion properties. The resulting 100% natural products were characterized in terms of their physico-mechanical properties.

2.2. Materials and methods

2.2.1. Materials

Native and sour cassava starch was purchased at a local supermarket in Porto, Portugal. Chitosan (molecular weight around 300 kDa, degree of deacetylation > 85%) was supplied by Golden-Shell Pharmaceutical Co. Ltd (Zhejiang, China). *Populus L.* fibers, commonly used in medium density fiber panels (MDF) production, was provided by Valbopan-Fibras de Madeira S.A (Nazaré, Portugal). Glycerol (≥ 95%) was supplied by Sigma-Aldrich (Steinheim, Germany). Wood particles with a moisture content of 4% used for the production of particleboards were supplied by Sonae Indústria PCDM (Oliveira do Hospital, Portugal).

2.2.2. Determination of amylose content

The amylose content determination was performed by Eurofins (Madrid, Spain). Sample was first defatted with dichloromethane/methanol and 75% of propanol, and then the starch was solubilized in 2 M sodium hydroxide solution. The amylose content was determined by potentiometric titration with in-situ formed I_2 (from iodate). This procedure is based on the method described by Banks *et al.* [29].

2.2.3. Scanning electron microscopy

The interior morphology of particleboards was observed by scanning electron microscopy, using a high resolution (Schottky) Environmental Scanning Electron Microscope with X-ray Microanalysis and Electron Backscattered Diffraction analysis: Quanta 400 FEG ESEM/EDAX Genesis X4M (FEI, Hillsboro, OR, USA). Samples were coated with a Au/Pd thin film, by sputtering, using the SPI Module Sputter Coater equipment. The analysis was performed at CEMUP (Centro de Materiais da Universidade do Porto, Porto, Portugal).

2.2.4. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of the native and sour cassava starch were recorder with a Vertex 70 spectrometer (Bruker, Karlsruhe, Germany). The samples were scanned using a Platinum-ATR single reflection diamond ATR module. The absorbance spectra were computed between 4000 and 500 cm^{-1} at 4 cm^{-1} resolution. Symmetrical interferograms on 66 scans were co-added for each spectrum.

2.2.5. Preparation of binder system

The formulation of the adhesive system is shown in Table 1. Sour cassava starch and distilled water were mixed first. Chitosan solution, at 5 wt% concentration, was prepared by adding chitosan to propionic acid solution (6 wt%), and then mixing for 3 h at 60 °C. This solution was then added to the binder adhesive in the proportion shown in Table 2.1. Finally, *Populus* fibres and glycerol were added and stirring was maintained for 5 min. The adhesive system is a brownish viscous liquid with a solid content of 38%.

Table 2.1. Formulation of the adhesive system.

Component	**Quantity (wt %)**
Sour cassava starch	30.5
Distilled water	30.5
Chitosan solution	33.4
Populus fibres	2.8
Glycerol	2.8

2.2.6. Foamability of sour and native cassava starch

Two formulations were prepared with each starch, as described in Section 2.5. The same amount of mixture (20 g) was placed in a glass beaker, and heated in an oven at 190 °C during 40 min. The volume of expansion was measured.

2.2.7. Particleboard production

Wood particles were manually blended with the adhesive. The adhesive/wood ratio was 1:1, based on weight of solid adhesive content and oven dry wood. Single layer mats were hand formed in square aluminium foil deformable containers (Lusoforma, Mem Martins, Portugal), with initial dimensions of 220 × 220 × 80 mm^3. A computer-controlled laboratory scale hot-press (homemade at our laboratory), equipped with a linear variable displacement transducer (LVDT), a pressure transducer and thermocouples, was used for producing the panels. The platen temperature was set to 190 °C. The adhesive/wood mixture was placed on the bottom platen, and the top platen was positioned at 25 mm height, during 30 min. Afterwards the top platen was slowly lifted until 28 mm thickness, over a 6 min period, and the final position maintained for 5 min.

About 12 h after production, part of the particleboards were subjected to heat post-treatment (HPT) in an oven, at 80 °C for 24 h. The remaining boards were not subjected to any kind of post-treatment. All boards were conditioned at 20 °C and a relative humidity of 65% until testing. The mass of wood/binder mixture used to produce the panels with different densities was between 276 and 725 g.

2.2.8. Particleboard characterization

The boards were tested according to the European standards for density (D) (EN 323), internal bond strength (IB) (EN 319), moisture content (MC) (EN 322) and thickness swelling (TS) (EN 317). In order to evaluate the variability of the measurements, 5 particleboards were produced from the same binder formulation and their properties measured. The coefficient of variation (ratio between standard variation and average value of measurement) obtained for each property were: density-4.0%, internal bond strength-2.7%, thickness swelling-10.7%, moisture content-7.5%.

2.3. Results and discussion

2.3.1. Foamability of sour cassava starch

The ability of native and sour cassava starches to expand during baking was compared. The formulation containing sour cassava starch increased about 700% in volume (Figure 2.2), while the one containing native starch increased about 200%. Water vaporization combined with good swellability and paste fluidity of sour cassava starch led to the formation of a foam with good an expansion ability upon heating, without the need for the addition of expansion agents [19].

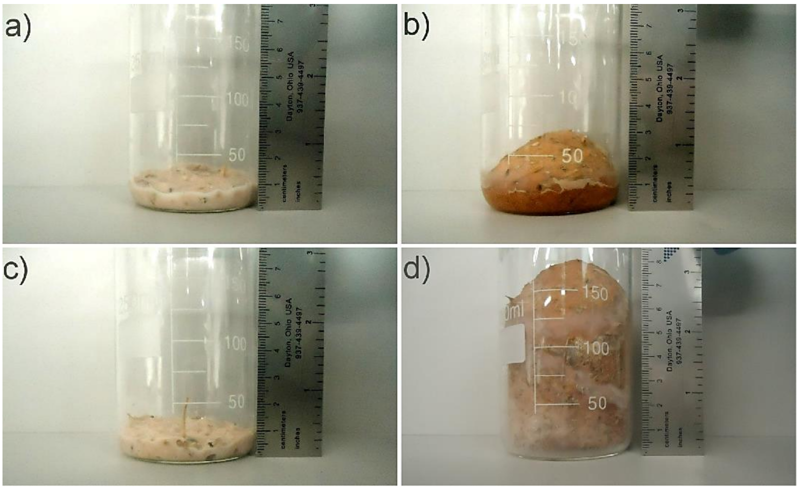


Figure 2.2. Expansion behavior of different types of cassava starches. (a,b) Native cassava starch before and after heating, respectively; (c,d) sour cassava starch before and after heating, respectively.

2.3.2. FTIR spectroscopy analysis

Figure 2.3 represents the FTIR spectra of native and sour cassava starches. The two spectra are very similar. The absorption peaks at 3291.2 cm^{-1} and 2930.7 cm^{-1} can be attributed to O–H and C–H bond stretching, respectively [30]. The absorption peak at 1455.4 cm^{-1} was attributed to C–H bending.

The absorbances at 1149.4 cm^{-1} and 1077.2 cm^{-1} are both assigned as the coupling of C–O, C–C and O-H bond stretching, bending and asymmetric stretching of the C–O–C glycosidic bridge [31]. The absorbance peak at 997.2 cm^{-1} can be attributed to the C–O–H bending and H–C–H related modes. The peak at 860.1 cm^{-1} can be assigned to C–O–C symmetrical stretching and C-H deformation [32].

Sour starch was expected to show higher carbonyl and carboxyl content than native starch, as a result of oxidation during the fermentation/sun drying production process [19]. Such differences are, however, not visible, in particular in terms of the expected carbonyl band at 1735 cm^{-1}. Similar results were obtained by Demiate *et al.* [33] and may be due to a low concentration of said groups not allowing detection.

The amylose content of native and sour cassava starches was determined by potentiometric titration, and a value of 18% (w/w) was obtained for both.

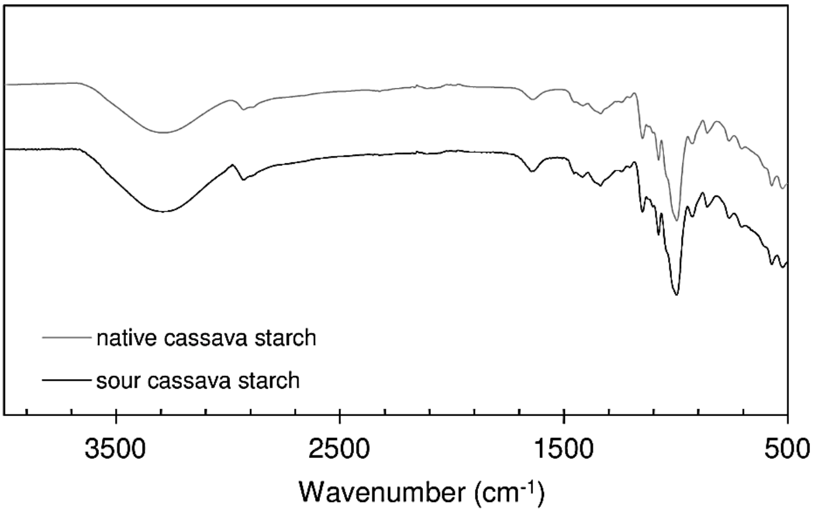


Figure 2.3. FTIR spectra of native and sour cassava starch in the (4000–500 cm^{-1}) spectral region.

2.3.3. Physico-mechanical properties of particleboards

Figure 2.4 depicts the particleboards produced with sour cassava starch–based binder. The boards, shown in Figure 2.4a, appear rigid and strong when handled, and have no noticeable smell after cooling. The wood particles show good cohesion and cannot be easily detached. Figure 2.4b shows that the particles are surrounded by a heterogeneous foam-like material, created by starch expansion. The internal morphology of the panel is seen more clearly in the SEM image depicted in Figure 2.4c. The foam fills the voids between the particles and seems to be well adhered to the wood particle surfaces. Wood fibres, present in the adhesive formulation, are visible within the foam cell walls. The binder’s foaming ability causes separation of the wood particles, allowing for the panel’s low density, hopefully maintaining good cohesion and therefore guaranteeing acceptable mechanical properties. Chitosan and wood fibre were added to the sour cassava starch formulation in order to improve the foam properties, based on previous evidence found in the literature [20]. In addition to the reinforcing role of wood fibre, highly compatible with the starch matrix, the interaction between the amino groups of chitosan and the hydroxyl groups of starch may provide mechanical strengthening and decreased water solubility. The formulation has not yet been fully optimized for this application, the purpose of the present work being to demonstrate the feasibility and potential of low-density particleboards produced using this type of binder.

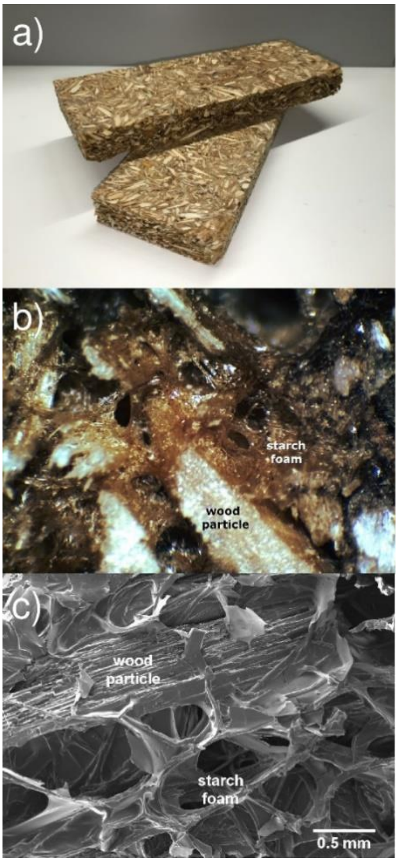


Figure 2.4. Particleboards produced with sour cassava starch–based binder. (a) Outside appearance; (b) close-up detail; (c) SEM image showing wood particles and surrounding foam, 100x magnification.

The particleboards were produced from different starting masses of wood/binder mixture, in order to identify an optimal combination of composite properties. The effect of the heat post-treatment (HPT of 80 °C for 24 h) after production was also evaluated. The results of the density of the final dry particleboards are shown in Figure 2.5, as a function of the expected density (ratio of the dry mixture mass to the volume corresponding to the thickness defined by the final press platen separation of 28 mm).

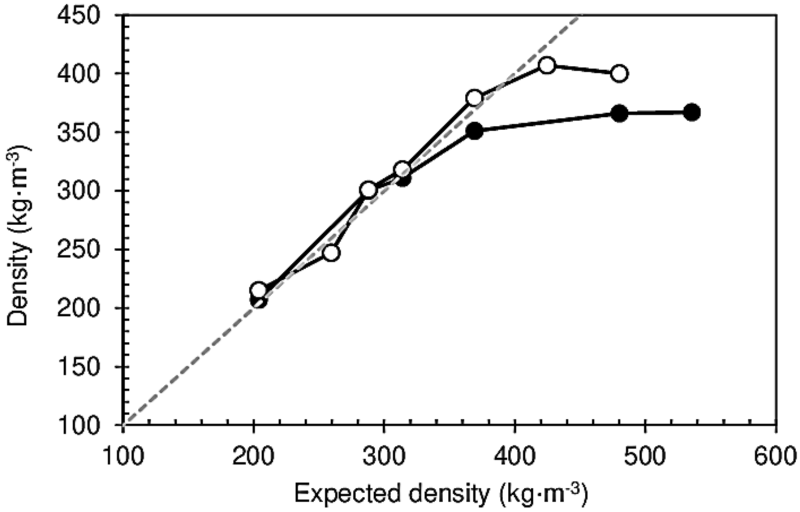


Figure 2.5. Density of dry particleboards bonded with sour cassava starch foam. White circles: without HPT; black circles: with HPT. Dashed line shows coincidence between measured and expected densities.

The minimum value of the density obtained was 215 kg·m^{-3}. Initially the densities of the particleboards increase with the increase of the total mass of mixture used, independent of being subjected or not to the heat post-treatment. The mixture expands until reaching the top press platen, which defines the maximum height of the particleboard. The measured values coincide with the expected ones: Greater mixture mass placed between the press platen implies higher density. However, for expected densities above about 350 kg·m^{-3}, the measured densities show a negative deviation. This is a consequence of the high amount of water vapor that is retained within the panel while it stays inside the press. After removal, this internal pressure results in a springback effect, causing the particleboard to expand, thus decreasing its density. For expected densities above around 550 kg·m^{-3}, this actually tends to cause internal bursting, since the cohesive strength of the binder, still warm and with high moisture content, is not sufficient to balance the internal stress caused by trapped vapor. Figure 2.6 shows close-up images of two boards, one produced with a low initial mass (a), showing uniform internal morphology, and another that has visibly delaminated due to the phenomena described above (b).

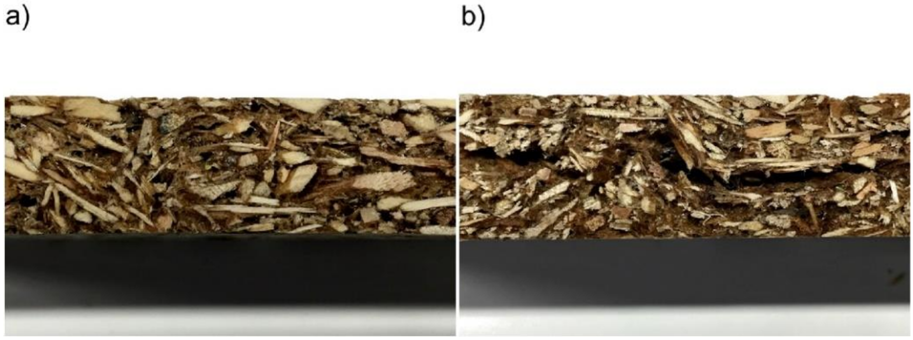


Figure 2.6. Detail of internal morphology of particleboards: (a) expected density of 313 kg·m^{-3}, showing uniform internal structure; (b) expected density of 550 kg·m^{-3}, showing internal delamination.

No significant difference was found in the equilibrium moisture content of the particleboards. This was in the range of 10.4% to 12.3% for non-heat-treated boards, and of 8.4% to 11.6% for heat-treated boards.

The internal bond strength (IB) provides an overall evaluation of the board's mechanical integrity, indicating how well the core material is bonded together. The IB values of the particleboards produced are given in Figure 2.7 Particleboards not subjected to HPT show an initial increase in the IB, as expected from the increased density, as it promotes more effective internal cohesion. A maximum value of 0.67 N·mm^{-2} was attained, corresponding to a density of 318 kg·m^{-3}. Note that according to European Technical Specification CEN/TS 16368, for lightweight particleboards type LP2 (the most demanding) with thicknesses between 20 and 25 mm, the minimum requirement for the IB is 0.30 N·mm^{-2} [4].

For expected densities above 313 kg·m^{-3}, the IB decreases, due to the higher board density causing vapor entrapment and, as a consequence of the resulting internal stress, rupture of inter-particle bonds. For the highest expected densities, this ends up leading to full delamination, as discussed before, and a virtually null IB. Heat post-treatment has two distinct effects on the IB of the particleboards. For expected densities up to 313 kg·m^{-3}, it leads to a lower IB. Heat treatment are used for the physical modification of starch granules, inducing crystalline rearrangement and promoting intramolecular bonds [34].

The actual outcomes of the treatment are highly dependent on the starch's botanical origin [35]. In the work presented here, HPT causes some degree of modification in the sour cassava starch that yields a weaker foam structure, probably due to increased brittleness. The heat treatment may be inducing retrogradation, i.e., recrystallization due to the rearrangement and intramolecular interactions during the expulsion of water. This is observed in the aging of thermoplastic starch, which is known to result in increased brittleness [36]. Interestingly, for the higher expected densities, the IB obtained for the heat-treated particleboards is actually higher than for the non-treated ones. The reasons for this strengthening are not yet clear, but may be related to the higher moisture content of these boards, shortly after production, resulting in a different physical rearrangement of starch during the heat treatment.

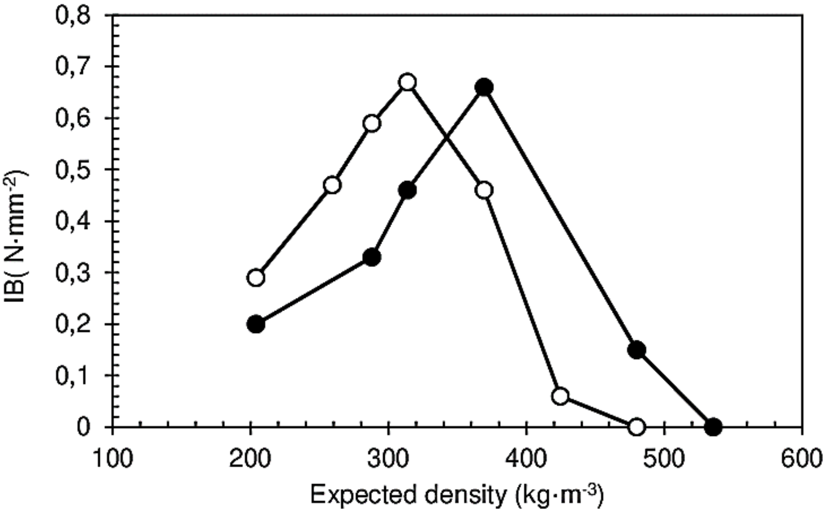


Figure 2.7. Internal bond of particleboards bonded with sour cassava starch foam. White circles: Without HPT; black circles: With HPT.

The thickness swelling (TS) results are shown in Figure 2.8. The TS tends to increase with the expected density, due to higher density causing higher water absorption. However, this effect is counterbalanced by the improvement in the internal bond strength, resulting in the dip in TS for expected densities between 300 and 350 kg·m^{-3}, where the IB shows a maximum value. Since the IB decreases for higher densities, thickness swelling increases again. It must be noted that the values obtained for the TS can be considered quite low. According to European Standard EN 312, for non-load-bearing boards for use in humid conditions with thicknesses between 20 and 25 mm, the maximum acceptable value for TS is 13% [37]. For the panel produced with a density of 318 kg·m^{-3}, which displayed the best IB result, the measured TS is 8.7%. It is important to note that these boards are intended for furniture use in dry conditions (standard value not specified).

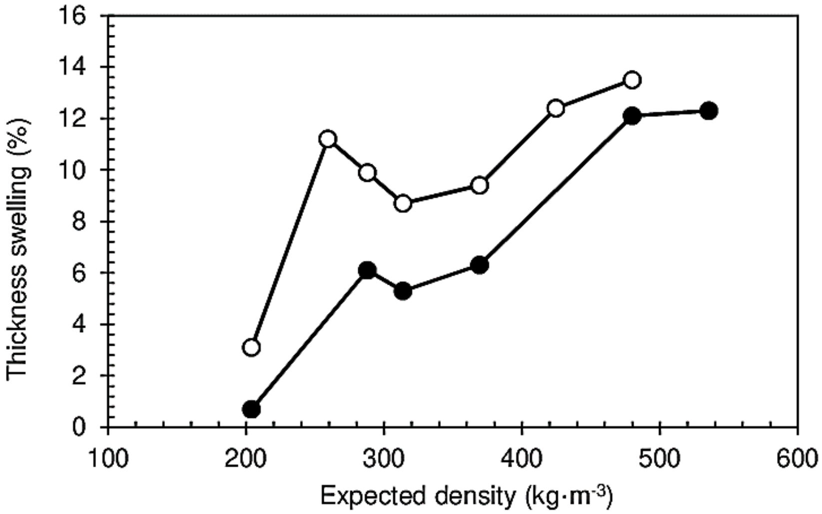


Figure 2.8. Thickness swelling of particleboards bonded with sour cassava starch foam. White circles: Without HPT; black circles: With HPT.

The heat post-treatment consistently causes a significant decrease in TS. Once again, this may be related to the physical modifications that are known to occur in starches subject to heating (increased crystallinity, reduced hydration, increased intramolecular interaction), which translate into reduced swelling power [34].

2.4. Conclusions

Lightweight particleboards, bonded with an adhesive system, based on sour cassava starch with added chitosan and wood fibers, were produced with densities between 207 kg·m^{-3} and 407 kg·m^{-3}. These low-density values were obtained thanks to the good self-foaming property of the starch, which allows for the separation of wood particles and the creation of low-density domains while maintaining good cohesion. Very good internal bond strength and thickness swelling values were obtained. The best overall performance corresponded to a panel with a density of 318 kg·m^{-3}, an IB of 0.67 N·mm^{-2}, and a TS of 8.7%. Heat post-treatment revealed to not be beneficial in terms of internal bond strength, but led to a decrease in the thickness swelling.

The use of this 100% natural adhesive system allows for producing low-density particleboards with excellent performance. Optimization of the adhesive formulation and production conditions will be the subject of future studies.

2.5. References

1. Mohanty, A.K.; Misra, M.; Drzal, T. Sustainable Bio-Composites from renewable resources: Opportunities and challenges in the green materials world. *J. Polym. Environ*. 2002, 10, 19–26.
2. Weiss, M.; Haufe, J.; Carus, M.; Brandão, M.; Bringezu, S.; Hermann, B.; Patel, M.K. A Review of the Environmental Impacts of Biobased Materials. *J. Ind. Ecol*. 2012, 16, 169–181.
3. European committee for standardization. Particleboards – Definition and classification. EN 309, 2005.
4. European committee for standardization. Lightweight Particleboards – Specifications. CEN/TS 16368, 2014.
5. Monteiro, S.; Dias, Â.; Martins, J.; Carvalho, L. Synthesis of Multihollow Polyester Particles in Supra- and Infra-Millimeter Size Ranges by Double Emulsion Process. *Polym. Eng. Sci*. 2016, 56, 590–597.
6. Ballerini, A.; Despres, A.; Pizzi, A. Non-Toxic, zero emission tannin-glyoxal adhesives for wood panels. *Eur. J. Wood Wood Prod*. 2005, 63, 477–478.

7. Valenzuela, J.; Leyser, E.V.; Pizzi, A.; Westermeyer, C.; Gorrini, B. Industrial production of pine tannin-bonded particleboard and MDF. *Eur. J. Wood Wood Prod*. 2012, 70, 735–740.

8. Mansouri, N.E.; Pizzi, A.; Salvado, J. Lignin-Based polycondensation resins for wood adhesives. *J. Appl. Polym. Sci*. 2007, 103, 1690–1699.

9. Liu, Y.; Li, K. Chemical modification of soy protein for wood adhesives. *Macromol. Rapid Commun*. 2002, 23, 739–742.

10. Liu, Y.; Li, K. Development and characterization of adhesives from soy protein for bonding wood. *Int. J. Adhes Adhes*. 2007, 27, 59–67.

11. Wescott, J.M.; Frihart, C.R.; Traska, E. High-Soy-Containing water-durable adhesives. *J. Adhes Sci. Technol*. 2006, 20, 859–873.

12. Lorenz, L.; Frihart, C.R.; Wescott, J.M. Chromatographic analysis of the reaction of soy flour with formaldehyde and phenol for wood adhesives. *J. Amer Oil Chem. Soc*. 2007, 84, 769–776.

13. Amini, M.H.M.; Hashim, R.; Hiziroglu, S.; Sulaiman, N.S; Sulaiman, O. Properties of particleboard made from rubberwood using modified starch as binder. *Compos. Part B Eng*. 2013, 50, 259–264.

14. Belgacem, M.; Gandini, A. *Monomers, Polymers and Composites from Renewable Resources*, 1st ed.; Elsevier: Oxford, UK, 2008; 321–342.

15. Mansouri, H.R.; Navarrete, P.; Pizzi, A.; Tapin-Lingua, S.; Benjelloun-Mlayah, B.; Pasch, H.; Rigolet, S. Synthetic-Resin-Free wood panel adhesives from mixed low molecular mass lignin and tannin. *Eur. J. Wood Wood Prod*. 2011, 69, 221–229.

16. Imam, S.H.; Mao, L.; Chen, L. Greene R V. Wood Adhesive from Crosslinked Poly(Vinyl Alcohol) and Partially Gelatinized Starch: Preparation and Properties. *Starch/Stärke* 1999, 51, 225–229.

17. Tharanathan, R.N. Starch – value addition by modification. *Crit. Rev. Food Sci. Nutr*. 2005, 45, 371–384.

18. Tondi, G.; Wieland, S.; Wimmer, T.; Schnabel, T.; Petutschnigg, A. Starch-Sugar synergy in wood adhesion science: Basic studies and particleboard production. *Eur. J. Wood Wood Prod*. 2012, 70, 271–278.

19. Zhu, F. Composition, structure, physicochemical properties, and modifications of cassava starch. *Carbohydr. Polym*. 2015, 122, 456–480.

20. Kaisangsri, N.; Kerdchoechuen, O.; Laohakunjit, N. Biodegradable foam tray from cassava starch blended with natural fiber and chitosan. *Ind. Crops Prod*. 2012, 37, 542–546.

21. Salgado, P.R.; Schmidt, V.C.; Ortiz, S.E.; Mauri, A.N.; Laurindo, J.B. Biodegradable foams based on cassava starch, sunflower proteins and cellulose fibers obtained by a baking process. *J. Food Eng*. 2008, 85, 435–443.

22. Fueangvivat, V.; Jarusombuti, S.; Hiziroglu, S.; Bauchongkol, P. Properties of Sandwich-Type Particleboard Panels Made from Rubberwood and Eastern Redcedar. *For. Prod. J*. 2014, 64, 72–76.

23. Okudoh, V.; Trois, C.; Workneh, T.; Schmidt, S. The potential of cassava biomass and applicable technologies for sustainable biogas production in South Africa: A review. Renew. Sustain. *Energy Rev*. 2014, 39, 1035–1052.

24. Pandey, A.; Soccol, C.; Nigam, P.; Soccol, V.; Vandenberghe, L.; Mohan R. Biotechnological potential of agro-industrial residues. I: Sugarcane bagasse. *Bioresour. Technol*. 2000, 74, 69–80.

25. Nassar, N.; Ortiz, R. Cassava improvement: Challenges and impacts. *J. Agric. Sci*. 2007, 145, 163.

26. Taiwo, K. Utilization Potentials of Cassava in Nigeria: The Domestic and Industrial Products. *Food Rev. Int*. 2006, 22, 29–42.

27. Sanginga, M. Root and Tuber Crops (Cassava, Yam, Potato and Sweet Potato).Available online: http://www.afdb.org/fileadmin/uploads/afdb/Documents/Events/DakAgri2015/Root_and_Tuber_Crops_Cassava_Yam_Potato and Sweet_Potato.pdf (accessed on 30 September 2016)

28. Tilman, D.; Socolow, R.; Foley, J.; Hill, J.; Larson, E.; Lynd, L.; Pacala, S.; Reilly, J.; Searchinger, T.; Somerville, C.; *et al*. Beneficial biofuels-the food, energy, and environment trilemma. *Science* 2009, 325, 270–271.

29. Banks, W.; Greenwood, C.T.; Muir, D.D. The characterization of starch and its components. Part 3: The technique of semi-micro, differentail, potentiometric, iodine titration and the factors affecting it. *Starch/Stärke* 1971, 21, 118–124.

30. Zhang, Y.R.; Wang, X.L.; Zhao, G.M.; Wang, Y.Z. Preparation and properties of oxidized starch with high degree of oxidation. *Carbohydr. Polym*. 2012, 87, 2554–2562.

31. Klein, B.; Vanier, N.L.; Moomand, K.; Pinto, V.Z.; Colussi, R.; Zavareze, E.; Dias, A.R.G. Ozone oxidation of cassava starch in aqueous solution at different pH. *Food Chem*. 2014, 155, 167–173.

32. Van Soest, J.J.G.; Tournois, H.; Wit, D.; Vliegenthart, J.F.G. Short-Range structure in (partially) crystalline potato starch determined with attenuated total reflectance Fourier-transform IR spectroscopy. *Carbohydr. Res*. 1995, 279, 201–214.

33. Demiate, I.M.; Dupuy, N.; Huvenne, J.P.; Cereda, M.P.; Wosiacki, G. Relationship between baking behavior of modified cassava starches and

starch chemical structure determined by FTIR spectroscopy. *Carbohydr. Polym*. 2000, 42, 149–158.

34. Zavareze, E.D.R.; Dias, A.R.G. Impact of heat-moisture treatment and annealing in starches: A review. *Carbohydr. Polym.* 2011, 83, 317–328.

35. Gunaratne, A.; Hoover, R. Effect of heat-moisture treatment on the structure and physicochemical properties of tuber and root starches. *Carbohydr*. *Polym*. 2002, 49, 425–437.

36. Nafchi, A.M.; Moradpour, M.; Saeidi, M.; Alias, A.K. Thermoplastic starches: Properties, challenges, and prospects. *Starch/Stärke* 2013, 65, 61–72.

37. European committee for standardization. Particleboards – Specifications. EN 312, 2010.

CHAPTER 3

Low-density wood particleboards bonded with starch foam: study of production process conditions

3. Low-density wood particleboards bonded with starch foam: study of production process conditions[3]

Abstract: It has been shown that wood particleboards bonded with sour cassava starch can display low density combined with good physico-mechanical performance, thanks to starch being able to produce a strong foam that fills the interparticular space. Here we optimize the pressing conditions for the production of these panels. The procedure involved hot-plate pressing in two stages: (1) lowering the top platen to a specified thickness for a duration designated as pressing time, followed by (2) raising the top platen to allow panel expansion for a duration designated as hold time. The parameters studied were the pressing time (10 to 150 s), the hold time (290 to 890 s), and the top platen temperature (80 to 190 °C). The hold time and pressing time showed to be crucial parameters. The best operating conditions corresponded to 600 s of press cycle time, comprising 60 s of pressing time and 540 s of hold time. The top platen temperature used was 190 °C. The particleboards produced had a density of 405 $kg{\cdot}m^{-3}$, an internal bond strength of 0.44 $N{\cdot}mm^{-2}$, and a thickness swelling of 13.2%. This can be considered as very good performance, taking into account the panels' low density.

---

[3] Monteiro, S.; Martins, J.; Magalhães, F.D.; Carvalho, L. Low-density wood particleboards bonded with starch foam: study of production process conditions. *Materials*. 2019, 12, 1975.

3.1. Introduction

Particleboards are composites made of wood particles (wood flakes, chips, shavings, saw-dust and similar) and/or other lignocellulose materials in particle form (flax shives, hemp shives, bagasse fragments and similar), with the addition of an adhesive, bonded together with an adhesive system under pressure and heat (EN 309). The most commonly used adhesives are formaldehyde-based resins, mainly urea-formaldehyde resins. Particleboard densities are usually in the range 600 to 750 $kg \cdot m^{-3}$ [1]. Particleboards with density below 600 $kg \cdot m^{-3}$ are designated as lightweight (CEN/TS 16368). That makes their application in furniture industry easier where low weight is required to facilitate transportation and assembly by the customer. Several strategies are available to produce lightweight particleboards, such as lower compaction of the wood mat, use of light wood species, use of sandwich panels with foam core (made of polyurethane or polystyrene foam) or cardboard-based honeycomb core, and production of extruded particleboards containing longitudinal tubular hollow spaces. However, density reduction always has a negative impact on mechanical resistance, in addition to other problems such as difficulty in surface finishing and post-forming [2].

Currently, biosourced and biodegradable materials assume great industrial importance due to environmental issues, in particular regarding replacement of petroleum-derived raw materials and degradability after disposal [3,4]. Biopolymers like tannins, lignin, and starch have been proposed to replace the synthetic adhesives used in particleboards [5–7]. Zhao *et al.* used a binder composed of tannin and sucrose to produce particleboards with a density of 800 $kg \cdot m^{-3}$. Thickness swelling ranged from 20 to 23% [7]. Selamat *et al.* produced particleboards bound with carboxymethyl starch, with densities between 600 and 800 $kg \cdot m^{-3}$ and thickness swelling between 20 and 12% [8].

On the other hand, starch is known to be self-foamable, which has led to it being proposed as a natural replacement for some synthetic foam applications [9–11]. This implies processing via hot mould baking. During this process, the starch granules gelatinize, forming a viscous paste, and the entrain vaporized water that causes the paste to expand. The foam is then dried to allow consolidation [12]. Combination of a starch binder that possesses foaming capability with wood particles seems like a promising strategy to obtain low-density particleboards with good internal cohesion. This approach has been described in our previous work, where a hot-mould was replaced by a hot-press, which is traditionally used among particleboard manufacturers. In this preliminary study, low-density particleboards with densities between 207 and 407 kg·m^{-3} were produced, based on sour cassava starch. Very good internal bond strength and thickness swelling values were obtained, the best performance corresponding to internal bond strength of 0.67 N·mm^{-2}, and thickness swelling of 8.7% for a density of 318 kg·m^{-3} [13]. However, in this proof-of-concept work the production process was not optimized, implying excessively long pressing times, in the order of 40 min, which was a major limitation concerning energy-efficiency and productivity. It is therefore relevant to study how these particleboards can be produced using more efficient pressing conditions.

The hot-pressing process is a key step in the production of particleboards, being also the most costly of the whole process. It requires strict control of all pressing parameters in order to ensure the intended physico-mechanical properties of the product and minimize production [14]. These parameters depended on the mat moisture content and the type of binder. High initial mat moisture content implies longer pressing times in order to allow for water vaporization in the centre of the board. In the current case, the hot-pressing conditions determine how the starch foam develops, contributing to create air-filled cells in between the wood particles, thus providing low density to the board while ensuring good cohesion and adhesion to the wood particle surfaces.

When heated in water, starch granules become hydrated, swell, and undergo disruption. The crystalline order within the starch is lost and amylose chains leach out from the granule and dissolve in water, causing the solution viscosity to increase significantly and forming a gel [15]. The gelatinization temperature for sour cassava starch is around 88 °C [16]. Above this temperature, water present in the gel vaporizes into trapped air bubbles, causing expansion and formation of the foam cell structure.

The present work studies how different production parameters affect the properties of low-density particleboards bonded with a foamable sour cassava starch formulation. The goal defined by us was to obtain panels with density no higher than about 400 $kg \cdot m^{-3}$ and internal bond strength not lower than 0.35 $N \cdot mm^{-2}$, keeping production time as low as possible.

3.2. Materials and methods

3.2.1. Materials

Sour cassava starch was supplied by A Colmeia do Minho S.A. (Seixal, Portugal). Glycerol (99.59%) and propionic acid (99%) were supplied by José Manuel Gomes dos Santos Lda. (Odivelas, Portugal). Chitosan (molecular weight around 300 kDa, degree of deacetylation > 85% was purchased from Golden-Shell Pharmaceutical Co. Ltd (Yuhuan, China). Recycled wood particles (eucalyptus, pine, etc.), with moisture content of 4%, used for the manufacture of particleboards were provided by Sonae Indústria PCDM (Oliveira do Hospital, Portugal). Pinus pinaster fibers was provided by Valbopan-Fibras de Madeira S.A. (Nazaré, Portugal).

3.2.2. Preparation of binder

The adhesive system was prepared as described in our previous work [13]. Table 3.1 shows the formulation composition. Initially, sour cassava starch and distilled water were mixed. Chitosan solution, at 5 wt% concentration, was prepared mixing chitosan and propionic acid solution (6 wt%), during 3 h at 60 °C. This solution was added to the starch and water mixture. Finally, Pinus pinaster fibres and glycerol were added and stirring was maintained for 5 min. The binder mixture shows a light brownish colour, has a solid content of 38% and a viscosity of 15000 cP (measured in a LVDV-IIIU Brookfield viscometer from Brookfield Engineering Laboratories (Middleboro, MA, USA) in the following conditions: temperature-23.3 °C, spindle-RV7, torque-39.5%, speed-10 RPM).

Table 3.1. Formulation of the adhesive system.

Component	**Quantity (wt%)**
Sour cassava starch	30.5
Distilled water	30.5
Chitosan solution	33.4
Pinus pinaster fibers	2.8
Glycerol	2.8

3.2.3. Scanning electron microscopy

The internal structure of particleboards was observed by Scanning Electron Microscope, using a high resolution (Schottky) Environmental Scanning Electron Microscope with X-ray Microanalysis and Electron Backscattered Diffraction analysis: Quanta 400 FEG ESEM/EDAX Genesis X4M (FEI, Hillsboro, OR, USA). Samples were coated with Au/Pd thin film, by sputtering, using the SPI

Module Sputter Coater equipment. The analysis was performed at CEMUP (Centro de Materiais da Universidade do Porto, Porto, Portugal).

3.2.4. Particleboard production

Wood particles were manually blended with the adhesive system. The adhesive/wood ratio was 1:1 based on weight of solid adhesive content and oven dry wood. Single layer particleboards were hand formed in square aluminium deformable container, with 220 × 220 × 80 mm^3. A computer-controlled laboratory scale press, equipped with a linear variable displacement transducer (LVDT), pressure transducer and thermocouples, was used to produce the particleboards.

The press bottom platen temperature was set to 190 °C, while the temperature of the top platen was varied between 80 and 190 °C. The adhesive/wood mixture was placed on the bottom platen and pressed to 16 mm thickness for a certain amount of time, designated as “pressing time”. After this, the top platen was raised to 28 mm thickness, and the panel maintained in the press for a duration designated as “hold time”, to allow foam expansion as water in the starch paste vaporizes. The “press cycle time” comprises the pressing and hold times. After pressing, panels were dried at (20 ± 2) °C and relative humidity of (65 ± 5)% till constant mass. During this process boards suffer shrinkage due to loss of water, attaining thickness of 16 – 20 mm depending on the production conditions, which results in different final densities. The mass of wood/binder mixture used to produce the panels was always 425 g, which corresponds to a target density of 318 $kg \cdot m^{-3}$. Four boards were produced for each condition tested. Figure 3.1 depicts the particleboards manufacturing process. Before testing, particleboards surfaces were calibrated by sanding in order to remove irregularities and guarantee flat parallel surfaces. Tested particleboards had a moisture content between 15.1 and 15.5%.

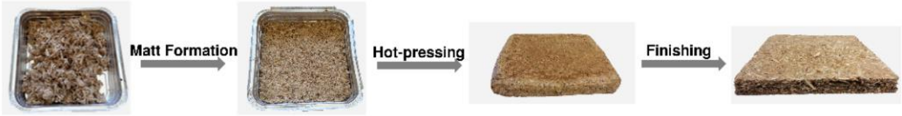


Figure 3.1. Steps of manufacture process of particleboards bonded with a sour cassava starch, starting with a mixture of wood particles and starch paste and ending with a finished particleboard.

Density measurements were performed according to EN 323. The samples were square shaped, with side length of 50 mm and thickness between 16 and 20 mm. Density was calculated using the mass and volume of specimen after drying. Four replicates were used for each experiment

Determination of internal bond strength, also known as tensile strength perpendicular to the plane of the board, was performed according to EN 319. The specimen has a square shape with 50 × 50 mm^2 and thickness between 16 and 20 mm. The test pieces are glued to the metal loading block using a hot-melt glue (ethylene vinyl acetate) The specimen is subject to a tensile force at constant speed until rupture occurs. Four replicates were used for each experiment.

Thickness swelling was determined according to the method described in EN 317. The increase in thickness of a specimen, with 50 × 50 mm^2 and thickness between 16 and 20 mm, was evaluated after complete immersion in water for 24 h. Four replicates were used for each experiment.

Moisture content was measured according to EN 322. It is the ratio between the weight loss of a sample, dried in an oven at (103 ± 2) °C till constant mass, and the mass of oven dry-board. The specimen had a square shape with 50 × 50 mm^2

and thickness between 16 and 20 mm. Four replicates were used for each experiment.

3.3. Results and discussion

In order to understand the influence of hold time on physico-mechanical properties of particleboards, different times (290 – 890 s) were tested, with both platens at a temperature of 190 °C. This temperature was chosen because it is typically used in industrial production of particleboards. After being placed on the lower platen, the mat made of wood particles mixed with starch paste was pressed to 16 mm thickness during 10 s, to ensure good particle contact and heat transfer. After this the top platen was lifted to 28 mm and held in this position for the intended hold time, allowing the particle/starch mixture to expand until reaching the top platen. The final densities of the panels for the different hold times are shown in Figure 3.2.

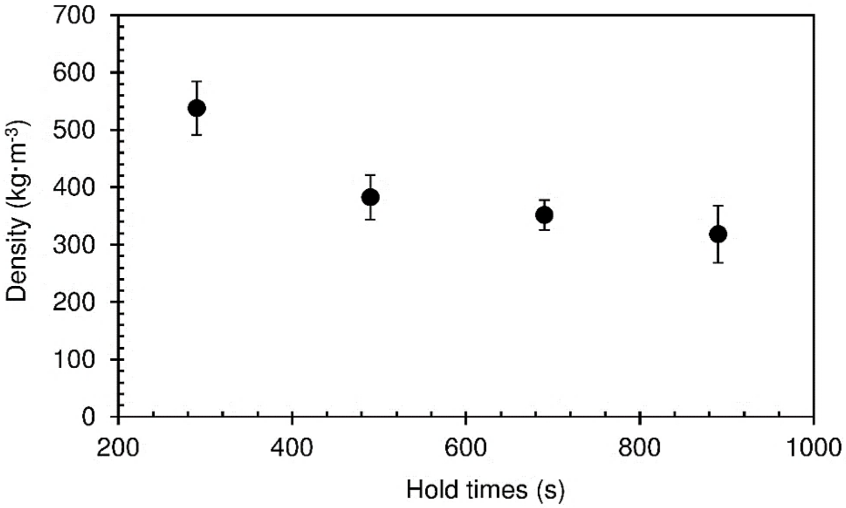


Figure 3.2. Density of particleboards bonded with sour cassava starch foam for different hold times at 190 °C. The pressing time used was 10 s.

The obtained densities range between 318 and 538 kg·m^{-3}, decreasing with the hold times. The particleboards produced at 290 s did not touch the top platen during expansion. For this reason, these panels had a final thickness of 15.24 mm after being removed from the press and their density is higher than de others. For longer, the panels expanded until reaching the 28 mm limit defined by the top platen. However, when removed from the press, all panels ended up abating as vapour escaped while the starch is still soft, allowing the foam to practically collapse. These panels had a final thickness between 18.31 and 20.62 mm (Table 3.2). The reduction in thickness after abatement is lower for the longer times due to progressive hardening of the starch foam as water vaporizes. This leads to the slight decrease in density observed for hold times between 490 and 890 s.

Table 3.2. Panels thickness measured immediately after removed from the press (results for four specimens).

Hold times (s)	Thickness of panels immediately after pressing (mm)
290	15.24 ± 0.07
490	18.31 ± 0.54
690	20.62 ± 0.95
890	20.56 ± 0.28

The internal bond strength of particleboards indicates the level of cohesion inside the panel, or, in other words, how well particles are bonded together. Figure 3.3 shows the results of internal bond strength obtained for the particleboards produced.

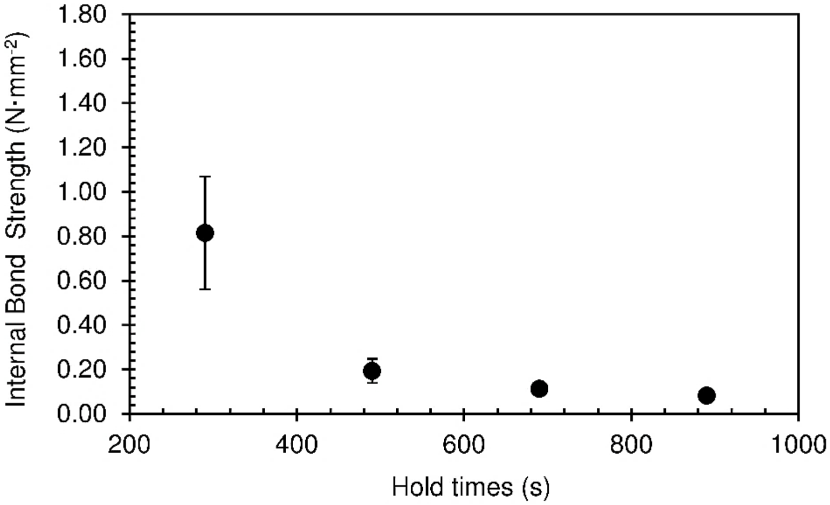


Figure 3.3. Internal bond strength of particleboards bonded with sour cassava starch foam for different hold times, produced at 190 °C. The pressing time used was 10 s.

The reduction in internal bond strength follows the decrease in density, which was expected since lower density implies lower internal cohesion. However, the very low values obtained for hold time of 490 s and above are actually attributable to rupture of the foam structure after the panel is removed from the press. The large amount of water vapour trapped inside the panel creates significant inner pressure, which causes very fast expansion followed by collapse when it is removed from the confinement of the press platens. This results in bursting of the foam cell walls, creating interior cracks that weaken the panel.

The relatively high variability observed in internal bond strength for the lower hold time, when the panels display higher strength, is attributable to several factors, like the heterogeneity of the particles, which are obtained from recycled wood, and the inhomogeneity of the adhesive/wood mixing process, which is done manually. This variability, observed also for other test conditions, could be reduced if more replicates were performed, but this would not have an effect on the key conclusions that can be drawn from the results.

The thickness swelling results are shown in Figure 3.4. As expected, thickness swelling follows the same trend as density. The lower the mass of material per unit volume, the lower will be the amount of water absorbed and thus the lower the swelling.

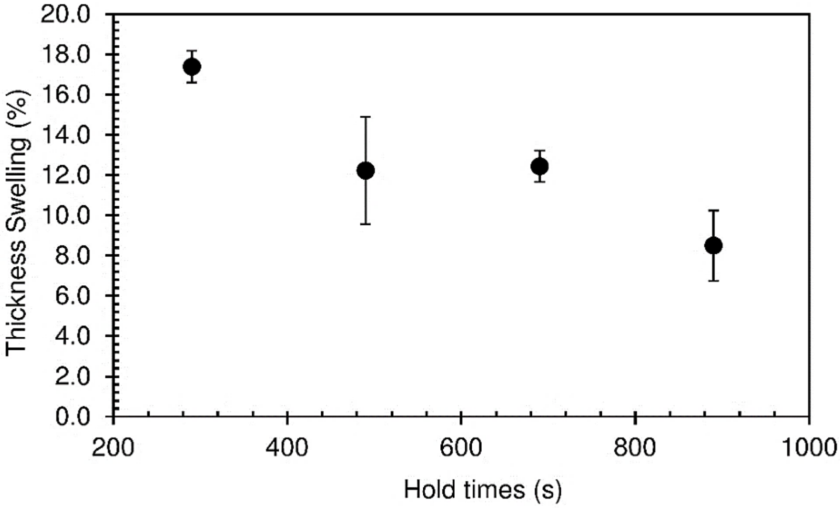


Figure 3.4. Thickness swelling of particleboards bonded with sour cassava starch produced at different hold times at 190 °C. The pressing time used was 10 s.

According to the European standard EN 312, for non-load bearing boards for use in humid conditions (P3 class), with thickness between 13 and 20 mm, the maximum thickness swelling allowed is 14%. Particleboards produced with longer hold times (490–890 s) meet this requirement.

Figure 3.5 shows an overview of the internal bond strength as a function of density for the particleboards produced at different hold times. The grey area in the graph represents the goal region of the present work: low-density particleboards (density ≤ 400 kg·m^{-3}) with good bonding quality (internal bond strength ≥ 0.35 N·mm^{-2}). It can be seen that none of the panels produced in these conditions satisfied the objectives. Low density implies low strength and good strength is obtained only with too high density.

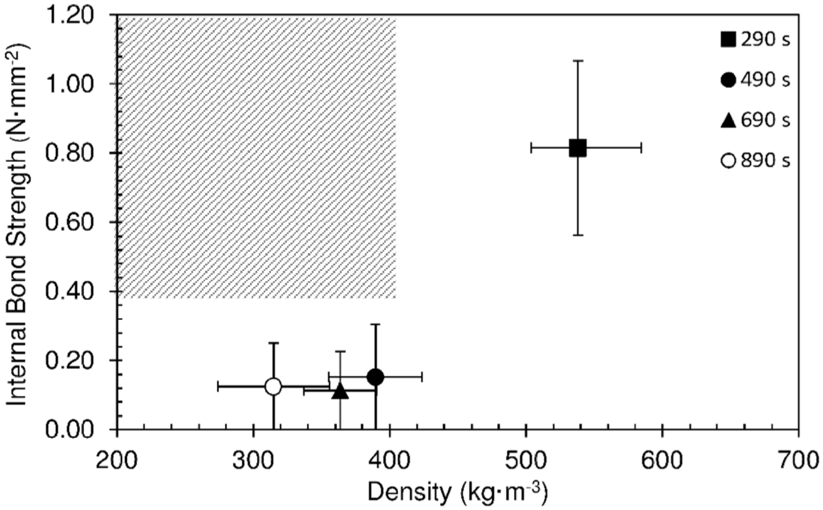


Figure 3.5. Internal bond strength as function of density for particleboards produced at different hold times and 190 °C. The pressing time used was 10 s.

Considering the previous results, a hold time of 490 s was selected and the effect of decreasing the top platen temperature was studied. The lower platen was kept at 190 °C. The particleboard density results are shown in Figure 3.6.

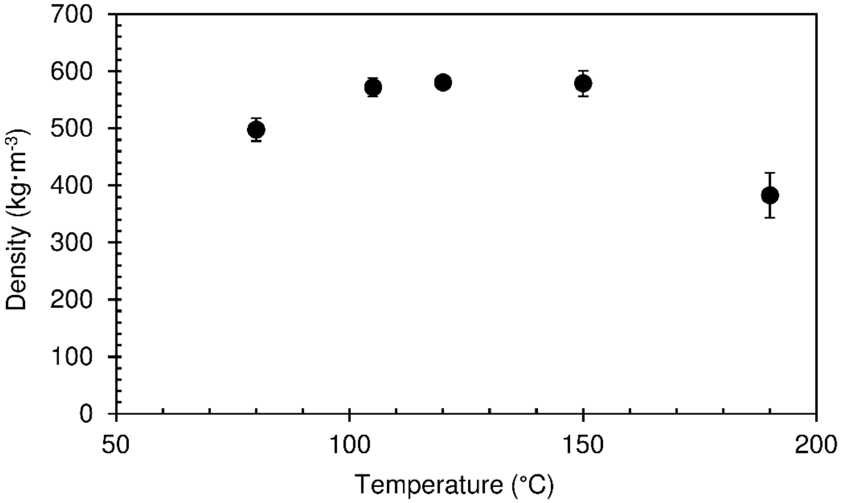


Figure 3.6. Density of particleboards produced with different top platen temperatures, for a hold time of 490 s. The pressing time used was 10 s.

For temperatures up to 150 °C, the density does not change significantly with temperature. On the other hand, for 190 °C it decreased from around 580 to 380 kg·m^{-3}. The high densities observed at low temperatures are a result of panel abatement after removal from the press. This occurs due to incomplete foam consolidation. Starch foam is formed as water vapor bubbles are trapped within the viscous paste of gelatinized starch [12]. Gelatinization is a condition for starch's crystalline double-helix chains to dissociate, breaking up the granules' structure and forming a waterborne network of hydrogen bonds [17]. Low temperatures in the top platen do not allow for complete starch gelatinization, and a fraction of starch chains remain within the granules. As a consequence, the foam cell walls do not develop the strength needed to hold the structure when the vapour escapes after the panel is removed from the press. At 190 °C, gelatinization within the mixture is complete and the panel undergoes significantly less abatement, allowing for lower final density.

The internal bond strength results are shown in Figure 3.7. Bond resistance increases very significantly for top platen temperatures between 80 and 120 °C, which is not relatable to the trend observed in the panel densities, which did not change significantly. This strength increase is coherent with a more extensive gelatinization as the mixture is heated more effectively, as discussed above. For 150 °C the measurements showed large variability, indicating that this is a point of instability. For 190 °C, the bond strength decreased to a very low value, which is a consequence of inner bursting of the foam when this panel with a more hardened foam structure was taken out of the press confinement, as mentioned before.

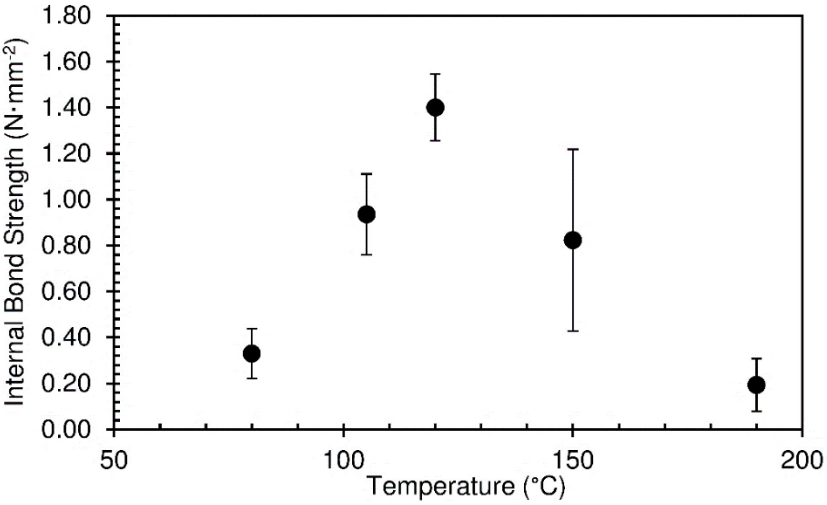


Figure 3.7. Internal bond of particleboards produced at different top platen temperatures, for hold time of 490 s. The pressing time used was 10 s.

The thickness swelling results are shown in Figure 3.8. Thickness swelling values vary between 12.2 and 17.4%, being once again relatable to the changes in density.

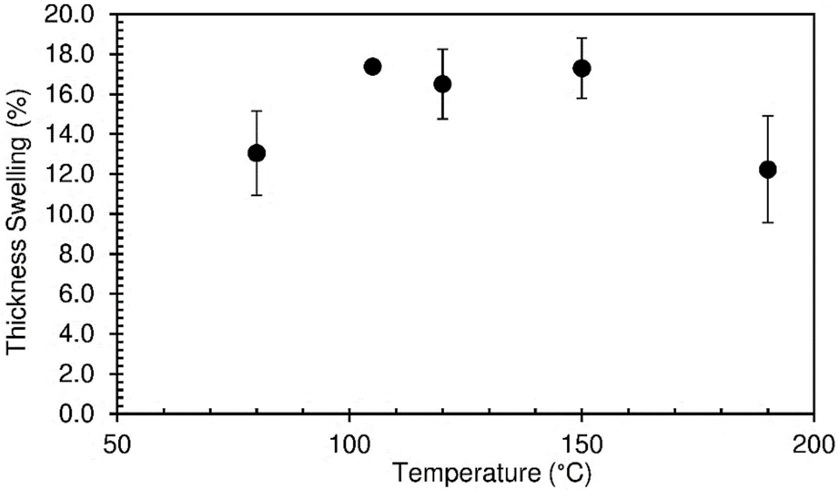


Figure 3.8. Thickness swelling of particleboards bonded with sour cassava starch foam produced at different pressing temperatures with a hold time of 490 s. The pressing time used was 10 s.

Figure 3.9 shows an overview of the results obtained for panels produced at different temperatures. Once again, none of the pressing conditions allowed us to obtain particleboards inside the target area. Decreasing the press top platen temperature mostly led to higher final densities, contradicting the intended goal.

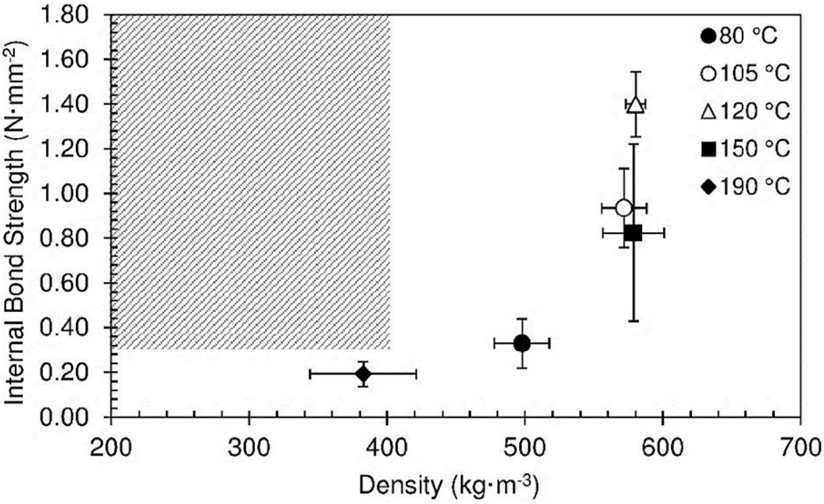
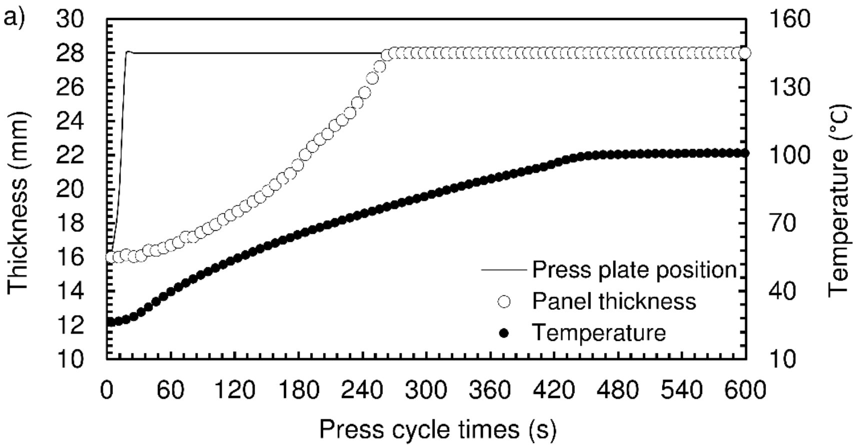


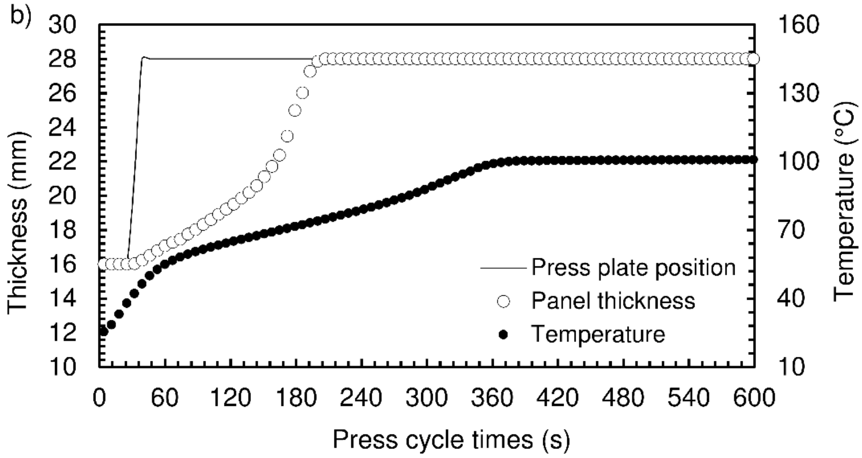
Figure 3.9**.** Internal bond strength as function of density for particleboards produced at different temperatures with a hold time of 490 s. The pressing time used was 10 s.

The previous studies indicated that manipulating the hold time and the top platen temperature did not allow attaining the combined density and internal bond strength goal. Since there was evidence that in some conditions complete starch gelatinization may be hindered, a closer look was taken at the temperature inside the particle/starch mat during the panel manufacture process. In addition, the expansion of the mat was monitored by image analysis.

The top platen temperature was kept at 190 °C, and different pressing times, at which the mat is pressed at 16 mm thickness, were tested: 10 s, 30 s, 90 s, 150 s. The total time in the press was 600 s.

Figure 3.10 shows the results obtained, in terms of mat thickness and inside temperature histories for the pressing times tested.


a)
Thickness (mm)
30
28
26
24
22
20
18
16
14
12
10
Temperature (°C)
160
130
100
70
40
10
0
60
120
180
240
300
360
420
480
540
600
Press cycle times (s)
Press plate position
Panel thickness
Temperature


b)
Thickness (mm)
30
28
26
24
22
20
18
16
14
12
10
Temperature (°C)
160
130
100
70
40
10
0
60
120
180
240
300
360
420
480
540
600
Press cycle times (s)
Press plate position
Panel thickness
Temperature

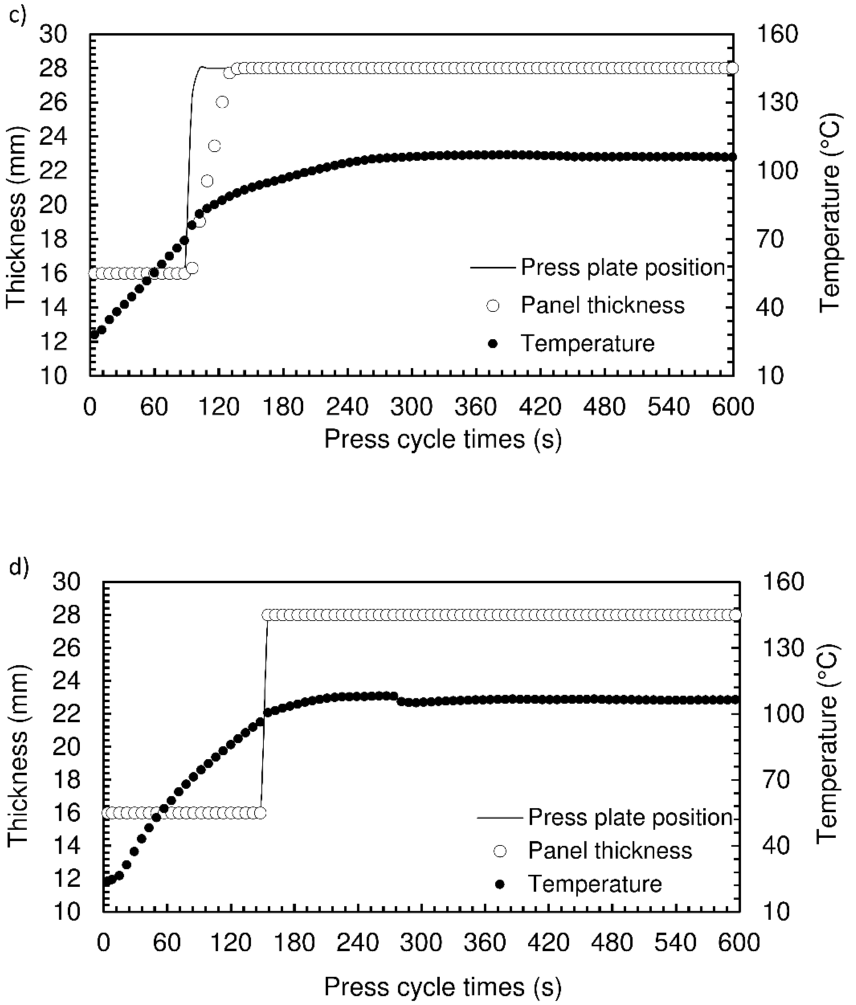


Figure 3.10. Expansion behavior profile of particleboards bonded with sour cassava starch for different pressing times: 10 s (a), 30 s (b), 90 s (c), and 150 s (d). The pressing temperature of experiments was 190 °C.

The temperature inside the mat increases relatively slowly when the pressing time is only 10 s, taking about 450 s to reach a maximum slightly above 100 °C (Figure 3.10a). This maximum temperature is dictated by the continuous evaporation of liquid water present in the starch paste. The foam expansion is also relatively slow. The mat reaches the top platen only about 250 s after the beginning of the process, corresponding to a hold time of 240 s. As the pressing time is increased, heating inside the mat is accelerated, as well as its expansion. When the pressing time is 150 s, the centre of the mat has almost reached the maximum temperature by the end of pressing, and the expansion actually follows the movement of the top platen as soon as it rises (Figure 3.10d). The pressing time is therefore seen to play an important role, since it corresponds to a highly effective heat transfer process that accelerates water evaporation and foam formation. However, it must be noted that the panels produced at the higher pressing times (90 and 150 s) exhibited internal fractures, associated with the vapour pressure build-up within the mat causing bursting of the foam structure when the top platen was raised. It was therefore decided to try a pressing time of 60 s in the subsequent panel productions, keeping the top platen temperature at 190 °C, and testing different hold times. The density results are shown in Figure 3.11.

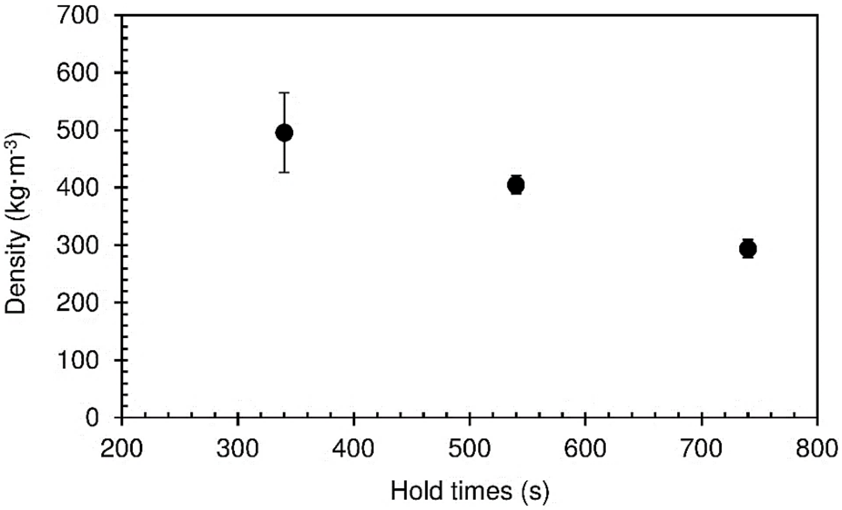


Figure 3.11. Density of particleboards bonded with sour cassava starch for different hold times at 190 °C. The pressing time used was 60 s.

The minimum value of density obtained was 294 kg·m^{-3} for a hold time of 740 s. The density of the panels decreases with the increase in hold time. Longer time in the press implies more water evaporation and hardening of the foam, therefore diminishing abatement when, after removal from the press, trapped vapour escapes through the panel surface. Figure 3.12 shows that the panels did not undergo internal rupture of the foam structure, since reasonably high values of internal bond strength were obtained. As expected, these followed the same trend as density.

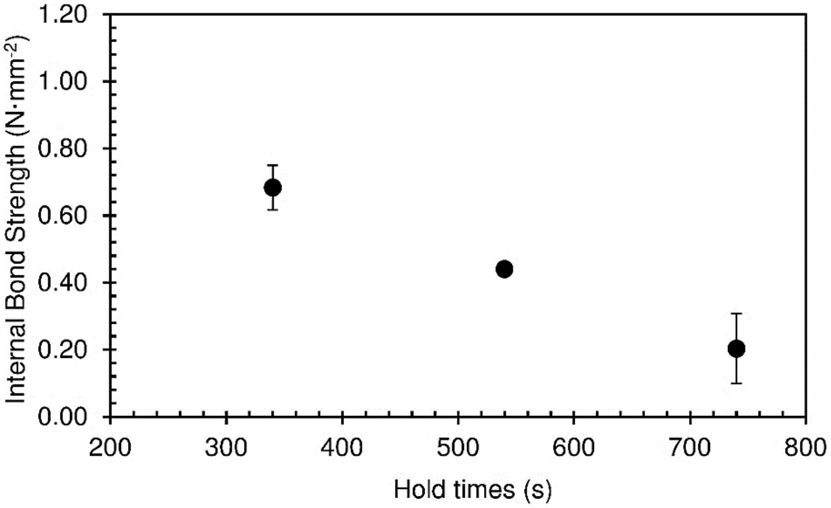


Figure 3.12. Internal bond of strength particleboards bonded with sour cassava starch for different hold times at 190 °C. The pressing time used was 60 s.

The thickness swelling results are shown in Figure 3.13. The values obtained ranged between 6.9 and 14.8%. As discussed before, these can be considered quite low when compared with particleboards produced with a bio-based adhesive reported in the literature.

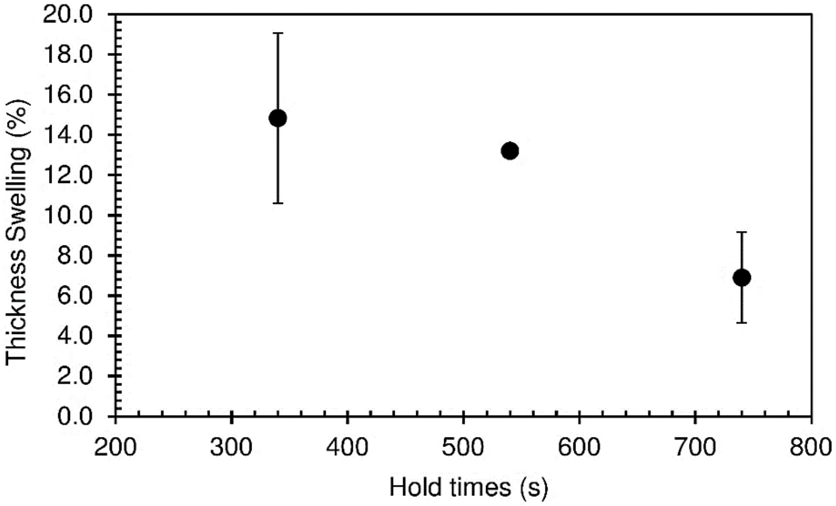


Figure 3.13. Thickness swelling of particleboards bonded with sour cassava starch for different hold times at 190 °C. The pressing time used was 60 s.

Figure 3.14 shows an overview of the results obtained for panels produced with the pressing time of 60 s for different hold times at 190 °C. The work's goals were attained with 540 s. These operating conditions allowed us to produce particleboards with density of 405 kg·m^{-3}, internal bond strength of 0.44 N·mm^{-2}, and thickness swelling of 13.2%. It is well known that particleboards produced with bio-based adhesives tend to have lower internal bond strength than those based on conventional urea-formaldehyde resins for the same densities. Zhang *et al.* [18] produced particleboards using bayberry tannin-based adhesive having internal bond strength obtained of 0.34 – 0.47 N·mm^{-2}, but with densities of 600 – 718 kg·m^{-3}. Ferreira *et al.* [6] used a binder system based on spent sulfite liquor and wheat flour, obtaining maximum internal bond strength of 0.46 N·mm^{-2} for boards with a density of 650 kg·m^{-3}.Sulaiman *et al.* [19] produced boards using epichlorohydrin-modified rice starch as binder.

They obtained internal bond strength of about 0.22 N·mm^{-2} for native rice starch, and 0.35 – 0.39 N·mm-^{2} for modified rice starch, with densities of 600 kg·m^{-3}.

The best performance corresponded to panels manufactured with epichlorohydrin-modified rice starch combined with urea-formaldehyde resin, yielding internal bond strength of 0.50 – 0.61 N·mm^{-2}.

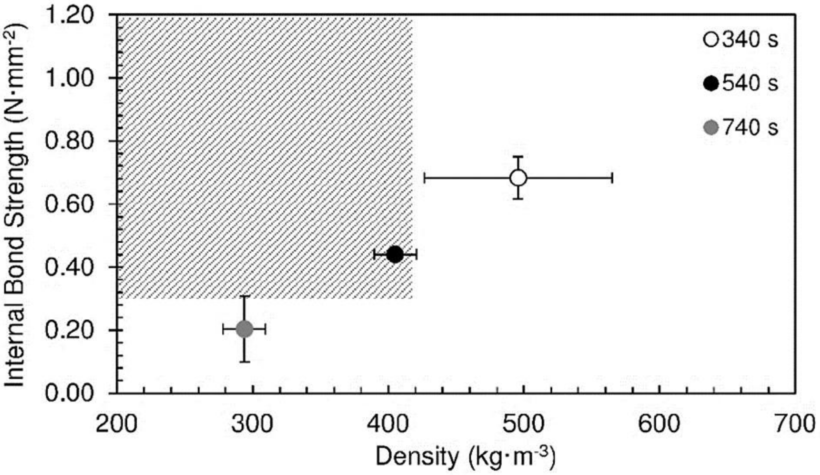


Figure 3.14. Internal bond strength as function of density for particleboards bonded with sour cassava starch for different hold times at 190 °C. The pressing time used was 60 s.

Figure 3.15 shows a SEM image of the interior of a panel. It is visible that the wood particles are surrounded by starch foam, and an apparently good interphase adhesion exists between the two. The starch foam effectively separates the wood particles, providing the panel`s low density, while providing cohesive strength, as demonstrated by the good internal bond resistance values obtained. Note that, according to European Technical Specification CEN/TS 16368, for lightweight particleboards type LP2 (the most demanding) with thickness between 13 and 20 mm, the minimum requirement for internal bond is 0.35 N·mm^{-2}.

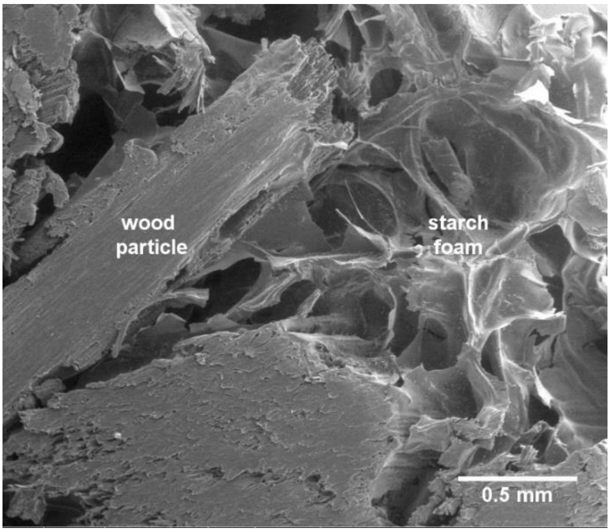


Figure 3.15. SEM image of the interior of the particleboards showing wood particle surrounding by a starch foam, 100 x magnification.

3.4. Conclusions

The present work studied the effect of different production parameters on the physico-mechanical properties of low-density particleboards bonded with a foamable sour cassava starch formulation. Our aim was to produce totally biosourced panels with density about 400 kg·m^{-3} and internal bond strength higher than 0.35 N·mm^{-2}, in the shortest production time possible.

The particleboards produced with hold times ranging from 290 to 890 s had densities between 318 and 538 kg·m^{-3}. Density decreased with hold time, however above 490 s the density variation was small. In this case the panels showed very low internal bond strength (< 0.20 N·mm^{-2}), due to bursting of the internal foam cell structure upon removal from the press, a consequence of the large amount of water vapour entrapped within the panel.

The pressing temperature affects starch gelatinization, and consequently the consolidation of the foam structure. Panels produced at low top platen temperatures (< 150 °C) showed high densities as a result of the foam structure abating after vapour escapes when the panel is removed from the press. Starch gelatinization is more effective at 190 °C, and lower densities can be obtained.

Longer pressing times accelerate foam expansion due to more effective heat transfer within the particle mat. Nonetheless, panels manufactured with too long pressing times (90 and 150 s) exhibited internal fractures due to vapour pressure build-up.

The selected operating parameters were: Pressing time of 60 s, platen temperature of 190 °C, and total hold time of 540 s. Particleboards produced under these conditions had density of 405 $kg \cdot m^{-3}$, internal bond strength of 0.44 $N \cdot mm^{-2}$, and thickness swelling of 13.2%. The internal bond strength obtained is above of the requirements of European Technical Specification CEN/TS 16368, for lightweight particleboards type LP2 (the most demanding) (0.35 $N \cdot mm^{-2}$).

3.5. References

1. Thoemen, H.; Irle, M.; Sernek, M. *Wood-Based Panels An Introduction for Specialists*, 1st ed.; Brunel University Press: London, UK, 2010; p. 117.
2. Monteiro, S.; Martins, J.; Magalhães, F.D.; Carvalho, L. Lightweight Wood Composites: Challenges, Production and Performance. *In Lignocellulosic Composite Materials*, 1st ed.; Kalia, S., Ed.; Springer International Publishing: Cham, Switzerland, 2018; Volume 1, pp. 293–322.

3. Zhang, C.W.; Li, F.Y.; Li, J.F.; Wang, L.M.; Xie, Q.; Xu, J.; Chen, S. A new biodegradable composite with open cell by combining modified starch and plant fibers. *Mater. Des*. 2017, 120, 222–229.
4. Francucci, G.; Rodriguez, E. Processing of Plant Fiber Composites by Liquid Molding Techniques: An Overview. *Polym. Compos*. 2016, 37, 718–733.
5. Lei, H.; Pizzi, A.; Du, G. Environmentally Friendly Mixed Tannin/Lignin Wood Resins. J. *Appl. Polym. Sci*. 2008, 107, 203–209.
6. Ferreira, A.M.; Pereira, J.; Almeida, M.; Ferra, J.; Paiva, N.; Martins, J.; Magalhães, F..; Carvalho, L. Biosourced Binder for Wood Particleboards Based on Spent Sulfite Liquor and Wheat Flour. *Polymers* 2018, 10, 1070.
7. Zhao, Z.; Umemura, K. Investigation of a new natural particleboard adhesive composed of tannin and sucrose. *J. Wood Sci*. 2014, 60, 269–277.
8. Selamat, M.E.; Sulaiman, O.; Hashim, R.; Hiziroglu, S.; Noor, W.; Wan, A.; Syuhada, N.; Zulhairie, M. Measurement of some particleboard properties bonded with modified carboxymethyl starch of oil palm trunk. *Measurement* 2014, 53, 251–259.
9. Glenn, G.M.; Orts, W.J.; Nobes, G.A.R. Starch, fiber and CaCO3 effects on the physical properties of foams made by a baking process. *Ind. Crops Prod.* 2001, 14, 201–212.
10. Uslu, M.-K.; Polat, S. Effects of glyoxal cross-linking on baked starch foam. *Carbohydr. Polym*. 2012, 87, 1994–1999.
11. Palma-Rodríguez, H.M.; Berrios, J.D.J.; Glenn, G.; Salgado-Delgado, R.; Aparicio-Saguilán, A.; Rodríguez-Hernández, A.I.; Vargas-Torres, A. Effect of the storage conditions on mechanical properties and

microstructure of biodegradable baked starch foams. *CYTA J. Food* 2016, 14, 415–422.

12. Soykeabkaew, N.; Thanomsilp, C.; Suwantong, O. A review: Starch-based composite foams. *Compos. Part A Appl. Sci. Manuf.* 2015, 78, 246–263.
13. Monteiro, S.; Martins, J.; Magalhães, F.D.; Carvalho, L. Low-density wood-based particleboards bonded with foamable sour cassava starch: Preliminary studies. *Polymers* 2016, 8, 354.
14. Ranita, J.; Martins, J.; Garrido, N.; Carvalho, L.H.; Costa, C. Influência do ciclo de prensagem na qualidade do aglomerado de partículas de madeira fabricado com teor elevado de partículas recicladas.In Proceedings of the Anais de Congresso Floresta Nacional-A Floresta e as Gentes, Viseu, Portugal, 16–18 May 2005.
15. Zhu, F. Composition, structure, physicochemical properties, and modifications of cassava starch. *Carbohydr. Polym.* 2015, 122, 456–480.
16. Marcon, M.J.A.; Kurtz, D.J.; Raguzzoni, J.C.; Delgadillo, I.; Maraschin, M.; Soldi, V.; Reginatto, V.; Amante, E.R. Expansion Properties of Sour Cassava Starch (Polvilho Azedo): Variables Related to its Practical Application in Bakery. *Starch/Stärke* 2009, 61, 716–726.
17. Yongfeng, A.; Jane, J. Gelatinization and rheological properties of starch. *Starch/Stärke* 2015, 67, 213–224.
18. Zhang, J.; Liang, J.; Du, G.; Zhou, X.; Wang, H.; Lei, H. Development and characterization of a bayberry tannin-based adhesive for particleboard. *BioResources* 2017, 12, 6082–6093.
19. Sulaiman, N.S.; Hashim, R.; Amini, M.H.M.; Sulaiman, O.; Hiziroglu, S. Evaluation of the properties of particleboard made using oil palm starch modified with epichlorohydrin. *BioResources* 2013, 8, 283–301.

CHAPTER 4

Low-density cardoon (Cynara cardunculus) particleboards bound with potato starch-based adhesive

4. Low-density cardoon (*Cynara carduncylus*) particleboards bound with potato starch-based adhesive[4]

Abstract: In the present work, and for the first time, totally biosourced low-density particleboards were produced using cardoon particles (a no added value by-product from the Portuguese cheese making industry), bound with a potato starch adhesive. Different starch/cardoon ratios (0.6, 0.8, 1 and 1.2) were tested, and the effect of different bio-based additives (chitosan, wood fibre and glycerol) on the performance of the adhesive system was evaluated. The best result was obtained for a formulation with a starch/cardoon weight ratio of 0.8, a chitosan/starch ratio of 0.05 and a water/starch ratio of 1.75. The particleboards produced had a density of 323 kg·m^{-3}, internal bond strength of 0.35 N·mm^{-2}, and thickness swelling of 15.2%. The values of density and internal bond strength meet the standard requirements of general-purpose lightweight boards for use in dry conditions according to CEN/TS 16368 specification.

---

[4] Submitted to Wood Science and Technology: Monteiro, S.; Nunes, L.; Martins, J.; Magalhães, F.D.; Carvalho, L. Low-density cardoon (*Cynara carduncylus*) particleboards bound with potato starch-based adhesive.

4.1. Introduction

Particleboards (PBs) are wood-based panels produced from wood particles and/or other lignocellulosic material, bonded with an adhesive system under pressure and heat. Particleboards with a density below 600 kg·m^3 are called lightweight particleboards and are usually used in furniture and flooring systems [1].

In general, the adhesives used in the production of particleboards are based in formaldehyde in combination with urea and/or melamine or phenol, due to their good adhesive performance, high reactivity and lower price [2–4]. However, the adhesive industry has been searching for alternatives that are more sustainable, eco-friendly and less dependent of fossil resources, while guaranteeing good bonding performance and economic viability [5].

Starch has been one of the most studied natural products due to its low cost, biodegradability, renewability and good binding properties, in particular for cellulosic substrates [6–9]. The Europe Union produces 9.3 million tonnes of starch, where 58% in food, 2% in feed and 40% in non-food applications (the majority for paper-related products)[10]. Potato starch is presented as large granules (< 110 mm) with an ellipsoidal shape. It has higher swelling capability and solubility than other starches, and low gelatinization temperature (60 - 72 °C) [11,12].

Cardoon (*Cynara cardunculus* L.) is native to the Mediterranean basin and belongs to Asteraceae Dumortier family. The aqueous extracts from its flowers have been used for centuries as coagulant in the traditional manufacture of ewes' milk cheese making, due to high content of aspartic proteases, and high milk-clotting activity. Cardoon extract confers particular texture and flavor to cheese products. Its use as coagulant in the production of some Portuguese and Spanish traditional ewes' milk cheeses is required by specific regulations for cheeses that have protected designations of origin (PDO) [13–15]. Even though this is its major current use, cardoon is a crop with a wide range of applications such as human nutrition (due to high amount of nutraceutical and bio-active compounds) [16], and medicine (compounds with anti-tumor, antibacterial and anti-HIV activity can be extracted from the plant) [17]. Cardoon can also be used for the production of lignocellulosic biomass and seed oil, for animal feed and as a raw material in paper pulp and plywood [11,18,19]. In Portugal, cardoon plants are cultivated mostly for the value of the flowers, used in the cheese industry. The stalks and branches are a by-product with no added value. The stalks (Figure 4.1) have a central pith surrounded by cortex, and an irregular thin epidermis [20]. Cardoon stalks have remarkably low-density, which has been determined be several authors. Gominho *et al.* [21] obtained a density of 208 $kg \cdot m^{-3}$ for stalk particles with 20-30 mm. The authors further determined densities of 218 $kg \cdot m^{-3}$ for depithed stalks (longitudinally section of stalk without pith) and 75 $kg \cdot m^{-3}$ for the pith material. Quilhó *et al.* [22] determined a density of 138 $kg \cdot m^{-3}$ for whole stalks and 160 $kg \cdot m^{-3}$ for the depithed stalks. Gil *et al.* [23] reported a density of 114 $kg \cdot m^{-3}$ for milled stalks and branches.

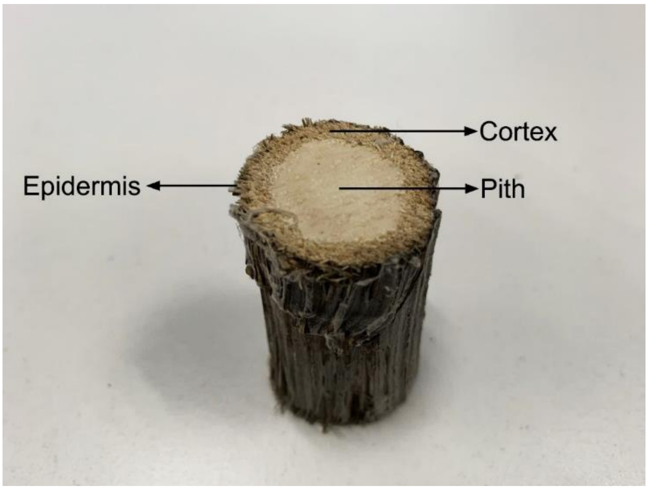


Figure 4.1.Stalks fraction of cardoon: a) pith, b) cortex and c) epidermis.

In a previous work we reported low-density particleboards using pine wood particles bound with a foamable sour cassava starch formulation. The starch foam formed during hot-pressing allowed for intercalation of the wood particles with a low-density but resistant foam, thus providing low-density and good cohesion to the panel. The best results were achieved for particleboards with internal bond strength (IB) of 0.67 $N \cdot mm^{-2}$, thickness swelling of 8.7% and a density of 318 $kg \cdot m^{-3}$ [24,25]. The present work, on the other hand, proposes to take advantage of cardoon particles' naturally low density to produce lightweight particleboards. Obtaining a starch foam is not therefore paramount, allowing for the use of potato starch, of Portuguese origin, instead of sour cassava starch as the binder.

The goal of the present work is therefore to evaluate the viability of producing low-density particleboards with cardoon particles and potato starch. The effect of adding other components to the adhesive system (chitosan, wood fibre and glycerol) is also studied. It is intended that the panels have low-density (specified here as ≤ 400 $kg \cdot m^{-3}$) and good mechanical properties (internal bond strength ≥ 0.30 $N \cdot mm^{2}$, according to the standard requirements for general purpose lightweight boards for use in dry conditions (Type LP2)-CEN/TS 16368).

4.2. Materials and methods

4.2.1. Materials

Potato starch was supplied by Diverembal Lda. (Alcabideche, Portugal). Glycerol (99.59%) and propionic acid (99%) were supplied by José Manuel Gomes dos Santos Lda. (Portugal). Chitosan (molecular weight around 300 kDa, degree of deacetylation > 85% was purchased from Golden-Shell Pharmaceutical Co. Ltd (Zhejiang, China). Cardoon was provided by Casa da Ínsua (Viseu, Portugal), and chipped at Polytechnic Institute of Viseu (IPV) into particles with size range between 0.5 and 2 mm and moisture content of 10%. *Pinus pinaster Ait*. fibres were provided by Valbopan-Fibras de Madeira S.A (Nazaré, Portugal).

4.2.2. Preparation of binder

A cassava starch-based binder formulation described in our previous works with pine wood particleboards [24,25] was used as reference for the optimization of the adhesive system in this work. Variable relative amounts of each formulation component were tested – water, starch, chitosan, wood fiber and glycerol. Initially, potato starch was added to distilled water. Chitosan solution, at 5 wt% concentration, was prepared by mixing chitosan and propionic acid solution (6 wt%), during 3 h at 60 °C. This solution was added to the starch and water mixture. Finally, Pinus pinaster fibres and glycerol were added and stirring was maintained for 5 min.

4.2.3. Particleboards production and characterization

Cardoon particles were blended manually with the adhesive system. All the particleboards produced were prepared with 200 g solids content. Single layer particleboards were hand formed in square aluminium deformable containers, with dimensions 220 × 220 × 80 mm^3. A computer controlled laboratory-scale press, equipped with a linear variable displacement transducer (LVDT), pressure transducer and thermocouples, was used to produce the particleboards.

The adhesive/cardoon mixture was placed on the bottom platen and pressed to 16 mm thickness for 60 seconds. After this, the top platen was raised to 22 mm thickness, and the panel maintained in the press during 240 seconds. The press platen temperature was 190 °C. After pressing, panels were dried at (20 ± 2) °C and relative humidity of (65 ± 5)% till constant mass. During this process boards suffer shrinkage, due to loss of water, attaining thickness between of 16 and 20 mm, depending on the adhesive formulation, which results in different final densities. Seven boards were produced for each adhesive formulation tested.

The boards were tested according to the European standards for density (EN 323), moisture content (EN 322), internal bond strength (EN 319) and thickness swelling (EN 317).

4.3. Results and discussion

4.3.1. Effect of starch/cardoon ratio

In the present work, different binder compositions were tested for the production of particleboards. Firstly, the impact of different starch/cardoon ratio on the physico-mechanical properties of the panels was evaluated. The starch/cardoon dry mass ratios tested were 0.6, 0.8. 1 and 1.2. The water/starch mass ratio was 2 and chitosan and wood fibre were not present in the formulation at this point.

The particleboards produced had a moisture content between (19.0 ± 0.4)% and (19.1 ± 0.6)%. The internal bond strength and the final densities of the particleboards produced with the different starch/cardoon ratios are shown in Figure 4.2.

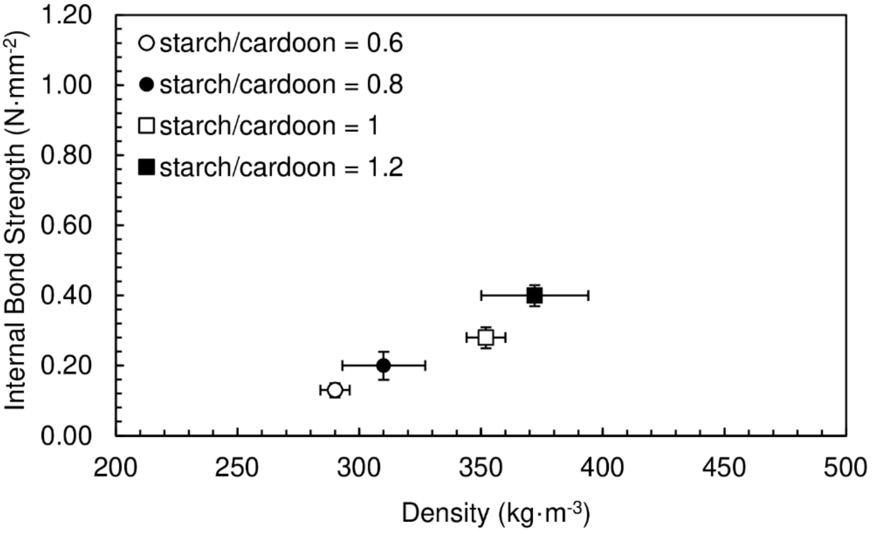


Figure 4.2**.** Internal bond strength of particleboards bonded with potato starch as function of density for starch/cardoon ratios of 0.6, 0.8, 1 and 1.2. All formulations had a water/starch ratio of 2.

The obtained densities vary between 290 and 372 kg·m^{-3}. The lowest densities were achieved for panels produced with the lowest starch/cardoon ratio, 0.6. This is an expected result taking into account that cardoon is less dense than potato starch. A decrease in starch/cardoon ratio leads to a decrease in the particleboard density, since it is increasing the fraction of the component with lower density.

The increase of internal bond strength follows the increase in density, which is expected since higher density implies higher internal cohesion. The internal bond strength values obtained vary between 0.13 and 0.40 N·mm^{-2}. The goal of the present work is to produce particleboards with the lowest density possible, maintaining good bond quality (internal bond strength ≥ 0.30 N·mm-^{2}. Note that, according to European Technical Specification CEN/TS 16368, the minimum requirement for internal bond of lightweight particleboards type LP2 (the most demanding) with thickness between 13 and 20 mm, is 0.30 N·mm^{-2}.

From the results above, only the formulation with starch/cardoon ratio of 1.2 provides intended internal bond strength within this goal.

The thickness swelling results are shown in Figure 4.3, the obtained values vary between 14.0 and 17.0%. As expected, the thickness swelling follows the same trend as density, panels with lower density absorb less water, and consequently the swelling tends to be slightly lower. The lower the mass of material per unit volume, the lower will be the amount of water absorbed and thus the lower the swelling. These water swelling results can be considered quite good considering that European standard EN 312 specifies maximum thickness swelling of 14% for use in humid conditions (P3 class), for non-load-bearing boards with thickness between 13 and 20 mm. The particleboards produced in this work are not intended for use humid conditions, but still present water swelling values close to the limit allowed for those conditions. Even when comparing with wood-based particleboards produced with synthetic adhesives, the results are remarkable. Pine wood particleboards bounded with urea-formaldehyde resins reported in the literature present thickness swelling values between 27 and 38% [25,26].

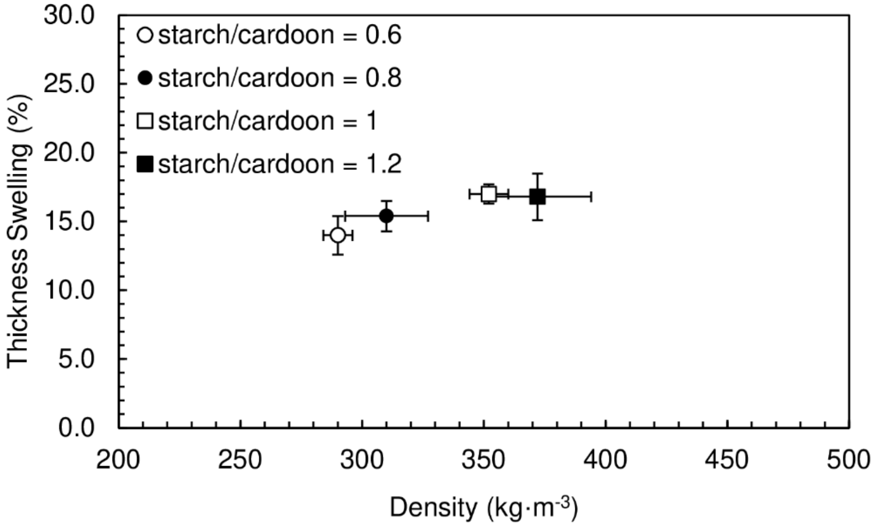


Figure 4.3. Thickness swelling of particleboards bonded with potato starch for starch/cardoon ratios of 0.6, 0.8, 1 and 1.2. All formulations had a water/starch ratio of 2.

4.3.2. Effect of chitosan content

Chitosan (cs) is known to have good affinity towards starch, both due to hydrogen bonding and electrostatic interaction between the amine groups of chitosan and the phosphate groups of potato starch [28]. The combination of the two polysaccharides is therefore generally beneficial for the binding performance of starch-based adhesive systems [29]. In addition, chitosan may also establish hydrogen bonding with the lignocellulosic wood components [30].

Chitosan was added to the previous formulations in order to obtain chitosan/starch ratios of 0.05. The results of internal bond strength and the densities for the particleboards produced are shown in Figure 4.4. The panels had moisture content between (16.4 ± 0.1)% and (19.2 ± 0.5)%.

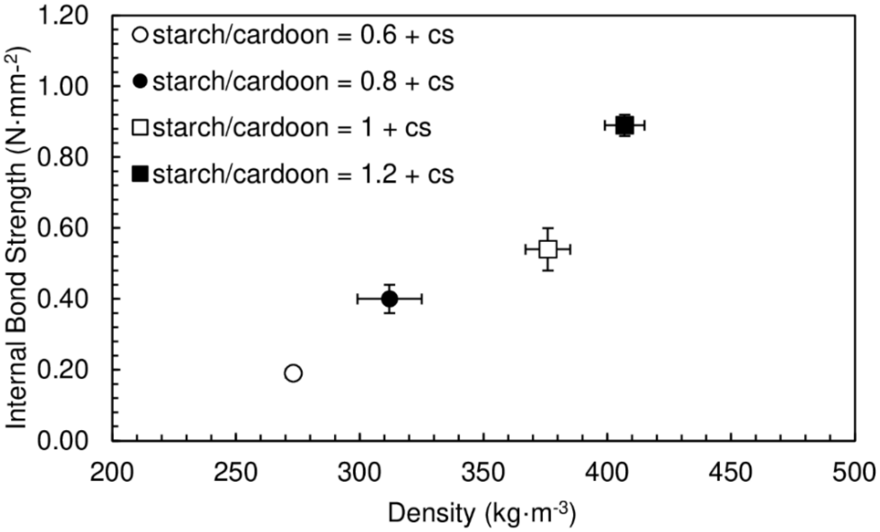


Figure 4.4. Internal bond strength of particleboards bonded with potato starch as function of density for starch/cardoon ratios of 0.6, 0.8, 1 and 1.2. All formulations had chitosan/starch ratio of 0.05 and water/starch ratio of 2.

The densities vary between 273 and 407 kg·m^{-3}, which is similar to the range obtained for particleboards produced without chitosan. On the other hand, a significant improvement is observed in internal bond strength: the values are, in some cases, about twice the ones obtained without chitosan. This confirms the predicted positive effect of the polysaccharide in the particleboard's cohesion. The internal bond strength is observed to increase with density, as expected.

The thickness swelling results are shown in Figure 4.5. The thickness swelling values vary between 14.8 and 20.7%, being similar to the ones previously obtained with starch alone.

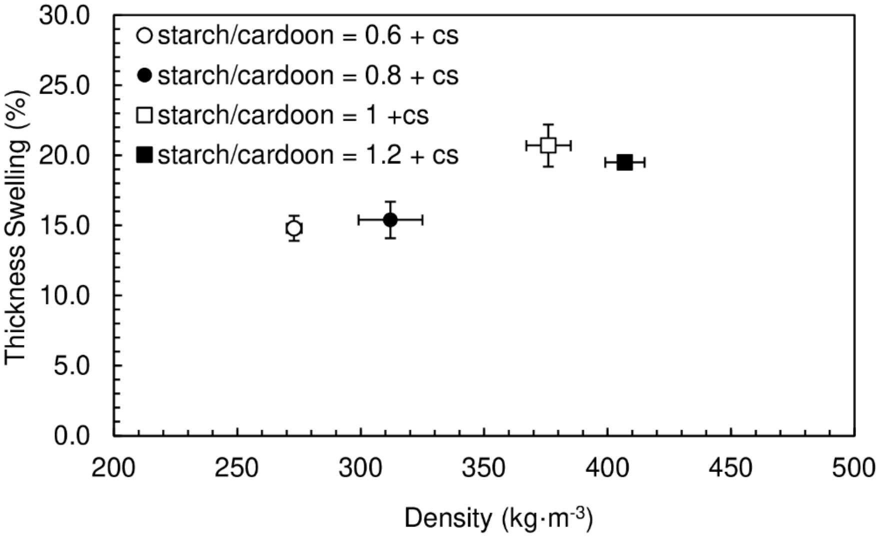


Figure 4.5. Thickness swelling of particleboards bonded with potato starch for starch/cardoon ratios of 0.6, 0.8, 1 and 1.2. All formulations had chitosan/starch ratio of 0.05 and water/starch ratio of 2.

Starch/cardoon ratios of 0.6 and 0.8 were selected to the ensuing studies, since these yielded the lowest densities, with mechanical resistances around the target threshold of 0.30 N·mm^{-2}.

4.3.3. Effect of fibre content

Wood fibre has been reported as being an effective reinforcing filler for starch foam [31]. In the current work particleboards were produced with starch/cardoon ratios of 0.6 and 0.8, with and without chitosan addition, and fibre/starch ratio of 0.05. A ratio of 0.1 was also tested, however the high amount of fibre increases the viscosity of the adhesive, hindering its dispersion significantly. As a consequence, the panels manufactured did not present enough cohesion to justify being subjected to mechanical testing.

The panels produced had a moisture content between (16.9 ± 0.1)% and (20.2 ± 0.2)%. The particleboards with a starch/cardoon ratio of 0.6 exhibit densities between 247 and 290 $kg \cdot m^{-3}$,while those produced with a starch/cardoon ratio of 0.8 had densities between 286 and 334 $kg \cdot m^{-3}$ (

Figure 4.6).

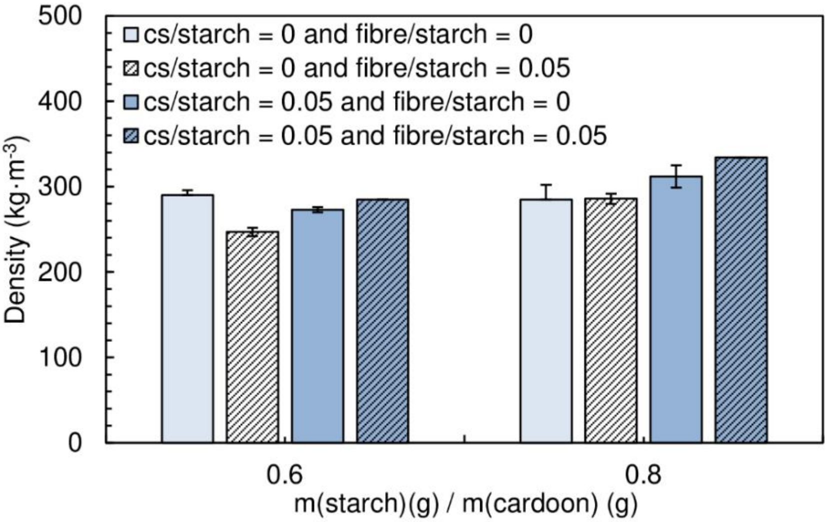


Figure 4.6. Density of the particleboards produced with fibre and fibre combined with chitosan. All adhesive formulations had a starch/cardoon ratio of 0.6 and 0.8.

Figure 4.7 shows the effect of the content of fibre on the internal bond strength of the panels.

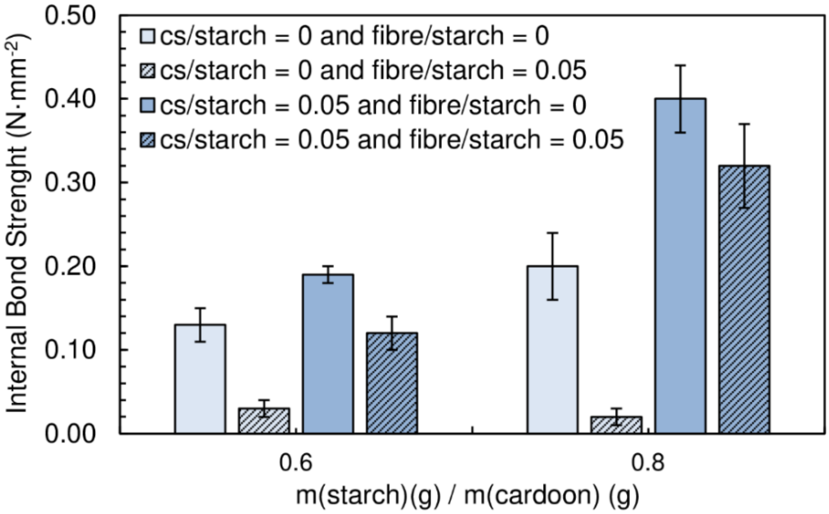


Figure 4.7. Effect of fibre content and the combined effect of chitosan and fibre on internal bond strength of the particleboards bonded with a potato starch. All adhesive formulations had a starch/cardoon ratio of 0.6 and 0.8.

The combination of wood fibre with starch decreases very significantly the internal bond strength of the panels. When chitosan is added, the performance decay is less notorious. Wood fibre is not easily dispersible in the starch suspension, tending to form agglomerates. This has a detrimental effect of mechanical resistance, since these act as defects with low cohesion. Chitosan was seen to facilitate significantly fibre deagglomeration/dispersion. This results from the joint effect of high shear, due to higher viscosity of the medium when chitosan is present, and the possible action of chitosan as a surfactant for the fibres dispersion in water. Nevertheless, the combination of chitosan and fibres does not provide better strength than chitosan alone. It must be noted that this binder formulation has very high viscosity and it is difficult to guarantee a homogeneous mixture with the cardoon particles.

The thickness swelling results are shown in Figure 4.8. No significant changes can be observed with the addition of fibres.

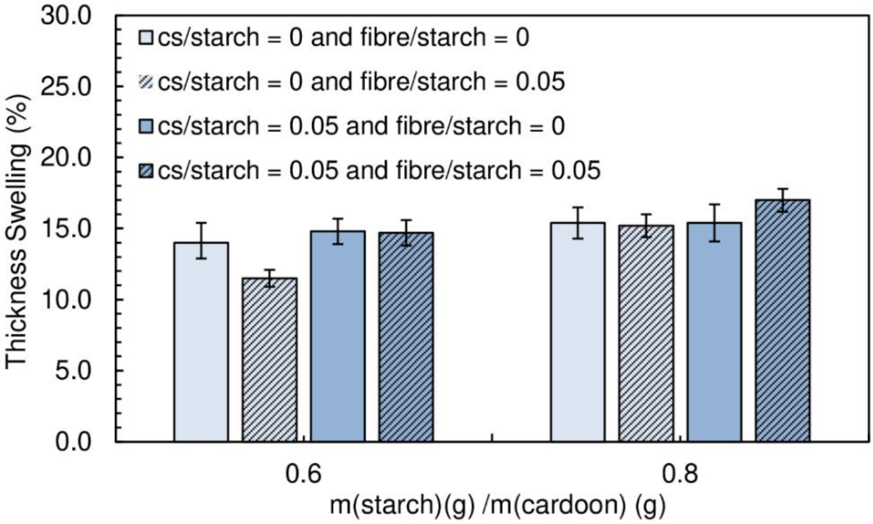


Figure 4.8. Effect of fibre content and the combined effect of chitosan and fibre on thickness swelling of the particleboards bonded with a potato starch. All adhesive formulations had a starch/cardoon ratio of 0.6 and 0.8.

4.3.4. Effect of glycerol content

Glycerol is an effective plasticizer for starch, as the intermolecular chain interactions (strong hydrogen bonding and chain entanglements) are replaced by weaker interactions with glycerol. This results in higher chain mobility, therefore decreasing stiffness [32,33]. This may benefit internal bond strength: higher flexibility of the binder may allow for slight displacements of the wood particles during application of stress without causing breakage of interparticular bonds.

The density of the particleboards produced with different glycerol/starch ratios (0.05, 0.1 and 0.2) are shown in Figure 4.9. The densities vary between 273 and

282 kg·m^{-3} for starch/cardoon ratio of 0.6, while for panels produced with starch/cardoon ratio of 0.8 the densities vary between 312 and 333 kg·m^{-3}.

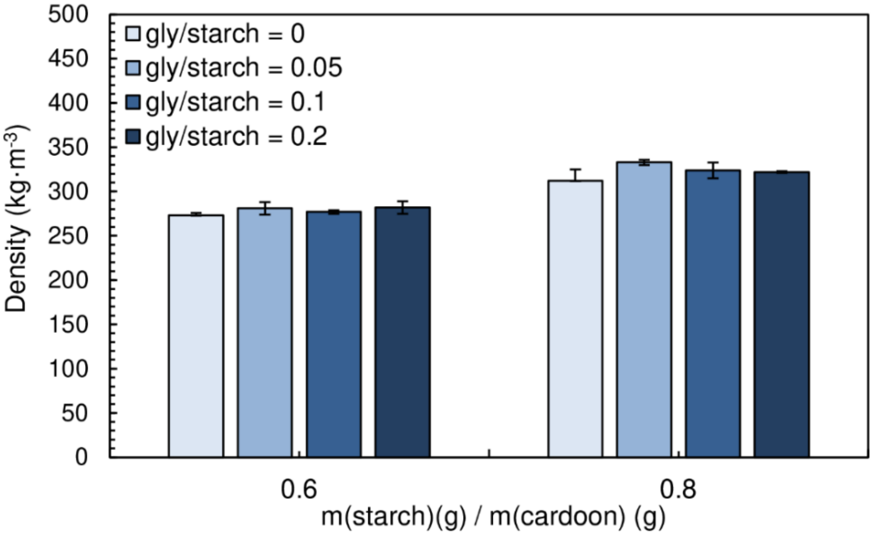


Figure 4.9. Density of the particleboards produced with different gly/starch ratios. All adhesive formulations had a starch/cardoon ratio of 0.6 and 0.8 and cs/starch ratio of 0.05.

Figure 4.10 presents the influence of the addition of glycerol (gly) on the internal bond strength of the particleboards. A chitosan/starch ratio of 0.05 was maintained for all formulations. The particleboards produced had a moisture content between (16.9 ± 0.1)% and (19.8 ± 0.1)%.

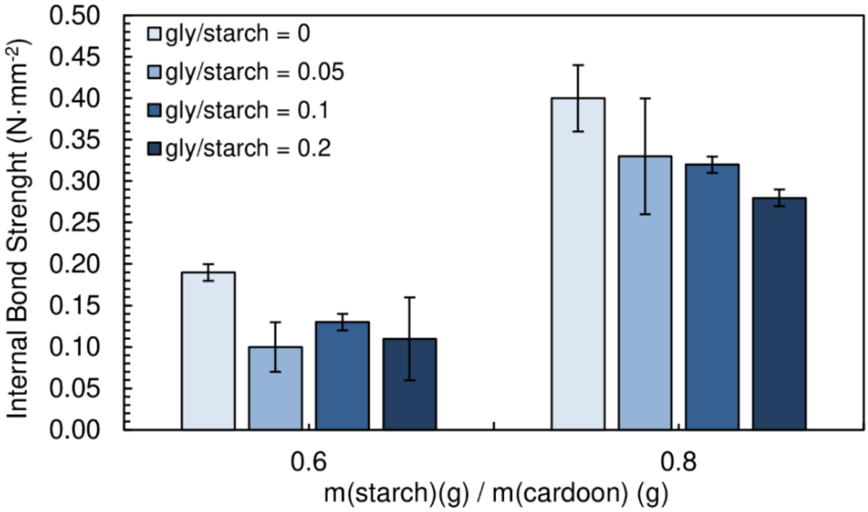


Figure 4.10. Effect of glycerol content on internal bond strength of the particleboards bonded with a potato starch. All adhesive formulations had a starch/cardoon ratio of 0.6 and 0.8 and cs/starch ratio of 0.05.

The addition of glycerol had no positive effect on the internal bond strength of the particleboards. In fact, it is possible to observe a decreasing trend on the resistance of the panels, due to the plasticized binder having lower strength.

The thickness swelling results are shown in Figure 4.11. Again, no significant influence can be observed with the addition of glycerol.

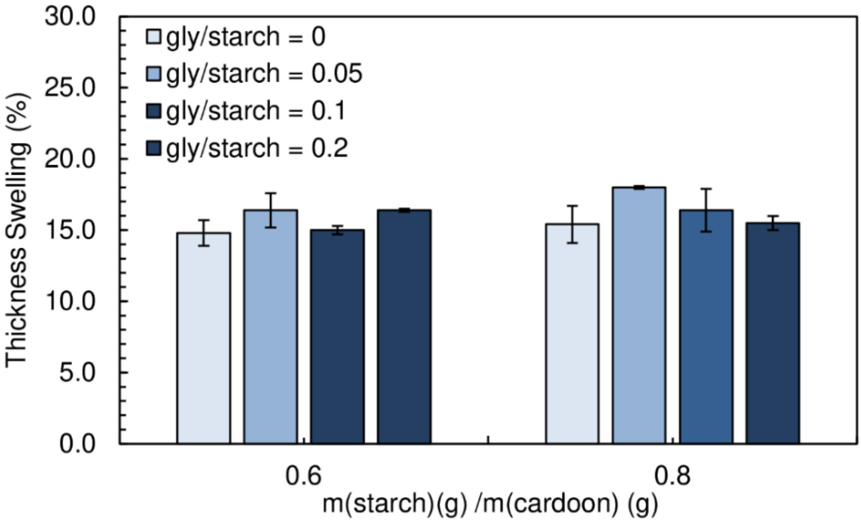


Figure 4.11. Effect of glycerol content on thickness swelling of the particleboards bonded with a potato starch. All adhesive formulations had a starch/cardoon ratio of 0.6 and 0.8 and cs/starch ratio of 0.05.

4.3.5. Effect of water content

Water plays a key role on the binder performance, since it is responsible for starch gelatinization, which is paramount for the adhesion process, so that interaction of starch chains with the particles surface is maximized. On the other hand, too much water lengthens the drying time of the particleboards [25]. Different ratios water/starch were tested (1, 1.3, 1.5, 1.75, 2 and 2.25), the densities of the produced panels are shown Figure 4.12.

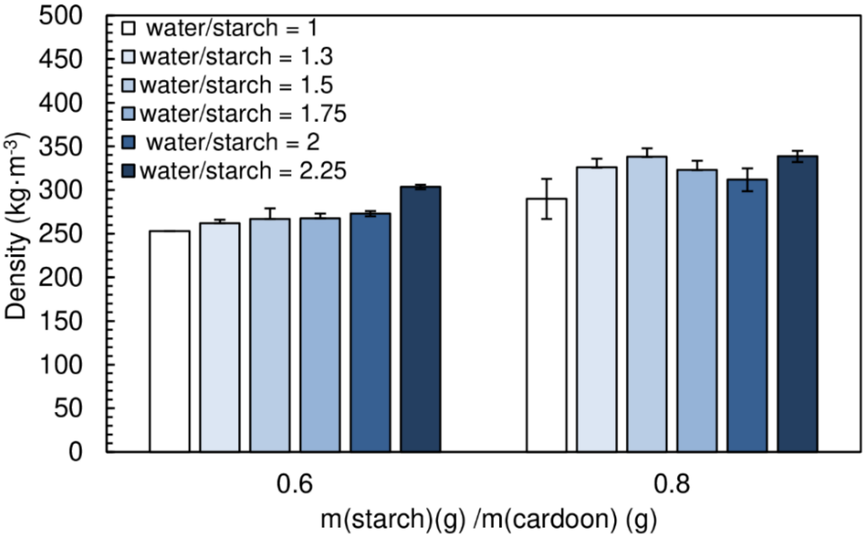


Figure 4.12. Density of the particleboards produced with different water/starch ratios. All adhesive formulations had a starch/cardoon ratio of 0.6 and 0.8 and cs/starch ratio of 0.05.

Figure 4.13 presents the effect of water content on the internal bond strength of the panels manufactured. Recall that the previous results were obtained for a water/starch ratio of 2. A chitosan/starch ratio of 0.05 was used in all formulations. The particleboards produced had a final moisture content between (16.9 ± 0.1)% and (19.2 ± 0.5)%.

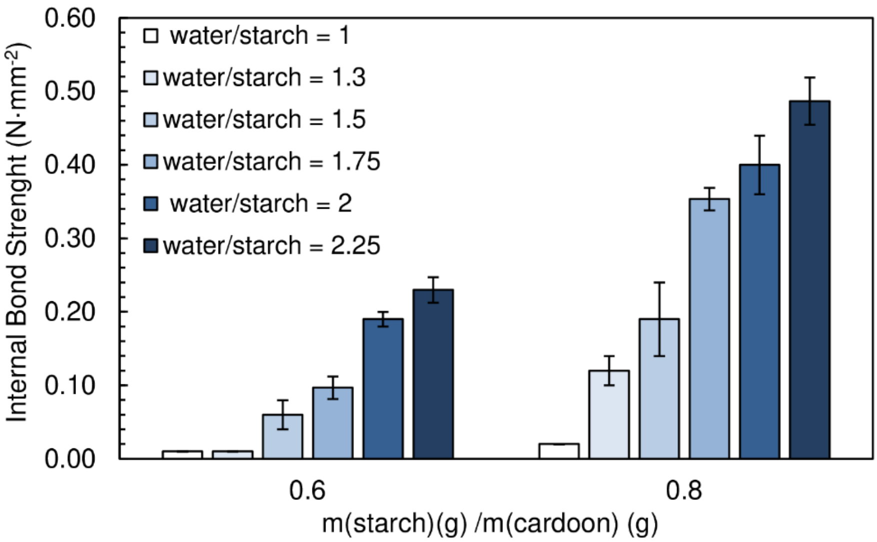


Figure 4.13**.** Effect of water content on internal bond strength of the particleboards bonded with a potato starch. All adhesive formulations had a starch/cardoon ratio of 0.6 and 0.8 and cs/starch ratio of 0.05.

Bond resistance increases steadily with the amount of water in the adhesive formulation. The best internal bond performance (0.49 N·mm^{-2}) was achieved for particleboards with a ratio water/starch of 2.25. This results from the more effective starch gelatinization process under excess water. Complete gelatinization is essential for starch's crystalline double-helix chains to dissociate, breaking up the granules and therefore exposing the hydroxyl groups for interaction with the substrate.

The particleboards produced with starch/cardoon ratio of 0.8 and water/starch ratio of 2.25 meet the proposed objectives, density ≤ 400 kg·m^{-3}) and internal bond strength ≥ 0.30 N·mm^{-2}. However, in order to minimise the drying time, the particleboards produced with a water/starch ratio of 1.75 satisfy the goal of this work. An example of a panel produced in these conditions is shown in Figure 4.14.

Figure 4.14. Cardoon particleboard with potato starch binder. Panel thickness is 16 mm.

Thickness swelling results are shown in Figure 4.15. The amount of water did not have a significant effect on the thickness swelling of the particleboards. The values obtained ranged between (14.0 ± 0.8)% and (17.4 ± 1.6)%.

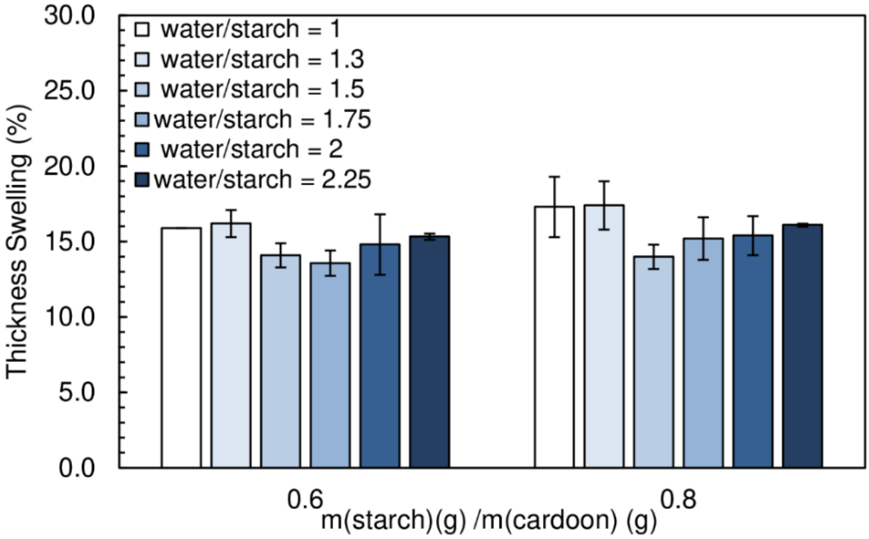


Figure 4.15. Effect of water content on thickness swelling of the particleboards bonded with a potato starch. All adhesive formulations had a starch/cardoon ratio of 0.6 and 0.8 and cs/starch ratio of 0.05.

The work's goals were attained with the adhesive formulation contained starch/cardoon ratio of 0.8, a cs/starch ratio of 0.05 and water/starch ratio of 1.75. The particleboards produced with this adhesive formulation have a density of 323 kg·m^{-3} with internal bond strength of 0.35 N·mm^{-2} and thickness swelling of 15.2%.

4.4. Conclusions

This work proposes the use of cardoon particles bound with potato starch adhesive for production of lightweight particleboards appropriate for interior furniture. The aim was to produce totally biosourced panels with density below 400 kg·m^{-3} and internal bond strength of at least 0.30 N·mm^{-2}.

The particleboards produced with starch/cardoon ratios ranging from 0.6 to 1.2 had densities between 290 and 372 kg·m^{-3} Density increases with the relative amount of potato starch. The internal bond strength follows the increase of density. The values obtained varied between 0.13 and 0.40 N·mm^{-2}.

The addition of chitosan to the starch adhesive leads to a notorious improvement in internal bond strength of the panels for all starch/cardoon ratios studied (0.19 to 0.89 N·mm^{-2}), with practically no change in density. The enhancement in mechanical properties may result from electrostatic interaction between amine groups of chitosan and phosphate groups of starch, as well as from hydrogen bonding between chitosan and cellulose.

The introduction of wood fibre in the formulation was detrimental to the mechanical properties of the particleboards due to poor dispersibility of fibres. The presence of chitosan was seen to improve the dispersion and consequently the mechanical performance of the panels. However, better results were obtained with chitosan alone, so it was concluded that the fibres do not provide a reinforcement effect in this system.

Glycerol, which is a well-known plasticizer for starch, was tested, since a reduction in the stiffness of the binder could be beneficial for the particleboards' resistance. However, no improvement was observed.

The amount of water proved to be an important component in the adhesive system. The internal bond strength of the cardoon panels improved with the increase of the water to starch ratio, probably due to more effective starch gelatinization, leading to better binder cohesion.

The best adhesive formulation was constituted by starch/cardoon ratio of 0.8, chitosan/starch ratio of 0.05, and water/starch ratio of 1.75. The particleboards produced with this adhesive formulation presented density of 323 $kg \cdot m^{-3}$, with an internal bond strength of 0.35 $N \cdot mm^{-2}$ and thickness swelling of 15.2%. The combination of cardoon particles with starch-based binder is therefore a promising biosourced solution for low-density particleboards appropriate, for example, for interior furniture.

4.5. References

1. Monteiro, S.; Martins, J.; Magalhães, F.D.; Carvalho, L. Lightweight Wood Composites: Challenges, Production and Performance.In Lignocellulosic Composite Materials, 1st ed.; Kalia, S., Ed.; Springer International Pulishing: Cham, Switzerland, 2018; volume 1, pp. 293–322.
2. Ferreira, A.M.; Pereira, J.; Almeida, M.; Ferra, J.; Paiva, N.; Martins, J.; Magalhães, F..; Carvalho, L. Biosourced Binder for Wood Particleboards Based on Spent Sulfite Liquor and Wheat Flour. *Polymers* 2018, 10, 1070.
3. Dunky, M. Urea-formaldehyde (UF) adhesive resins for wood. *Int. J. Adhes. Adhes.* 1998, 18, 95–107.

4. Gonçalves, C.; Martins, J.; Magalhães, F.; Carvalho, L.; Paiva, N.T.; Ferra, J.M.; Barros-Timmons, A. Utilization and characterization of amino resins for the production of wood-based panels with emphasis on particleboards (PB) and medium density fibreboards (MDF). A review. *Holzforschung* 2018, 72, 653–671.

5. Norström, E.; Demircan, D.; Fogelström, L.; Khabbaz, F.; Malmström, E. Green Binders for wood Adhesives. In *Applied Adhesive Bonding in Science and Technology*; Özer, H., Ed.; IntechOpen Limited, London, 2018; volume. 1, pp.50-70.

6. Patel, A.K.; Mathias, J.D.; Michaud, P. Polysaccharides as adhesives: A critical review. *Rev. Adhes. Adhes.* 2013, 1, 312–345.

7. Ferdosian, F.; Pan, Z.; Guchuhan, G.; Zhao, B. Bio-Based Adhesives and Evaluation for Wood Composites Application. *Polymers* 2017, 9, 70.

8. Hemmilä, V.; Adamopoulos, S.; Karlsson, O.; Kumar, A. Development of sustainable bio-adhesives for engineered wood panels – A Review. *RSC Adv.* 2017, 7, 38604–38630.

9. Heinrich, L.A. Future opportunities for bio-based adhesives-advantages beyond renewability. *Green Chem.* 2019, 21, 1866–1888.

10. European Starch Industry Association EU Starch Market Data. Available online: https://starch.eu/the-european-starch-industry/(accessed on Sep 16, 2019).

11. Singh, N.; Singh, J.; Kaur, L.; Sodhi, N.S.; Gill, B.S. Morphological , thermal and rheological properties of starches from different botanical sources. *Food Chem.* 2003, 81, 219–231.

12. Wang, W.; Chen, W.; Yang, H.; Cui, M. Textural and rheological properties of potato starch as affected by amino acids. *Int. J. Food Prop.* 2018, 20, S3123–S3134.

13. Barracosa, P.; Oliveira, J.; Barros, M.; Pires, E. Morphological evaluation of cardoon (*Cynara cardunculus L.*): assessing biodiversity for applications based on tradition, innovation and sustainability. *Genet. Resour. Crop Evol.* 2018, 65, 17–28.

14. Roseiro, L.B.; Viala, D.; Besle, J.M.; Carnat, A.; Fraisse, D.; Chezal, J.M.; Lamaison, J.L. Preliminary observations of flavonoid glycosides from the vegetable coagulant *Cynara L.* in protected designation of origin cheeses. *Int. Dairy J.* 2005, 15, 579–584.

15. Guiné, R.P.F.; Tenreiro, M.I.C.; Correia, A.C.; Correia, P.M.R.; Barracosa, P. Analysis of factors influencing the physical, chemical and sensorial properties of Serra da Estrela cheeses. *J. Food Meas. Charact*. 2016, 10, 643–657.

16. Pandino, G.; Lombardo, S.; Mauromicale, G.; Williamson, G. Phenolic acids and flavonoids in leaf and floral stem of cultivated and wild Cynara cardunculus L. genotypes. *Food Chem.* 2011, 126, 417–422.

17. Mileo, A.M.; Di Venere, D.; Linsalata, V.; Fraioli, R.; Miccadei, S. Artichoke polyphenols induce apoptosis and decrease the invasive potential of the human breast cancer cell line MDA-MB231. *J. Cell. Physiol.* 2012, 227, 3301–3309.

18. Fernández, J.; Curt, M.D.; Aguado, P.L. Industrial applications of *Cynara cardunculus L.* for energy and other uses. *Ind. Crops Prod.* 2006, 24, 222–229.

19. Gominho, J.; Lourenço, A.; Palma, P.; Lourenço, M.E.; Curt, M.D.; Fernández, J.; Pereira, H. Large scale cultivation of *Cynara cardunculus L.* for biomass production-A case study. *Ind. Crops Prod.* 2011, 33, 1–6.

20. Gominho, J.; Curt, M.D.; Lourenço, A.; Fernández, J.; Pereira, H. *Cynara cardunculus L.* as a biomass and multi-purpose crop: A review of 30 years

of research. *Biomass and Bioenergy* 2018, 109, 257–275.

21. Gominho, J.; Fernandez, J.; Pereira, H. *Cynara cardunculus L.*-A new fibre crop for pulp and paper production. *Ind. Crops Prod.* 2001, 13, 1–10.

22. Quilhó, T.; Gominho, J.; Pereira, H. Anatomical characterisation and variability of the thistle *Cynara cardunculus* in view of pulping potential. *IAWA J.* 2004, 25, 217–230.

23. Gil, M.; Arauzo, I.; Teruel, E.; Bartolomé, C. Milling and handling *Cynara Cardunculus L.* for use as solid biofuel: Experimental tests. *Biomass and Bioenergy* 2012, 41, 145–156.

24. Monteiro, S.; Martins, J.; Magalhães, F.D.; Carvalho, L. Low-density wood-based particleboards bonded with foamable sour cassava starch: Preliminary studies. *Polymers* . 2016, 8.

25. Monteiro, S.; Martins, J.; Magalhães, F.D.; Carvalho, L. Low-density wood particleboards bonded with starch foam-study of production process conditions. *Materials* 2019, *12*.

26. Pereira, P.; Pereira, J.; Paiva, N.T.; Ferra, J.M.; Martins, J.M.; Carvalho, L.H.; Magalhães, F.D. Copolymerization of UF resins with dimethylurea for improving storage stability without impairing adhesive performance. *Materials* 2018, 11, 1032.

27. Gonçalves, C.; Pereira, J.; Almeida, M.; Paiva, N.T.; Ferra, J.M.; Martins, J.M.; Magalhães, F.D.; Barros-Timmons, A.; Carvalho, L.H. Impact of alkaline–acid and strongly acid process on the synthesis of urea–formaldehyde resins and derived composites: a comparison study. *Eur. J. Wood Wood Prod.* 2019, 77, 1177–1187.

28. Soykeabkaew, N.; Thanomsilp, C.; Suwantong, O. A review: Starch-based composite foams. *Compos. Part A Appl. Sci. Manuf.* 2015, 78, 246–

263.

29. Kaisangsri, N.; Kerdchoechuen, O.; Laohakunjit, N. Biodegradable foam tray from cassava starch blended with natural fiber and chitosan. *Ind. Crops Prod.* 2012, 37, 542–546.

30. Patel, A.K.; Michaud, P.; Petit, E.; De Baynast, H.; Grédiac, M.; Mathias, J.D. Development of a chitosan-based adhesive. Application to wood bonding. *J. Appl. Polym. Sci.* 2013, 127, 5014–5021.

31. Salgado, P.R.; Schmidt, V.C.; Molina Ortiz, S.E.; Mauri, A.N.; Laurindo, J.B. Biodegradable foams based on cassava starch, sunflower proteins and cellulose fibers obtained by a baking process. *J. Food Eng.* 2008, 85, 435–443.

32. Paiva, D.; Pereira, A.M.; Pires, A.L.; Martins, J.; Carvalho, L.H.; Magalhães, F.D. Reinforcement of thermoplastic corn starch with crosslinked starch/chitosan microparticles. *Polymers* 2018, 10, 1–14.

33. Esmaeili, M.; Pircheraghi, G.; Bagheri, R. Optimizing the mechanical and physical properties of thermoplastic starch via tuning the molecular microstructure through co-plasticization by sorbitol and glycerol. *Polym. Int.* 2017, 66, 809–819.

CHAPTER 5

Conclusions and future work

5. Conclusions and future work

5.1. General conclusions

The objective of this PhD thesis was the development of low-density particleboards with suitable mechanical properties, bonded with a starch-based adhesive.

The main conclusions of this work were:

- It was demonstrated that starch can be used as binder in the production of two different types of low-density particleboards: one manufactured with wood particles and the other with cardoon particles. In both cases the panels produced had very low density (between 207 and 538 $kg \cdot m^{-3}$) combined with good mechanical properties. The particleboards produced meet the standard requirements for general-purpose lightweight boards for use in dry conditions, according to CEN/TS 16368 specification.

- In the case of particleboards produced with wood particles, it is necessary to use a starch with self-expansion properties to achieve low densities. The good self-foaming property of sour cassava starch allowed the separation of wood particles and creation of low-density domains, while maintaining good cohesion.

- The main challenge of this work thesis was to establish the manufacturing process for this type of panels, which turned out to be very different from the traditional process for particleboards. The procedure involved hot-plate pressing in two stages: 1) lowering the top platen to a specified thickness during a certain period of time designated as pressing time, followed by 2) raising the top platen to allow panel expansion during a certain period of time designated as hold time. The pressing time is crucial to accelerate the foam expansion, however, when this time is too long it leads to internal fracture due to the vapour pressure build-up. The density decreases with the hold time, however above certain limit value the density variation was small, due to the bursting of the internal foam cell structure caused by the amount of water vapour inside the panel, leading to low internal bond strength. The starch gelatinization is more effective when the panels were produced at 190 °C, which contributes to the formation of foam with higher cohesion.

- Cardoon particles are, by themselves, a low-density raw material. For this reason, it was possible to use a national starch (potato starch), with negligible self-expansion capability, in the formulation of the adhesive system. The effect of different starch/cardoon ratios and different bio-based additives on the performance of the adhesive system were studied. The presence of chitosan leads a substantial improvement in the internal bond strength of the particleboards, possibly due to electrostatic interaction between amine groups of chitosan and phosphate groups of starch, as well as from hydrogen bonding between chitosan and cellulose. The amount of water in the formulation revealed to be important to allow effective starch gelatinization, and therefore insure good internal bond strength.

- This composite can be moulded, which allows to produce furniture parts that do not have flat shape, a promising solution for furniture applications.

5.2. Future work

This type of product, starch-bonded particleboards, is a promising bio-sourced solution for low-density particleboards, taking in account the demand of society to use more sustainable products, either because they increase the options of the life cycle of a material or transform a waste in to a new raw material for a new value chain always maintaining their high biodegradability. It will be interesting to study other agro-food wastes such as silage grain (corn, maize or rice), grape stems and nut shells. It can be also used wastes from forestry operations such as pruning (branches, leaves, shrubs) and debarking as substitutes of cardoon.

Other important study that should be carried out is the cost assessment of raw materials and production of this composite. This evaluation is crucial to determine the economic feasibility of this product comparing with the traditional low-density particleboards presented in the market.

Further studies concerning the formulation adhesive system can be also done, such as testing different amounts of chitosan. It is well known that the starch-based adhesive has poor resistance to water which is the main challenge to overcome when it comes to natural adhesives. Some strategies can be used in further studies, such as the modification of starch through grafting polymerization by inserting hydrophobic segments in the starch molecule, such as acrylic chains, in order to provide water resistance.

APPENDIX A

6. Appendix A: Proof of concept

One advantages of this product when compared with synthetic binders is the possibility that it can be moulded. This product can be used in the production of furniture parts that have and do not have flat shape. In this part of the document is presented some flat and non-flat parts that were produced with this composite.

Figures A.1 shows shelves for cheese ripening produced with the developed composite; the furniture piece was produced with the optimised adhesive formulation described in Chapter 4. Cardoon particles were blended manually with the adhesive system. Single layer particleboards were hand formed in square aluminium deformable containers, with dimensions 300 × 300 × 80 mm^3. The adhesive/cardoon mixture was placed on the press bottom platen and pressed to 16 mm thickness for 60 seconds. After this, the top platen was raised to 25 mm thickness, and the panel maintained in the press during 240 seconds. The press platen temperature was 190 °C. After pressing, panels were dried at (20 ± 2) °C and relative humidity of (65 ± 5)% till constant mass.

Figure A.1. Shelves for cheese ripening produced with a cardoon particles and a potato starch-based adhesive. The panels were pressed at 16 mm during 60 s, then the top platen was raised at 25 mm and the panel was maintained in the press during 240 s. The temperature of press platens was 190 °C. This piece of furniture was on display in London Design Fair and Salone del Mobile Milano 2019.

Figure A.2 shows a sideboard for cheese and wine produced according to the same procedure used in the manufacture of the shelves for cheese ripening.

Figure A.2. Sideboard for cheese and wine produced with a cardoon particles and a potato starch-based adhesive. The panels were pressed at 16 mm during 60 s, then the top platen was raised at 25 mm and the panel was maintained in the press during 240 s. The temperature of press platens was 190 °C. This piece of furniture was on display in London Design Fair and Salone del Mobile Milano.

Non-flat pieces were also produced, in figure A.3 can be seen a fruit bowl produced with the same composite used in the manufacture of the cheese trays.

Figure A.3. Fruit bowl produced with a cardoon particles and potato starch-based adhesive. The piece was produced at 190 °C using a mould.

To produce this piece, the cardoon particles were blended manually with the adhesive system, then the mixture was placed into a mould with volume of

1230.88 cm^3 (Figure A.4). The mould was placed in the press during 300 s at 190 °C. After production, the piece was dried at (20 ± 2) °C and relative humidity of (65 ± 5)% till constant mass.

Figure A.4. Mould used in the production of the fruit bowl.