



UNIVERSITÀ DEGLI STUDI DI CAMERINO

School of Advanced Studies

DOCTORATE COURSE IN

“Chemical and Pharmaceutical Sciences and Biotechnology: Chemical Science”

XXXII Cycle

**“A FORMALDEHYDE-FREE BIO-ADHESIVE FOR
PLYWOOD AND PARTICLEBOARDS BASED ON
SOY FLOUR, MAGNESIUM OXIDE AND A PLANT-
DERIVED ENZYMATIC HYDROLYSATE”**

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1. INTRODUCTION

1.1 SUMMARY

At present, the particleboard industry, which together with the plywood industry dominate the wood-based panels' production volume worldwide, uses almost exclusively urea-formaldehyde (UF) resins (Eastin et al. 2015)¹. However, environmental sustainability and consumer demand for healthier products have contributed to an increase in research efforts to find substitutes for these petroleum-based thermosetting adhesives. Formaldehyde has been reclassified as a human carcinogen compound by the International Agency for Research on Cancer already in 2004 (IARC 2004)² while a new classification entered into force for the European Union in June 2014 following the CLP (Harmonised Classification, Labelling and Packaging) Commission Regulation 2015/491. The discussion on both the availability of fossil resources for producing million tons of amino resins every year and the restrictions on formaldehyde emissions from the finished wood composite products is expected to intensify (Salthammer 2010³; Hammilä et al. 2019a⁴). The US Environmental Protection Agency (EPA)⁵ adapted the California Air Resources Board (CARB)⁶ emission limits in 2017 (EPA 2017), and formaldehyde in indoor environment is a current legislation topic in other places of the world. The latest example comes from Germany, where lowered legal limits for formaldehyde emissions (from the European emission level E1 of 0.10 ppm to 0.05 ppm) and a new proposed test method will come into effect as from 1st of January 2020 (Bundesministerium für Umwelt Naturschutz und nukleare Sicherheit 2018)⁷.

¹ Eastin, I., Brose, I., Maplesden, F., and Novoselov, I. (2015). "Wood-based panels," in: *Forest Products: Annual Market Review 2014-2015*, F. Guerrieri and C. F. Christian Friis Bach (eds.), UNECE/FAO, ECE/TIM/SP/39, UNITED NATION PUBLICATIONS, pp. 65-75.

² IARC. (2004). IARC Classifies Formaldehyde as Carcinogenic to Humans, International Agency for Research on Cancer (IARC), Lyon, France, Press Release June 15, No. 153.

³ Salthammer, T., Mentese, S., and Marutzky, R. (2010). "Formaldehyde in the indoor environment," *Chem Rev* 110, 2536-2572.

⁴ Hemmilä, V., Meyer, B., Larsen, A., Schwab, H., and Adamopoulos, S. (2019a). "Influencing factors, repeatability and correlation of chamber methods in measuring formaldehyde emissions from fiber- and particleboards," *Int. J. Adhes. Adhes.*, 94, 102420.

⁵ EPA. (2017). Code of Federal Regulations (CFR) 40 CFR § 770 on Formaldehyde Standards for Composite Wood Products Act, Title VI to the Toxic Substances Control Act, TSCA; US Environmental Protection Agency.

⁶ CARB (2008) Final Regulation Order 93120 Airborne Toxic Control Measure to Reduce Formaldehyde Emissions from Composite Wood Products

⁷ Bundesministerium für Umwelt Naturschutz und nukleare Sicherheit. (2018). *Bekanntmachung analytischer Verfahren für Probenahmen und Untersuchung für die in Anlage 1 der Chemikalien-Verbotsverordnung genannten Stoffe und Stoffgruppen*, Bundesanzeiger, BAnz, AT 26.11.2018 B2.

Adhesives based on alternative, renewable resources can satisfy the need for formaldehyde-free solutions and have the additional benefit of increased sustainability. The recent years, there have been several reviews on sustainable bio-adhesives for wood composites, based mainly on lignin, starch, tannin and proteins (Pizzi 2006⁸; Ferdosian et al. 2017⁹; Hemmilä et al. 2017¹⁰; Heinrich 2019¹¹; Solt et al. 2019¹²). It has been shown that bio-based adhesives are still at a development laboratory phase and suffer from several issues that hinder their application at the industry. The most common limitations have to do with the availability of raw materials, low reactivity and need for modification, high viscosity, slow curing, low water resistance, and higher costs in comparison with the conventional formaldehyde-based adhesives (Hemmilä et al. 2017). Depending on the biopolymer used, crosslinking with different, mostly synthetic, agents is required to achieve acceptable bonding performance. Solt et al. (2019) provided a thorough overview of the various crosslinking agents, their chemical structure and toxicological information. Although, there is a wish to develop bio-based crosslinkers it seems that isocyanates can be regarded as the most viable formaldehyde-free candidates. The use of isocyanates is well established in North America while a small production of pMDI-bonded particleboards (approx. 1% of the total annual production) is industrially available in Europe (Mantanis et al. 2017)¹³. On the other hand, although mixtures of different biopolymers with pMDI have resulted in acceptable bonding performance of laboratory composites, it is questionable if the addition of such compounds

⁸ Pizzi, A. (2006), "Recent developments in eco-efficient bio-based adhesives for wood bonding: Opportunities and issues," *J. Adhes. Sci. Technol.*, 20(8), 829-846.

⁹ Ferdosian, F., Pan, Z., Gao, G., and Zhao, B. (2017). "Bio-based adhesives and evaluation for wood composites application," *Polymers*, 9(2), 70.

¹⁰ Hemmilä, V., Adamopoulos, S., Karlsson, O., and Kumar, A. (2017). "Development of sustainable bio-adhesives for engineered wood panels—A Review," *RSC Adv.*, 7, 38604-38630.

¹¹ Heinrich, L. A. (2019). "Future opportunities for bio-based adhesives – advantages beyond renewability," *Green Chem.*, 21, 1866-1888.

¹² Solt, P., Konnerth, J., Gindl-Altmutter, W., Kantner, W., Moser, J., Mitter, R., and van Herwijnen, H.W.G. (2019). "Technological performance of formaldehyde-free adhesive alternatives for particleboard industry," *Int. J. Adhes. Adhes.*, 94, 99-131.

¹³ Mantanis, G. I., Athanassiadou, E. Th., Barbu, M. C., and Wijnendaele, K. (2018). "Adhesive systems used in the European particleboard, MDF and OSB industries," *Wood Mater. Sci. Eng.*, 13(2), 104-116.

is really contributing to the adhesion (El Mansouri et al. 2007¹⁴; Amaral-Labat et al. 2008¹⁵, Pizzi 2014¹⁶, Hemmilä et al. 2019b).

Currently, soy protein adhesives seem to have a lead than the other bio-based counterparts. A thorough overview of soy-based adhesives can be found in Vnučec et al. (2017)¹⁷. Soy protein comes as a by-product of the soybean oil extraction process, and depending on the purification steps it is available with different qualities from the low-priced soy flour to the more expensive protein isolates. The world production of soy beans was estimated to be over 317×10⁶ t in 2015, and large quantities of soy flour floor can be used as wood adhesives as they do not have any human food applications (Frihart 2014¹⁸; Zhang et al. 2018¹⁹). The adhesive performance of soy proteins is mainly affected by a number of factors such as the protein content, but other properties such as their structure, particle size, surface quality, viscosity and pH are important (Frihart and Satori 2013²⁰; Frihart and Birkeland 2014²¹). In general, drawbacks of soy protein adhesives refer to low water resistance, sensitivity to biological degradation, high viscosity at high solid content and relatively low bonding strength of wood composites (Hemmilä et al. 2017). Denaturation of soy protein is performed with various chemicals, such as acids, alkalis, detergents, salts, and chaotropic agents, with the aim to expose more polar groups for an improved solubility and interaction bonding via hydrogen bonds (Vnučec et al. 2017). Water resistance of soy protein adhesives is imparted by soy protein molecular modifications, i.e. grafting reactive groups of chemical

¹⁴ El Mansouri, N.-E., Pizzi, A., and Salvadó, J. (2007). "Lignin-based wood panel adhesives without formaldehyde," *Holz Roh. Werkst.*, 65, 65-70.

¹⁵ Amaral-Labat, G. A., Pizzi, A., Gonçalves, A. R., Celzard, A., Rigolet, S., and Rocha, G. J. M. (2008). "Environment-friendly soy flour-based resins without formaldehyde," *J. Appl. Polym. Sci.*, 108, 624-632.

¹⁶ Pizzi, A. (2014). "Synthetic adhesives for wood panels: chemistry and technology - a critical review," *Rev. Adhes. Adhes.*, 2, 85-126.

¹⁷ Vnučec, D., Kutnar, A., and Goršek, A. (2017). "Soy-based adhesives for wood-bonding – a review," *J. Adhes. Sci. Technol.*, 31(8), 910-931.

¹⁸ Frihart, C. R., and Birkeland, M. J. (2014). "Soy Properties and Soy Wood Adhesives," in: *Soy-Based Chemicals and Materials*, R. P. Brentin (ed.), ACS Symposium Series, American Chemical Society, Washington, DC, pp. 167-192.

¹⁹ Zhang, M., Zhang, Y., Chen, M., Gao, Q., and Li, J. (2018). "A high-performance and low-cost soy flour adhesive with a hydroxymethyl melamine prepolymer," *Polymers*, 10, 909.

²⁰ Frihart, C. R., and Satori, H. (2013). "Soy flour dispersibility and performance as wood adhesive. *J. Adhes. Sci. Technol.*, 27(18-19), 2043-2052.

²¹ Frihart, C. R., and Birkeland, M. J. (2014). "Soy Properties and Soy Wood Adhesives," in: *Soy-Based Chemicals and Materials*, R. P. Brentin (ed.), ACS Symposium Series, American Chemical Society, Washington, DC, pp. 167-192.

reagents onto protein molecules (Qin et al. 2013²²; Gui et al. 2016²³). These groups react with polar groups of soy protein during the hot press process and form a cross-linked network after curing (Kim and Sun 2014²⁴; Zhu and Damodaran 2014²⁵). The most developed crosslinker for soy protein is polyamidoamine-epichlorohydrin (PAE), while other protein crosslinkers include polyamides, polyethyleneimines (PEI), pMDI and ketones (Li et al. 2004²⁶; Li 2007²⁷; Hamarneh et al., 2010²⁸; Gu and Li 2011²⁹). Unlike the other biopolymers, there are exist several commercial adhesives systems (Kymene®, SOYBABY®, OZERO®, Soyad™, Prolia™) based on soy proteins, and are used mainly for interior plywood and engineered wood flooring (Vnučec et al. 2017). Their acceptance for particleboards is limited while the high amount of moisture introduced during adhesive application is considered as a serious issue (Solt et al. 2019).

The present study proposes a novel bio-adhesive for particleboards based on the natural materials soy flour, magnesium oxide (MgO) and a plant-derived enzymatic hydrolysate.

MgO was used in the mixture with the aim to increase the water resistance of the adhesive (Jang and Li 2015³⁰) while the solubility and emulsifying properties of soy flour could be enhanced by adding the protein hydrolysate (McCarthy et al. 2013³¹).

The characterization of the natural adhesive was realized through DSC, TGA /DTA, pH, Viscosity, microbiological, Headspace, SEM analysis.

²² Qin, Z., Gao, Q., Zhang, S., and Li, J. (2013). "Glycidyl methacrylate grafted onto enzyme-treated soybean meal adhesive with improved wet shear strength," *BioResources*, 8, 4, 5369-5379.

²³ Gui, C., Zhu, J., Zhang, Z., and Liu, X. (2016). "Research progress on formaldehyde-free wood adhesive derived from soy flour," in: *Adhesives: Applications and Properties*, A. Rudawska (ed.), IntechOpen, Rijeka, Croatia, pp. 187-200.

²⁴ Kim, M. J., and Sun, X. S. "Adhesion properties of soy protein cross linked with organic calcium silicate hydrate hybrids," *J. Appl. Polym. Sci.*, 131: 8615-8623.

²⁵ Zhu, D., and Damodaran, S. (2014). "Chemical phosphorylation improves the moisture resistance of soy flour-based wood adhesive," *J. Appl. Polym. Sci.*, 131: 40451.

²⁶ Li, K., Peshkova, S., and Geng, X. (2004). "Investigation of soy protein-kymene adhesive systems for wood composites," *J. Am. Oil Chem. Soc.*, 81(5), 487-491

²⁷ Li, K. (2007). *Formaldehyde-free Lignocellulosic Adhesives and Composites Made from the Adhesives*, U.S. Patent No. 7252735B2.

²⁸ Hamarneh, A. I., Heeres, H. J., Broekhuis, A. A., Sjollem, K. A., Zhang, Y., and Picchioni, F. (2010). "Use of soy proteins in polyketone-based wood adhesives," *Int. J. Adhes. Adhes.*, 30(7), 626-635.

²⁹ Gu, K., and Li, K. (2011). "Preparation and evaluation of particleboard with a soy flour-polyethylenimine-maleic anhydride adhesive," *J. Am. Oil Chem. Soc.*, 88(5), 673-679.

³⁰ Jang, Y., and Li, K. (2015). "An all-natural adhesive for bonding wood," *J. Am. Oil Chem. Soc.*, 92, 431-438.

³¹ McCarthy, A. L., Yvonne C. O'Callaghan, Y. C., and O'Brien, N. M. (2013). "Protein hydrolysates from agricultural crops-Bioactivity and potential for functional food development," *Agriculture*, 3, 112-130.

The natural adhesive was compared and combined by using different percentages of other common synthetic crosslinker as Urea Formaldehyde (UF), Polyamidoamine-Epichlorohydrin (PAE), Phenol Formaldehyde (PF), Polymeric Methylene Diisocyanate (PMDI) (natural adhesive and synthetic crosslinker of 0:100 %, 33:67 %, 50:50 %, 67:33 % and 100:0 %) to verify the changes in properties. In fact, although the main challenge is to obtain a 100% organic binder, it is already considered important to be able to lower the synthetic percentage and introduce a significant percentage of organic origin.

The effect of the natural adhesive and combinations was verified making plywood (also curved plywood) and particleboard prototypes at Lab scale level.

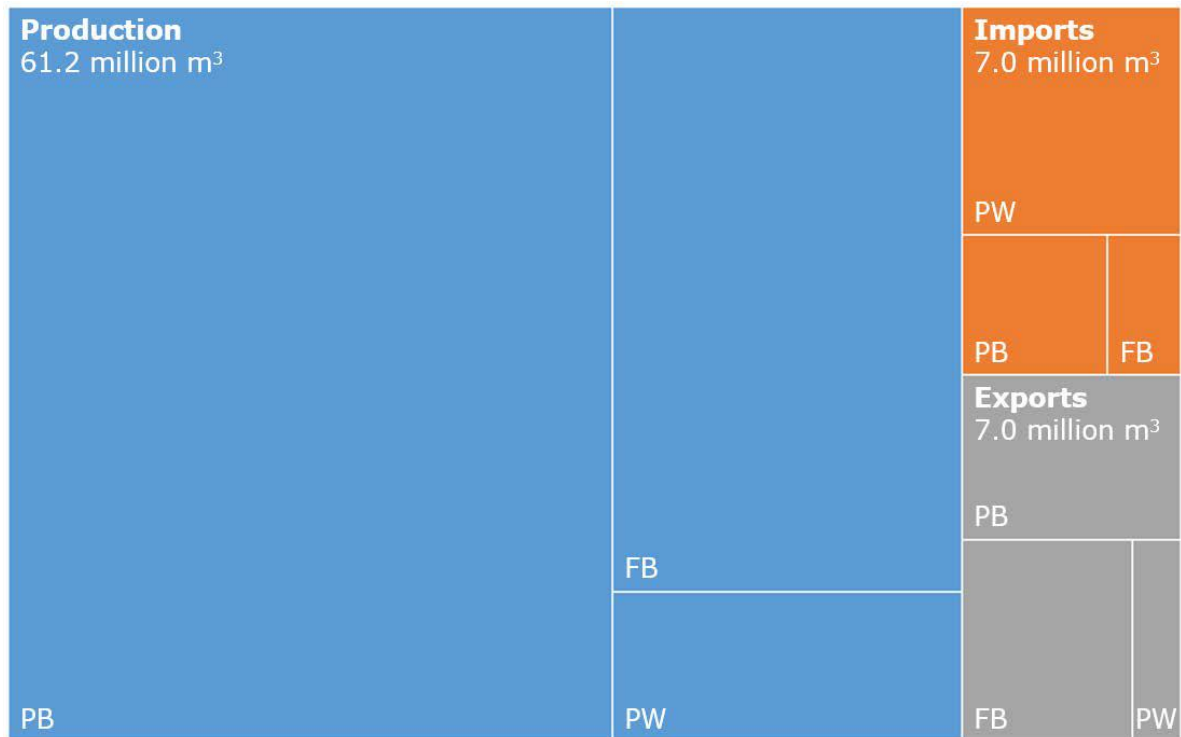
According to the main international reference standards, mechanical, water resistance and formaldehyde content tests were carried out on plywood and particleboard samples.

The overall results suggest that the combination of the natural materials soy flour, MgO and plant-derived enzymatic hydrolysate show good potential for developing formaldehyde-free adhesives for particleboards. Further work on such formulations should focus on optimum levels of PAE as a crosslinker, appropriate solids content and viscosity, and reduced press times.

1.2 OVERVIEW ON THE WOOD-BASED PANEL INDUSTRY

In Europe the production of particleboard represent the 63% of the total production of wood base panels (WBP) on the over 61 million m³ WBP produced in 2016. Other panel types produced are fibreboard, representing the 29% of the total production and plywood (7%).

The following Figure (Fig. 1) summarizes the wood-based panels market in EU: one-tenth of the total production is imported, and the 60% of the total imported is constituted by plywood.

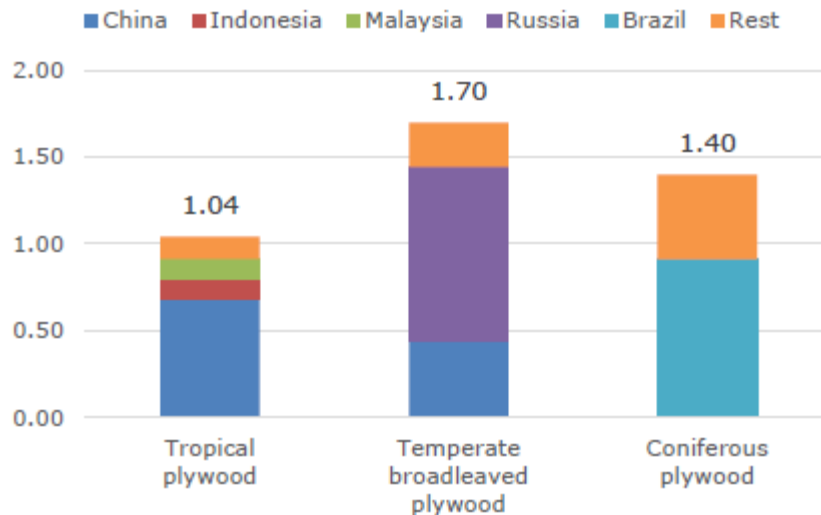


PW = Plywood, PB = Particleboard (incl. OSB), FB = Fibreboard (comprises MDF, hardboard and other fibreboard) Source: Eurostat (2018c) and FAO (2018)

Source: ECHA - ANNEX XV RESTRICTION REPORT – Formaldehyde and formaldehyde releasers.

Fig. 1. EU production and extra-EU trade of wood-based panels, 2016.

As shown in the next figure (Fig.2) the main plywood sub-groups imported are tropical plywood, temperate broadleaved plywood and coniferous plywood, and the main trading partners for these products are China, Indonesia, Malaysia, Russia and Brazil. The Brazil is the main supplier of Coniferous plywood, that is classified by the EN 13986 into the E1 emission class, while the tropical plywood (mainly exported by China, Indonesia and Malaysia) it is included in the E2 emission class.



Source: EPF (2017)

Fig.2: Extra-EU imports of plywood, 2016 (million m³)

In the Table 1, the EU’s total consumption of wood-based panels and their respective formaldehyde emission classes are showed. Looking at data, the amount of E2 panels coming from EU production, is around 1.9 million m³—corresponding at 3% of the total wood-based panel production- while the total amount of panels coming from extra-UE exports, is about 2 million m³. This means that about 4 million m³ of panels, around 6.5% of all wood-based panels classified as E2 formaldehyde class are produced and may potentially elevate formaldehyde concentrations in indoor air.

In this direction the European Chemicals Agency (ECHA) is evaluating an EU-wide restriction for wood-based panels commercialized in the EU in order to avoid high formaldehyde emission and to contribute to the harmonization of the rules on formaldehyde emissions across the EU.³²

³² ECHA - ANNEX XV RESTRICTION REPORT – Formaldehyde and formaldehyde releasers.

Table 1. EU consumption of class E1 and E2 wood-based panels, 2016 (1000 m³)

	All panels	E1 panels	E2 panels
EU production	61 166	59 235	1 932
Plywood	4 559	4 423	137
Particleboard	38 687	37 140	1 547
Of which: OSB	6 997	6 997	0
Fibreboard	17 920	17 672	248
Of which: MDF	12 381	12 133	248
Extra-EU imports	6 974	4 716	2 258
Plywood	4 303	2 797	1 506
Particleboard	1 784	1 231	553
Of which: OSB	67	50	17
Fibreboard	887	688	199
Of which: MDF	523	324	199
Extra-EU exports	6 963	6 778	186
Plywood	842	817	25
Particleboard	3 177	3 050	127
Of which: OSB	1 052	1 052	0
Fibreboard	2 944	2 911	33
Of which: MDF	1 670	1 637	33
Apparent EU consumption ¹	61 177	57 173	4 004
Plywood	8 020	6 402	1 617
Particleboard	37 294	35 321	1 973
Of which: OSB	6 013	5 996	17
Fibreboard	15 863	15 450	413
Of which: MDF	11 233	10 821	413

EU production plus extra-EU imports minus extra-EU exports.

Source: Eurostat (2018c), FAO (2018) and own calculations based on industry information

1.3 REGULATORY FRAMEWORK

The use of formaldehyde and its consequences on human health and on the indoor air pollution has been studied and continue to be a topic of central interest.

The WHO Guideline for Indoor Air Quality³³ for formaldehyde of 0.1 mg/m³ (30-minute average concentration) represents a guideline to prevent risks linked to acute and chronic irritation and long-term consequences like cancer in the population with a special focus on the most sensitive components like children or older people.

³³World Health Organization (2010). Who guidelines for indoor air quality [Available at: http://www.euro.who.int/_data/assets/pdf_file/0009/128169/e94535.pdf].

Until 2004, formaldehyde was classified by the World Health Organization (WHO) as a 2A Group substance, namely “probably carcinogenic to humans”; after that date, the International Agency for Research on Cancer (IARC), on the basis of new evidences and data classified the formaldehyde as a 1 Group substance “carcinogenic to humans” and that causes cancer³⁴, causing a general alarm situation on a world level and inspiring a number of solutions to limit the formaldehyde emissions at European and National level.

The first institute to issue a directive aimed at defining new limit values and test methods for the control of formaldehyde emission for E1 class panels production (1981) was the DIBT institute, the German Institute for Construction Technology.

Another relevant restriction proposal is represented by the EU’s Construction Products Regulation, a voluntary agreement of the European wood-based panels industry and a national legislation in a number of EU Member States.

The **Construction Products Regulation** (EU) No 305/2011 (CPR) became effective on 1 July 2013 and lays down harmonised rules about the essential requirements for construction products in order to be placed on the internal market and outlines the CE marking and the related obligations of manufacturers and other operators.³⁵ In order obtain the CE marking, the construction products must comply with the harmonized European standard, that for the wood-based panels is EN 13986 (CEN, 2004,b)³⁶.

The standard EN 13986 specifies the requirements and the appropriate test methods to determine these characteristics for wood-based panels used in construction market; in particular, as is shown in the following table (Table 2), the Annex B of this standard, sets out the limit values of emissions for E1 or E2 classes. It is necessary to underline that this standard does not limit the placing in the market of class E2 wood-based panels, i.e. the panels with formaldehyde release > 0.124 mg/m³, but several industry agreements exist at European level.

³⁴ IARC. International Agency for Research on Cancer (2004). Press release N° 153, WHO.

³⁵ European Commission. Construction Products Regulation (CPR). [Available at: https://ec.europa.eu/growth/sectors/construction/product-regulation_en Accessed on: 9/10/2019]

³⁶ EN 13986:2004+A1:2015 Wood-based panels for use in construction - Characteristics, evaluation of conformity and marking

Table 2. Formaldehyde emission class E1 according to EN 13986

		Panel product		
		Unfaced	Unfaced	Coated, overlaid or veneered
		Particleboard OSB MDF	Plywood Solid wood panels LVL	Particleboard OSB MDF Plywood Solid wood panels Fibre boards (wet process) Cement bonded particleboards LVL
Initial type testing ^a	Test method	ENV 717-1		
	Requirement	Release ≤ 0,124 mg/m ³ air		
Factory production control	Test method	EN 120	EN 717-2	
	Requirement	Content ≤ 8 mg/100 g oven dry board See NOTE 3	Release ≤ 3,5 mg/m ² h or ≤ 5 mg/m ² h within 3 days after production	
^a For established products, initial type testing may also be done on the basis of existing data with EN 120 or EN 717-2 testing, either from factory production control or from external inspection.				

Source: EN 13986:2004+A1:2015. Wood –based panels for use in construction- Characteristics, evaluation of conformity and marking.

In detail, the members of the European Panel Federation (EPF) adopted an internal agreement that allow only the production of class E1 wood-panel in conformity with the EN 13986 and avoiding the commercialization of class E2 panels in EU market. Looking at data, the majority of wood-panels in the market belong from E1 class, class E2 panels are still marketed in the EU mainly because not all the EU manufacturers comply with the voluntary agreement and because of the products imported by extra-EU operators.

Currently, as it is shown in the table 3, eight EU Member States – Austria, Denmark, Germany, Greece, Italy, Lithuania, the Netherlands and Sweden (see below table 3) – have adopted **national legislation to limit formaldehyde** emissions from wood-based panels, corresponding to the E1 emission class (EPF, 2017).

In 2008, two new formaldehyde emission limits by IKEA and by EPF were introduced. IKEA presented the legislation IOS-MAT 0003, corresponding to a perforator (EN 12460-5) value of max. 4.0 mg/100 g for particleboards (5.0 mg/100g for MDF >8mm) correlating to 0.060 ppm chamber value (EN 717-1). EPF emission standard correspond at 4mg/100g for particleboard, 5 mg/100g for MDF, (EUWID, 2008).

The German Chemicals Prohibition Ordinance (Chemikalien-Verbotsverordnung, ChemVerbotsV)³⁷ restricts, among other things, formaldehyde emission from coated and uncoated wood-based materials (particleboards, plywood, veneer boards and fiberboards) and furniture containing wood-based materials to no more than 0,1 ppm. This restriction limit also applies to an entire piece of furniture containing wood-based materials.

In November 2018, the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (Bundesministerium für Umwelt, Naturschutz und nukleare Sicherheit, BMU) announced EN 16516 as the new reference method for formaldehyde emission (in a chamber) from coated and uncoated wood-based materials under the Chemicals Prohibition Ordinance.

The announcement, published in the Federal Register (Bundesanzeiger, BAnz AT 26.11.2018 B2), allows the existing EN 717-1 method to be used in parallel with the new method, but requiring the concentration value of formaldehyde in EN 717-1 to be multiplied by a factor of two (2). It also allows EN ISO 12460 Parts 3 and 5 standards only to be used for correlations in production control under certain prerequisites.

According to the announcement, the following methods are only valid until December 31, 2019:

- Bundesgesundheitsblatt 34, 10 (1991), pages 488-499 as a test method for wood-based materials and products manufactured from wood-based materials
- EN 717-1 'Wood-based panels – Determination of formaldehyde release – Part 1: Formaldehyde emission by the chamber method' as a reference method for emission measurements in a chamber for all wood-based materials;
- EN ISO 12460-3 'Wood-based panels – Determination of formaldehyde release – Part 3: Gas analysis method' as a derived method for raw plywood boards and coated boards;
- EN ISO 12460-5 'Wood-based panels – Determination of formaldehyde release – Part 5: Extraction method (called the perforator method) as a derived method for raw particleboards and raw fiberboards.

³⁷ https://www.gesetze-im-internet.de/chemverbotsv_2017/BJNR009410017.html

The use of EN 16516, and EN 717-1 by multiplying the concentration of formaldehyde by two, for formaldehyde emission measurements in a chamber will become effective on January 1, 2020.

The changes to the reference method stem from a research project by the Federal Environmental Agency and the Federal Institute for Materials Research (BAM) where measurements for formaldehyde emissions from wood-based materials should be adapted to more realistic conditions.³⁸

Recently IKEA has introduced a new standard, named IOS MAT 0181, which specifies the requirements for raw and coated panels to which its suppliers must comply in order to respond to the German Prohibition of Chemicals Ordinance (The German Chemikalien-Verbotsverordnung).

A novelty is the introduction of finished furniture, which could cause repercussions in terms of tests and verifications also for furniture manufacturers and not only for panel manufacturers.

Table 3. Legislation to limit formaldehyde emissions in selected Member States

Member State	Legal act	Limit value	Test method
Austria	Formaldehydverordnung (BGBl. Nr. 194/1990) § 1	0.1 ppm (0.124 mg/m ³)	Test chamber
Denmark	BEK nr 289 af 22/06/1983	0.15 mg/m ³	Test chamber
Denmark	Draft Order 2017/89/DK	0.124 mg/m ³	EN 717-1
France	Draft Order 2017/0023/F	Emission classes	ISO 16000-9, EN 717-1
Germany	Chemikalien-Verbotsverordnung, Anlage 1 (zu § 3)	0.1 ppm (0.124 mg/m ³)	Test chamber
Italy	DECRETO 10 ottobre 2008	0.1 ppm (0.124 mg/m ³)	EN 717-1
Sweden	KIFS 2017:7	0.124 mg/m ³	EN 717-1

Source: ECHA - ANNEX XV RESTRICTION REPORT – Formaldehyde and formaldehyde releasers

³⁸ <https://www.sgs.com/en/news/2019/03/safeguards-04019-germany-announces-new-test-standard-for-formaldehyde-emission>

Beyond Europe Japan has emitted on the July 2003 the “Building Standard Law”, in which the furniture supplier could only sell without restrictions Wood based panels with less than 0.3 mg/l formaldehyde emissions (limit value to be evaluated through the test method JIS A 1460³⁹) to resolve the sick house syndrome.

The Air Resources Board of California (CARB) adopted a new regulation (93120 ATCM) to reduce the formaldehyde emissions from composite wood products, including particleboard, MDF and hardwood plywood (Airborne Toxic Control measure, ATCM). The modified version of this regulation was finally approved in April 2008. This regulation proposes the reduction of formaldehyde emission standards in two phases. Phase 1 limits (effective from January 2009) are roughly equivalent to the European E1 emission class that is the Japanese F** class. Phase 2 limits (effective from January 2010 and January 2011) are comparable to the Japanese F*** limits. The regulation establishes more stringent formaldehyde emission limits on wood products in the United States: 0,08 ppm from 2009 (0,05 from 2010) for plywood, 0,18 ppm from 2009 (0,09 from 2011) for particleboards and 0,21 ppm from 2009 (0,11 from 2011) for MDF panels. The measure method is described in US standard ASTM E 1333-14⁴⁰ that foreseen the use of a “big chamber method”, or in alternative ASTM D 6007-14⁴¹ (with a smaller size of the test chamber).

On December 12, 2016, EPA published in the Federal Register a final rule (TSCA Title VI) to reduce exposure to formaldehyde emissions from certain wood products produced domestically or imported into the United States. EPA worked with the California Air Resources Board (CARB) to help ensure the final national rule was consistent with California’s requirements for similar composite wood products.

The Formaldehyde Emission Standards for Composite Wood Products Act of 2010 established emission standards for formaldehyde from composite wood products and directed EPA to finalize a rule on implementing and enforcing a number of provisions covering composite wood products. As of June 1, 2018, and until March 22, 2019, composite wood products sold, supplied, offered for sale, manufactured, or imported in the United States were required to be labeled as CARB ATCM Phase II or TSCA Title VI compliant. After

³⁹ JIS A 1460 Determination Of The Emission Of Formaldehyde From Building Boards - Desiccator Method

⁴⁰ ASTM E1333 - 14 Standard Test Method for Determining Formaldehyde Concentrations in Air and Emission Rates from Wood Products Using a Large Chamber

⁴¹ ASTM D6007 - 14 Standard Test Method for Determining Formaldehyde Concentrations in Air from Wood Products Using a Small-Scale Chamber

March 22, 2019, composite wood products must be labeled as TSCA Title VI compliant. These products include: hardwood plywood, medium-density fiberboard, and particleboard, as well as household and other finished goods containing these products.

The final rule also established a third-party certification program for laboratory testing and oversight of formaldehyde emissions from manufactured and/or imported composite wood products.⁴²

On June 29, 2019, the proposed Formaldehyde Emissions from Composite Wood Products Regulations were published in the Canada Gazette, Part I, for a 75-day public comment period ending on September 12, 2019. Comments and information received during the public comment period will be considered in the development of the final regulations, targeted for publication in 2020.

The regulations would help reduce exposure of Canadians to formaldehyde emissions in indoor air from composite wood products sold, offered for sale or imported into Canada. The regulations would place limits on the amount of formaldehyde that composite wood products can emit. Further to the requirements to meet emission limits, the regulations would impose requirements on industry for record-keeping, labelling, and reporting. They would also align Canadian requirements for composite wood products with similar requirements in the United States (U.S.), thereby helping to minimize burden for businesses operating in both Canada and the U.S.⁴³

1.4 SCIENTIFIC AND TECHNICAL SCOPE OF THE WORK

There is a growing appreciation that resource management needs to be improved nationally, regionally and globally, and the waste and pollution needs to be reduced. Surplus natural renewable resources have great potential to be tapped as a source for biodegradable products that could replace many of the existing hazardous chemicals, but this implies a need for a radical technology shift to be adopted by the chemical industry. Green chemistry aims to initiate a paradigm shift in the chemical industry from being based on fossil resources to renewable raw materials for manufacture of "green" chemicals.

⁴² EPA (US Environmental Protection Agency) website (Date modified: 2019-08-21): <https://www.epa.gov/formaldehyde/formaldehyde-emission-standards-composite-wood-products>.

⁴³ Government of Canada website (Date modified: 2019-06-28): <https://www.canada.ca/en/health-canada/services/chemical-substances/other-chemical-substances-interest/formaldehyde.html>

Wood based products are realized through various technological processes bringing to several classes of final products such as particleboards, plywoods, OSB, MDF, HDF. Due to the very high contents of lignocellulosic materials, wood based panels cannot be processed by means of the usual processing technologies used for composites, such as extrusion or injection moulding or compression moulding. They are realized through the application of synthetic resins, such as UF resins, that are undergone to a curing process in order to realize the final products.

Within this class of materials, more than 90 wt% of the constituents are already obtained from renewable resources. Nevertheless, environmental impact still need significant improvements in order to reduce the emission of hazardous substances, the energy consumption during the production process and to replace synthetic binders with innovative biomass derived binders.

As described, in the previous paragraph, the formaldehyde emission still represents a relevant problem during the lifetime of wood-based products. In order to improve indoor air quality (IAQ), new regulation have limited in Europe the formaldehyde emission of wood panels to the E1 class. Nevertheless, further reductions are expected in the next years, in order to fulfil stricter EU and market requirements. In this regard, after the introduction of the EU Regulation 605/2014, formaldehyde is now classified for the first time as carcinogenic, thus modifying older regulatory measures, where it was considered only as suspected carcinogenic.

Within this work a new approach is proposed: instead of step-by-step reducing formaldehyde emission, the aim is to realize eco-sustainable wood-based panels (in particular plywood and particleboard), through the application of intrinsically formaldehyde-free binders, with a relevant social impact in terms of health and life conditions. Therefore, the activity will contribute to achieve the decrease in formaldehyde emissions by developing new binder 100% formaldehyde free. It's important to highlight that binders and coatings represent the most significant source of formaldehyde, but a low quantity of this composite is however contained within untreated or recycled wood.

Furthermore, the realization of a new class of wood based panels fully constituted by biomass materials, would allow a subsequent total independence from fossil resources and a complete biodegradability. To reach this result it is necessary to go through intermediate steps, both through comparisons with the traditionally used resins, but also

with the realization of hybrid resins (natural and synthetic) where some essential properties of the panel cannot yet be reached by the only natural binder.

This trend and need to avoid the use of synthetic resins is aligned with the European strategy of the implementation of the Circular Economy Action Plan⁴⁴ published on the 4th March 2019. This agrees with the decision of the EU Commission strategy which contains reduction targets such as 20 percent lower greenhouse gas (GHG) emissions.

1.5 ANALYSIS METHODS

In order to evaluate the chemical-physical characteristics of the Natural Adhesive proposed in this work, a preliminary characterization was investigated at UNICAM (University of Camerino) through the following analysis:

- Thermogravimetric analysis (TGA) and differential thermal analysis (DTA);
- Differential Scanning Calorimetry (DSC);
- Rheological analysis (Viscosity);
- Microbiological tests;
- Headspace Gas Chromatography-Mass Spectrometry (GC-MS);
- Field Emission Scanning Electron Microscope (FESEM).

The equipment and instrumentation used at UNICAM are described in the chapter 3 Methods, and the results are commented in the chapter 5 Experimental part.

After the characterization, the natural adhesive was compared and combined with the traditional crosslinker used in the plywood and particleboard industry (UF, PAE, PF, pMDI). TGA/DTA analysis were carried on the hybrid combinations (natural adhesive and synthetic crosslinker of 0:100 %, 33:67 %, 50:50 %, 67:33 % and 100:0 %) to verify the changes in properties.

In order to evaluate the effect the same combinations of natural adhesive and synthetic resins (UF, PAE, PF, pMDI) were used for making prototypes of wood base panels: in particular plywood (flat and curved) and particleboard. All these prototypes have been manufactured at Laboratory scale (at IKEA Industry Lab, CMR srl, NIS srl, CGM srl), using

⁴⁴ Circular Economy Action Plan published on the 4th March 2019 (<http://ec.europa.eu/environment/circular-economy/>)

different technologies depending on the typology of wood-based panels (plywood, curved plywood, particleboard).

According to the main international reference standards properly dedicated to wood-based panels mechanical performances, water resistance and formaldehyde content tests were carried out at IKEA Orla Lab and at the Laboratory of Cosmob (accredited Laboratory in compliance with UNI EN ISO 17025) on the plywood and particleboard prototypes.

Two European standards were used as a reference:

- EN 312 Particleboard specification
- EN 636 Plywood specifications

Within these two classification standards the following test methods are mentioned and used for the purpose of this work:

- EN 310:1993 Determination of elasticity modulus in bending and flexural strength;
- EN 314-1:2004 Plywood – Bond quality – Test methods;
- EN 319:1993 Determination of tensile strength perpendicular to the plane of the panel;
- EN 317:1993 Determination of swelling in thickness after immersion in water;
- EN 322:1993 Determination of moisture content;
- EN 323:1993 Determination of density;
- UNI EN ISO 12460-3:2015 Determination of formaldehyde release. Gas-analysis method;
- UNI EN ISO 12460-5:2016 Determination of formaldehyde content. Perforator method.

Statistical analysis was performed with SPSS Version 21.0 statistic software package (IBM Corp., Armonk, NY, USA). Analysis of variance (ANOVA) and Tukey HSD test were performed on the particleboard testing data to indicate significant differences at a 95% confidence level.

2. MATERIALS

2.1 INTRODUCTION

The wood industry is characterized by the wide use of adhesive in the production process; in fact the adhesives used in the wood sector represent the 65% of the volume of the adhesives used in the world⁴⁵. More in detail, the most used adhesives are UF (92%) mostly applied in the production of MDF, melamine-urea-formaldehyde (MUF, 7%) and isocyanates (pMDI, 1%)⁴⁶ mostly used for the production of OSB (75%) together with, to a lesser extent, MUF (15%) and UF (10%)⁴⁷, while the phenol-formaldehyde (PF) it is mostly used for OSB production in United States.⁴⁸

The following table summarizes the main benefits and disadvantages of the traditional synthetic adhesives used in wood-based panel industry.⁴⁹

Table 4. Main benefits and disadvantages of synthetic adhesives used in manufacturing of wood-based panel industry.

Adhesives				
Properties	UF	MUF	PF	pMDI
Price	Low	Medium to high	Medium	High
Cure temperature	Low	Medium	High	Medium
Pressing time	Short	Medium	Medium to long	Short
Susceptibility against wood species	High	Medium	Low	High
Efficiency	Low	Medium to high	Medium to high	High
Compatibility with bio-based raw-materials	Medium	Medium	Medium to high	High
Manipulations	Easy	Easy	Easy	Difficult
Resistant against hydrolysis	No	Medium to high	High	High
Use in wet conditions	No	Partially yes	Yes	Yes
Formaldehyde emission	E1. CARB I possible	E1. CARB II possible	Very low emission	No

Source: A. Kumar, PhD, Universiti Malaysia Pahang, 2013.

⁴⁵ Pizzi, A. (2016). Wood products and green chemistry. *Annals of forest science*, 73(1), 185-203.

⁴⁶ Kutnar A, Burnard MD. The past, present, and future of EU wood adhesive research and market. In: FPS, editor. *International Conference on wood adhesives. Proceedings*; 2013 Oct 9-11; Toronto, Canada. Madison (WI): Forest Products Society; 2014. p. 22-35

⁴⁷ Kutnar et. Al. *Ibidem*.

⁴⁸ Vnućec, D., Kutnar, A., & Goršek, A. (2017). Soy-based adhesives for wood-bonding—a review. *Journal of Adhesion Science and Technology*, 31(8), 910-931. doi:10.1080/01694243.2016.1237278).

⁴⁹ A. Kumar, PhD, Universiti Malaysia Pahang, 2013.

Hence the formaldehyde-based adhesives are the most used in wood product industry, but there are some challenges related to its application linked to the fact that formaldehyde-based adhesives are derived from non-renewable fossil and linked to the problem of formaldehyde emissions, that are carcinogenic for human and animal and are becoming topics of great interest in recent years⁵⁰ inspiring new researchers on formaldehyde-free adhesives from renewable bio resource.⁵¹ One of the main problems deriving from the use of synthetic adhesives, is their non-renewable origin and the fact that are not completely biodegradable, in opposition to the society recognition of the needs of the introduction of natural biodegradable resources, and the consequent use of bio-based adhesives in the wood industry.⁵² A comparative analysis on petrochemical (urea-formaldehyde, UF) and bio (protein-lignin composite) adhesives in a Life Cycle Assessment (LCA) perspective, showed as while the natural-based adhesives are biodegradable, their emission of volatile organic compound (VOCs) are low and they may be involved in different recycling process like composting of food production, the petrochemical adhesives environmental impacts are higher (about 22%).⁵³ In this direction, researches on natural-based adhesives aimed at improving some mechanical characteristics and water resistance, are being carried out⁵⁴, including soy-based adhesive, due to its abundant availability and low cost of this raw material.⁵⁵

“Bio-based product” is a commercial or industrial product composed in a significant part by biological products or renewable domestic agriculture material or materials produced by forestry.⁵⁶

⁵⁰ Gui, C., Wang, G., Wu, D., Zhu, J., & Liu, X. (2013). Synthesis of a bio-based polyamidoamine-epichlorohydrin resin and its application for soy-based adhesives. *International Journal of Adhesion and Adhesives*, 44, 237-242. doi:10.1016/j.ijadhadh.2013.03.011)

⁵¹ Gui, C., Wang, G., Wu, D., Zhu, J., & Liu, X. (2013). *Ibidem*

⁵² Vnučec, D., Kutnar, A., & Goršek, A. (2017). Soy-based adhesives for wood-bonding—a review. *Journal of Adhesion Science and Technology*, 31(8), 910-931. doi:10.1080/01694243.2016.1237278)

⁵³ Vnučec, D., Kutnar, A., & Goršek, A. (2017). *Ibidem*.

⁵⁴ Vnučec, D., Kutnar, A., & Goršek, A. (2017). Soy-based adhesives for wood-bonding—a review. *Journal of Adhesion Science and Technology*, 31(8), 910-931. doi:10.1080/01694243.2016.1237278)

⁵⁵ Gui, C., Wang, G., Wu, D., Zhu, J., & Liu, X. (2013). Synthesis of a bio-based polyamidoamine-epichlorohydrin resin and its application for soy-based adhesives. *International Journal of Adhesion and Adhesives*, 44, 237-242. doi:10.1016/j.ijadhadh.2013.03.011)

⁵⁶ Hemmilä, V., Adamopoulos, S., Karlsson, O., & Kumar, A. (2017). Development of sustainable bio-adhesives for engineered wood panels-A review. *RSC Advances*, 7(61), 38604-38630. doi:10.1039/c7ra06598a

In the specific case of adhesives, there are different ways to introduce renewable materials in their production such as using natural products with adhesive proprieties (i.e. proteins); a second possibility is combining building block or monomers that can be derived from renewable sources to make polymers (this procedure requires more effort at the beginning of procedures, but one advantages is linked to the application end); and combine them to make polymers closely resembling synthetic adhesives; adding bio-based materials into synthetic adhesive preparations.⁵⁷

The bio-based industrial adhesives now available for the production of panels, have an high cost and for this reason are used for the production of premium panels or are used in combination with synthetic adhesives in order to have the required characteristics at an affordable cost for the mainstream panel production.

The most used bio-based adhesives is the soy protein, but some industrial application exist for tannin and starch and for lignin-based adhesives available in the market thanks to the new types of bio-refineries.⁵⁸

The new market trends based on the use of renewable materials, represent a good opportunity to investigate how further applications of adhesives can provide benefits in terms of environment and profits.⁵⁹

2.2 NATURAL ADHESIVE

The present study proposes a novel bio-adhesive for plywood and particleboard based on the following natural materials:

- Soybean flour (200 µm mesh), containing 38 wt% protein, 28 wt% carbohydrates, and 6 wt% moisture was purchased by Lameri S.p.A. (San Bassano, Italy).
- A water-free liquid hydrolysate obtained from enzymatic hydrolysis of an agricultural crop, having a density of 1300 kg/m³ and pH of 4.5, was supplied by NIS s.r.l (Vallefoglia, Italy). The hydrolysate contains large amounts of fulvic acids (23%) and proteins (18.75%), and a small amount of humin acids (2%).
- MgO, magnesium oxide was purchased by General Abrasivi s.r.l. (Carrara, Italy), obtaining by burning limestone at temperatures ranging from 550 to 650 °C.

⁵⁷ Green Chem., 2019, 21, 1866

⁵⁸ Hemmilä, V., Adamopoulos, S., Karlsson, O., & Kumar, A. (2017). Development of sustainable bio-adhesives for engineered wood panels-A review. RSC Advances, 7(61), 38604-38630. doi:10.1039/c7ra06598a

⁵⁹ Green Chem., 2019, 21, 1866

2.2.1 RAW SOY PROTEIN

Raw soybean is a component of the investigated natural adhesive, which increase the protein content of the binder, being a rich source of protein. Raw soybean flour may be contained in the binder mixture in an amount of 10% to 70% by weight, preferably 38,9%.

Soybeans are industrial cultivations produced almost in United States of America, Brazil, Argentina e Chile used for the production of both human (like oil, milk, flours, tofu and other products of different form) and for animal feedstock⁶⁰, which production and demand increase rapidly in the recent years. Another use of soy protein is the industrial use: in fact it can be used in the production of bio-composited, candles, ink and wood adhesives⁶¹.

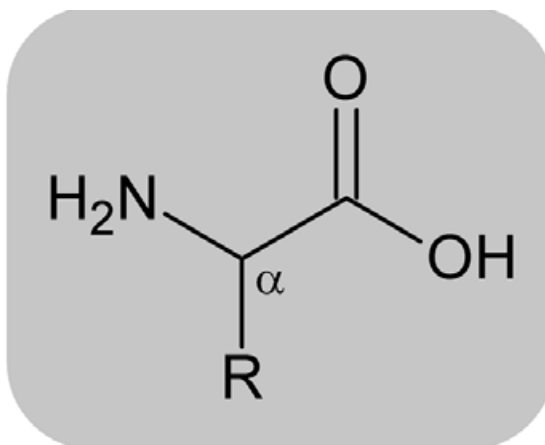
Soy proteins are composed for the 10 % by albumins, that can be extracted by water and for the 90 % by globulins that can be extracted by dilute salt solution. Four water-extractable fraction, 11S, 7S, 2S and 15S, are part of the soy globulins, where the S means Svedberg units- determined by sedimentation chromatography- and can be isolated based on their sedimentation coefficients. The 11S (glycinin) and 7S (β -conglycinin) constitute 65-80% of the total protein fractions and are both storage proteins. In detail, the glycinin (is a hexamer with six acidic and six basic subunits) constitutes about 52% while the β -conglycinin (a trimeric protein with three different subunits) are around 35% of the total seed proteins.

Soy protein molecules are complex macromolecules composed by 20 different amino acids. In the following figure (Figure 3) is shown as each amino acid has a common backbone- the amino group (NH₂), the α -carbon and the carboxylic group (COOH) - and different -chain (R)⁶².

⁶⁰ Vnućec, D., Kutnar, A., & Goršek, A. (2017). Soy-based adhesives for wood-bonding—a review. *Journal of Adhesion Science and Technology*, 31(8), 910-931. doi:10.1080/01694243.2016.1237278)

⁶¹ Vnućec et al. *Ibidem*.

⁶² Vnućec, D., Kutnar, A., & Goršek, A. (2017). Soy-based adhesives for wood-bonding—a review. *Journal of Adhesion Science and Technology*, 31(8), 910-931. doi:10.1080/01694243.2016.1237278)



Source: Vnučec, D., Kutnar, A., & Goršek, A. (2017). *Soy-based adhesives for wood-bonding—a review*.

Figure 3. The chemical structure of an amino acid. Backbones are the same for all amino acids, while side-chains (R) are different for each amino acid.

The use of soy protein as an adhesive dates back to before the 1930s: in fact, before this date, the soy proteins were used mostly as a blinder in coating and paint, while the first use of soy protein as a wood adhesive began after that time⁶³.

The soy protein, in order to be used as a wood adhesive, were typically denaturalized by a caustic treatment⁶⁴, and its use was linked to several advantages: the low cost, low press temperature and high capacity of binding with high moisture content⁶⁵. However, many disadvantages have to be underlined such as the poor biological stability, slow pressing times, very poor water resistance⁶⁶ and a general low strength that caused the substitution of this adhesive with more water resistant adhesives, the formaldehyde-based ones⁶⁷. In fact, in the 1960s, the synthetic adhesives started to replace the soy-based adhesives⁶⁸, that had actually a great potential if techniques to overcome their disadvantages were developed⁶⁹.

The use of soy protein as a wood adhesive, represents an inexpensive and easy solution as due to low pressing temperatures and the ability of bond wood with relatively high moisture

⁶³ Peshkova, S., & Geng, X. (2004). Investigation of soy protein-kymene® adhesive systems for wood composites. *JAOCs, Journal of the American Oil Chemists' Society*, 81(5), 487-491. doi:10.1007/s11746-004-0928-1

⁶⁴ Hemmilä, V., Adamopoulos, S., Karlsson, O., & Kumar, A. (2017). Development of sustainable bio-adhesives for engineered wood panels-A review. *RSC Advances*, 7(61), 38604-38630. doi:10.1039/c7ra06598a

⁶⁵ Peshkova Ibidem.

⁶⁶ Hemmilä, V., Adamopoulos, S., Karlsson, O., & Kumar, A. (2017). Development of sustainable bio-adhesives for engineered wood panels-A review. *RSC Advances*, 7(61), 38604-38630. doi:10.1039/c7ra06598a

⁶⁷ Peshkova Ibidem.

⁶⁸ Hemmilä, V. Ibidem

⁶⁹ Peshkova Ibidem.

content. However, some soy adhesives characteristics, such as high viscosity, short pot lives, sensitiveness to temperature and pH, influence the quality of the wood products bound with them that are relatively weak and characterized by a low water tolerance that make difficult their application.

Some solutions in order to overcome these difficulties have been evaluated: first of all, being the adhesive properties influenced by the protein content, one solution in order is to lower the high viscosity by using low solid's content or use hydrolysis. One disadvantage is linked to the fact that breaking down the protein macromolecules into small fragment leads to an inferior bond strength⁷⁰. Another less evaluated aspect is the application of soy adhesives in particleboard produced from straw that result to be more suitable than formaldehyde-based adhesives because the straw surface is hydrophobic due to silica and wax components⁷¹.

Although the soy protein adhesives are now used in the namely "green panels", they still have a great potential due to their main advantages: controlling denaturation and creating good crosslinking in an economical way are the key parameters to create industrially practical solutions⁷².

2.2.2 LIQUID PLANT HYDROLYSATE

Another component of the Natural Binder is a liquid plant hydrolysate (preferably 13,9%), a water free component obtained from demolition of cellulose with a density of 1300 kg/m³ and pH = 4,5.

An example of liquid plant hydrolysate is produced by Bioiberica company⁷³, and in this case it is a product of sugarcane bagasse demolition, remaining from sugar extraction, having a large amounts of fulvic acids (from 22 to 24%) and a large amounts of proteins (from 18 to 19%) and a small amount of humic acids (from 1 to 3%) which does not affect water resistance.

The first two components are chemically reactive, due to their property of containing carboxy groups, aldehyde and ketone groups, phenol groups, quinone groups,

⁷⁰ Hemmilä, V. Ibidem

⁷¹ Hemmilä, V. Ibidem

⁷² Hemmilä, V. Ibidem

⁷³ <https://www.bioiberica.com/en/company>

namely amide groups (- NH₂) and the acidic groups (-COOH), which increase the protein content of the soybean.

Humic acids are soluble in the original acidic environment but are insoluble in a basic environment.

2.2.3 AN ALKALINE EARTH METAL OXIDE, MgO

A third component, obtained by burning limestone at temperatures ranging from 550 to 650 °C, is an alkaline earth metal, preferably magnesium oxide, that is highly reactive and may be contained in the binder mixture in an amount from 2% to 5% by weight, preferably 2,8%.

Magnesium oxide acts as binder activator because it forms magnesium hydrate (or brucite) in the presence of water, providing a strongly basic environment, and adding the proteins of the hydrolysate to soybean proteins, enter into a solution and interact with one another, thereby creating aminoplast chains.

2.2.4 WATER

Deionized water is added 44,4% by weight.

2.3 SYNTHETIC RESINS

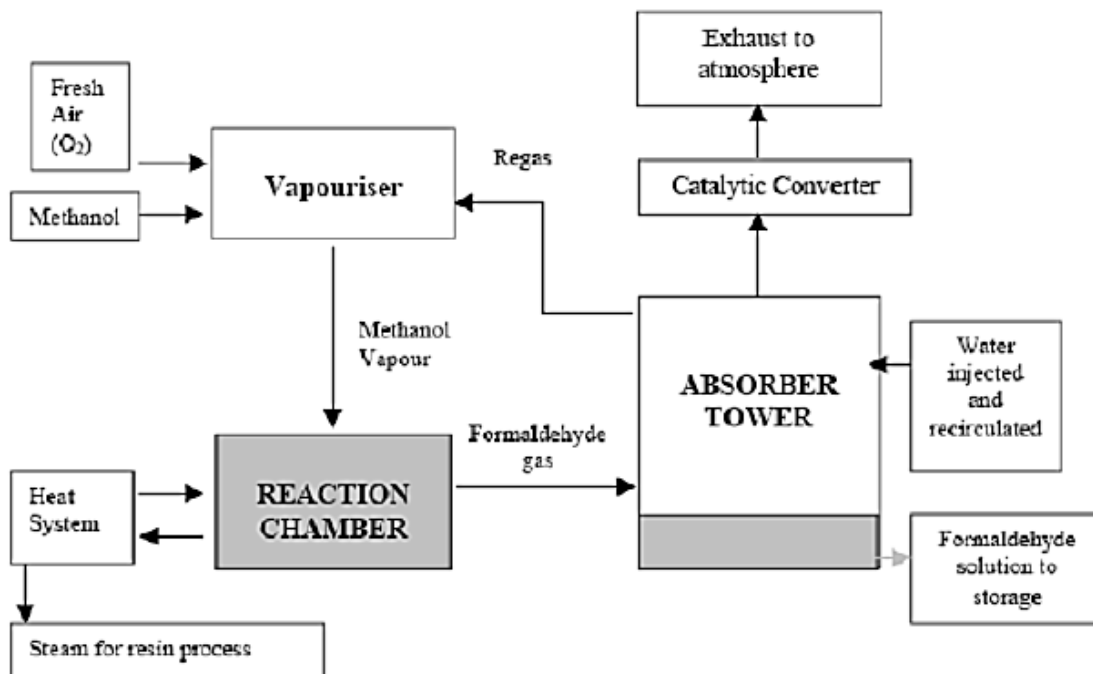
About the synthetic resins that were compared and mixed with the natural adhesive, the references are as follows:

- UF, U208 was provided by OMNIA KOLL s.r.l.;
- PAE, Polyamide Epichlorohydrin Resin (PAE 12.5%) was purchased at Wuhan Golden Wing Industry & Trade Co., Ltd.
- PF, MARFEN 100 was provided by Saglamlar Plywood.
- PMDI, Protopur PN was purchased at COLLANTI CONCORDE s.r.l.

2.3.1 UF (UREA FORMALDEHYDE)

Formaldehyde has been produced commercially since 1889 by the catalytic oxidation of methanol. Various specific methods were used in the past, but only two are widely used currently: the metal oxide catalyst process and the silver catalyst process. In the first process, the methanol is oxidised with excess air in the presence of a modified iron-molybdenum-

vanadium oxide catalyst at a specific temperature of 250-400 °C and a specific atmospheric pressure (methanol conversion, 98-99%).⁷⁴ The following Figure (Fig. 4) summarizes the formaldehyde manufacturing process by metal-oxide conversion. In the second process, methanol is directly converted into formaldehyde and hydrogen at 600-780 °C.



Source: Formacare (2018)

Fig. 4: Formaldehyde manufacturing process

In most of the sites in which formaldehyde is manufactured (according to ECHA, the sites are 73 in 21 EU Member State)⁷⁵, the formaldehyde manufacturing takes place with the manufacturing of formaldehyde-based resins and/or other chemicals, while in some sites (\pm 11 non-integrated sites) large volumes of formaldehyde-based organic chemicals such as (MDI) -methylene diphenyl diisocyanate and polyols – and some others specialty chemicals.

The quantity of formaldehyde registered under REACH result to be >1 million tonnes per year.⁷⁶ According to Formacare (2008), in 2015 the total pure formaldehyde production in the 28 countries, Norway and Switzerland was around 3.2 million tonnes, corresponding to 8.6 million tonnes as 37% water solution⁷⁷ and as underlined by Eurostat (2018), a part of formaldehyde become from imports from extra-EU countries:

⁷⁴ IARC, (2006). Formaldehyde, 2-Butoxyethanol and 1-tert-Butoxypropan-2-ol. Volume 88.

⁷⁵ ECHA (2019) - ANNEX XV RESTRICTION REPORT – Formaldehyde and formaldehyde releasers.

⁷⁶ ECHA (2019), *ibidem*.

⁷⁷ ECHA (2019), *ibidem*

between 2015 and 2017, in fact 20-30 thousand tonnes annually have been imported from extra-EU countries.

Formaldehyde-derived products

As it has been introduced before, the production of formaldehyde-based resins or other chemical production, as a central role and represent almost the 98% of the total formaldehyde produced or imported. The most common substances obtained from formaldehyde are ⁷⁸: *Urea formaldehyde (UF)*, *Phenol formaldehyde (PF) resins*, *Melamine formaldehyde (MF) resins*, *Methylene diphenyl diisocyanate (MDI)*, *Polyoxymethilenes (POM)*, *1,4-Butanediol (BDO)*, *Pentaerythritol (Penta)* and *Hexamine*. In the following table (table 5), the main formaldehyde-based resins and their application are summarized.

Table 5: Substances obtained by formaldehyde manufacturing and main applications

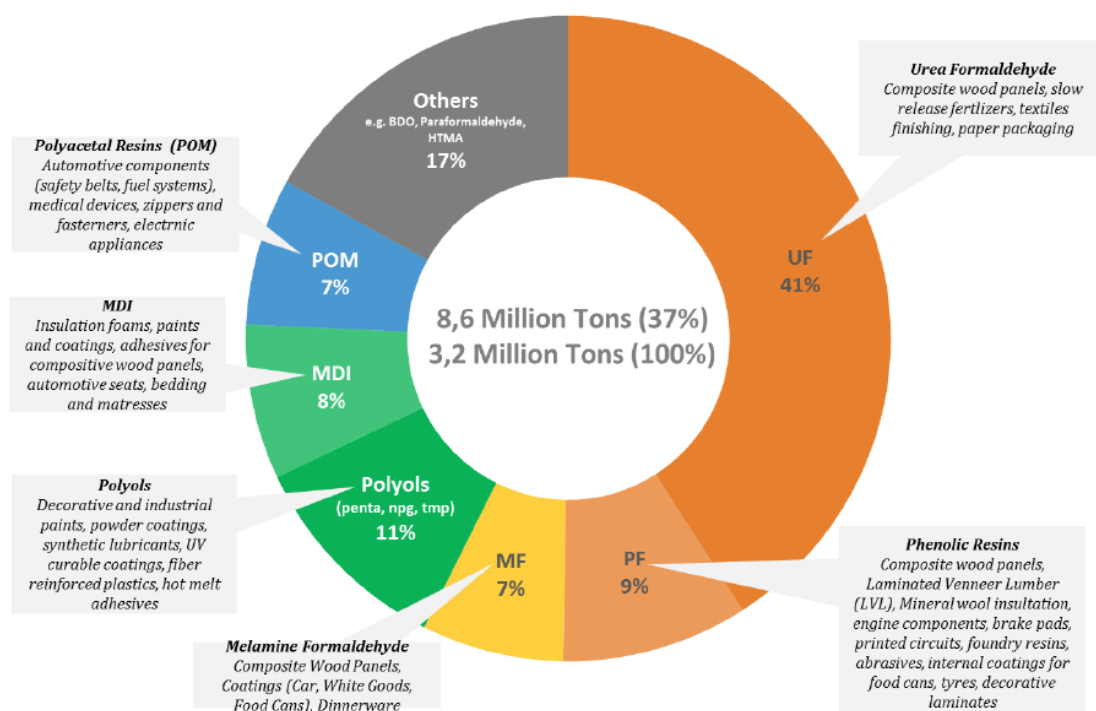
Substances	Application	Sectors
Urea formaldehyde (UF) resins	<ul style="list-style-type: none"> ○ Binders or adhesives (low cost, dimensional stability, hardness, clear glue line, fast curing times) ○ Urea-based fertilisers 	<ul style="list-style-type: none"> ○ Wood-based panel production ○ Agriculture
Phenol formaldehyde (PF) resins	<ul style="list-style-type: none"> ○ Insulation binder, wood-based products, laminates ○ Friction materials ○ Foundry binders 	<ul style="list-style-type: none"> ○ Building and construction industry ○ Automobile
Melamine formaldehyde (MF) resins	<ul style="list-style-type: none"> ○ Laminates and surface coatings 	<ul style="list-style-type: none"> ○ Building and construction industry ○ Automotive sector a ○ Housewares
Methylene diphenyl diisocyanate (MDI)	<ul style="list-style-type: none"> ○ Insulation materials ○ Appliance use (refrigerators, freezers, air conditioners) 	<ul style="list-style-type: none"> ○ Construction and automotive sector

⁷⁸ ECHA (2019), *ibidem*

	○ Packaging of electronics	
	○ Transportation	
Polyoxymethylenes (POM)	○ Precision parts	○ Industrial and automotive sectors
1,4-Butanediol (BDO)	○ Intermediate in tetrahydrofuran (THF) and polybutylene (PBT) resins	○ Textile industry ○ Automotive ○ Electrical industry
Pentaerythritol (Penta)	○ Paints	○ Automotive industry
	○ Polyol esters for engines lubricants	
Hexamine	○ Epoxy resins	
	○ Rubber vulcanization	

Source: our elaboration on ECHA 2019.

The following figure (Fig. 5) details the main uses of formaldehyde and its derived products in 2015, and shows the relevance of each substances on the total production.



Source: Formacare (2018)

Fig. 5: Main uses of formaldehyde and formaldehyde-derived products, 2015

As it has been showed, while the formaldehyde-based resins are used for the production of adhesives used for bonding particleboard, MDF, plywood, or laminating adhesives, the

main disadvantage is related to the fact that they originate formaldehyde emissions during the production and the use of bounded products. The environmental regulations and legislation led the significant reduction of panel product's emissions of the last decades, and are inspiring panel manufacturers, adhesive suppliers and researchers to develop systems, which further decrease formaldehyde emissions.⁷⁹

In detail, the types of products involved in the use of formaldehyde are: solid wood, wood-based products, and furniture.

Solid wood: Solid wood products are involved in the emission of small quantities of formaldehyde as formaldehyde is a decomposition product of lignin.

Wood-based products: the wood-based panels are used in the production of furniture and flooring, and represent the main source of formaldehyde emission in indoor air (Marquart et al., 2013⁸⁰), even if they are usually covered with layers that contribute to reduce formaldehyde emissions.⁸¹

The formaldehyde-based resins are used in different applications depending on the desired result in the finished product.

In detail, the UF resins, which application is suitable only for indoor products as they are not water resistant, are used in raw and covered wood-based materials, laminates, furniture, windows, and doors. Average formaldehyde emission rates, caused by moisture, for UF-based wood products (raw) are 164 $\mu\text{g}/(\text{m}^2\text{h})$ (range 8,6-1580 $\mu\text{g}/(\text{m}^2\text{h})$).⁸²

PF resins are used in indoor and outdoor products, as they are water resistant and their emission rates are in the range of 4.1-9.2 $\mu\text{g}/(\text{m}^2\text{h})$ ⁸³.

Melamine formaldehyde (MF) resins and Melamine urea formaldehyde (MUF) are suitable for indoor and outdoor products and their emission rate is lower than the one

⁷⁹ Vnučec, D., Kutnar, A., & Goršek, A. (2017). Soy-based adhesives for wood-bonding—a review. *Journal of Adhesion Science and Technology*, 31(8), 910-931. doi:10.1080/01694243.2016.1237278

⁸⁰ H. Marquart, K. Verbist, S. Dieperink-Hertsenberg (2013). Analysis of Consumer Exposure Associated with the Use of Products and Articles Containing Formaldehyde-based Resins

⁸¹ Aldag, N., Gunschera, J., & Salthammer, T. (2017). Release and absorption of formaldehyde by textiles. *Cellulose*, 24(10), 4509-4518.

⁸² Salthammer, T., Mentese, S., & Marutzky, R. (2010). Formaldehyde in the indoor environment. *Chemical reviews*, 110(4), 2536-2572.

⁸³ Salthammer, T., Mentese, S., & Marutzky, R. (2010). *Ibidem*.

related to UF resins (around one-fifth)⁸⁴ for MF and 50% for MUF compared to the UF resins.⁸⁵

Urea-formaldehyde (UF) resins are the most applied for the production of plywood products intended for internal use; one of the mayor defects of UF resins, is that they are not water resistant, and for this reason they are fortified with to water attack, fortification with melamine.⁸⁶

Furniture: The wood-based panels are used for the production of furniture that is contributing to indoor air formaldehyde emission, compounded by the use of acid-curing for veneering and preparation of furniture⁸⁷, and by foams applied in the furniture.⁸⁸

The formaldehyde emissions from these product decline over time: it starts with a rapid decline during the first days of their production, and then gradually decreases over the time. This process has been studied in literature, but according to Salthammer and Gunschera (2017) just a low number of studies approach this emission behaviour. Colombo et al. (1994) studied the behaviour of plywood formaldehyde emission and particleboard: comparing the initial emission rates (after 28 days) and the emission rates after one year and two years, they found out that for plywood there was an emission reduction of 33% and 42% respectively for the first and the second years; in the case of particleboard the reduction consisted in 45% after one year and 66% after two years. Another study conducted by Brown (1999) on the emission rates from particleboard and MDF, found out that while the emission in the first few weeks was of 300-400 mg/(m²h), after six months was 80-240 mg/(m²h). Another study conducted by Liang (2015) follow this line and found an emission reduction of 20-60% from MDF boards after two years⁸⁹. The UF used in this study was the U208, commercially sold for manufacturing wood based panels E1 compliant according the EN 13986.

⁸⁴ BAAQMD (2012). Emission offset program deferral equivalence demonstration. 2012 Report for Years 2009, 2010 and 2011.

⁸⁵ Salem, M. Z., Böhm, M., Barčík, Š., & Beránková, J. (2011). Formaldehyde Emission from Wood-Based Panels Bonded with Different Formaldehyde-Based Resins. *Wood Industry/Drvna Industrija*, 62(3).

⁸⁶ Mansouri, H. R., Pizzi, A., & Leban, J. M. (2006). Improved water resistance of UF adhesives for plywood by small pMDI additions. *Holz als Roh-und Werkstoff*, 64(3), 218.

⁸⁷ Jensen, L. K., Larsen, A., M lhave, L., Hansen, M. K., & Knudsen, B. (2001). Health evaluation of volatile organic compound (VOC) emissions from wood and wood-based materials. *Archives of Environmental Health: An International Journal*, 56(5), 419-432.

⁸⁸ H.V. Andersen, H.B. Klinke, L.W. Funch, L. Gunnarsen (2016). Emission of Formaldehyde from Furniture, The Danish Environmental Protection Agency, Copenhagen

⁸⁹ ECHA (2019) - ANNEX XV RESTRICTION REPORT – Formaldehyde and formaldehyde releasers.

2.3.2 PAE (POLYAMIDEAMINE-EPICHLOROHYDRIN)

Another formaldehyde-based resin is the Polyamideamine epichlorohydrin (PAE) resin, a water soluble additive available in the market from the 1950s and still used in the preparation of wet strengthened papers because of the low cost and the good performance, while the data about the chemical proprieties are still limited in literature. In order to be synthesized, the PAE follows a three steps process: condensation between adipic acid diethylenetriamine; addition of epichlorohydrin at the secondary amine group in polyamideamine in order to form, respectively, polyamideamine and N-(3-chloro-2-hydroxypropyl) polyamideamine, and a last step of formation of four-membered azetidinium ring (AZR) from the 3-chloro-2-hydroxypropyl group.⁹⁰

PAE is a known crosslinker that has helped soy protein adhesives to get commercial acceptance by improving their wet strength properties (Li 2007). PAE and soy protein molecules are capable of forming reversible ionic complexes before curing while further reactions between PAE with the proteins and wood can take place during curing (Zhong 2007)⁹¹. Most of research refers to interactions between PAE and soy protein isolates while it has been reported a different curing ability of soy flour due to its carboxylic acid functionality (Hunt et al. 2010)⁹². It has also been shown that curing with PAE, and consequently interaction with wood and bond strength, are little affected by the type of soy flour with varying levels of protein dispersibility index (Frihart and Satori 2013)⁹³.

The PAE resin together with the SF, is a component of an adhesive system developed by Li, the soy protein-KymeneR used for interior plywood, engineered wood flooring, and particleboard. At the origin, the soy protein-KymeneR was produced with the purified SPI, but now it is commercialized with SF, which level of dispersible protein (PDI) and particle sized do not affect the bond strength of SF-PAE adhesives. Furthermore, the resins combined with SF, form the Soyad™ adhesives, which are durable water resistant

⁹⁰ Siqueira, E. J. (2012). Polyamidoamine epichlorohydrin-based papers: mechanisms of wet strength development and paper repulping (Doctoral dissertation, Grenoble).

⁹¹ Zhong, Z., Sun, X. S., and Wang, D. (2007). Isoelectric pH of polyamide-epichlorohydrin modified soy protein improved water resistance and adhesion properties. *J. Appl. Polym. Sci.*, 103, 2261-2270.

⁹² Hunt, C. G., O'Dell, J., and Frihart, C. R. (2010). "High-temperature performance of soy adhesives," in: *Wood adhesives 2009*, C. R. Frihart, C. G. Hunt, and R. J. Moon (eds.), Madison, WI: Forest Products Society, pp. 214-219.

⁹³ Frihart, C. R., and Satori, H. (2013). "Soy flour dispersibility and performance as wood adhesive. *J. Adhes. Sci. Technol.*, 27(18-19), 2043-2052.

thermosetting adhesive which strength and performance is comparable to UF-based adhesives. They are used to produce hardwood plywood, particleboard, MDF and engineered wood flooring.⁹⁴

SOYBABYR and OZEROR are used for the productions of MDF, HDF and laminated floor products on a large scale in China. The main advantages of SOYBABYR are linked to the better water resistance than UF resins, while the main disadvantages are the high hot pressing temperature of SOYBABYR (more than 170°C) and the high viscosity for OZEROR (more than 50,000 mPas).

The combination of the polyamidoamine resins, a new CAs (curing agent) with maleic anhydride (MA), allow a better water resistance of the SF-based adhesives, to the same extent of bonding type-II plywood, and it is used in the production of interior plywood panels. The particleboards bonded with adhesive based on SF and CA derived from ammonia and epichlorohydrin are M-2 particleboards. In addition, the new bio-based CA itaconic acid-based polyamidoamine-epichlorohydrin (PAE) was synthesised from renewable itaconic acid. The adhesive resulting from this combination can be classified according the requirements for type-II plywood.⁹⁵

2.3.3 PF (PHENOL-FORMALDEHYDE)

The first plastic resins available in the market, are the phenol-formaldehyde resins (PF), formed by phenols and formaldehyde solutions reaction, that in contrast to celluloids, are made from pure synthetic materials.⁹⁶ Today resins based on natural polyphenolic materials are starting to be used industrially- the so called condensed tannin resins- but the first work on these resins date back to 1872 with Adolf Bayer and subsequently with Losekam, while the real first commercialization began in 1902, when the PF resins started to substitute the shellac. In 1907 with the “heat and pressure” patents by Dr. Leo H. Baekeland and the subsequently creation of the General Bake-lite Company, the use of phenolic resins was spread, thanks to these new methods that allowed a more cost effectively produce moulded parts, that until this time, was expensive and a long process.

⁹⁴ Vnučec, D., Kutnar, A., & Goršek, A. (2017). Soy-based adhesives for wood-bonding—a review. *Journal of Adhesion Science and Technology*, 31(8), 910-931. doi:10.1080/01694243.2016.1237278

⁹⁵ Vnučec, D., Kutnar, A., & Goršek, A. (2017). Soy-based adhesives for wood-bonding—a review. *Journal of Adhesion Science and Technology*, 31(8), 910-931. doi:10.1080/01694243.2016.1237278

⁹⁶ Pizzi, A., & Ibeh, C. C. (2013). *Handbook of Thermoset Plastics: 2. Phenol-Formaldehydes*. Elsevier Inc. Chapters.

In fact, the new development, enabled to overcome the problems of bubble formation and the fragility of cured phenolic resin.⁹⁷

During the time, the PF resins have continued to be popular despite the development of newer plastic resins; some data from the 1993, show as the PF resins has a consumption of 3.07 billion pounds, following just the polyurethane⁹⁸. Nowadays, PF resins are used in different sectors such as automotive industry, electrical devices production, and adhesives.

As it has been underlined before, one of the main advantages of PF resins is the cost effectiveness of the Phenol-formaldehyde condensation products. With reference to the condensation reaction of PF to carry out, there are two possibilities: it can be carried out under basic condition- in this case it produces “resols”, that can be further condense at 130-200 °C, with formation of methylene ether and bridges- or with acidic condensation- and in this case “novolacs”, thermoplastic materials, are produced. In the case of novolacs, they require the addition of formaldehyde donor for cross-linking. PF are used for bonding leather, wood, wood-based panel (in particular in some countries for plywood) and rubber or as tackifiers and are available in the market in form of powders, aqueous dispersions or solutions in alcohol or acetone, while heat-activated resols are available as tapes. Furthermore, due to their good adhesion in metal, hybrids have been developed (in combination of epoxies, poly(vinyl acetal), neoprene or methanes.

For developing high bonding strength and environmental-friendly wood composites, a soybean/PF resin based (SP) adhesive was investigated (Gao et al. 2010)⁹⁹ and applied in the manufacture of plywood. The result had shown the optimum formula of SP adhesive was: soy-based adhesive was 70%, PF resin was 30%; the optimum technical parameters of the plywood manufacture were: hot-pressing temperature was 160 °C, hot-pressing time was 80 s/mm, pressure intensity was 1.2 MPa, and glue content was 160 g /m²; Properties of plywood made under the optimum technical parameters were: the bonding strength was 1.30 MPa, the formaldehyde emission was 0.32 mg/L. It completely meets the type plywood requirement type I and low level of formaldehyde emission (Gao et al. 2010).

⁹⁷ Pizzi, A., & Ibeh, C. C. (2013). *Ibidem*.

⁹⁸ Fabris, H. J., & Knauss, W. G. (1989). Synthetic polymer adhesives.

⁹⁹ Gao Q, Dang R, Sang ZT, et al. Investigation of soybean/PF resin based adhesive applying on plywood. *Adv. Mat. Res.* 2010;113–116:2007–2011.

2.3.4 pMDI (POLYMERIC DIPHENYL METHANE DIISOCYANATE)

The polymeric diphenyl methane diisocyanate (pMDI), is an unconventional adhesive compared with the Formaldehyde-based ones; it is in fact, free of acidic and alkaline (like in the case of UF and PF), free of catalytic salts and free of formaldehyde. It is a liquid polymer, and it derives from crude oil and its mayor feedstock is benzene. Since the first development of isocyanate resins during World War II, it has been considered an adhesives that can “bond anything to anything”¹⁰⁰ and its diffusion has grown significantly, after the their introduction in German particleboard market in 1970s.

More in general, MDI binders are used in the production of oriented strand board (OSB) and in medium density fibreboard (MDF) in Europe and North America, and its production is now in excess of 1,500,000 tons annually. MDS, as a synthetic chemical, is a complex mixture of the isomers of di- and tri-isocyanates and high polymeric species and are sold as PMDI. MDI binders main advantages in their suitability for the production of lignocellulosic furnish: in fact they can that they react with moisture in the material and with the hydroxyl groups.¹⁰¹

pMDI’s propensity for water lies the clue for its curing. pMDI reacts with active hydrogen atoms. Wood surfaces are covered with -OH groups with active hydrogens. Lignocellulosic materials such as wood always have moisture adsorbed to surfaces; water has active hydrogens. Therefore, once it is sprayed, pMDI’s curing begins. Its shelf life is then measured in minutes. Curing is accelerated and completed during hot pressing. pMDI’s curing consists of two reactions occurring simultaneously but at different speeds and initiated by its NCO-groups. Beginning rather slowly, pMDI forms with water the so-called polyurea. In a fast reaction, pMDI forms with the hydroxyl groups of wood the urethane bonds—a true chemical bond (the “double lock” effect).

The reaction is an addition reaction, which result is a cross-linked, substituted urea and carbon dioxide¹⁰². As it is shown in Fig. 6. the MDI reaction with cellulosic hydroxyls yields a water-resistant chemical bond that has the same benefits of MDI-bonded composite

¹⁰⁰ MARRA, A. A. 1992. Technology of wood bonding: Principles in practice, 1 Ed., Van Nostrand Reinhold, New York. Pp. 76–80.

¹⁰¹ Rowell, R. M., R. Moisuk, and J. A. Meyer (1982). "Wood-Polymer Composites: Cell Wall Grafting With Alkylene Oxides and Lumen Treatments With Methyl Methacrylate." Wood Sci. 15(2): 90-96.

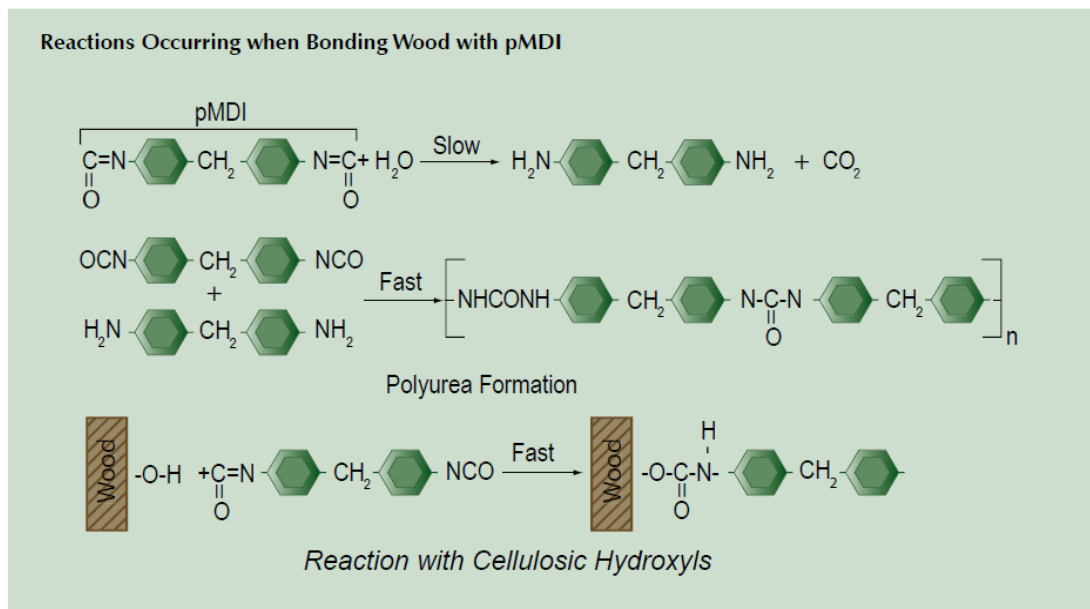
¹⁰² Lay DG, Cranley P(1994) Polyurethane adhesives. Chapter 24. In:A. Pizzi and K. L. Mittal (eds) In: Marcel-Decker, Inc., New York,N.Y. pp. 405–429

panels, i.e.: low resin dosage, an high moisture resistance, low swelling and an high strength.¹⁰³

pMDI can be use in addition of UF resins, in order to improve the UF glue line water resistance.¹⁰⁴

pMDI is not thermoplastic, it will not reverse the thermoset achieved during the curing process in the press, unlike some other bonding resins that are thermoplastic and are reversible due to heat, thus losing their bond. The resin is also unaffected by UV light and water.

At equal application rates, pMDI's bonding is superior to that of UF, MUF, and PF in a dry environment and vastly superior (even relative to PF) in a water-soaked environment. pMDI contains no formaldehyde with no formaldehyde emission.



Source: lignor.com

Fig. 6. Reactions occurring when bonding wood with pMDI

2.4 WOOD BASED PANELS

In Europe, the most commonly produced wood-based panels are particleboard and medium density fibreboard (MDF). Furthermore the market offer some other products as oriented strand board (OSB), interior and exterior plywood, insulation board and hardboard. There are also more recent products that include laminated veneer lumber (LVL), oriented strand lumber (OSL),

¹⁰³ Papadopoulos, A. N., Hill, C. A. S., Traboulay, E., & Hague, J. R. B. (2002). Isocyanate resins for particleboard: PMDI vs EMDI. *European Journal of Wood and Wood Products*, 60(2), 81-83.

¹⁰⁴ Mansouri, H. R., Pizzi, A., & Leban, J. M. (2006). Improved water resistance of UF adhesives for plywood by small pMDI additions. *Holz als Roh-und Werkstoff*, 64(3), 218.

parallel strand lumber (PSL), laminated strand lumber (LSL), glued laminated timber (also called glulam), wooden I-beams, light density fibreboard (LDF), high density fibreboard (HDF), cross-laminated timber (CLT), etc.

Most notably, hot pressing and the concurrent adaptability of thermosetting resins have improved composites produced from particles and strands (particleboard, OSB, OSL, PSL, LSL), fibres (as MDF, HDF) and veneers (plywood, LVL).¹⁰⁵

In order to appreciate the effects of the glues, different prototypes of wood-based panels (WPB) were realized; in particular in this work two kinds of WPB were considered:

- Plywood (flat and curved), where the veneer sheets were in both low (4-6%) and high (6-8%) moisture content; the veneers were supplied from an IKEA supplier (Sakuona);
- Particleboard, where the particles were supplied from IKEA and NIS srl.

2.4.1 PLYWOOD

Plywood is a useful product that result to be attractive for some characteristics: it provide an high performance under hazardous conditions; it is available in a range wood species (softwood such as spruce or pine; temperate or tropical hardwoods such as birch, poplar, eucalyptus) and resins; provide panels with stability and good strength resistance.

There are two typologies that can be distinguished talking about plywood:

- Veneer plywood (complete term of plywood): its plies are made of wood veneers orientated with their plane parallel to the surface of the panel, a grand ar right angles and with the outer and inner plies placed symmetrically at the central ply or may consist of two adjacent veneers;
- Core plywood: is an assembly of plies bonded together i.e. blockboard or laminboard.

Plywood is produced with resin bonds and are suitable for interior and exterior use and for their production the main adhesives used are UF, PF and MUF, that can influence the bonding quality.

Veneer plywood

For the production of plywood veneer, it is used a lathe, which peels with the blade parallel to the log that is generally soaked or steamed before the process in order to increase the

¹⁰⁵ Vnučec, D., Kutnar, A., & Goršek, A. (2017). Soy-based adhesives for wood-bonding—a review. *Journal of Adhesion Science and Technology*, 31(8), 910-931. doi:10.1080/01694243.2016.1237278)

moisture content and to produce a smoother veneer. The defect may be repaired using plugs or filter, and in some cases small strips of veneer may be jointed into full-size sheets. As it has been introduced before, the main resins used for plywood production are UF, PF, and MUF, and are applied using roller spreader, spray, extrusion or curtain coating. The use of one adhesive influence their bonding characteristics and the suitability of panels in the different kinds of products.

The Urea-formaldehyde based panels are in fact suitable for interior use, while Phenol-formaldehyde based panels are suitable for both internal and external use, due to the moisture resistance of PF.

The durability of the veneer species must also be considered when selecting plywood for uses where it may be exposed to prolonged high moisture content (standard reference: CEN/TS 1099 Plywood. Biological durability. Guidance for the assessment of plywood for use in different use classes).

Melamine-urea-formaldehyde based is used in some types of plywood; generally, the most used are UF and PF, but thanks to the development of new technologies, MUF is used in the manufacturing of exterior and marine plywood.

The output of the first step of the manufacturing is then subjected to pressure and heat, generally using a multi-opening press, producing a cured panel, that is cooled, trimmed to size and sanded.

In some case, such as in some forms of plywood coming from China, the plywood can be subjected to a further process of adding face and back veneers in order to produce very thin veneers with an high quality.

Surface appearance

The plywood can be classified in relation to the surface appearance that is influenced by the grade of veneer used for the surface.

The plywood can be classified according to the *EN 635 plywood- Classification by surface appearance* that is intended for determine the visual appearance of the panel. The standard classified the surface appearance according to different grades of veneers of surface, and

some furnish criteria such as knots, splits, insect holes, bark and resin pockets, decay, veneer joints, repairs, edge defects.

The final colour is affected also by the species of veneer used and by the effects of weathering and ageing.

The parameters that can affect the surface appearance are quality of sanding, minimum appearance class, thickness, defects in first inner ply and bonding class, etc. according to CEN/TS 635-4:2007 Plywood - Classification by surface appearance - Part 4: Parameters of ability for finishing, guideline.

Specification

The standards of reference for plywood manufactured are:

- the Construction Products Regulation (CPR): the harmonized European standard EN 13986;
- the specification of the product standard EN 636 that gives the minimum values for each of the classes;
- EN 12369-2 Wood-based panels. Characteristic values for structural design. Plywood, that provides corresponding characteristic values for use with each of these classes.

The EN 636 considers three classes, in order to represent respectively dry, humid and exterior condition of use. According to this standard this are the characteristics for the three situations:

Table 6. Classification according to EN 636

Condition	Application	Use class classification	Moisture content
Dry conditions	Interior applications	1	20°C and 65% of humidity
Humid conditions	Protected exterior applications	2	20°C and 85% of humidity
Exterior condition	Unprotected external applications	3	Above 20%

Source: Panel Guide Version 4, Wood panel Industries Federation, 2014

EN 636 also proposes bending strength and modulus classes based on bending tests specified in EN 310 Wood-based panels, in order to determine elasticity and bending strength in order to give a designated strength (F) and modulus (E). In this case the example of designation would therefore be F10/20, E30/40.

Table 6. shows requirements for plywood defined in EN 636.

The standard EN 314-2 provides a three-bonding class classification, while the *EN 314-1 Plywood. Bonding quality. Test methods* provides tests to evaluate the glue bond performance at determined conditions and according the environment class of use.

Physical properties

The wood-based panel products are hygroscopic and their dimension tend to change due to humidity conditions, much more across the grain. In the case of plywood, thanks to the cross-laminated structure, the longitudinal veneers in one ply tend to restrain the perpendicular veneers in the adjacent ply, causing just a small dimensional movements (to give an example 1% change in moisture content influence the length and width of plywood of 0,15 mm, and the thickness change is about 0,3 % to 0,4 %).

The factors that modify the material proprieties, like the moisture content that influence the strength and stiffness, are given in EN 1995-1-1 (Eurocode 5).

Another relevant standard regarding plywood is the European standard EN 335, that specifies the risk linked to biological attack of plywood in relation to Use classes 1,2,3 and 4 (in contact with ground or fresh water) and 5 (sea water). In fact, it is not just the glue bond quality to affect the durability of plywood, but a relevant factor is given by the biological attack.¹⁰⁶

2.4.2 PARTICLEBOARD

The particleboard (PB) is a wood-based panel, designed so that the wood particles are bonded together with a synthetic adhesive produced with resins.

The manufacture of particleboards was introduced with the purpose of scrap re-use; for this reason, at the beginning the manufacturing process was rough compared to the current one and the reproducibility of the quality was relatively poor. Over the years, the application of new technologies in the production and control, together with the dimensional optimization

¹⁰⁶ Panel Guide Version 4, Wood panel Industries Federation, 2014

of wood particles and the use of more sophisticated resin systems, have led to the production of large amount of high-performance panels.

PB is made with wood chips prepared in a mechanical chipper and generally coming from natural species or recycled material, consisting in particles bonded with synthetic resins composed of urea-formaldehyde (UF), melamine urea-formaldehyde (MUF), and more rarely phenol-formaldehyde (PF) and the polymeric methylene di-isocyanate (PMDI). The success of UF resins is due to their high reactivity and good mechanical performance, combined with low cost. However, they have an important disadvantage: the release of formaldehyde.

The bonding system used depends on the end use envisaged. In detail, the relevance in mass of each PB component is described here below:

- 83-88% chips;
- 6-8% formaldehyde based resins on or 2-3% of PMDI;
- 5-7% water;
- 1-2% paraffin wax solid parts.

PB has smooth and polished surfaces. To obtain this characteristic, the density is increased in the external faces by the use of small particles of wood bonded with a higher percentage of resin with respect to the central core of the panel.

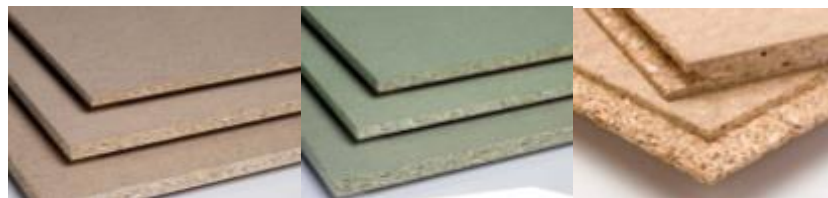


Fig. 7. Examples of PB panels [Source: Archiexpo]

Generally, PB has a light yellow colour; however, for identification purposes, the entire product or individual layers that compose can be dyed according to the end use or to specific properties (e.g. green for the panels with a great resistance to moisture, red for fully treated panels with fire retardant chemicals). The density of the panel, influenced by the typologies of particles and by the process, varies depending on the product. In general, typical densities are about 600 – 680 kg/m³. Thus, for example, a panel of 2400 x 1200 x 19 mm will weigh approximately 36 kg.

Applications and specifications. The specific properties of the PB imply several benefits that are transformed into a wide range of applications. In this regard, the good mechanical performance, uniform throughout the panel, together with the availability also in large dimensions, make these panels suitable especially for the furniture sector. Large quantities of PB with laminate finishing are also used in the manufacture of kitchen cabinets, working tops and furniture for dining rooms and bedrooms.

PB must comply with European standard EN 312¹⁰⁷, which is also a reference for the standard EN 13986 containing the requirements for the different typologies individuated by EN 312 (here listed in Table 7).¹⁰⁸

Table 7. Definition and application of different typologies of PB

Type	Definition from EN 13986	Applications
P1	Panel of wood particles bonded with resin for internal use as non-structural component in dry conditions	Internal applications, packaging of materials, furniture manufacturing
P2	Panel of wood particles bonded with resin for interior equipment (including furniture) in dry conditions	Furniture manufacturing, partition walls, kitchen cabinets, internal applications.
P3	Panel of wood particles bonded with resin for internal use as non-structural component in wet conditions	Bathroom and kitchen cabinets
P4	Panel of wood particles bonded with resin for internal use as structural component in dry conditions	Partition walls, floors, furniture subjected to heavy loads.

¹⁰⁷ EN 312:2010 Particleboard specification

¹⁰⁸ Panel Guide Version 4, Wood panel Industries Federation, 2014

P5	Panel of wood particles bonded with resin for internal use as structural component in wet conditions	Roofs, attics, floors, wall panels
P6	Panel of wood particles bonded with resin for use as structural component for heavy loads in dry conditions	Partition walls, lofts
P7	Panel of wood particles bonded with resin for internal use as structural component in dry conditions for heavy loads in wet conditions.	Partition walls, lofts

3. METHODS

A natural adhesive was prepared by mixing the soy flour, MgO and the plant hydrolysate at ambient temperature. The fulvic acids of the plant hydrolysate can potentially crosslink with the amino and fatty acids contained in the soy protein while its proteins further enhance the protein content of the final adhesive. MgO in the presence of water forms magnesium hydrate, and thus provides a strong basic environment that is necessary for the solubility of the soy flour and plant hydrolysate proteins and their interaction. A first mixture was prepared by adding MgO (2.8 % wt) and then soy flour (38.9 % wt) in deionized water (44.4 % wt) by constant stirring.

The plant hydrolysate (13.9 % wt) was added to prepare the final mixture by mixing for 1 min with the help of a hand-held kitchen mixer. The final mixture was grinded in a RETSCH MM400 (Retsch GmbH, Haan, Germany) ball mill for size reduction and homogenization, with 3 cycles of 2 min each at 30 Hz. The total solids content of the resulting natural adhesive was 44 %.

Viscosity measurements of the natural adhesive were performed as a function of rotation speed (rotary stress) at 10, 25 and 40 °C. The rotational rheometer used (HR-1 Discovery Hybrid Rheometer with Trios V4.2.1.36612 software, both TA instruments, New Castle, USA) is a flat disc type with a diameter of 6 cm and the sample thickness between the two disks is 1 mm.

The curing behaviour of the natural adhesive before and after size reduction and homogenization was determined using the Differential Scanning Calorimetry (DSC) instrument Pyris 1 equipped with an Intracooler 2P cooling device (both Perkin Elmer, Norwalk, USA). DSC was calibrated for temperature and heat flow using a pure sample of indium and zinc standards. A total of 20 mg of freshly blended adhesive mixture was heated from -20 to 200 °C at a heating rate of 10 °C min⁻¹ under a nitrogen flow of 20 mL/min.

The thermal stability of the cured natural adhesive was tested using the Pyris 1 instrument (Perkin Elmer, Norwalk, USA) with a simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA). Powdered samples of 3 mg were weighed in an alumina crucible and scanned from 30-500 °C at a heating rate of 10 °C/min in a nitrogen environment. The weight change of the samples was recorded throughout.

Headspace Gas Chromatography was carried out in order to verify the absence of emissions of harmful substances from both the enzymatic liquid and the natural adhesive. The analyses were carried out with a 6890N gas chromatograph with 7683N autosampler coupled with 5973N electronic impact mass detector by GC-MS instrument (Agilent Technologies, Santa Clara, USA) at a temperature of 40 °C.

About the antimicrobial activity, two samples have been compared: Natural Adhesive grinded and Natural Adhesive not grinded (with the addition of 0,01% of Ag). The following controls have been realized:

- *Escherichia coli* Graphs (Negative-Gram);
- *Staphylococcus aureus* Graphs (Positive-Gram);
- *Pseudomonas aeruginosa* Graphs (Positive-Gram).

Air-dried thin films of the natural adhesive before after treatment with the ball mill were placed on glass pieces and viewed under a Sigma 300 Field Emission Scanning Electron Microscope (FESEM) (Carl Zeiss Microscopy GmbH, Jena, Germany) to reveal details of adhesive's morphology.

The results of the analysis carried on at the UNICAM are reported and commented at the paragraphs 4.1 e 4.2.

After the evaluation of the chemical-physical characteristics of the 100% natural adhesive (here named Bio44T), the Bio44T itself was compared with the traditional ones used by the plywood and PB manufacturers (especially UF) and it was also checked the properties when mixed with other synthetic resins (after named hybrids samples):

- Urea Formaldehyde (UF),
- Polyamideamine-epichlorohydrin (PAE),
- Phenol Formaldehyde (PF),
- Polymeric Methylene Diisocyanate (PMDI).

TGA/DTA analysis were performed at UNICAM on the hybrids (par. 4.4).

These analysis were fundamental in order to characterize and compare the proposed combinations.

After this stage the best compromises between organic rate and performance behaviour has been selected and used for making prototypes of plywood (flat and curved) and particleboard (PB) at Laboratory scale, in particular:

- the plywood prototypes were realized at NIS, CGM and CMR, as described at the paragraph 4.2.1;
- the PB prototypes were realized at IKEA Industry's Laboratory in Orla (Poland) and at NIS srl, as described at the paragraph 4.2.2.

According to the main international reference standards properly dedicated to wood-based panels, mechanical, water resistance and formaldehyde emissions tests were carried out at the Laboratory Cosmob¹⁰⁹ (accredited Laboratory in compliance with UNI EN ISO 17025) on the plywood and particleboard (PB) samples in order to verify and compare the performances with the traditional made using UF adhesives.

In particular, two European standards were used as a reference, defining the performance characteristics and classifications for particleboard and plywood panels:

- EN 312 Particleboard specification
- EN 636 Plywood specifications

Within these two classification standards the following test methods are mentioned and used for the purpose of this work:

- EN 310:1993 Determination of elasticity modulus in bending and flexural strength
- EN 314-1:2004 Plywood – Bond quality – Test methods
- EN 319:1993 Determination of tensile strength perpendicular to the plane of the panel
- EN 317:1993 Determination of swelling in thickness after immersion in water
- EN 318:2002 Determination of the dimensions change associated to the variation in relative humidity
- EN 320:1993 Determination of resistance to axial withdrawal of the screws
- EN 322:1993 Determination of moisture content
- EN 323:1993 Determination of density
- UNI EN ISO 12460-3:2015 Determination of formaldehyde release. Gas-analysis method (for plywood)
- UNI EN ISO 12460-5:2016 Determination of formaldehyde content. Perforator method (for particleboards)

¹⁰⁹ <http://www.cosmob.it/en/>

Statistical analysis was performed with SPSS Version 21.0 statistic software package (IBM Corp., Armonk, NY, USA). Analysis of variance (ANOVA) and Tukey HSD test were performed on the particleboard testing data to indicate significant differences at a 95% confidence level.

4. EXPERIMENTAL PART

4.1 CHARACTERIZATION OF THE NATURAL ADHESIVE

4.1.1 INTRODUCTION

It has been shown that bio-based adhesives are still at a development laboratory phase and suffer from several issues that hinder their application at the industry. The most common limitations have to do with the availability of raw materials, low reactivity and need for modification, high viscosity, slow curing, low water resistance, and higher costs in comparison with the conventional formaldehyde-based adhesives (Hemmilä et al. 2017)¹¹⁰. Depending the biopolymer used, crosslinking with different, mostly synthetic, agents is required to achieve acceptable bonding performance.

Currently, soy protein adhesives seem to have a lead than other bio-based counterparts. Adhesive performance of soy proteins is mainly affected by a number of factors such as the protein content, their structure, particle size, surface quality, viscosity and pH (Frihart and Satori 2013¹¹¹; Frihart and Birkeland 2014¹¹²). In general, drawbacks of soy protein adhesives refer to low water resistance, sensitivity to biological degradation, high viscosity at high solid content and relatively low bonding strength of wood composites (Hemmilä et al. 2017)¹¹³.

The present study proposes a novel bio-adhesive for particleboards based on the natural materials soy flour, magnesium oxide (MgO) and a plant-derived enzymatic hydrolysate. The fulvic acids of the plant hydrolysate can potentially crosslink with the amino and fatty acids contained in the soy protein while its proteins further enhance the protein content of the final adhesive. MgO in the presence of water forms magnesium hydrate, and thus provides a strong basic environment that is necessary for the solubility of the soy flour and plant hydrolysate proteins and their interaction.

Different rates of the three main components of the natural adhesive (soy flour, MgO and the plant hydrolysate at ambient temperature) were chosen on the base of the type of materials to be glued (for example wood particles, veneers, fibres, etc.) or of the relative industrial

¹¹⁰ Hemmilä, V., Adamopoulos, S., Karlsson, O., and Kumar, A. (2017). "Development of sustainable bio-adhesives for engineered wood panels—A Review," *RSC Adv.*, 7, 38604-38630.

¹¹¹ Frihart, C. R., and Satori, H. (2013). "Soy flour dispersibility and performance as wood adhesive. *J. Adhes. Sci. Technol.*, 27(18-19), 2043-2052.

¹¹² Frihart, C. R., and Birkeland, M. J. (2014). "Soy Properties and Soy Wood Adhesives," in: *Soy-Based Chemicals and Materials*, R. P. Brentin (ed.), ACS Symposium Series, American Chemical Society, Washington, DC, pp. 167-192.

¹¹³ Hemmilä et al. (2017). *Ibidem*

process to be used to manufacture a specific wood-based panel (i.e. plywood, particleboard or fibreboard).

The effect on plywood and particleboard properties by using various proportions of others common synthetic crosslinker (UF, PAE, PF, pMDI) for proteins was also investigated.

4.1.2 LIST OF THE SAMPLES AND ANALYSIS

In order to characterize the natural adhesive and to investigate on its properties (i.e. water content, homogeneity, crosslinking temperatures, etc.), different recipes were analysed at UNICAM (Table 8), through the equipment already describer at the paragraph 3.

Table 8. Tests performed on different samples of the natural adhesive

Samples Identification	Description	Analysis
U208	Reference sample (OMNIA KOLL srl): Urea Formaldehyde traditionally used for manufacturing PB of E1 class emission (according to table 1 of the EN 13986)	- DSC, TGA/DTA
Bio50	Natural binder with 50% H ₂ O	- DSC , TGA/DTA - Viscosity measurements at 10, 25 and 40 ° C
Bio44	Natural binder with 44% H ₂ O	- DSC, TGA/DTA - Viscosity measurements at 10, 25 and 40 ° C,
Bio44T	Natural binder grinded with 44% H ₂ O (ball mill 3 cycles of 2min. 30Hz)	- DSC - Viscosity measurements at 25 and 40 ° C, - Biological Tests to verify resistance to bacteria strains.

BioAg44T	Natural binder milled with 44% H ₂ O binder grinded with 44% H ₂ O (ball mill 3 cycles of 2min. 30Hz) with the addition of 0.01% of Ag	- Biological Tests to verify resistance to bacteria strains.
Bio44Tfilm	Film of Natural binder milled with 44% H ₂ O, air dried	- SEM analysis
Bio44film	Film of Natural binder with 44% H ₂ O, air dried	- SEM analysis

4.1.3 ANALYSIS AND MAIN RESULTS OBTAINED

4.1.3.1 THERMO-GRAVIMETRIC ANALYSIS (TGA)

The thermograms of the samples **Bio44** and **Bio50** (Fig. 8 and 9) show the same trend. Water loss starts at room temperature and ends 140-150 °C. In the range of 150-230 °C a relative stability is observed, while above 230 °C a progressive decomposition begins which ends at about 500 °C, leaving a 5% white residue consisting mainly of MgO.

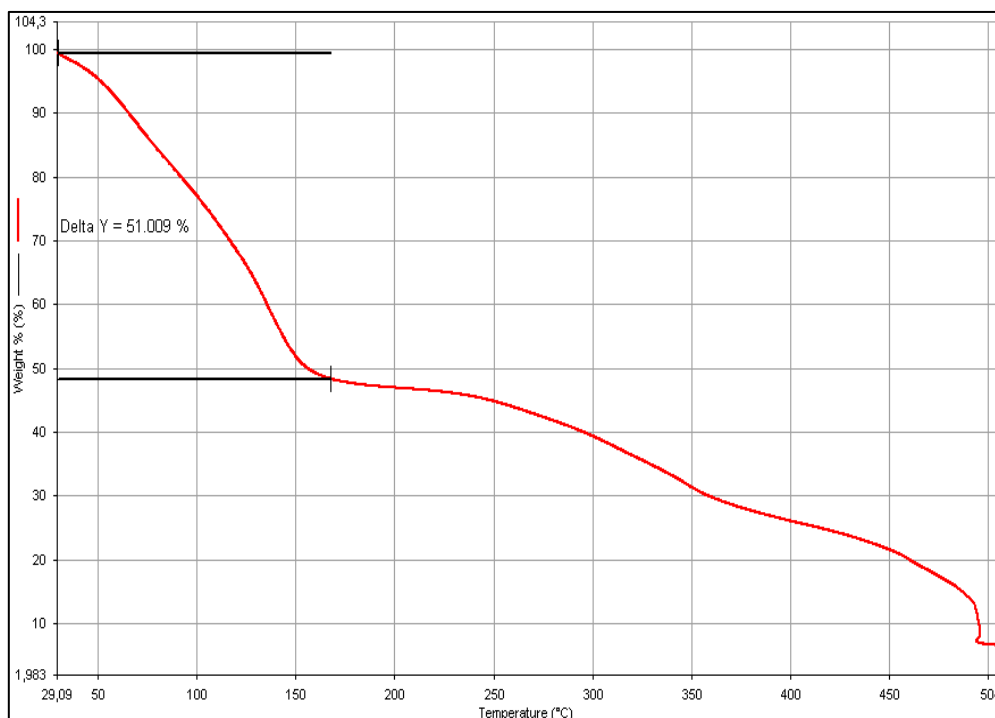


Fig. 8. TGA of the samples Bio44

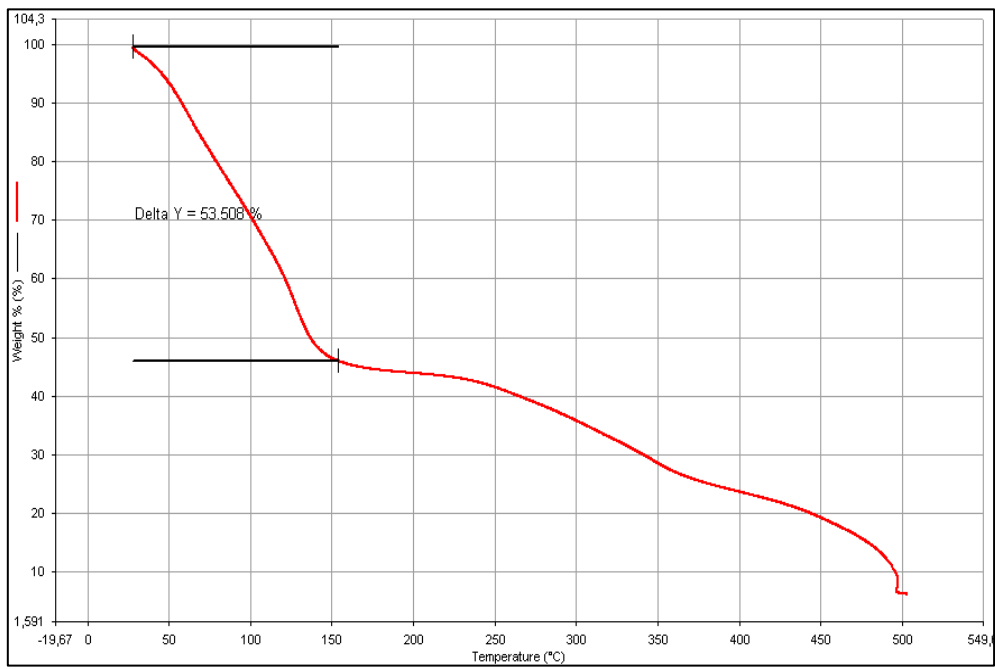


Fig.9. TGA of the samples Bio50

4.1.3.2 DSC CALORIMETRIC ANALYSIS

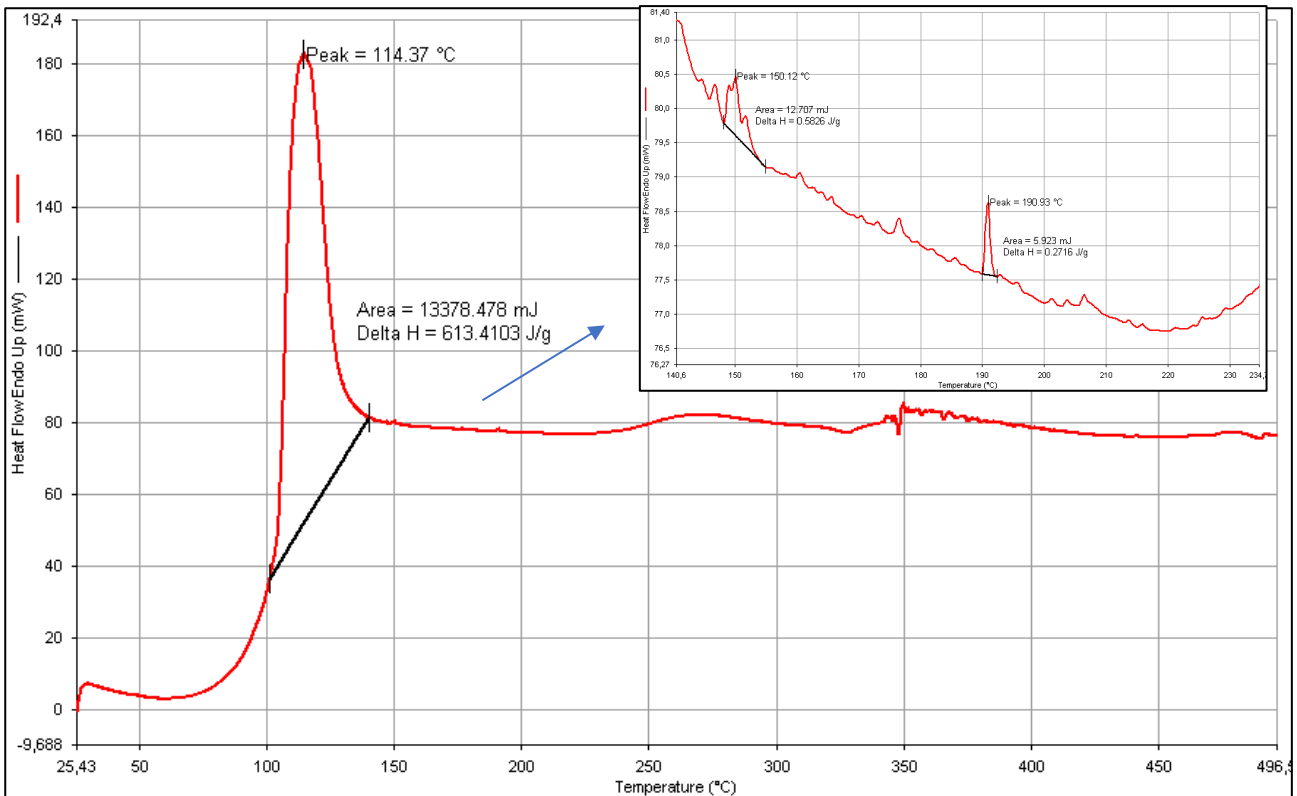


Fig. 10. DSC sample Bio44.

The DSC thermogram of the sample **Bio44** shows an intense endothermic signal ($\Delta H = 613 \text{ J / g}$) due to water evaporation. In the range 140-230 °C (enlarged image) some endothermic signals are observed, but their size is practically negligible and does not provide useful information. Above 250 °C there are degradation processes, around 350 °C both endothermic and exothermic decomposition and thermal degradation processes are observed.

The thermal analysis of the sample **Bio44T**, treated at the ball mill, (fig. 11) shows substantially the same trend as the sample **Bio44**, even if the **Bio44T** it seems to get rid of water more easily, in fact the energy needed to remove the water is lower $\Delta H = 424 \text{ J / g}$ (although the lower value could also be due to a smaller amount of water, which could have been eliminated during the ball mill milling process). In addition, the maximum of the endothermic elimination of the water signal falls to 110 °C instead of 114 °C. In the range 140-230 °C the small endothermic signals observed in the sample **Bio44** disappear completely.

In both samples **Bio44** and **Bio44T** there are no exothermic signals associated with a possible cross-linking, or they fall within a temperature range of 115-140 °C and are therefore covered by the intense water signal. It seems that may be useful to dry the sample at room temperature and carry out the DSC analysis on the dry to reduce the water signal to better explore the 115-140 °C range.

In fig.12 it is shown the trend UF resin (U208) in order to have a reference.

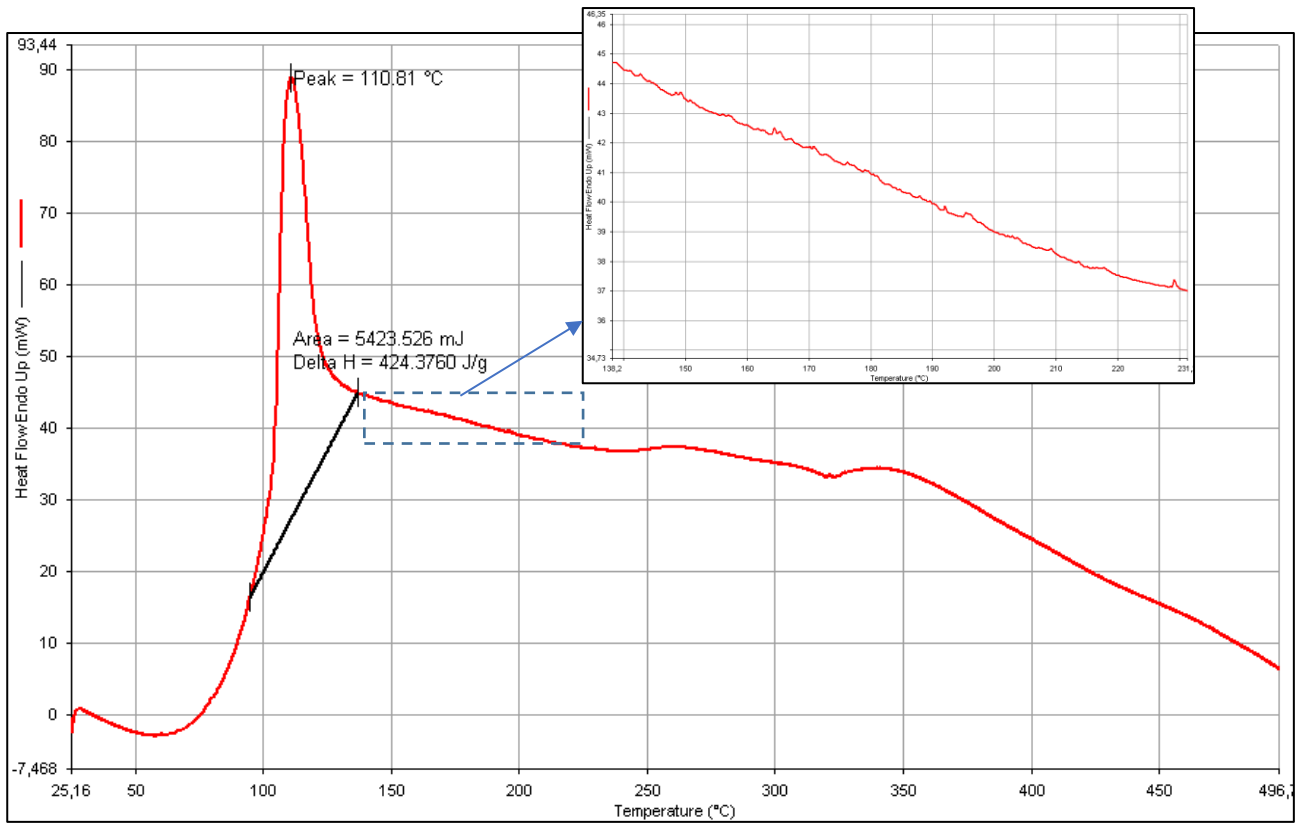


Fig. 11. DSC of the sample Bio44T.

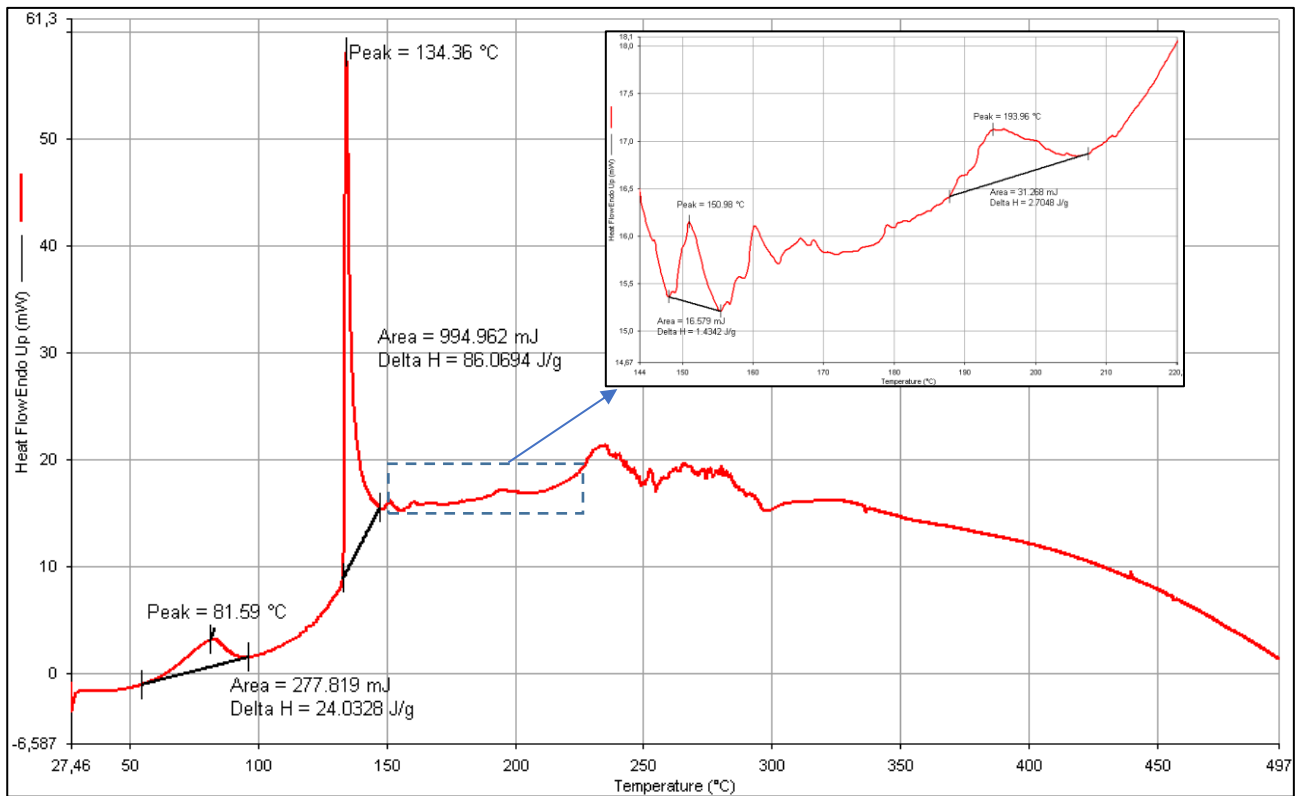


Fig. 12. DSC of UF (sample U208).

4.1.3.3 TGA-DTA ANALYSIS

The thermogram in fig.13 shows a trend of the TGA curve completely similar to that already observed in fig. 8. The DTA curve has the strong energy absorption necessary to remove the water but the peak does not it is symmetrical and the presence of a shoulder at about 120 ° C would seem to indicate the concomitant presence of an endothermic phenomenon not directly linked to the elimination of water, this confirms the above mentioned hypothesis of the existence of other phenomena covered by the signal of the water that could be better investigated by repeating the analyses on the dry sample.

In fig.14 the TGA-DTA trend of the UF resin (U208) is plotted.

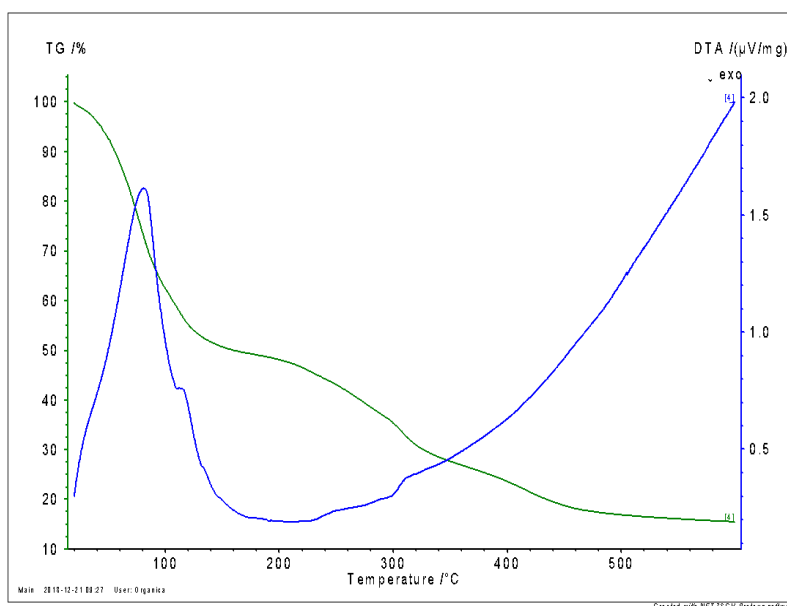


Fig.13. TGA-DTA thermogram of the sample Bio44. TGA green curve, DTA blue curve.

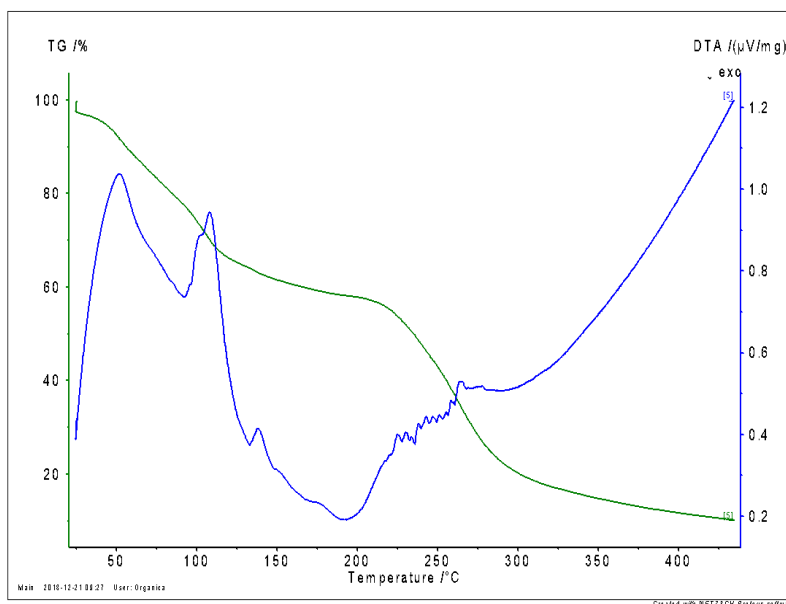


Fig. 14. TG-DTA thermogram of the sample U208. TG green curve, DTA blue curve.

4.1.3.4 RHEOLOGICAL ANALYSIS

The viscosity of adhesive is an important factor affecting bond strength and is dependent on the size and shape of adhesive's molecules, the solids content and amount of additives (Hong and Park 2017)¹¹⁴.

Thus, in this study the viscosity of the natural adhesive was determined.

On the first test, viscosity measurements were performed only at room temperature (25 °C) through the Brookfield viscometer. The measured value was approximately 96000 cP even if the measurement was probably not completely reliable as the type of viscometer was more suitable for oily fluids and not for aqueous mixtures. In fact the viscometer needle tended to drag part of the mixture in a non-homogeneous way, leaving air bubbles behind it, in such conditions the measurement cannot be considered completely reliable. However, the viscosity value detected is plausible and in good agreement with the rheological measurements described in the following paragraph.

In fact, after that the viscosity measurements were performed as a function of rotation speed (rotary stress). The rotational rheometer used is a flat disc type with a diameter of 6 cm (Fig.15) . The sample thickness between the two disks is one millimetre.

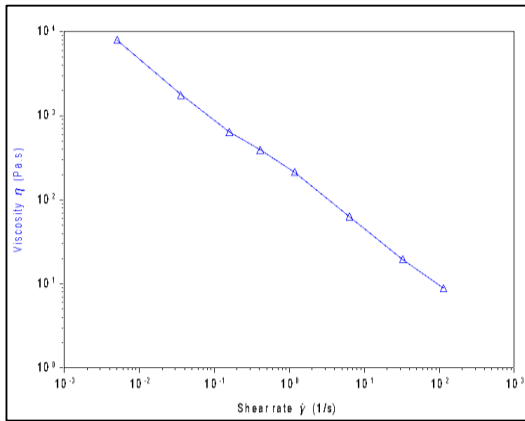
¹¹⁴ Hong, M. -H., Park, B. -D. (2017). "Effect of urea-formaldehyde resin adhesive viscosity on plywood adhesion," J. Korean Wood Sci. Technol., 45(2), 223-231.



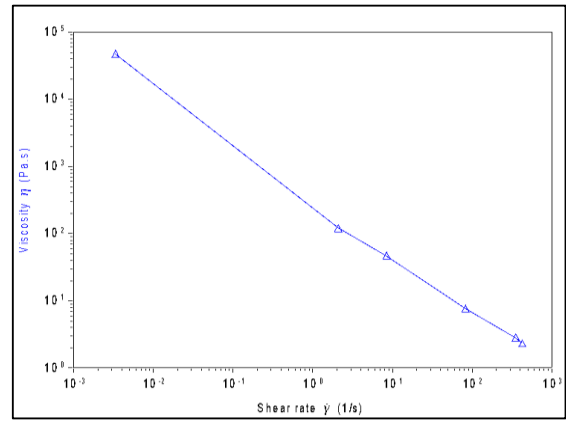
Fig. 15. Rheometer

The graphs in figure 16 show the viscosity values as a function of the plate rotation speed, with a rather wide range of shear stress. At the beginning the system is almost stopped, very little perturbed, while as the speed increases there is a collapse of the viscosity due to the energy supplied to the sample, at this point strongly disturbed. Such behaviour is typical of **fluids thixotropic** which tend to pass from the state of pasty (almost solid) fat to that of liquid.

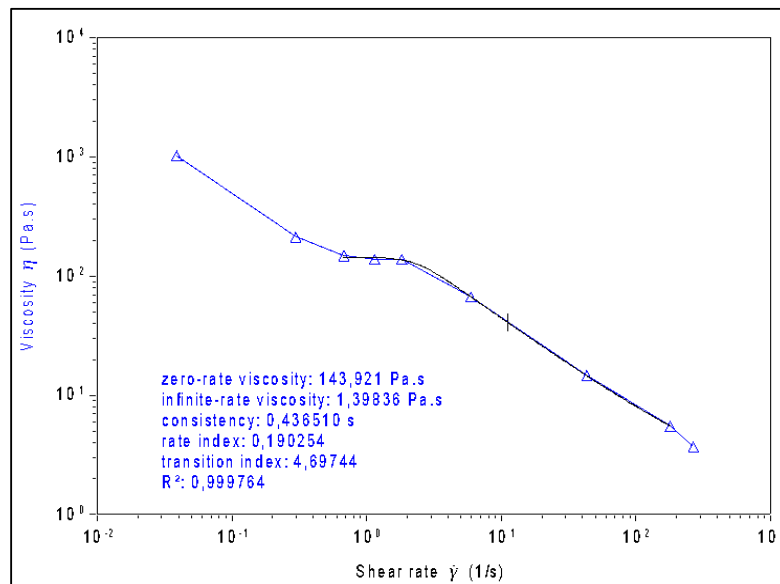
The pseudo-Newtonian behaviour is clearly seen only on curves at 25 ° C, which have an area in which the viscosity tends to remain constant (plateaux), it is more difficult to interpret the other curves at temperatures other than 25 ° C. The viscosity values that we can therefore consider as certainly more reliable are those taken when reaching the plateau area of the curve or in any case in the central position of the curve.



Bio44 at 10°C



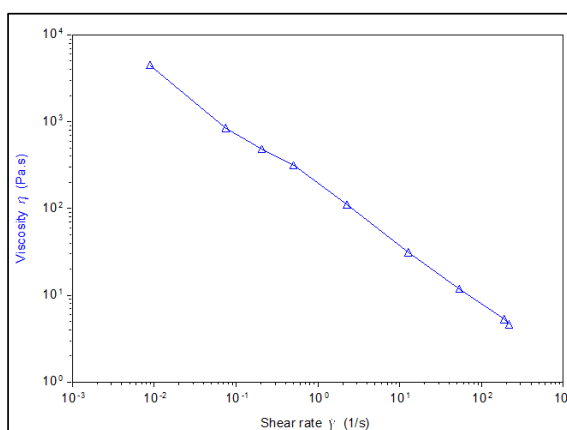
Bio44 at 40°C



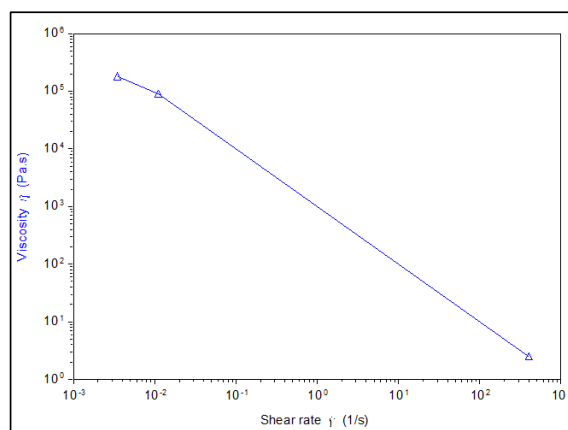
Bio44 at 25°C

Fig. 16. Viscosity of the natural adhesive (sample Bio44) as a function of rotation speed (rotary stress) at 10, 25 and 40 °C.

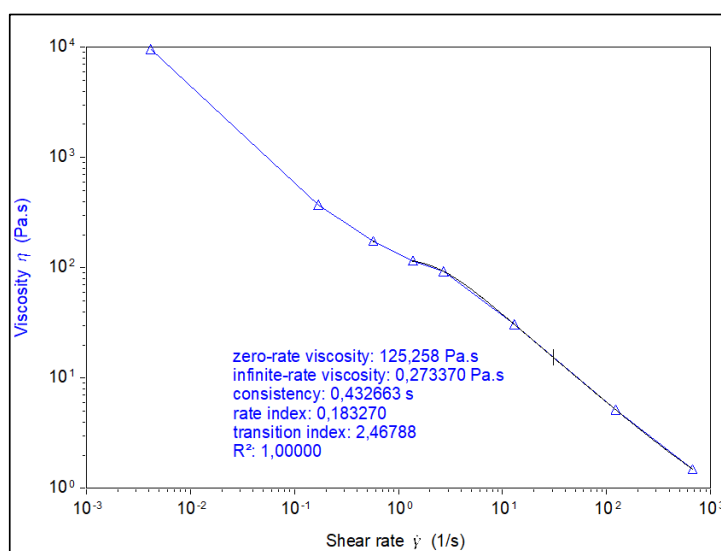
A similar behaviour to the Bio44 (not grindid) it was observed also for the Bio50, which was with an higher water content(Fig.16).



Bio50 at 10°C



Bio50 at 40°C



Bio50 at 25°C

Fig.17. Viscosity of the natural adhesive (sample Bio50) as a function of rotation speed (rotary stress) at 10, 25 and 40 °C.

In the case of the milled sample through Ball mill (Bio44T), a similar trend to that already observed in the corresponding previous measurements can be observed (Fig. 18), even if there is an increase in viscosity at temperatures of 10 and 25 °C compared to the previous measurements carried out on the Bio44 (not grinded sample).

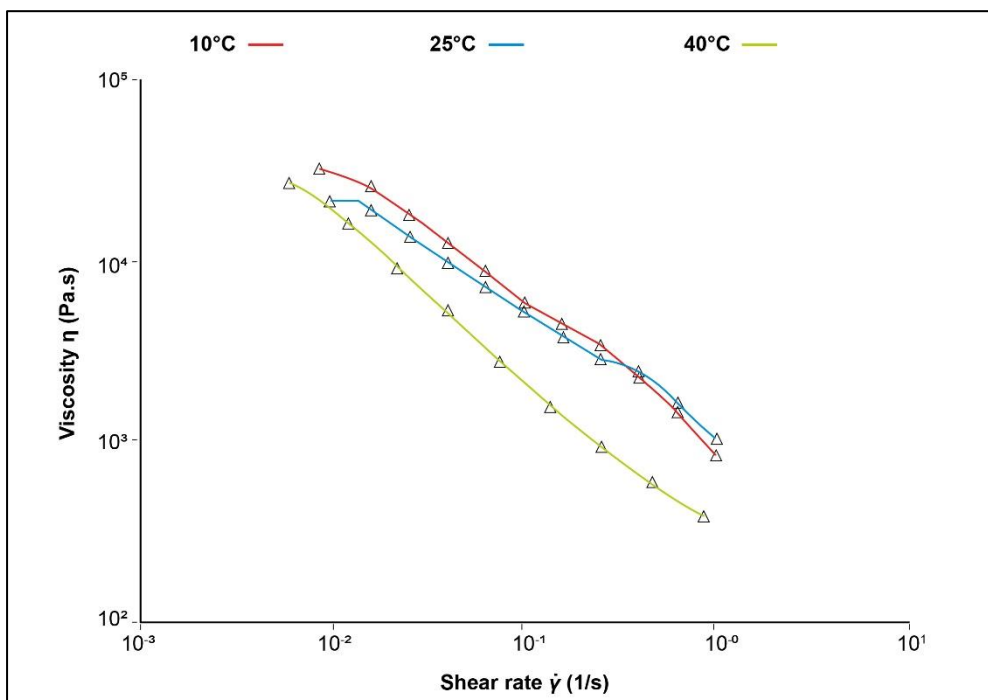


Fig. 18. Viscosity of the natural adhesive (Bio44T) as a function of rotation speed (rotary stress) at 10, 25 and 40 °C

In the following table 9 are reported the viscosity of the samples (Bio44, Bio50, Bio44T) obtained with different temperature.

Table 9. Viscosity values of the samples (Bio44, Bio50, Bio44T) obtained with different temperature

Temperature (°C)	Bio 44 Viscosity (Pa·s)	Bio 50 Viscosity (Pa·s)	Bio 44T Viscosity (Pa·s)
10	214	316	1550
25	140	125	510
40	120	100	175

Viscosity values of the natural adhesive were found to decrease with increasing the temperature of determination from 10 to 40 °C. The viscosity values of the sample named Bio44T at 10, 25 and 40 °C were respectively 1550, 510 and 175 Pa·s at shear rate of one rotation per second. These results

suggest a good operability of the natural adhesive at 25 °C since viscosity is low enough to give appropriate spreading and penetration into wood chips (Chen et al. 2017)¹¹⁵. However, the balance between viscosity and solids content is also important. The lower solids content of the natural adhesive (44%) than that of UF resins (typically 66%) implies excess water that might cause steam related internal voids (blows) during the particleboard manufacturing process (Dunky 1998)¹¹⁶. At each temperature level, the natural adhesive became thinner with the increase in shear force and the viscosity decreased (Fig. 18). The natural adhesive can thus be characterised as a shear thinning fluid that shows a non-Newtonian behaviour, as has been reported previously for soy protein adhesives (Zhang et al. 2005¹¹⁷; Frihart and Satori 2013¹¹⁸; Feng et al. 2018¹¹⁹).

4.1.3.5 ELECTRON MICROSCOPE ANALYSIS (SEM)

The following images (Fig.19) were taken on two air-dried samples:

- **Bio44 film** obtained by forming a thin film on glass and air dried.
- **Bio44T film** obtained as above but starting from the bio-glue treated in the ball mill 3 cycles of 2min 30Hz.

¹¹⁵ Chen, N., Zheng, P., Zeng, Q., Lin, Q., and Rao, J. (2017). "Characterization and performance of soy-based adhesives cured with epoxy resin," *Polymers* 9, 514.

¹¹⁶ Dunky, M. (1998). "Urea-formaldehyde (UF) adhesive resins for wood," *Int. J. Adhes. Adhes.*, 18, 95-107.

¹¹⁷ Zhang, J. T., Yang, X. Q., and Huang, L. X. (2005). "Changes of viscosity during preparation of soy protein isolate adhesives and their adhesive properties. *China Oils Fats*, 30, 68-70.

¹¹⁸ Frihart, C. R., and Satori, H. (2013). "Soy flour dispersibility and performance as wood adhesive. *J. Adhes. Sci. Technol.*, 27(18-19), 2043-2052.

¹¹⁹ Feng, C., Wang, F., Xu, Z., Sui, H., Fang, Y., Tang, X., and Shen, X. (2018). "Characterization of soybean protein adhesives modified by xanthan gum," *Coatings*, 8, 342.

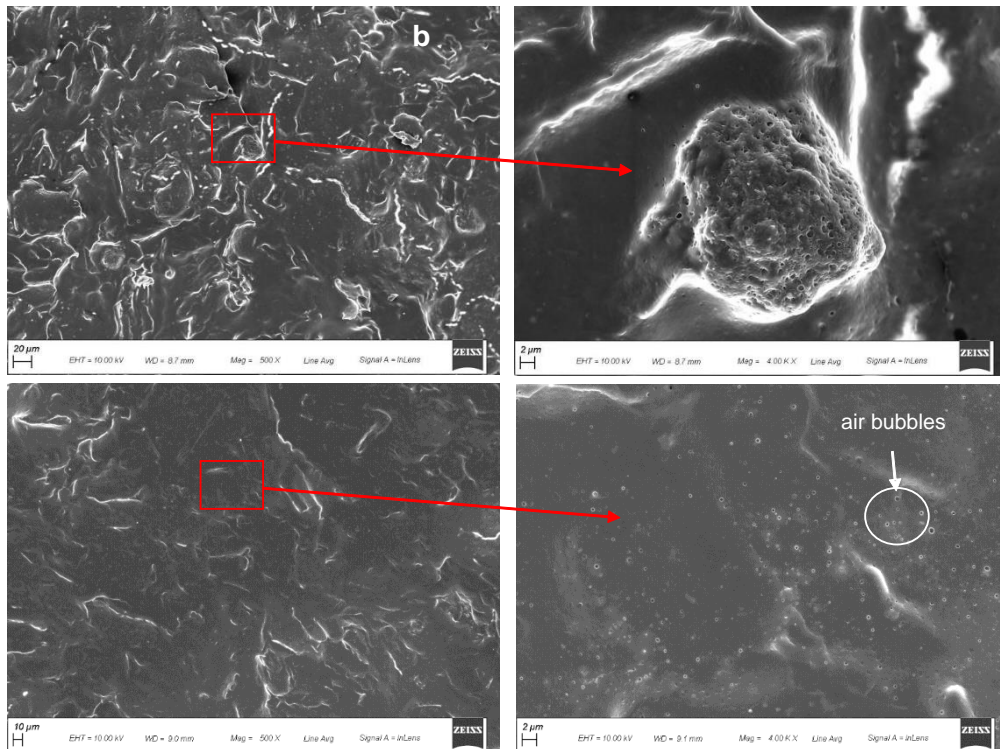


Fig. 19. SEM images on cured films of the natural adhesive before (a, b) and after (c, d) grinding with a ball mill for size reduction and homogenization. Images at the left (b, d) show enlarged details of the surface morphologies

The surface morphology of the cured adhesive samples with and without grinding of the adhesive mixture were examined using SEM analysis. The results showed that the surface morphologies of the samples varied in coarseness (Fig. 19). Without grinding, it was noted the presence of numerous granules with variable diameters ranging from 10 to 30 microns (Fig 19a). Morphological details of a single grain can be seen in Fig.19b. The grinded adhesive showed a smoother and more uniform surface with no granules (Fig.19). The finer particle size of the grinded natural adhesive should provide more surface area and greater bond strength. Closer examination revealed the presence of very small air bubbles (diameter < 0.5 μ m) (Fig. 19d), probably due to the ball mill treatment. An indication that these structures are small bubbles and not granules is given by their perfectly circular shape.

4.1.3.6 BIOLOGICAL TESTS

About the **antimicrobial activity**, two samples have been compared: Bio44T and BioAg44T (with the addition of 0,01% of Ag). The following controls were realized:

- ***Escherichia coli* Graphs (Negative-Gram)**

- *Staphylococcus aureus* Graphs (Positive-Gram)
- *Pseudomonas aeruginosa* Graphs (Positive-Gram)

Here are reported graphs and results obtained:

Escherichia coli Graphs (Negative-Gram)

Regarding E. coli, is observed by both glue samples a reduction in the viable cells from the first hours of treatment with respect to trend of growth of the bacterial strain of control.

By calculating the percentage of cells remaining viable compared to the control already starting from the 4 hours of treatment, a vitality is observed about 1% in both BIO 44T and BIO Ag 44T; after the 8 hours of treatment with BIO Ag 44T in the sample the percentage of bacterial cells remaining viable is equal to 0. In the sample treated with BIO 44T instead we still have a number of viable cells, although close to 0 of 0.12% at 8h and 0.05% at 12h (Fig. 20, 21 and 22).

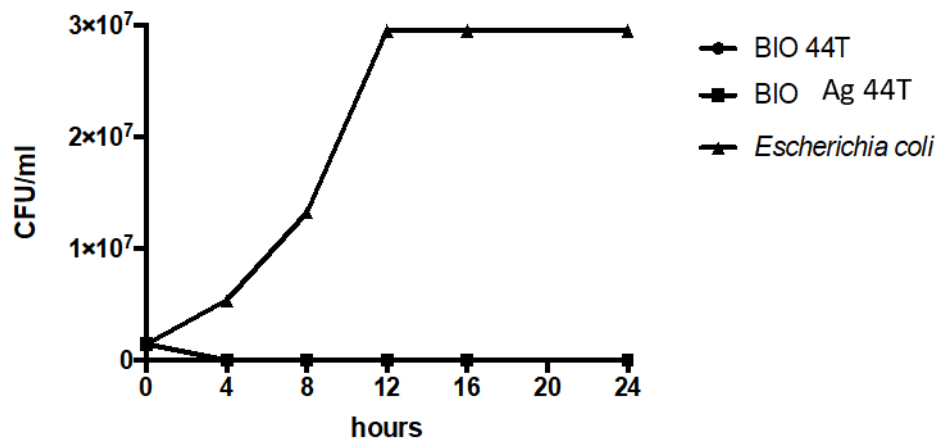


Fig. 20. Trend of the bacterial strain of control E. coli and viable cells (CFU / ml)

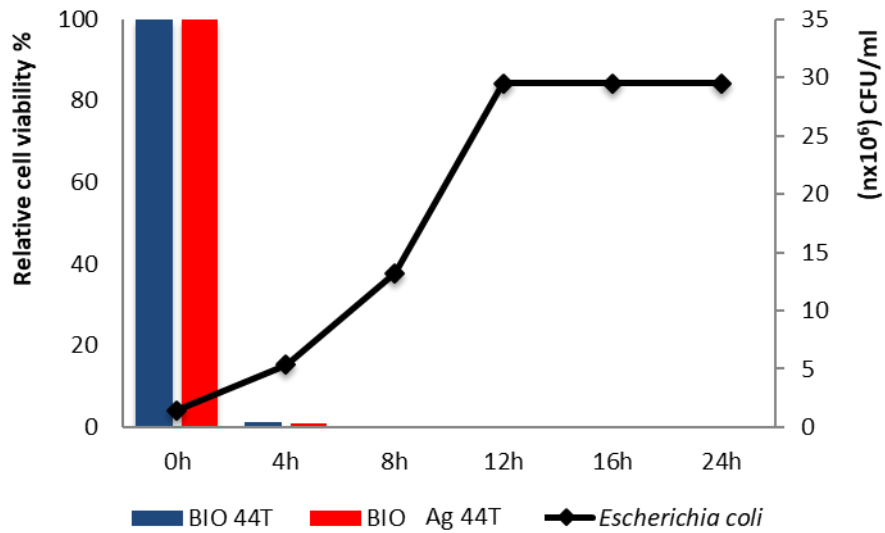


Fig.21. % of relative cells viability/hours in the control and in the two treatments

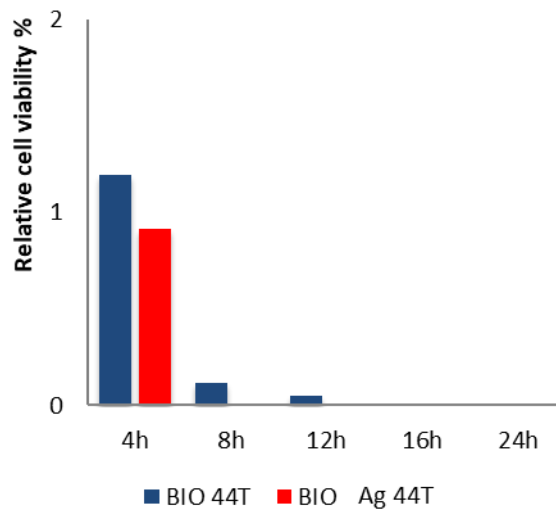


Fig. 22. % of relative cell vitality/hours in the two treatments

***Staphylococcus aureus* Graphs (Positive-Gram)**

Concerning *S. aureus*, a reduction in the viable cells from the first hours of treatment by both glue samples is observed with respect to the growth of the bacterial control strain. In particular, in chart a) it can be seen that BIO Ag 44T acts more quickly than BIO 44T within 4 hours.

This trend can be better appreciated by the percentage value of the cells remaining viable compared to the control (Fig. 23, 24 and 25).

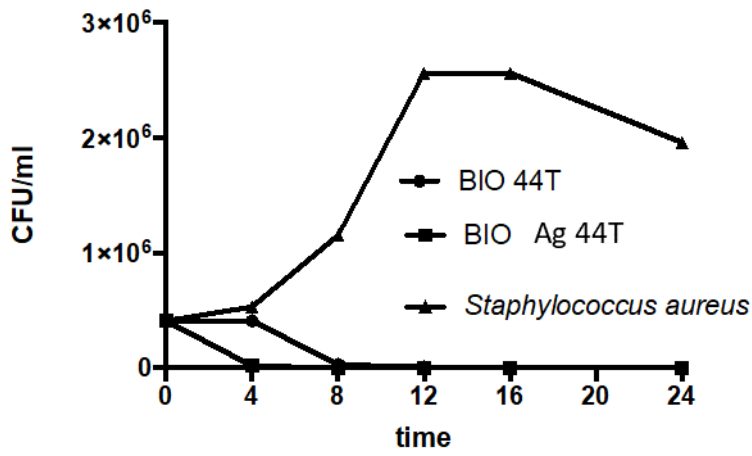


Fig. 23. Trend of the bacterial strain of control *S. aureus* and viable cells (CFU / ml)

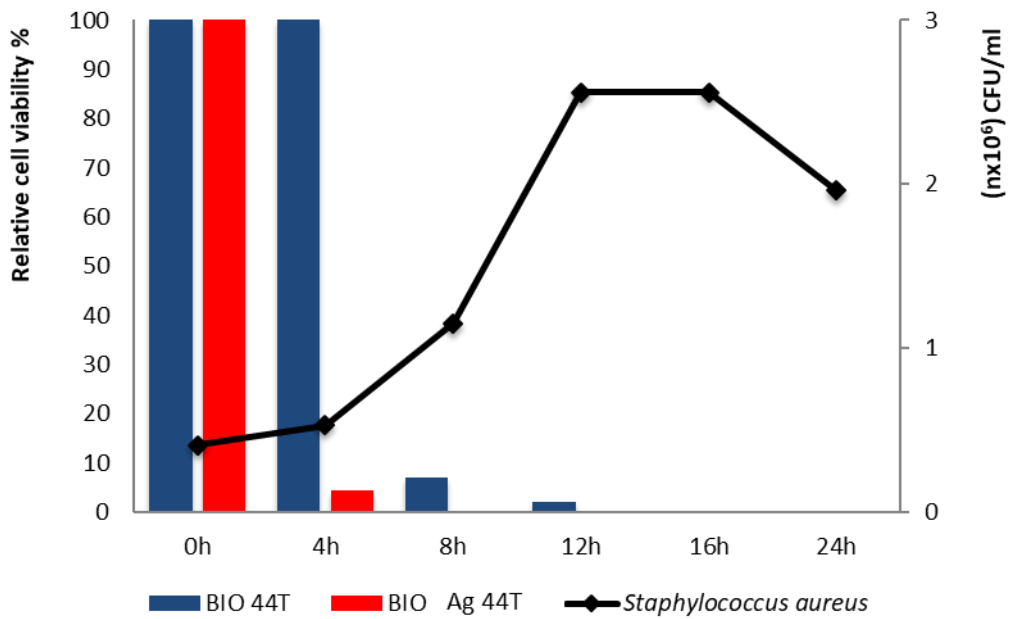


Fig. 24. % of relative cells viability/hours in the control and in the two treatments

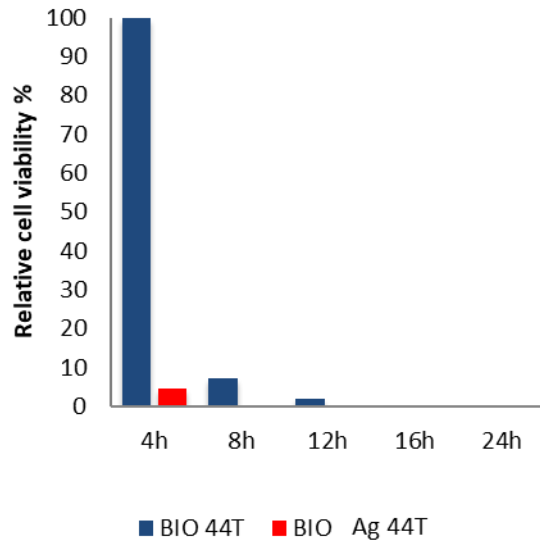


Fig. 25. % of relative cell vitality/hours in the two treatments

***Pseudomonas aeruginosa* Graphs (Positive-Gram)**

As regards *P. aeruginosa*, a bacterium capable of producing resistant biofilms on wet surfaces, a reduction of the viable cells from the first hours of treatment by both glue samples is observed with respect to the growth of the control bacterial strain. In particular, in chart a) it can be seen that BIO Ag 44T acts more quickly than BIO 44T within 4 hours.

This trend can be better appreciated by the percentage value of the cells remaining viable compared to the control. The graph b) shows in fact a% equal to 8 of cells left vital after the 8h of treatment with BIO 44T (Fig. 26, 27 and 28).

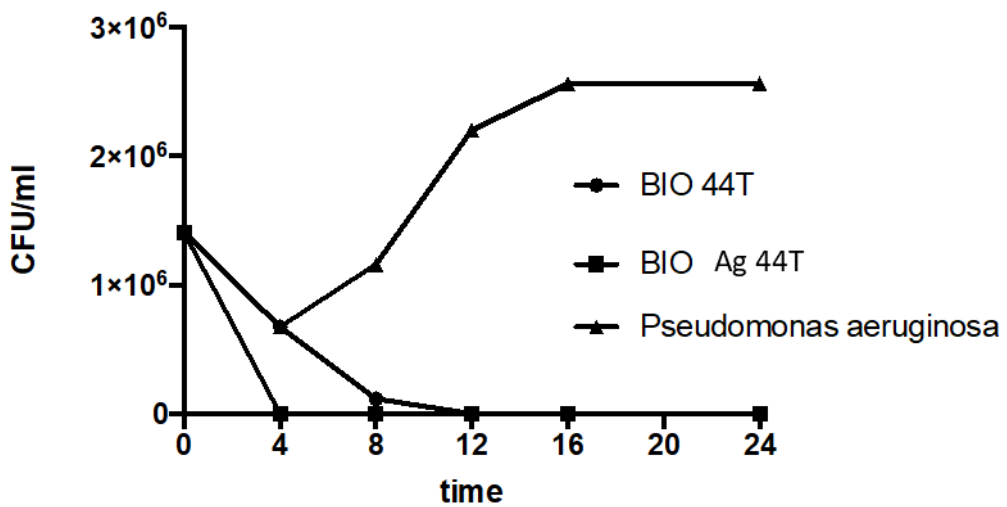


Fig. 26. Trend of the bacterial strain of control *P. aeruginosa* and viable cells (CFU / ml)

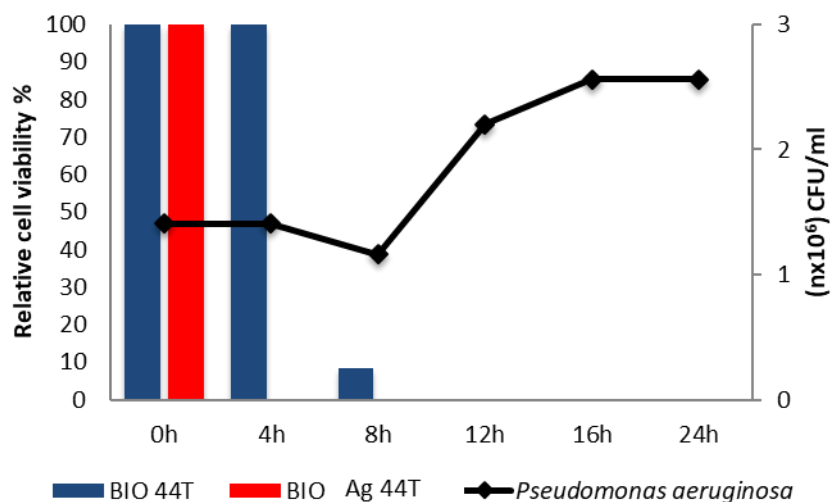


Fig. 27. % of relative cells viability/hours in the control and in the two treatments

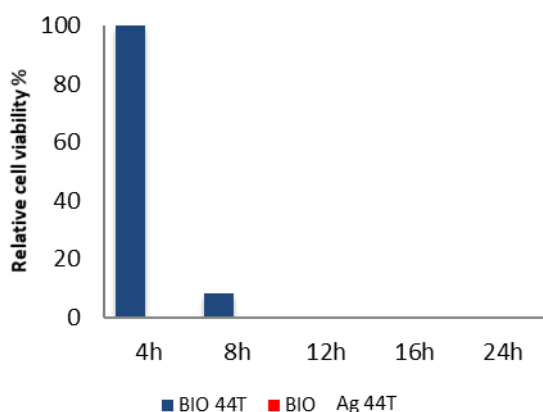


Fig. 28. % of relative cell vitality/hours in the two treatments

The main conclusions about the antimicrobial activity tests is that in all of them is observed by both glue samples a reduction in the viable cells from the first hours of treatment with respect to trend of growth of the bacterial strain of control. In general, BIO Ag 44T acts more quickly than BIO 44T within 4 hours.

4.1.3.7 HEADSPACE GAS CHROMATOGRAPHY-MASS SPECTROMETRY (HEADSPACE GC-MS)

Headspace Gas Chromatography-Mass Spectrometry (Headspace GC-MS) analysis were carried out in order to verify the absence of emissions of harmful substances both from the natural adhesive and from the liquid enzymatic hydrolysate, in order to assess possible risks

not only in the use of the glue, but also in the realization process. The analyses were carried out at a temperature of 40 °C (Fig. 29 and 30, Table 9 and 10).

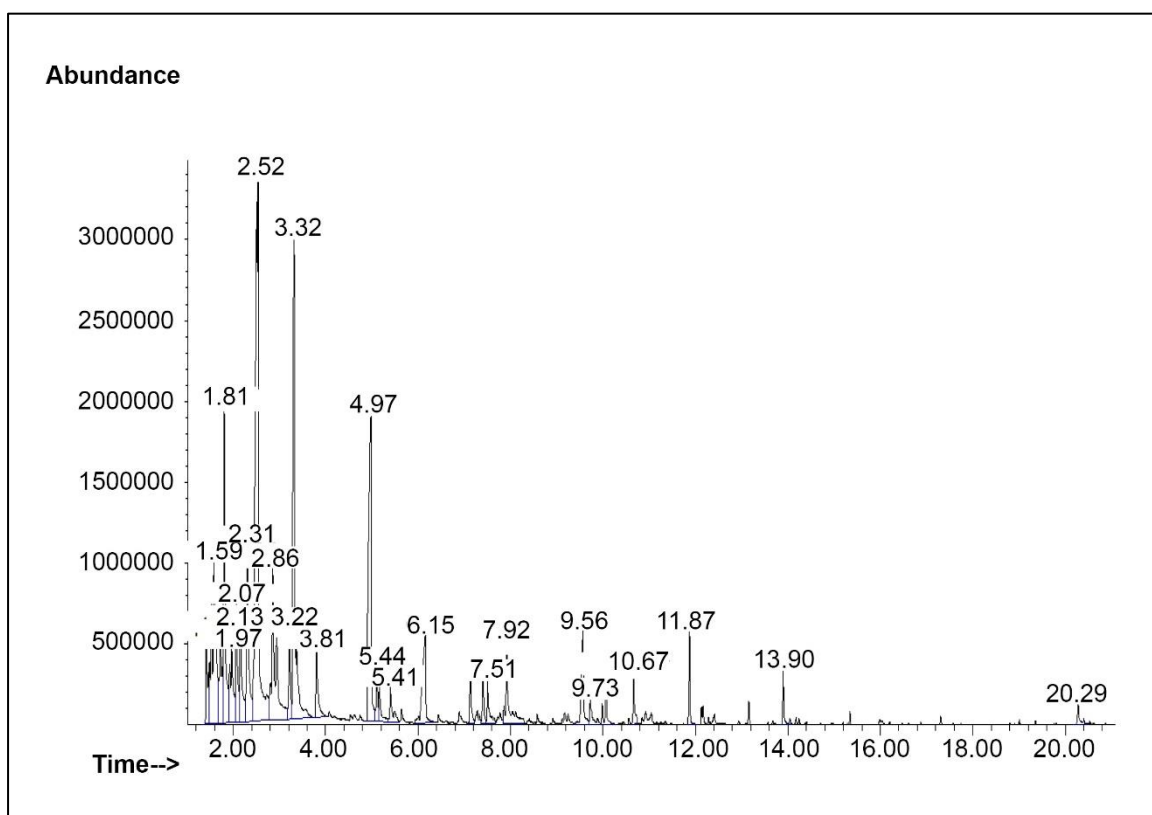


Fig. 29 Headspace Gas Chromatography-Mass Spectrometry (Headspace GC-MS) of the natural adhesive

Table 9. Compounds Identified and Correspondence in the GC-MS of the Natural Adhesive

Retention Time (RT)	Compound identified	CAS number	Correspondence
1.73	1,3-Butanediol	000078-93-3	42%
1.81	1-Propanol, 2-methyl-	000078-83-1	95%
1.97	Butanal, 2-methyl-	000096-17-3	49%
2.07	1-Penten-3-ol	000616-25-1	72%
2.31	Silanediol, dimethyl-	001066-42-8	64%
2.52	1-Butanol, 2-methyl-	001565-80-6	78%

2.87	1-Pentanol	000071-41-0	90%
3.31	Hexanal	000066-25-1	83%
4.97	1-Hexanol	000111-27-3	78%
5.40	2-Heptanone	000110-43-0	91%
6.14	Oxime-, methoxy-phenyl-	1000222-86-6	90%
7.41	1-Octen-3-ol	003391-86-4	90%
7.92	Cyclotetrasiloxane, octamethyl-	000556-67-2	91%
10.67	Cyclopentasiloxane, decamethyl-	000541-02-6	94%

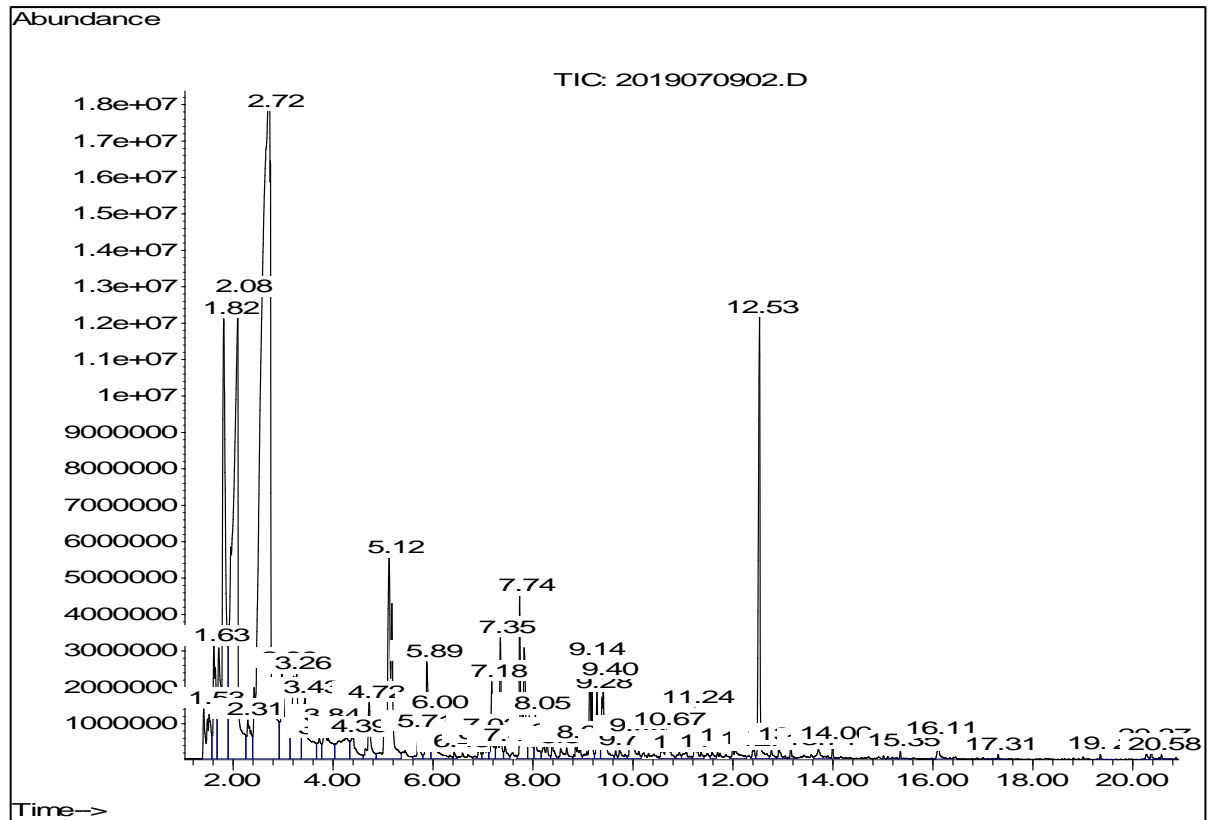


Fig. 30 Headspace Gas Chromatography-Mass Spectrometry (Headspace GC-MS) of Liquid Enzymatic hydrolysate.

Table 10. Compounds Identified and Correspondence in the GC-MS of the Liquid Enzymatic hydrolysate.

Retention Time (RT)	Compound identified	CAS number	Correspondence
1.63	1-Propanol	000071-23-8	72%
1.82	1-Propanol, 2-methyl-	000078-83-1	94%
2.08	Acetic acid	000064-19-7	91%
2.72	1-n-Butoxy-2,3-dimethyldiaziridine	343928-70-1	50%
5.12	1-Butanol, 3-methyl-, acetate	000123-92-2	90%
12.53	Benzene, 1-methoxy-4-(1-propenyl)-	000104-46-1	98%

According to Headspace Gas Chromatography-Mass Spectrometry (Headspace GC-MS) analysis GC-MS results, no dangerous volatile substances were released from the natural adhesive in thermal equilibrium condition at 40°C (Fig. 29 and Table 9). The main volatile molecules detected in the headspace are alcohols and chitons. Cyclotetrasiloxane and cyclopentasiloxane, also detected, are cyclic dimethyl polysiloxane compounds and are commonly used in cosmetic products. The Cosmetic Ingredient Review Expert Panel has concluded that these ingredients are safe in the present practices of use and concentration. In detail, available data on these compounds did not suggest skin irritation or sensitization potential, and also, it is not likely that dermal exposure would cause significant systemic exposure (Johnson Jr et al. 2011)¹²⁰.

Considerations

The main considerations after the analysis performed at UNICAM on the natural adhesive under study are:

¹²⁰ Johnson Jr, W., Bergfeld, W. F., Belsito, D. V., Hill, R. A., Klaassen, C. D., Liebler, D. C., Marks Jr, J. G., Shank, R. C., Slaga, T. J., Snyder, P. W., and Andersen, F. A. (2011). "Safety assessment of cyclomethicone, cyclotetrasiloxane, cyclopentasiloxane, cyclohexasiloxane, and cycloheptasiloxane," *Int. J. Toxicol.*, 30, 149-227.

- The thermal analysis of the Bio44T sample, treated on the ball mill, (fig.11) shows substantially the same behaviour as the Bio44 sample, even if the Bio44T seems to get rid of water more easily, in fact the energy needed to remove the water is lower $\Delta H = 424 \text{ J / g}$ (although the lower value could also be due to a smaller amount of water, which could have been eliminated during the ball mill grinding process).
- Furthermore the maximum of the endothermic water elimination signal falls to 110 degrees instead of 114 ° C.
- In both Bio44 and Bio44T samples there are no exothermic signals associated with a possible cross-linking, or they fall within a temperature range of 115-140 ° C and are therefore covered by the intense water signal.
- At 25 °C a rheological analysis showed a typical behaviour of thixotropic fluids which tend to pass from the state of pasty (almost solid) fat to that of liquid.
- The Bio44T sample grinded by ball mill, analysed the morphology with a SEM for both magnifications (500 and 4000 times), had a much more regular surface and it wasn't detect the presence of any granules.
- In the Headspace GC-MS analysis on Bio44T and liquid enzymatic hydrolysate no dangerous substances are detected. The detected Cyclotetrasiloxane and Cyclopentasiloxane, inert substances, normally used to produce creams for body use, could provide lubricating properties and be helpful in improving the viscosity characteristics of the binder.
- At the end of the characterization activities and described on the previous paragraphs, it results that the natural adhesive named **Bio44T** (where it means *Natural Adhesive with 44% in H₂O, grinded (T) in the ball mill 3 cycles of 2min at 30Hz*) has shown promising characteristics in order to be used as binder for plywood and particleboard applications.

4.1.4 HYBRID RESINS: SYNTHETIC RESINS MIXED WITH NATURAL ADHESIVE (BIO44T)

After the characterization, the Natural Adhesive (Bio44T) was mixed with other commercial resins (UF, PAE, PF, PMDI), Table 11 and 12.

Each combination was prepared 3 times (in total 51 samples).

The effects of these mixes were evaluated through TGA/DTA Analysis (Table 13) and on the particleboard prototypes (par. 4.2.3 and par. 4.2.4)

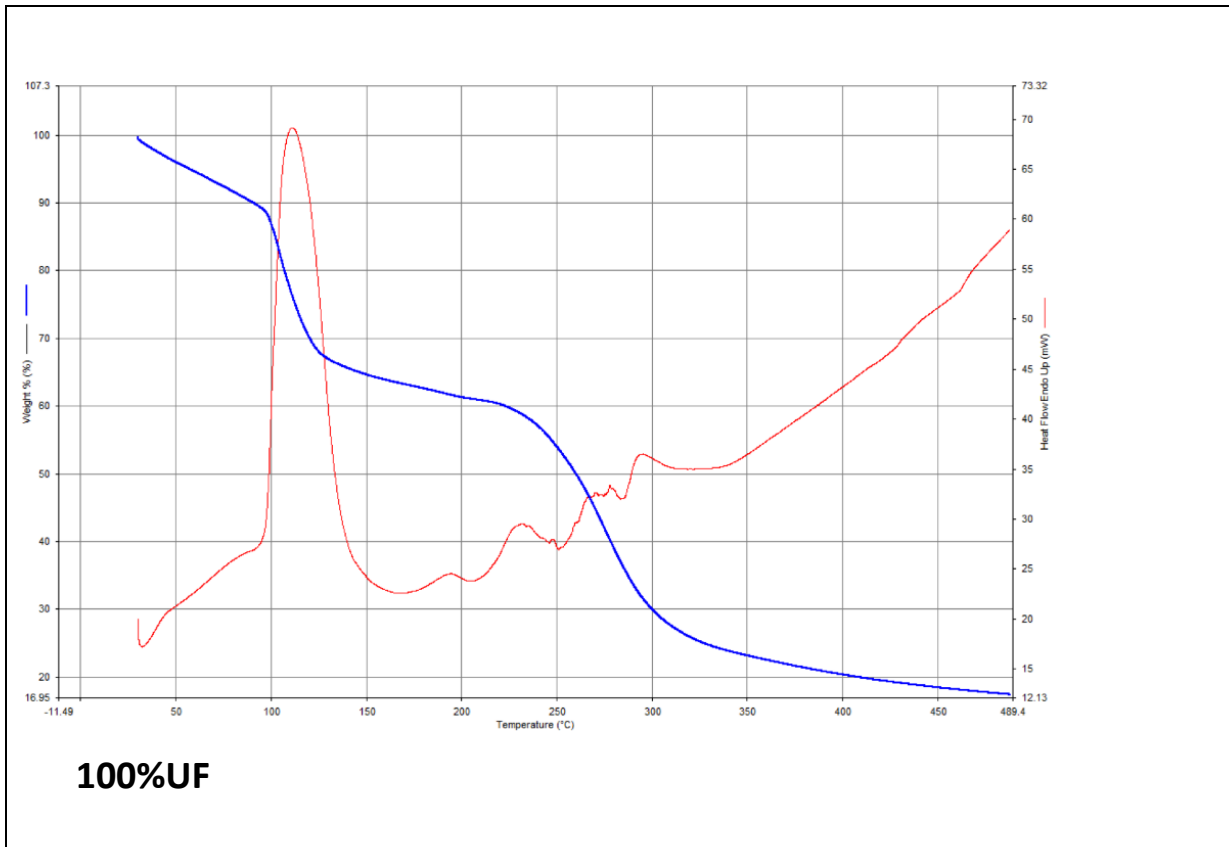
Table 11. Commercial resins selected and used in this work

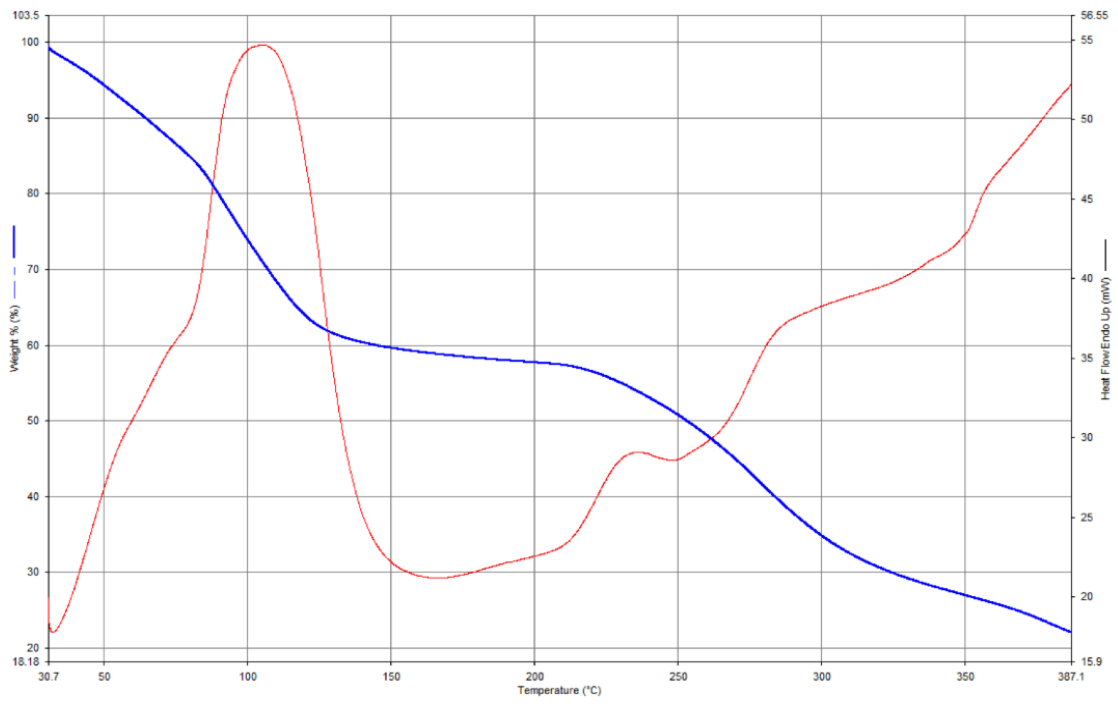
Synthetic (S) Resin	Commercial resins selected
Urea Formaldehyde (UF)	Urea Formaldehyde, U208 by OMNIA KOLL s.r.l (see Technical sheet)
Polyamideamine-epichlorohydrin (PAE)	Polyamide Epichlorohydrin Resin (PAE 12.5%) was purchased by Wuhan Golden Wing Industry & Trade Co., Ltd.
Phenol Formaldehyde (PF)	Phenol Formaldehyde MARFEN 100 was provided by Saglamlar Plywood
Polymeric Methylene Diisocyanate (PMDI)	PMDI, Protopur PN was purchased at COLLANTI CONCORDE s.r.l.

Table 12. Percentages of Synthetic (S) resins and Natural Adhesive (N) used

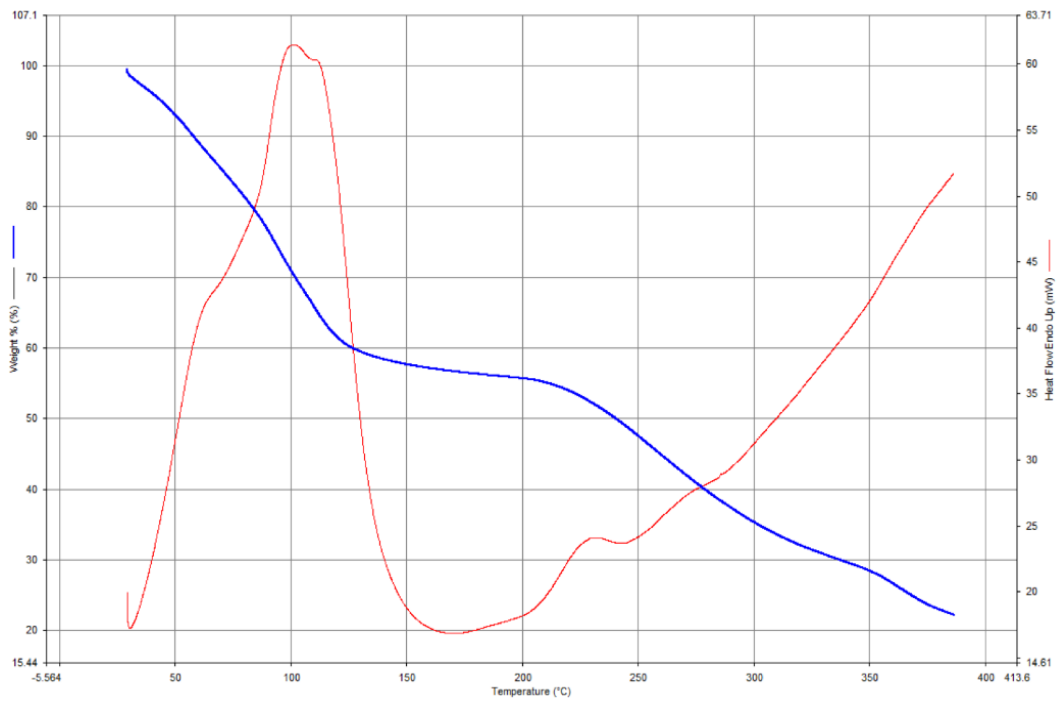
% Synthetic (S)	% Natural Binder (N)
100	0
67	33
50	50
33	67
0	100

Table 13. TGA-DTA (TGA blue curve, DTA red curve) results of the mix between natural adhesive and synthetic crosslinkers (UF, PAE, PF, pMDI) of 0:100 %, 33:67 %, 50:50 %, 67:33 % and 100:0%

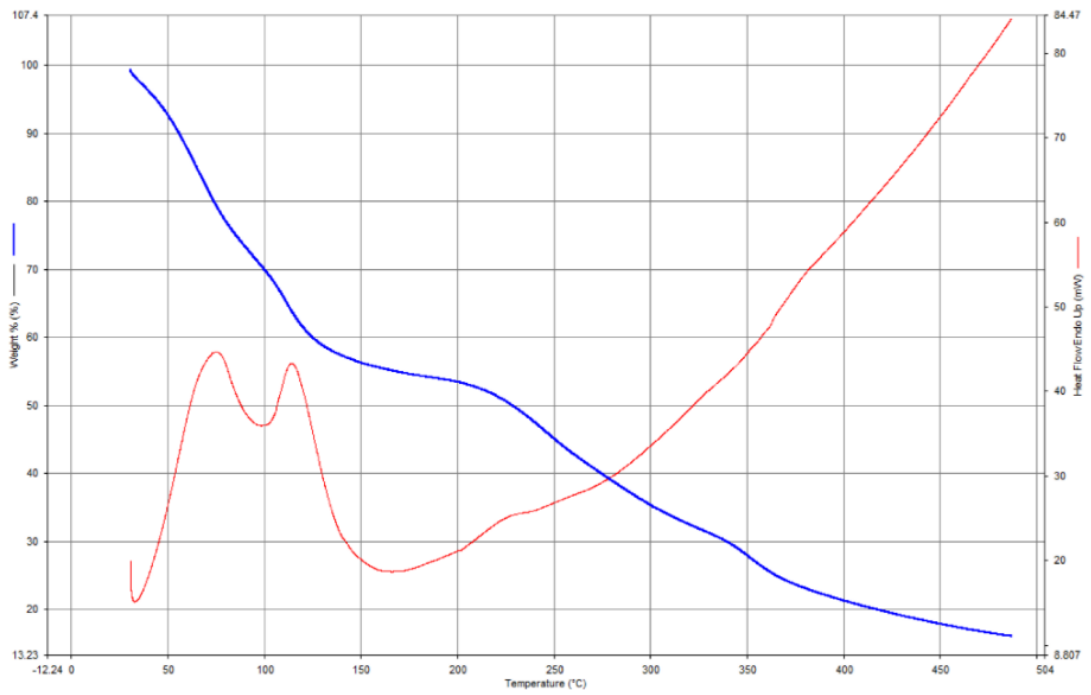




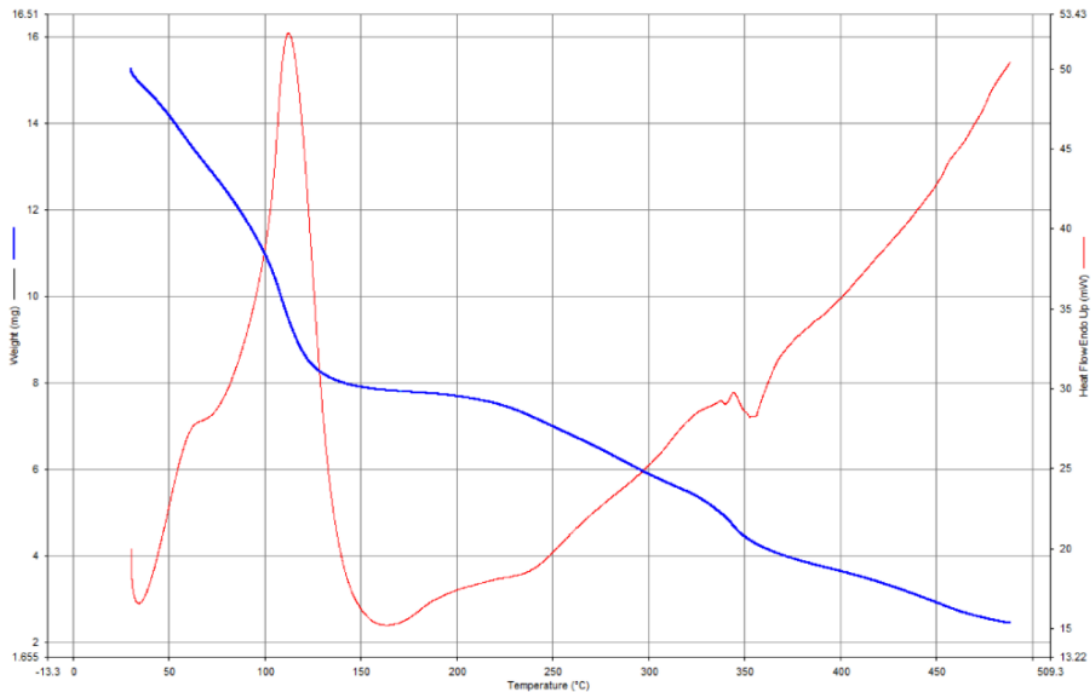
33%Bio44T: 67%UF



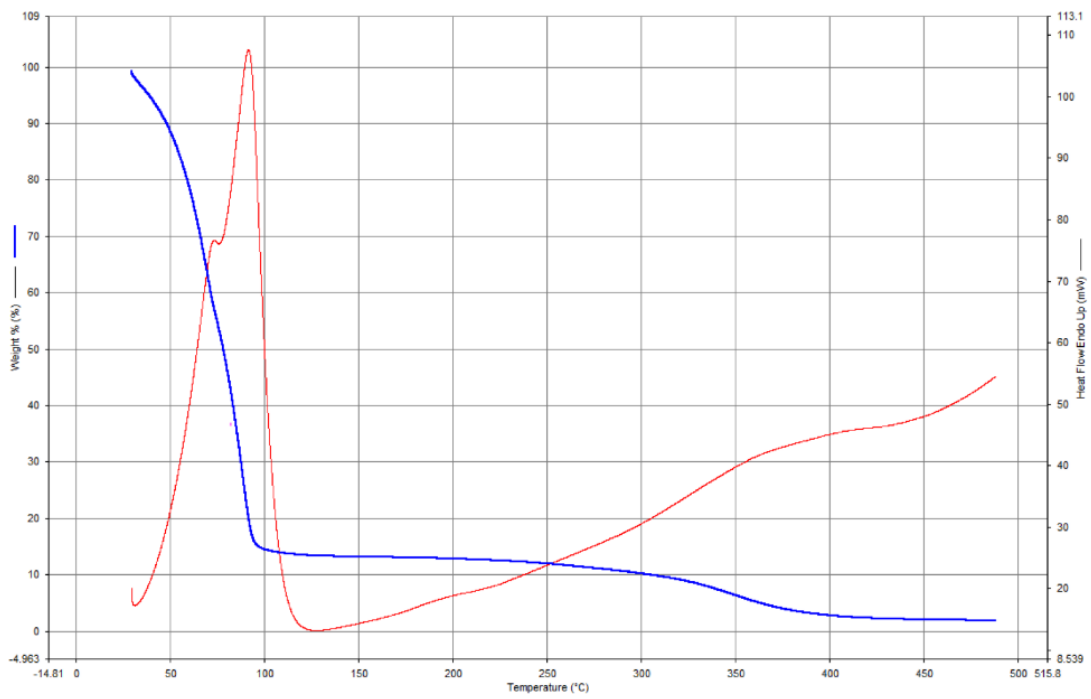
50%Bio44T: 50%UF



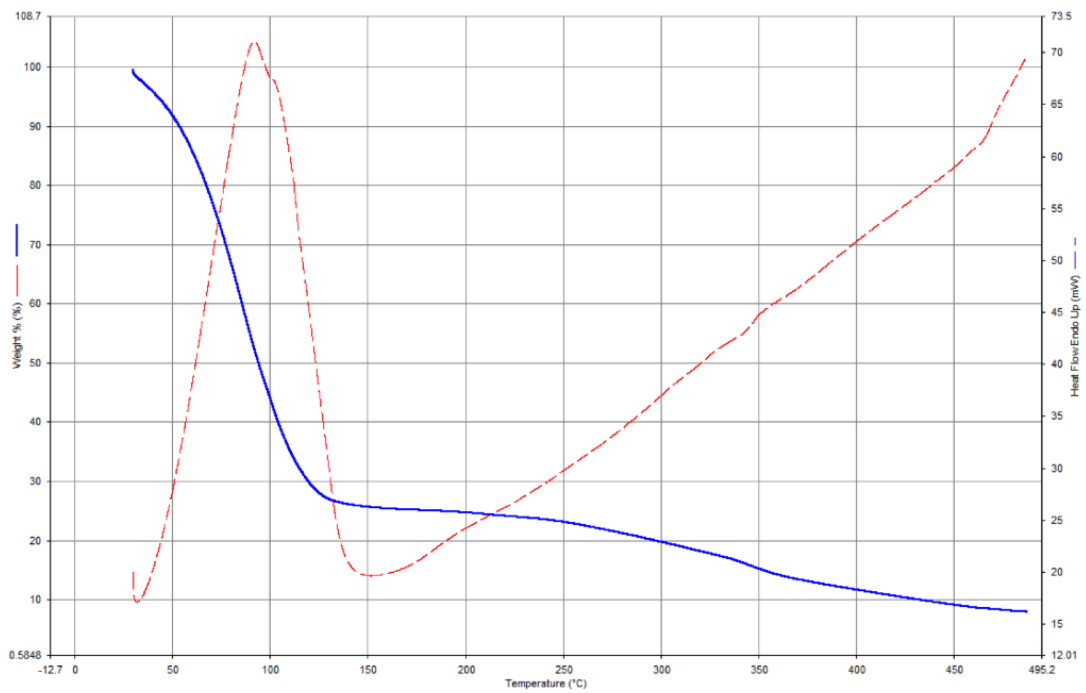
67%Bio44T:33%UF



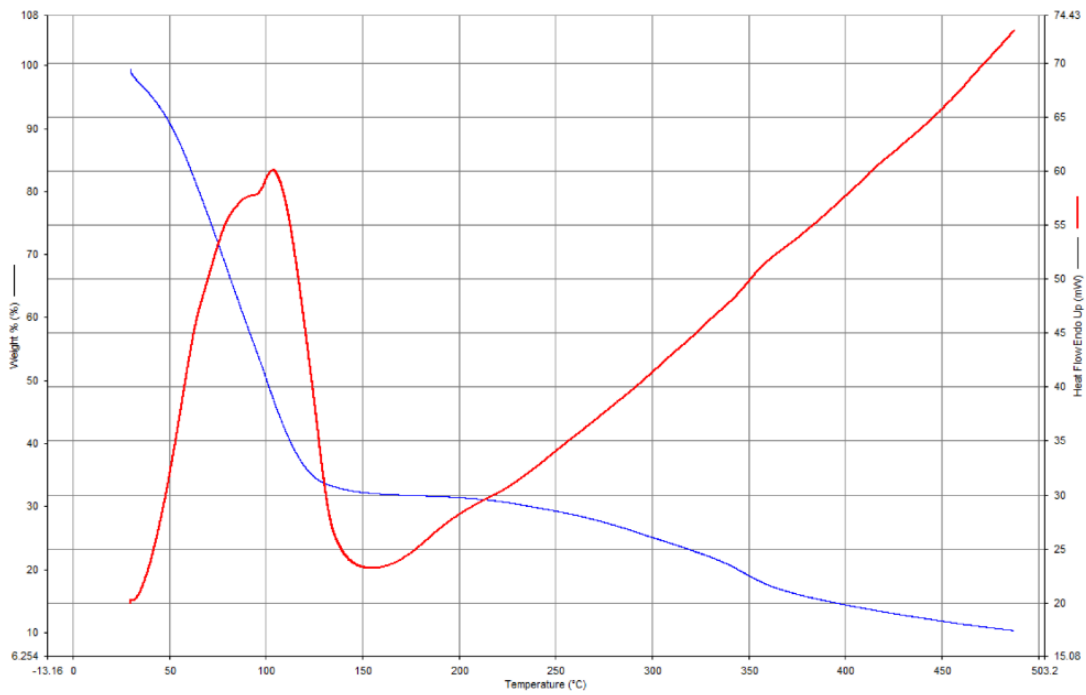
100%Bio44T



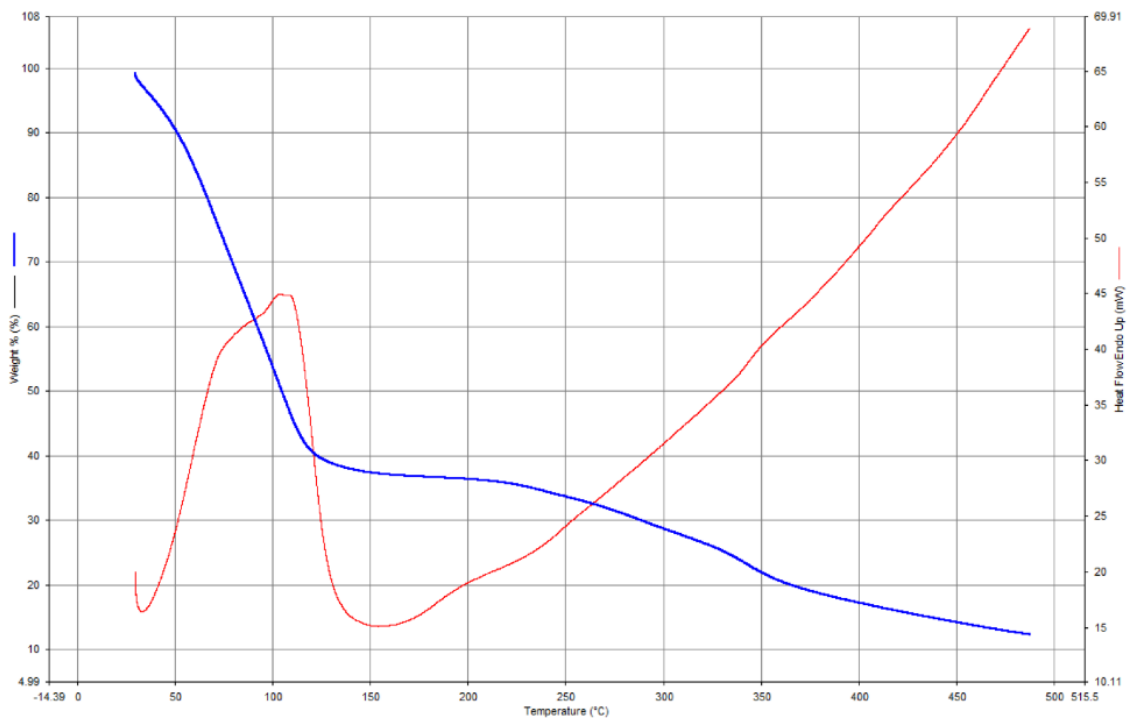
100%PAE



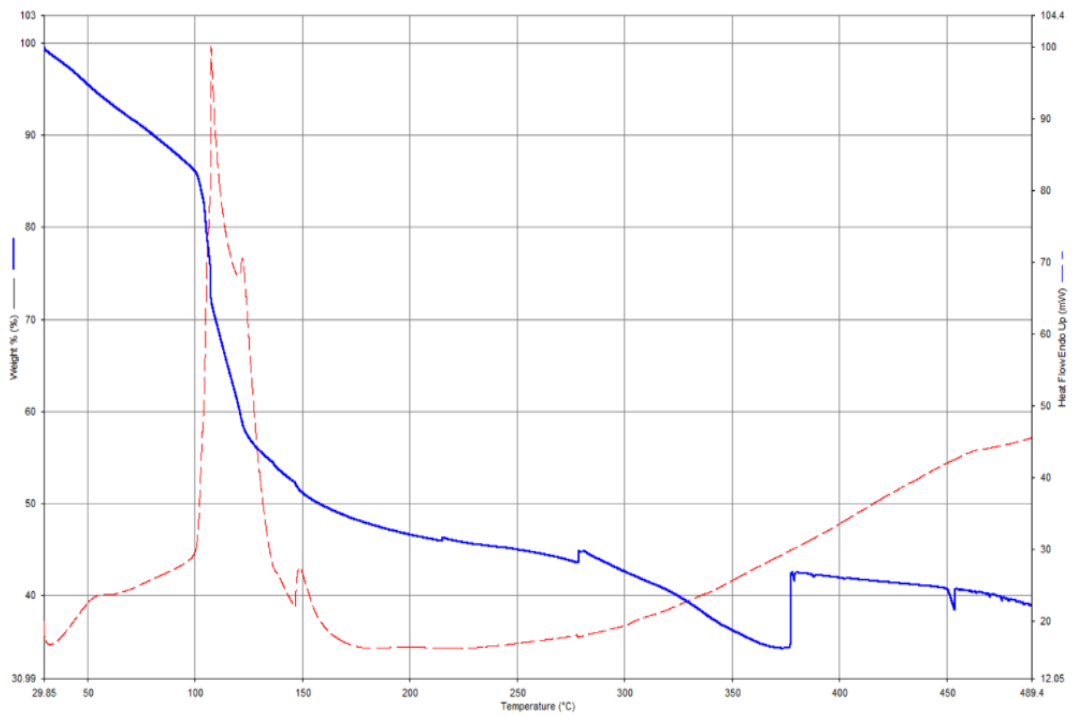
33%Bio44T:67%PAE



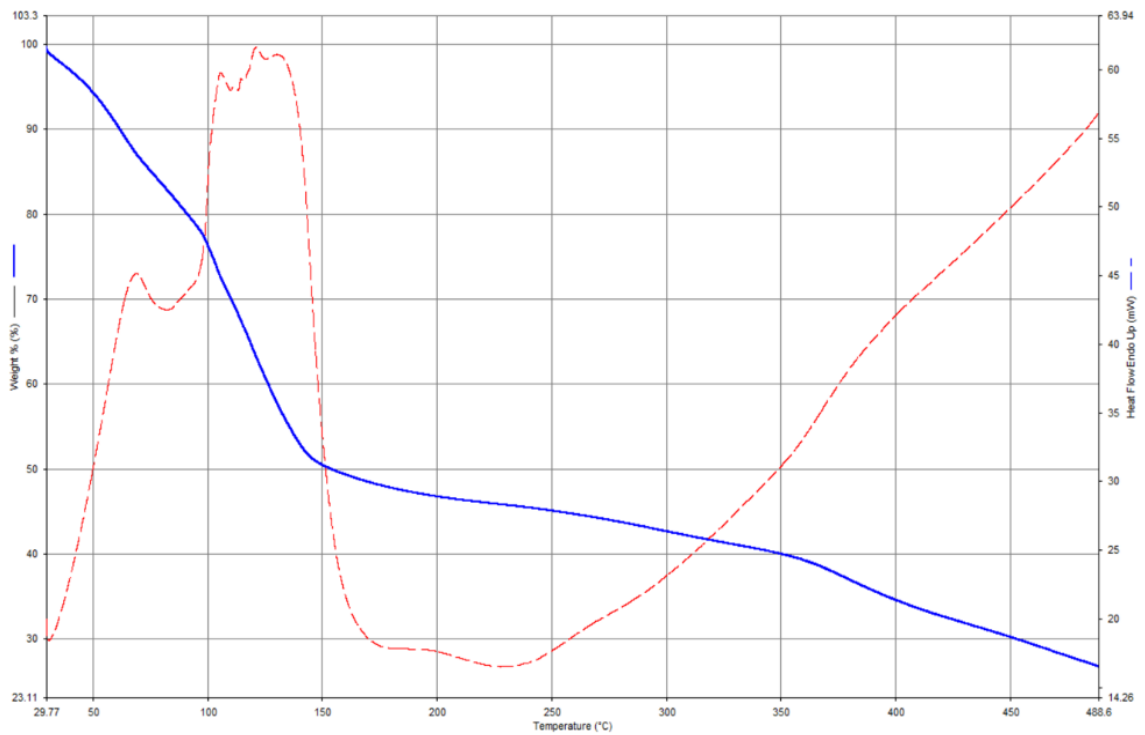
50%Bio44T:50%PAE



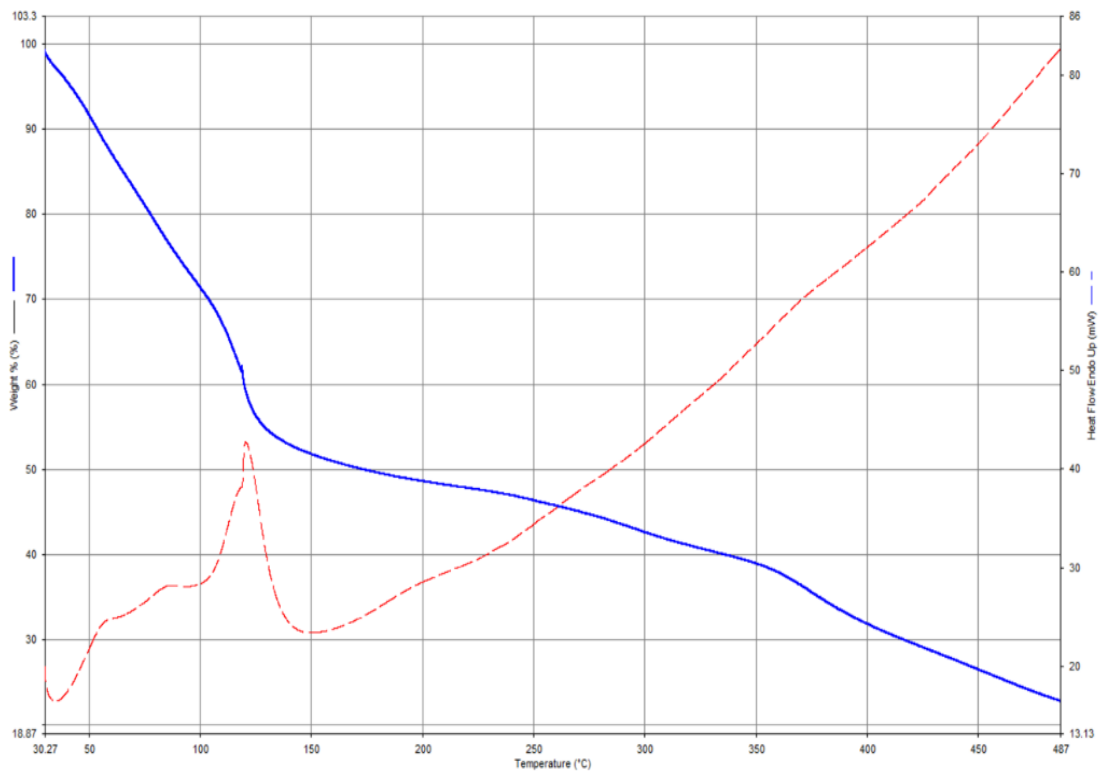
67%Bio44T:33%PAE



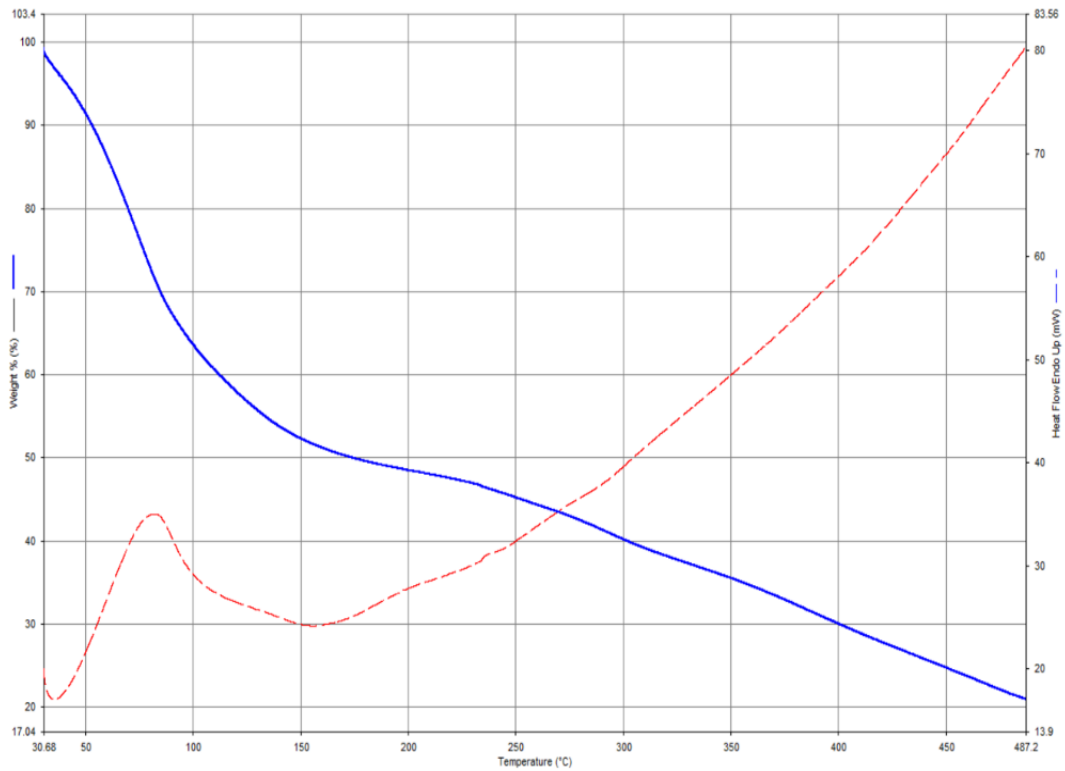
100%PF



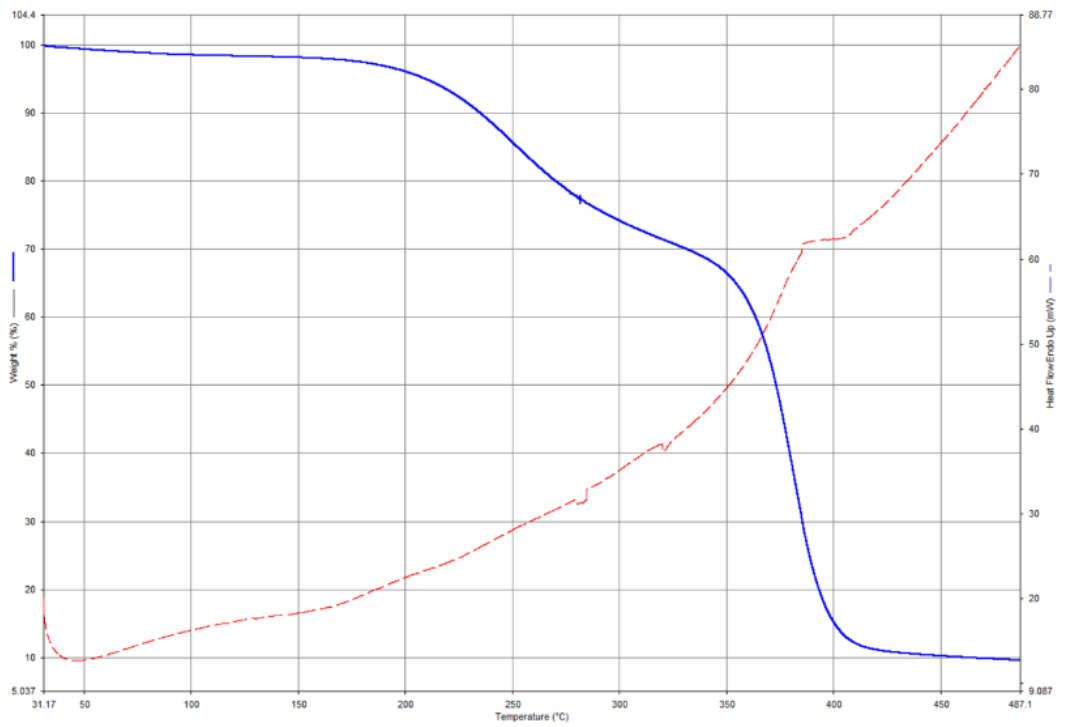
33%Bio44T:67%PF



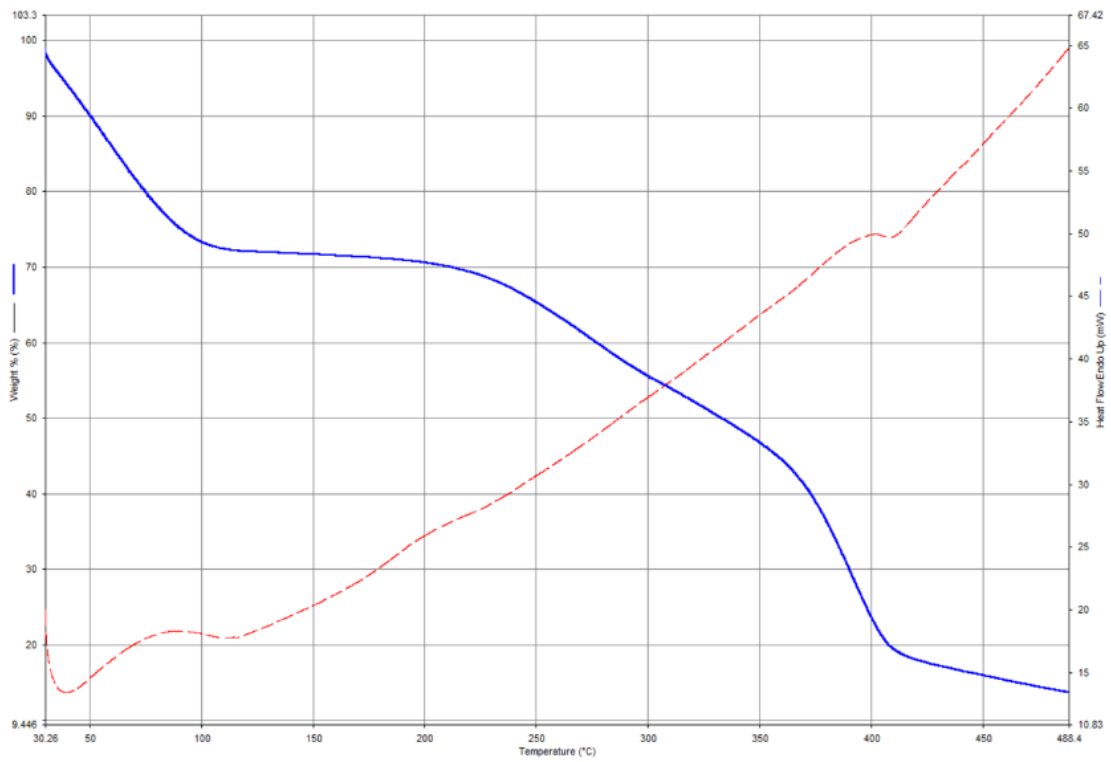
50%Bio44T:50%PF



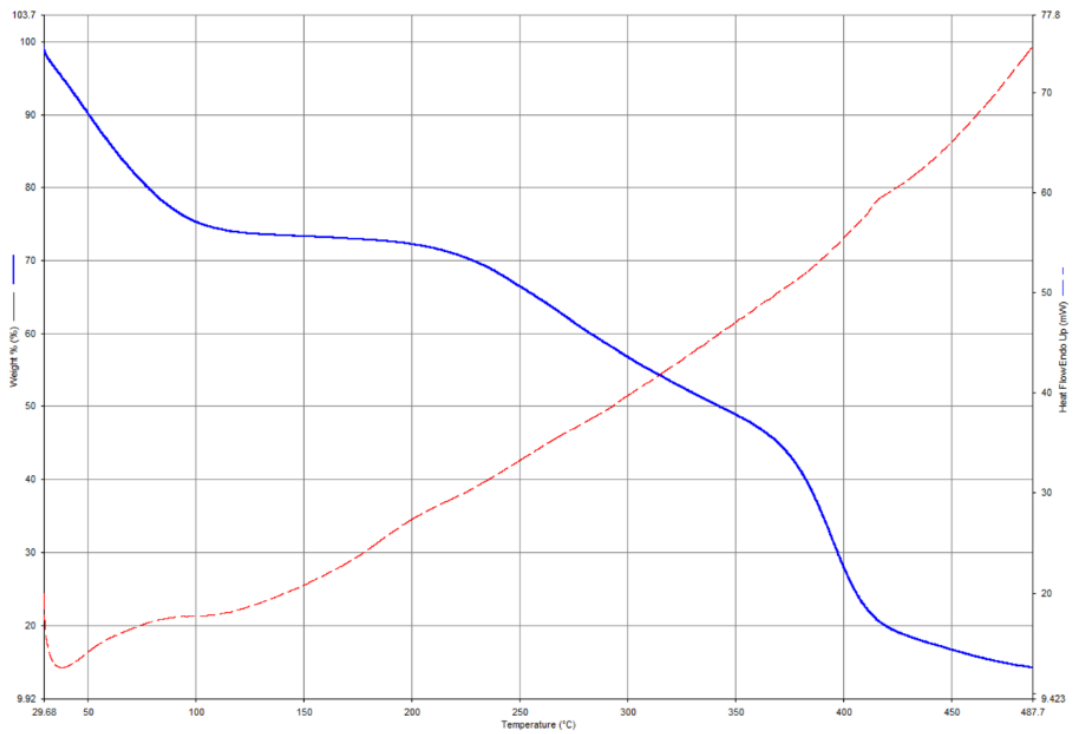
67%Bio44T:33%PF



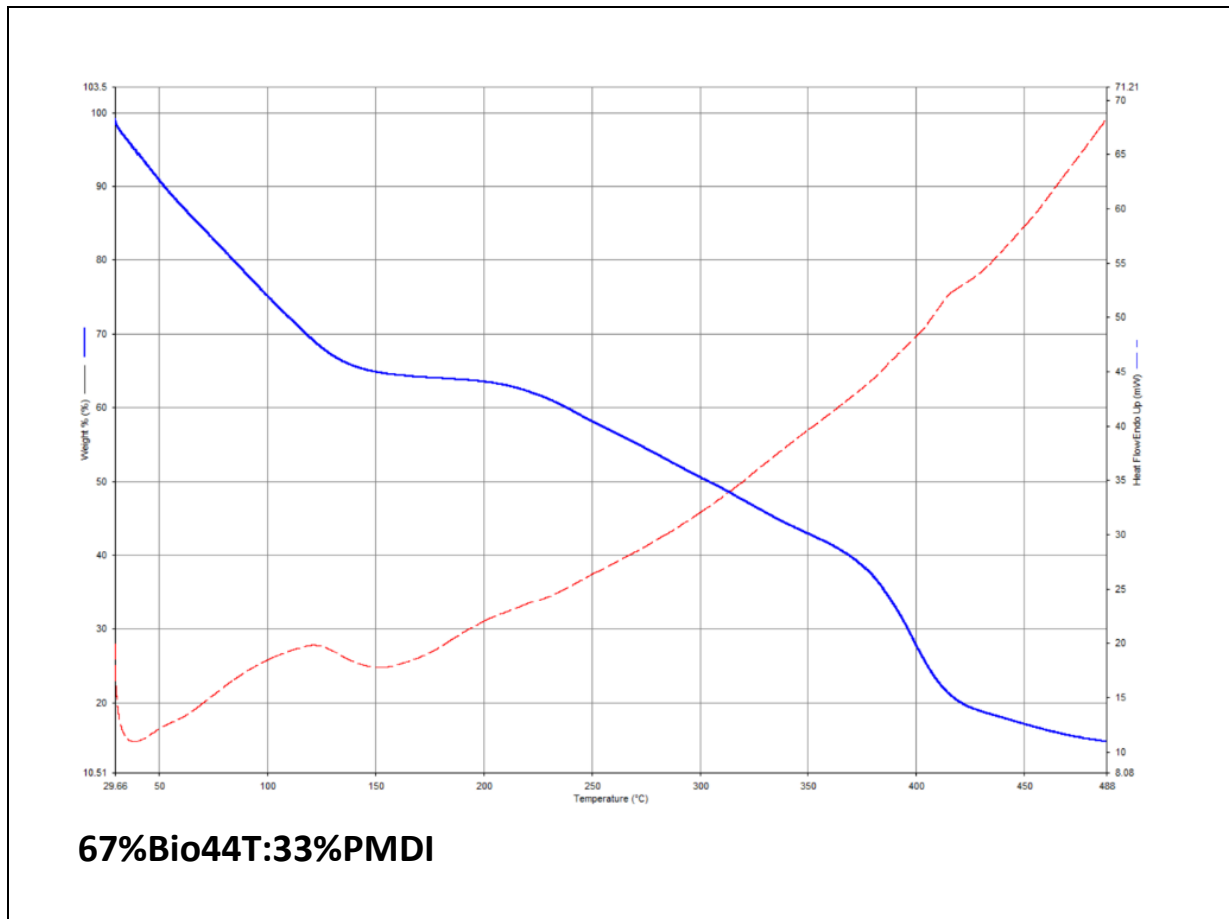
PMDI100%



33%Bio44T:67%PMDI



50%Bio44T:50%PMDI



The TGA results in Table 13 show that the natural adhesive (100%Bio44T) almost confirmed the previous results. It halved in mass in the temperature range 30-130 °C, mainly due to water loss. From 130 to 230 °C the sample weight remain constant to indicate thermal stability, the adhesive showed no major degradation of its proteins and other major components, in accordance with the absence of signal in the DTA and DSC curves in the same temperature range. Mass loss observed from 230 to 500 °C is related to the progressive thermal degradation associated with the break of some bonds and to the emission of small molecules moiety, and finally with the degradation of the polymeric skeleton structure of the adhesive (Zhang et al. 2018). The thermal degradation is confirmed by the endothermic and exothermic signals around 350 °C present in the DTA curve. Observing instead the behaviour of the mix between natural adhesive (Bio44T) and UF, the TGA shows a trend similar to that of natural adhesive alone; instead for the DTA, especially in the 67% Bio44T: 33% ratio the water content of the natural adhesive inhibits the reaction with formaldehyde. The 100% PAE reduces its weight to 100 °C by about 80%, while when combined with the natural adhesive it reduces the weight by 40% and at a higher temperature (about 120 °C).

With PF, a similar behaviour was observed with that of natural adhesive with UF.

Natural adhesive with pMDI, we observe that the weight lost occurring in the TGA is very small till 200 °C, probably for a difficult interaction between natural adhesive and pMDI (at any percentage between the two components).

4.2 WOOD BASED PANELS PROTOTYPES AND TESTING

4.2.1 PLYWOOD PROTOTYPES

4.2.1.1 INTRODUCTION

One of the scope of this work is to investigate the use of the natural adhesive for manufacturing plywood, especially curved plywood.

The curved plywood, like the flat plywood, consists of the overlapping of wood sheets (veneers) of the desired species (i.e. beech, birch), between which a layer of glue is applied (urea-formaldehyde, vinylic, mix of the previous ones). To obtain this arrangement, veneers without glue alternate with veneers glued on both sides to form the desired sandwich.



Fig. 31. example of curved plywood

The application of the glue on the sheets takes place by means of a double grooved rubberized roller film-maker, each roller is equipped with a feed tank with dosing blade. The sheet is inserted between the rollers that drag it while applying the glue to the surfaces and is ejected from the opposite side ready to be stacked (Fig.32).



Fig. 32. Process of gluing using a roller glue spreader

The sheets are then overlapped alternately (glued or not) and the direction of the fibers can be crossed to obtain the desired resistance (Fig.33). The first and the last sheet can be of the same specie or a different from the others if the finished detail needs an aesthetic value.



Fig. 33. Manual process of overlapping the wood sheets

Then the pack of sheets obtained is placed in the mould for forming. Different technologies, as specified in the next paragraph, may be used in order to obtain a curved plywood.

4.2.1.2 *TECHNOLOGY USED FOR MAKING THE PROTOTYPES OF CURVED PLYWOOD*

In order to verify the correct functionality and verify the versatility of the adhesive, different types of technologies currently used industrially to produce curved plywood panels were used during the research activity in particular:

- Radio frequency technology;
- Press with heated hot plate.

The two technologies are different, in fact:

- The radiofrequency process works much like a microwave oven, where electricity is used to quickly cure the glue from the inside out. This allows a relatively fast press cycle and lends itself to multilayer pressing, driving costs down. Because radiofrequency technology can result in warping on large pieces, this process works best on smaller upholstered pieces. The radiofrequency process for curing adhesives has been used for many years in the production of curved plywood.
- The press with heated hot plate is the most used technology for the curved plywood production. After the sheets are laid-up to form the desired thickness of plywood, the billet of veneers is pre-pressed to begin the consolidation process. Following the prepressed the billet is hot-pressed, generally in a multi-daylight press (usually for flat plywood), to consolidate the panel. The plates of the hot pressed are heated to a temperature of around 130 °C for UF resin, and higher for PF resin. The press pressure and thickness are carefully controlled to ensure an even thickness in the final panel and the duration of pressing will depend on the panel thickness: thicker panels requiring longer press times to ensure that the core veneers reach a temperature sufficient to fully cure the resin.

The following companies' facilities were used within this work:

- Built in house, hot press plate, at NIS Laboratory, in order to have preliminary information;
- Radiofrequency equipment at CGM;
- Hot plate press at CMR.

4.2.1.3 *PRELIMINARY TRIALS*

Flat plywood samples were realized at NIS srl, a start-up involved in the ideation and patenting of eco-friendly products.

The aim of this first trial was to have preliminary verification about:

- Distribution of the glue during the spreading on the veneer;
- Behavior using a Microwave pre-activation;
- Behavior using a heated press;
- Mechanical performance.

The glue recipe (Bio44) was prepared as written in the previous paragraph (for these prototypes not grinded by mill)

Table 14. Natural Adhesive preparation for trials at NIS Lab

Recipe	Bio44
Quantity of water (%)	44,4
Quantity of MgO (%)	2,8
Quantity of Soy Flour (%)	38,9
Quantity of LE (%)	13,9
Additive for pH correction	-
Additive for fast reactivity	-
Temperature of water (°C)	15

The first activity was to control the glue spreading, in terms of application and amount. In the following table 15 are reported weight and size of veneers used during this trial: birch veneer sheets in both low (4-6%) and high (6-8%) moisture content, supplied from an IKEA supplier (Sakuona).

Table 15. Weight and size of the veneers

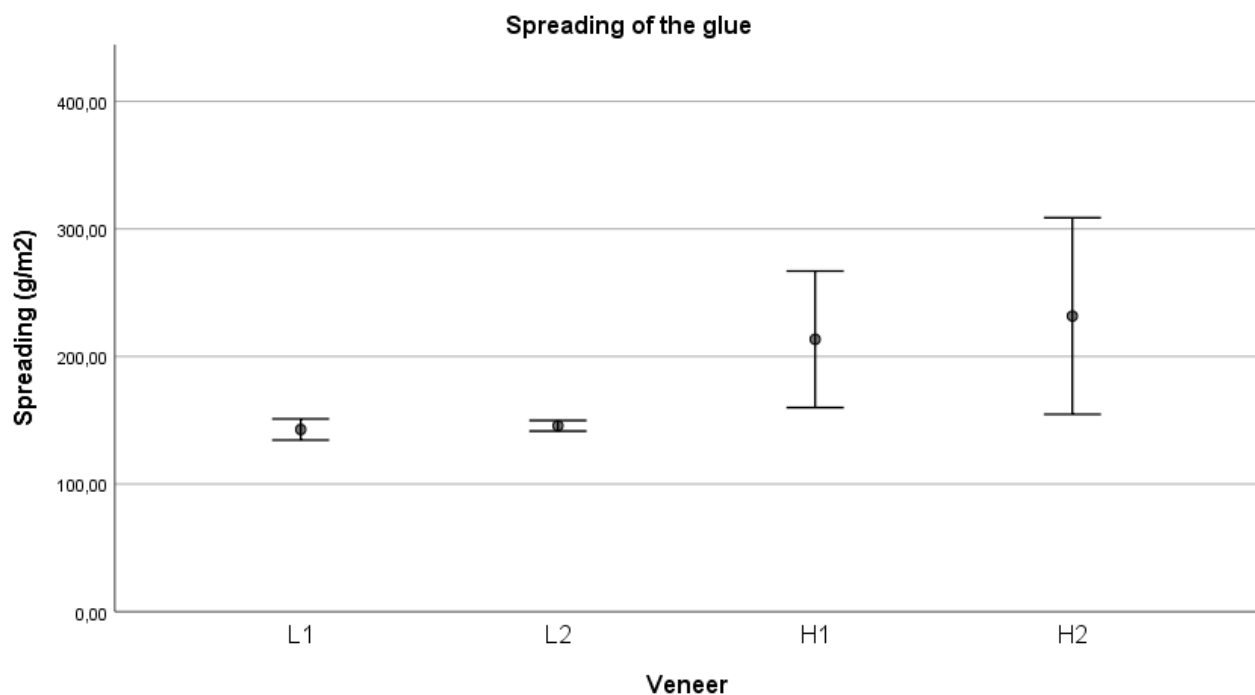
Panel weight (g)	140	130	156
Panel length (mm)	960	960	960
Panel width (mm)	180	180	180

In the table 16 are reported different samples using an high (H) and low (L) amount of glue using a roller spreader. Each series was composed by 6 samples. A total of 24 samples were realized.

Table 16. Samples made using different moisture content and quantity of glue

Series	Number of samples	Moisture content of veneers	Quantity of glue (g/m ²)	Media (g/m ²)	Dev Standard
L1	6	Low	142,7	144,2	2,0
L2	6	High	145,6		
H1	6	Low	213,5	222,6	12,9
H2	6	High	231,7		

In the graph (Fig.34) is reported the variation of the glue distribution uniformity according to the quantity of glue: High amount (H)/Low amount (L) of glue; it is observed that increasing the amount of glue, proportionally increase the standard deviation (meaning irregular distribution of the glue quantity). Probably the high viscosity of the binder, not grinded, does not allow the distribution of the film in a homogeneous manner. This problem could be overcome by increasing the quantity of water, but this means lowering the solid content. The balance between viscosity and solids content is also important. The lower solids content of the natural adhesive (44%) than that of UF resins (typically 66%) implies excess water that might cause steam related internal voids (blows) during the manufacturing process (Dunky 1998)¹²¹.



¹²¹ Dunky, M. (1998). "Urea-formaldehyde (UF) adhesive resins for wood," *Int. J. Adhes. Adhes.*, 18, 95-107.

Fig. 34. Glue spreading amount (g/m²) in function of the moisture content of the veneers

After that different plywood panels were prepared.

The hand-formed mats were pressed using a built-in house hot-press plate; the main parameters of each pressed panels are reported in the table 17.

Table 17. Process parameters of plywood prototypes made at NIS Lab.

	Sample	L1	L2	H1	H2
Panel forming	Quantity of glue (g/m²)	142,75	145,64	213,45	231,73
	Weight of glue (g)	-	-	-	-
	Area of sheets (m²)	0,173	0,173	0,228	0,228
	Thickness of sheets (mm)	1,5	1,5	1,5	1,5
	Layers (nr)	7	7	7	7
	Time for forming the panel (min)	< 5 min	< 5 min	< 5 min	< 5 min
	Glue Recipe (nr)	1	1	1	1
Pre-activation	Microwave power (W)	30000	30000	30000	30000
	Time (s)	40	40	40	40
	Panel temperature (°C)	-	-	-	-
Press	Pressure (bar)	125	125	75	125
	Microwave power (W)	ON	ON	ON	ON
	Press temperature (°C)	-	-	-	-
	Panel temperature (°C)	-	-	-	-
	Time (s)	120	120	120	120
Cooling	Time (s)	300	300	300	300
	Pressure (bar)	125	125	75	125
	Total time (sec)	460	460	460	460

The test results of the plywood prototypes realized in NIS are reported in paragraph 4.3.1.

4.2.1.4 TRIALS USING RADIOFREQUENCY

Introduction

Trials for making prototypes of curved plywood with Bio44 glue using radiofrequency technology were realized at CGM srl¹²², which is an industrial manufacturer of curved furniture components.

Different shapes were considered:

- bed slats;
- seat legs;
- seat shells.

These three products were realized with different number of layers (each layer of about 1.5mm of veneer): 7 for the bed slats, 14 for the seat leg and 9 for the seat shell.

A different radius of curvature was used: the minimum for the bed slats (of about R30) and the maximum for the seat shell (of about R75).

Procedure and parameters

The following steps were made:

- 1) The day before the demonstration, the glue Bio44 was prepared as described in the previous paragraph (in this case it was not grinded in the ball mill);
- 2) Spread the glue on the sheets controlling the weight of the glue per sheet using a precision balance (accuracy 0.1 g);
- 3) Manual Pre-Formation of the panel with the alignment of the veins;
- 4) Positioning of the panel in the mould/press (about 1 minute without radiofrequency in which the temperature was not over 110°C);
- 5) Press with a radiofrequency, about 180-190 bar (about 2/3 minutes depending from the thickness);
- 6) Cooling: kept the press closed without radiofrequencies (about 5/6 minutes).

Before starting the trials, initial parameter were established (Table 18).

¹²² <http://www.cgmcuvati.com/>

Table 18. Initial parameters designed for the trials using radiofrequency

Parameter	CGM Test Conditions
Wood species	Birch
Moisture content of the veneers %	low (4-6%) and high (6-8%)
Glue application method	Roller glue spreader (see the photo)
Open time (after the application of the glue till the layers are built)	More then 10 min
Press type	Radio frequency press
Pressure	About 180-190 bar
Pressing time	About 8/10 min
Press temperature	Radio Frequency, to be verified during the trials
Glue spread	120g-130 g/m ² (wet glue).
Conditioning time	12 h - 24 h

The trials

After the preparation described of the samples (par. 4.2.1.1), the pack of sheets obtained was placed in the mould for forming. In the specific case of the natural adhesive, it was introduced a pre-

activation phase (Fig.34) using a high frequency current generator, which serves to trigger the polymerization reaction: during this phase no pressure was applied and the frequency was modulated according to the dielectric capacity of the body in press and set the exposure time.

The natural binder appeared, before activation, as a mixture without adhesive properties; pressing the pack in this phase generates a filter effect of the wood towards the liquid part of the mixture, separating it; for this it was necessary to bring the temperature to 100 ° C without applying pressure to the pack of sheets.



Fig. 35. Pre-activation phase

Considering that the polymerization is exothermic, the reaction was monitored following the temperature trend in the period following the pre-activation (Fig.35).

At this point, the pressing phase is completed by closing the mould at a pressure of 180 bar and supplying other energy by means of a high frequency alternating current for a suitable time depending on the size and thickness of the part to be obtained (Fig. 36 and 37).



Fig. 36. Pressing phase



Fig. 37. Radiofrequency controller

Finally, after a cooling time in a press without heating, the mould was opened, and the exceeding parts of the glue were removed, trimming along the external.



Fig. 38. Cooling phase outside the mould.

4.2.1.5 TRIALS USING HOT PLANE PRESS

At CMR¹²³, company specialized in the production of hot plane press, were realized 6 different flat plywood panels.

As glue recipe it was always prepared and used the same Bio44 (not grinded), here in the table 19 are reported the quantity.

Table 19. Natural Adhesive preparation for trials at CMR

Recipe	Bio44
Quantity of water (%)	44,4
Quantity of MgO (%)	2,8
Quantity of Soy Flour (%)	38,9
Quantity of LE (%)	13,9
Additive for pH correction	-
Additive for fast reactivity	-
Temperature of water (°C)	15

Each sample was made with 7 layers, for a total thickness 9,6 mm.

¹²³ <http://www.cmrimpianti.com/>

Birch veneer sheets in low (4-6%) moisture content were used with dimensions reported in the table 20.

Table 20. Veneer sheet dimensions

Sample length (mm)	465
Sample width (mm)	480
Sample Area (m²)	0,22

The first activity was application of the glue made using a spray-gun as visible from the fig. 39.



Fig. 39. Glue spreading

The glue spreading control and application amount is reported in the following table 21:

Table 21. Natural Adhesive spreading and application amount

Sample	1	2	3	4	5	6
Glue on Layer 1 (g)	130	51	44	52	51	67
Glue on Layer 2 (g)	85	56	49	58	68	66

Glue on Layer 3 (g)	68	58	48	58	52	50
Glue on Layer 4 (g)	60	64	50	62	54	64
Glue on Layer 5 (g)	58	68	53	58	50	58
Glue on Layer 6 (g)	60	50	50	62	56	52
Media (g)	77	58	49	58	55	60
Standard deviation (g)	28	7	3	4	7	7
Mean of glue spreaded (g/m²)	344	259	220	261	247	267
Standard deviation of glue spreaded (g/m²)	125	32	13	16	30	33
Standard deviation of glue spreaded (in %)	36,3	12,3	6,1	6,3	12,0	12,3

After the application of the natural adhesive, the boards were pressed. The pressing phase was divided in two steps:

- Pre-activation at about 90°C (Hot plates fixed at 110°C);
- Press at about 130°C (Hot plates fixed at about 160°C);

A temperature probe was fixed inside the panel to control the steps of the process, and the duration of each step was in function of the panel temperature.



Fig. 40. Press equipment used in CMR.

In the following table 22 are reported the main process parameters records during the prototyping.

Table 22. Process parameters for making the prototypes using hot plane press at CMR

	Sample	1	2	3	4	5	6
Panel forming	Quantity of glue (g/m²)	344,2	259,1	219,5	261,4	247,2	266,6
	Weight of glue (g)	76,8	57,8	49,0	58,3	55,2	59,5
	Area of sheets (m²)	0,22	0,22	0,22	0,22	0,22	0,22
	Thickness of sheets (mm)	1,5	1,5	1,5	1,5	1,5	1,5
	Layers (nr)	7	7	7	7	7	7
	Time for forming the panel (min)	6	6	6	6	6	6
	Glue Recipe (nr)	Bio44	Bio44	Bio44	Bio44	Bio44	Bio44

Pre-activation	T press (°C)	110	80	110	110	110	110
	Time (s)	108	170	94	146	142	72
	P (bar)	5	9	7	6	7	7
	Panel temperature (°C)	89	80	108	90	90	90
	t pause (s)	/	40	34	/	/	/
Press	Pressure (Kg/cm²)	10	10	10	10	10	10
	T press (°C)	160	160	160	160	160	160
	Panel temperature (°C)	130	130	132	130	128	144
	Time (sec)	260	360	330	225	261	232
Cooling	Time (min)	123	105	39	110	110	140
	Pressure (Kg/cm²)	10	10	10	10	10	10
	Total time (sec)	491	570	497	481	513	444

Test results of the mechanical performance of the plywood prototypes realized are reported in the following paragraph 4.2.2.

4.2.2 TESTING ON PLYWOOD PROTOTYPES

The reference standard for plywood is EN 636 Plywood specifications¹²⁴. This European Standard specifies the requirements for plywood for both general purpose use (non-structural application) and structural application in dry, humid or exterior conditions. It also gives a classification system based on the bending properties.

In particular the tests were performed at Cosmob according to standards:

- EN 310 Wood-based panels - Determination of modulus of elasticity in bending and of bending strength
- EN 322 Wood-based panels – Determination of moisture content

¹²⁴ EN 636:2012+A1:2015 Plywood specifications

- EN 314-1 Plywood – Bond quality – Test methods
- EN ISO 12460-3¹²⁵ Formaldehyde emission, with the gas analysis method

Furthermore on the prototypes realized at CGM, IKEA IOS MAT specifications were used, in particular what IKEA call “intermediate product quality verification” where some simple product verification test are done at factory after pressing/conditioning and before Mechanical Tests.

4.2.2.1 TESTING ON SAMPLES MADE DURING THE PRELIMINARY TRIALS

In the table 23 are reported the results according to EN 310 Wood-based panels - Determination of modulus of elasticity in bending and of bending strength.

Table 23. Results on plywood samples (L1, L2, H1, H2) according to EN 310

L1 Samples	Modulus of Elasticity Em (N/mm²)	Bending resistance fm (N/mm²)	Delamination
1	12525,80	110,26	YES
2	13702,81	138,77	NO
3	13420,57	148,71	NO
4	13647,90	136,13	YES
5	13954,81	158,92	NO
6	13168,06	148,48	NO
Average value	13403,33	140,21	33% of delamination
Standard deviation σ	505,83	16,77	
L2 Samples	Modulus of Elasticity Em (N/mm²)	Bending resistance fm (N/mm²)	Delamination
1	12374,63	143,86	NO
2	14400,00	151,09	NO
3	13644,38	152,54	NO
4	13734,30	149,54	NO
5	13708,50	134,02	NO
6	12748,25	144,32	NO

¹²⁵ EN ISO 12460-3:2015 Wood-based panels — Determination of formaldehyde release — Part 3: Gas analysis method

Average value	13435,18	146,06	0% of delamination
Standard deviation σ	739,92	9,77	
H1 Samples	Modulus of Elasticity E_m (N/mm²)	Bending resistance f_m (N/mm²)	Delamination
1	14572,36	93,38	SI
2	13991,56	137,47	NO
3	13105,45	80,53	SI
4	14135,32	132,16	NO
5	13123,22	82,21	SI
6	14112,32	123,10	NO
Average value	13840,04	108,14	50% of delamination
Standard deviation σ	595,66	25,74	
H2 Samples	Modulus of Elasticity E_m (N/mm²)	Bending resistance f_m (N/mm²)	Delamination
1	13499,83	132,57	SI
2	15513,13	180,77	NO
3	13792,51	155,43	SI
4	15541,51	166,59	NO
5	14094,58	161,02	NO
6	11287,54	136,69	SI
Average value	13954,85	155,51	50% of delamination
Standard deviation σ	1569,28	18,28	

About the formaldehyde emissions, all the samples were tested according to EN ISO 12460-3 and they were under the limit of quantification (tested by COSMOB Laboratory, accredited Laboratory according to the EN ISO IEC 17025 and the EN ISO 12460-3 is included in their scope of accreditation).

Conclusions on the plywood samples realized at NIS Lab

- Prototypes showed very good results in terms of adhesion and bending resistance;
- it was confirmed the process conditions (repeatability);
- According to EN 636, the samples can be considered E120 and F80 classified;

- Standard deviations of the test results were low;
- It was noted that reducing the amount of glue, the delamination (during the EN 310 tests) and standard deviations were lowering, maintaining good values of bending resistance and modulus of elasticity.

4.2.2.2 *TESTING ON SAMPLES REALIZED USING RADIOFREQUENCY*

Results

The prototypes made with natural adhesive were immediately stable after forming, both after 2 hours and after 24 hours, however after the destructive tests, a lack of adhesion (delamination) could occur between some of the plywood sheets, which is therefore result not having the resistance required by the final product. The layers of glue also showed the shape given by the striped rollers after the pressing, a sign that the polymerization reaction had already been completed when the material had not yet been pressed, so the glue had to be already hard and was not stretched well. Unfortunately, the impossibility of knowing in detail the parameters of the process to be able to control them, was the determining factor in arriving at a partial result only.

Conclusions on the trials and tests made using radiofrequency

Notwithstanding that the result obtained were satisfactory for the category of bio-adhesives, the next studies need to demonstrate that it is possible to make specimens using natural adhesives that are sufficiently resistant to the plywood sheet separation tests, considering that:

- the power used on the RF machine was too high (20 KW) respect the lab trials (750 W). It is necessary to tune up the machine with the support of the equipment constructor.
- It seems that the glue was completely cured before the pressing step (e.g. seat shell maintains their shape but easily delaminates). The thesis is that it was provided too much energy in the pre-activation step (see previous point).
- The better samples obtained were with the stool legs. The relevant difference from the other samples (bad slats and seat shells) was not in the process but in the thicker plywood layers (about 21 mm for stool legs, 13 mm for seat shell and 9 mm for bed slats).
- It was impossible to reduce the glue spread on the layer with the rolling glue machine. Probably the viscosity of the glue was too high.

- It is necessary a reduction of the particle size: it could be initially used a ball mill in order to make the Bio44T; next step it will be to identify an industrial mixer;
- The solid content of the Bio44 has to be reduced; furthermore it is necessary to verify the sprayable viscosity in order to use an airless system for spreading the glue.

4.2.2.3 TESTING ON SAMPLES REALIZED USING HOT PLANE PRESS

In the table 24 are reported the results according to EN 310 Wood-based panels - Determination of modulus of elasticity in bending and of bending strength:

Table 24. Results according EN 310 Wood-based panels - Determination of modulus of elasticity in bending and of bending strength, for the plywood realized at CMR

Samples	E_m (N/mm ²)	f_m (N/mm ²)
1	10906,65	71,12
Th=9,7		
Layers=7		
2	7186,17	53,54
Th=9,6		
Layers=7		
3	10058,38	69,39
Th=9,5		
Layers=7		
4	10209,78	64,6
Th=9,6		
Layers=7		
5	6977,89	56,54
Th=9,6		
Layers=7		
6	10602,08	64,48
Th=9,5		

Layers=7		
Average	9323,49	63,28
St. Dev.	1762,77	6,96
EN 636 Classification	E100*	F40*

* E120 classified according EN 636, if excluding samples 2 and 3

The moisture content of the prototypes were all around 6-7 %, according to EN 322.

In the table 25 are reported the results according to EN 314-1 Plywood – Bond quality – Test methods.

Table 25. Results according EN 314-1 Plywood – Bond quality – Test methods, on the plywood prototypes realized at CMR

Sample	Max Load (N)	Max Load tensile strength (MPa)	Time (s)	Wood Fibre Failure (%)
1	1591,6	3,27	19,2	100%
2	2173,1	3,28	18,9	100%
3	1714,2	3,27	19,2	100%
4	1890,7	3,27	20,9	100%
5	2091,7	3,24	20,2	100%
6	1825,0	3,26	18,3	100%
7	2173,1	3,27	32,8	100%
8	1104,2	3,25	16,1	100%
9	1679,9	3,28	19,4	100%
10	2142,7	3,26	27,6	100%
11	2173,1	3,26	18,3	100%
12	2173,1	3,28	20,1	100%
13	2173,1	3,26	33	100%
14	2173,1	3,26	29,1	100%
15	2173,1	3,28	23	100%
Av.	1950,11	3,27	22,41	100%
St. Dev.	315,91	0,01	5,48	0,00

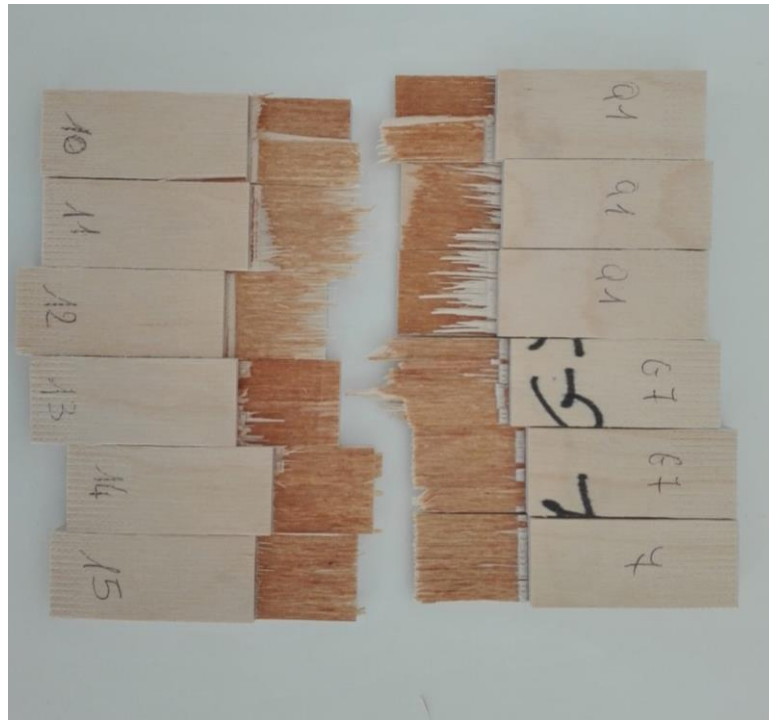


Fig. 41. Rupture of the sample after the EN 314-1 test on the plywood prototypes realized at CMR

About the formaldehyde emissions, all the samples were tested according to EN ISO 12460-3 and they were under the limit of quantification (tested by COSMOB, accredited Laboratory according to the EN ISO IEC 17025; EN ISO 12460-3 is included in its scope of accreditation).

Conclusions on plywood samples realized at CGM:

- Prototypes showed very good results in terms of adhesion and bending resistance;
- It was confirmed the process conditions (repeatability);
- According to EN 636, the samples can be considered E120 and F80 classified;
- Standard deviation of the results of the test is low;
- Good results obtained with the “dry test” EN 314 (Max Load tensile strength $\geq 3,25$ MPa). The specimens, however, have not undergone pre-treatment in water for 24 hours. In fact some samples have been soaked in water, but so far it is an excessive treatment for the natural adhesive; in order to withstand 24 hours in water will have to be combined with other crosslinkers (as shown in the prototypes and tests carried out for particleboards, for example by combining the natural binder with PAE).

4.2.3 PARTICLEBOARD (PB) PROTOTYPES

4.2.3.1 INTRODUCTION

The particleboard (PB) is a wood-based panel, in which the wood particles (coming from natural species or recycled material) are usually bonded with synthetic resins composed of urea-formaldehyde (UF), or melamine urea-formaldehyde (MUF), or more rarely phenol-formaldehyde (PF), or the polymeric methylene diisocyanate (PMDI). The main successful is UF resin due to its high reactivity and good mechanical performance, combined with low cost. However, it has an important disadvantage: the release of formaldehyde and that it is petroleum derived.

The manufacture of particleboards was introduced with the purpose of scrap re-use; for this reason, at the beginning the manufacturing process was rough compared to the current one and the reproducibility of the quality was relatively poor. Over the years, the application of new technologies in the production and control, together with the dimensional optimization of wood particles and the use of more sophisticated resin systems, have led to the production of large number of high-performance panels¹²⁶.

For the purposes of this work, different PB samples were realized but not using an industrial press but Laboratory presses. The main process parameters for the realization of the boards (i.e. temperature, press speed) were recorded.

Initially PB panels were made using only the Bio44 binder (not grinded): this activity was carried out at the IKEA Laboratory located in Orla (Poland).

Subsequently, further PB samples were made at NIS srl (Italy) using Bio44T grinded and mixed respectively with UF, PAE, PF and PMDI (weight combinations of the grinded natural adhesive and a synthetic crosslinkers of 0:100 %, 33:67 %, 50:50 %, 67:33 % and 100:0 %.).

All the samples made were then tested at Cosmob and partly at the IKEA Laboratory in Orla.

Statistical analysis was performed with SPSS Version 21.0 statistic software package (IBM Corp., Armonk, NY, USA). Analysis of variance (ANOVA) and Tukey HSD test were performed on the particleboard testing data to indicate significant differences at a 95% confidence level.

4.2.3.2 PB PROTOTYPES MADE USING NATURAL ADHESIVE (BIO44)

As mentioned before trials using natural adhesive for making PB was performed in the IKEA Laboratory facilities at Orla (Poland).

¹²⁶ Panel Guide Version 4, Wood panel Industries Federation, 2014

The glue (Bio44) was prepared 4 times, always using the same recipe described in the previous paragraphs (not grinded by ball mill). Standard industry core and surface layer wood chips from mixed Scots pine and Norway spruce were oven-dried to 1.0 ± 0.3 % moisture content. The adhesive solutions were sprayed onto wood particles in a blender at a resin content (solid content) of about 10 wt % (calculated based on the weight of oven dried wood particles). In the following table is reported the standard parameters usually set by IKEA's Laboratory in Orla (Poland) for the realization of a reference sample (see Table 26, reference sample 1):

Table 26: Process parameters used for forming the particleboards during the trials at Ikea Laboratory in Orla (Poland)

	Dry Particle (%)	Thickness (mm)	UF Glue (%)	Moisture content (%)
Surface Layer (SL)	20	3	10	9-10
Core Layer (CL)	60	12	9	7-8
Surface Layer (SL)	20	3	10	9-10
Thickness (mm)	18			
Density (kg/m ³)	620			
Press time (s/mm):	8-10			
Press temperature (°C):	200			
Mold length (mm)	600			
Mold width (mm)	600			
Mold thickness (mm)	250			



Fig 42. Making the glue, drying the particles, forming the board, pressing the board, during the trials at Ikea Laboratory in Orla (Poland).

List of PB prototypes made during the trials at Ikea’s Laboratory (the first sample was used as reference because made with a traditional MUF adhesive) at the table 27.

Table 27: List of PB prototypes made during the trials at IKEA Laboratory Orla

1	REFERENCE sample using MUF resin, 10s/mm	TEMPERATURE of the press - 200°C
2	Prepressing at 100 °C for 15 min (core T=80,5 °C); 18s/mm pre-pressed	
3	Prepressing at 100 °C for 9 min (core T=66 °C); 10s/mm pre-pressed	
4	3h drying + re-watering of the resinated particles; 18s/mm	
5	18s/mm	
6	24s/mm	
7	18s/mm	
8	24s/mm	
9	15s/mm	
10	12s/mm	

Test results performed on the particleboard prototypes are reported in the paragraph 4.2.4.

4.2.3.3 PB PROTOTYPES MADE USING HYBRID RESINS

Standard industry core and surface layer wood chips from mixed Scots pine and Norway spruce were oven-dried to 1.0 ± 0.3 % moisture content. Dried chips were then blended with weight combinations of the grinded natural adhesive and a synthetic crosslinkers (using UF, or PAE, or PF, or PMDI) of 0:100 %, 33:67 %, 50:50 %, 67:33 % and 100:0 %. The adhesive solutions were sprayed onto wood particles in a blender at a resin content (solid content) of 10 wt % (calculated based on the weight of oven dried wood particles).

The moisture content of the blended particles with the adhesives ranged from 8 % to 10 %. No wax or any other additives were applied for the manufacturing of the laboratory boards. The resinated chips were placed in a mold with dimensions of 200×200 mm² to produce 3-layer particleboards

(60% core share) with a thickness of 15 mm and a target density of 600 kg/m³. The hand-formed mats were pressed using a built in house parallel plate hot-press with pressing time of 18 s/mm and pressing temperature of 220 °C. UF-bonded boards were also prepared as above, and served as controls.

A total of 57 PB prototypes were realized at NIS Lab as reported in the following table 28:

Table 28. List of PB prototypes made in NIS Lab, using hybrid resins (natural adhesive and synthetic resin)

%UF + %Bio 44T		%PAE+ %Bio 44T		%PF + %Bio 44T		%PMDI + %Bio 44T	
Sample	Description	Sample	Description	Sample	Description	Sample	Description
1.1	100% Bio44T, 10% of Glue/PB Thickness of PB=15mm						
1.2							
1.3							
2.1	33% UF + 67% Bio44T, 10% of glue/PB Thickness of PB=15mm	8.1	33% PAE + 67% Bio44T, 10% of glue/PB Thickness of PB=15mm	12.1	33% PF + 67% Bio44T, 10% of glue/PB Thickness of PB=15mm	16.1	33% PMDI + 67% Bio44T, 10% of glue/PB Thickness of PB=15mm
2.2		8.2		12.2		16.2	
2.3		8.3		12.3		16.3	
3.1	50% UF + 50% Bio44T, 10% of glue/PB Thickness of PB=15mm	9.1	50% PAE + 50% Bio44T, 10% of glue/PB Thickness of PB=15mm	13.1	50% PF + 50% Bio44T, 10% of glue/PB Thickness of PB=15mm	17.1	50% PMDI + 50% Bio44T, 10% of glue/PB Thickness of PB=15mm
3.2		9.2		13.2		17.2	
3.3		9.3		13.3		17.3	
4.1	67% UF + 33% Bio44T, 10% of Glue/PB Thickness of PB=15mm	10.1	67% PAE + 33% Bio44T, 10% of Glue/PB Thickness of PB=15mm	14.1	67% PF + 33% Bio44T, 10% of Glue/PB Thickness of PB=15mm	18.1	67% PMDI + 33% Bio44T, 10% of Glue/PB Thickness of PB=15mm
4.2		10.2		14.2		18.2	
4.3		10.3		14.3		18.3	
5.1	100% UF 10% of Glue/PB	11.1	100% PAE 10% of Glue/PB	15.1	100% PF 10% of glue/PB	19.1	100% PMDI 10% of glue/PB
5.2		11.2		15.2		19.2	

5.3	Thickness of PB=15mm	11.3	Thickness of PB=15mm	15.3	Thickness of PB=15mm	19.3	Thickness of PB=15mm
6.1	100% Bio44T,						
6.2	16% of Glue/PB						
6.3	Thickness of PB=15mm						
7.1	100% Bio44T,						
7.2	25% of Glue/PB						
7.3	Thickness of PB=15mm						

After cooling to room temperature, the boards were trimmed and conditioned at 20 ± 2 °C and $65 \pm 3\%$ relative humidity before testing. Internal bond (IB) was tested according to EN 319 and thickness swelling (24 h) values were determined according to EN 317. Finally, the formaldehyde content of the particleboards was determined by using the perforator method according to EN ISO 12460-5.

Test results performed on the particleboard prototypes are reported in the following paragraph 4.2.4.2.

4.2.4 TESTING ON PB PROTOTYPES

4.2.4.1 TESTING ON SAMPLES MADE USING NATURAL ADHESIVE (BIO44)

In the following table are reported the test results of the samples made at Ikea's Laboratory at Orla (Poland) (as describe in the paragraph 4.2.3.2).

Table 29. Test results on the PB made during the trials in IKEA Lab (Orla).

Sample	Description	EN 323		EN 322 (%)	EN 319 (N/mm ²)	EN 317 (mm)		EN 310 (MPa)	
		Raw density (kg/m ³)	Thickness (mm)			in 2 h	in 24 h	MoE	MoR
1	Reference samples (MUF resin)	613,40	18,63	13,73	0,18	18,46	37,68	1811	6,79

2	Prepressing at 100 °C for 15 min (core T=80,5 °C); 18s/mm pre-pressed	595,17	19,22	16,34	0,14	49,09	61,14	939	3,85
3	Prepressing at 100 °C for 9 min (core T=66 °C); 10s/mm pre-pressed	588,05	19,70	16,46	0,15	40,21	51,76	940	3,47
4	3h drying + re-moustering of the resinated particles; 18s/mm	587,50	18,39	15,92	0,08	79,33	91,42	-	-
5	Press speed 18s/mm	612,48	18,29	15,73	0,13	36,26	49,60	1282	4,28
6	Press speed 24s/mm	646,05	18,03	15,47	0,14	38,41	52,75	1363	4,74
7	Press speed 18s/mm	602,34	18,32	16,12	0,15	35,31	44,96	1691	7,05
8	Press speed 24s/mm	620,54	18,29	15,96	0,18	36,27	45,75	1553	6,19
9	Press speed 15s/mm	598,07	18,46	16,02	0,12	38,11	48,48	1597	5,76
10	Press speed 12s/mm	597,98	18,93	16,01	0,10	39,65	50,62	1634	5,60

Comments about the test results on the PB made in Ikea Lab at Orla (Poland):

- The results of the samples 8 and 9, internal Bond (IB) and Modulus of Rupture (MoR), were in line with the results for the reference sample (sample 1);
- The swelling properties in conventional dipping tests (2 and 24 h) show that the MUF resin contributes to less swelling than the Bio44 adhesive (very clear for 2 h);
- Properties for Bio44 glue (not grinded, thus without desired particle size) can be achieved down to 15 sec/mm; instead 12 sec/mm is on the limit;

- During the trials it was not possible to use a pre-activation procedure (lack of equipment) as it was shown by the results obtained with samples 2 and 3;
- Drying of resinated particles, and then re-moisturing (sample 4), does not lead to similar board properties as pressing directly of high moisture content particles;
- The same samples were also tested on the workability of the panel, in particular of the edging process: through the support of the Biesse Group all the samples listed above were edged and then the good adhesion of the panel was verified through both of the visual observations of the Biesse technicians and both with the a pull-out test (following the Italian standard UNI 9240¹²⁷) carried out at the Cosmob testing laboratory, reporting values over 1,0 MPa.

4.2.4.2 TESTING ON HYBRID: NATURAL ADHESIVE (BIO44T) / SYNTHETIC RESINS

Bio44T/UF

Table 30. Test results on the PB made during the trials in NIS Lab, using Bio44T and UF.

Sample	Description	EN 12460-5 (mg/100g)	EN 322 (%)	EN 319 (N/mm ²)	EN 317 (% in 24 h)	EN 323 (kg/m ³)
1.1	100% Bio44T,	0,2	8,3	0,13	44,2	587,0
1.2	10% of Glue/PB	0,1	8,0	0,15	45,3	583,0
1.3	Thickness of PB=15mm	0,2	7,8	0,11	46,3	578,0
2.1	33% UF + 67% Bio44T,	4,3	6,9	0,18	32,1	515,0
2.2	10% of Glue/PB	4,1	6,5	0,16	34,2	541,0
2.3	Thickness of PB=15mm	4,5	6,9	0,17	33,4	531,0
3.1		7,5	6,9	0,22	23,1	510,0
3.2		7,3	6,8	0,21	25,2	540,0

¹²⁷ UNI 9240:2016 Mobili - Determinazione dell'adesione delle finiture al supporto mediante prova di strappo

3.3	50% UF + 50% Bio44T, 10% of glue/PB Thickness of PB=15mm	7,6	6,7	0,23	24,2	537,0
4.1	67% UF + 33% Bio44T, 10% of glue/PB Thickness of PB=15mm	9,2	7,5	0,26	16,3	605,0
4.2		8,8	7,3	0,28	15,7	615,0
4.3		9,1	7,6	0,23	15,9	609,0
5.1	100% UF 10% of Glue/PB Thickness of PB=15mm	6,4	5,9	0,35	38,3	645,0
5.2		6,0	5,5	0,33	39,2	651,0
5.3		6,5	6,0	0,38	37,6	653,0
6.1	100% Bio44T, 16% of Glue/PB Thickness of PB=15mm	0,3	8,2	0,19	40,1	603,0
6.2		0,1	8,5	0,18	39,8	606,0
6.3		0,1	8,3	0,22	41,3	598,0
7.1	100% Bio44T, 25% of Glue/PB Thickness of PB=15mm	0,0	8,4	0,21	27,1	689,0
7.2		0,1	8,1	0,20	28,2	675,0
7.3		0,1	8,6	0,21	29,1	681,0

Bio44T/PAE

Table 31. Test results on the PB made during the trials in NIS Lab, using Bio44T and PAE.

Sample	Description	EN 12460-5 (mg/100g)	EN 322 (%)	EN 319 (N/mm ²)	EN 317 (% in 24 h)	EN 323 (kg/m ³)
8.1	33% PAE + 67% Bio44T, 10% of Glue/PB Thickness of PB=15mm	0,3	9,2	0,41	20,2	501
8.2		0,2	10,3	0,39	21,1	491
8.3		0,1	9,5	0,40	20,6	495
9.1	50% PAE + 50% Bio44T, 10% of glue/PB Thickness of PB=15mm	0,4	12,5	0,47	21,0	530
9.2		0,3	11,5	0,43	23,1	512
9.3		0,2	12,0	0,45	22,2	524
10.1		0,1	12,1	0,49	19,8	523

10.2	67% PAE + 33% Bio44T,	0,2	11,2	0,48	20,1	521
10.3	10% of glue/PB	0,1	11,3	0,50	18,9	510
	Thickness of PB=15mm					
11.1	100% PAE	0,2	10,1	0,51	18,7	512
11.2	10% of Glue/PB	0,3	10,3	0,52	19,3	513
11.3	Thickness of PB=15mm	0,1	10,4	0,50	18,1	491

Bio44T/PF

Table 31. Test results on the PB made during the trials in NIS Lab, using Bio44T and PF.

Sample	Description	EN 12460-5 (mg/100g)	EN 322 (%)	EN 319 (N/mm ²)	EN 317 (% in 24 h)	EN 323 (kg/m ³)
12.1	33% PF + 67% Bio44T,	0,1	9,4	0,31	30,2	516
12.2	10% of Glue/PB	0,1	9,2	0,30	29,9	523
12.3	Thickness of PB=15mm	0,1	9,6	0,32	31,0	521
13.1	50% PF + 50% Bio44T,	0,4	8,5	0,26	35,2	546
13.2	10% of glue/PB	0,5	8,0	0,25	36,1	541
13.3	Thickness of PB=15mm	0,4	8,4	0,26	34,3	551
14.1	67% PF + 33% Bio44T,	1,0	7,8	0,39	15,2	547
14.2	10% of glue/PB	0,9	8,2	0,35	16,1	540
14.3	Thickness of PB=15mm	1,1	7,3	0,36	15,5	533
15.1	100% PF	1,3	9,8	0,41	19,0	512
15.2	10% of glue/PB	1,2	9,4	0,42	18,7	515
15.3	Thickness of PB=15mm	1,4	9,9	0,41	19,5	510

Bio44T/PMDI

Table 32. Test results on the PB made during the trials in NIS Lab, using Bio44T and pMDI.

Sample	Description	EN 12460-5 (mg/100g)	EN 322 (%)	EN 319 (N/mm ²)	EN 317 (% in 24 h)	EN 323 (kg/m ³)
16.1	33% PMDI + 67% Bio44T,	LOQ	8,3	0,32	25,3	498
16.2	10% of Glue/PB	LOQ	7,6	0,51	23,9	512
16.3	Thickness of PB=15mm	LOQ	7,9	0,39	24,6	509

17.1	50% PMDI + 50% Bio44T,	LOQ	7,0	0,23	31,1	471
17.2	10% of glue/PB	LOQ	7,4	0,27	29,1	489
17.3	Thickness of PB=15mm	LOQ	7,2	0,27	30,1	480
18.1	67% PMDI + 33% Bio44T,	0,1	7,3	0,24	29,1	542
18.2	10% of glue/PB	0,1	7,7	0,37	27,2	521
18.3	Thickness of PB=15mm	0,1	7,5	0,32	28,2	531
19.1	100% PMDI	0,3	6,9	0,37	27,2	512
19.2	10% of glue/PB	0,4	6,5	0,33	30,1	520
19.3	Thickness of PB=15mm	0,3	6,7	0,39	28,9	516

In the following graphs (from Fig.42 to Fig.46) are reported the test results of particleboards produced with combinations of the natural adhesive (Bio44T) and synthetic resins (UF, PAE, PF and pMDI). Error bars represent standard errors with 95% confidence interval for means.

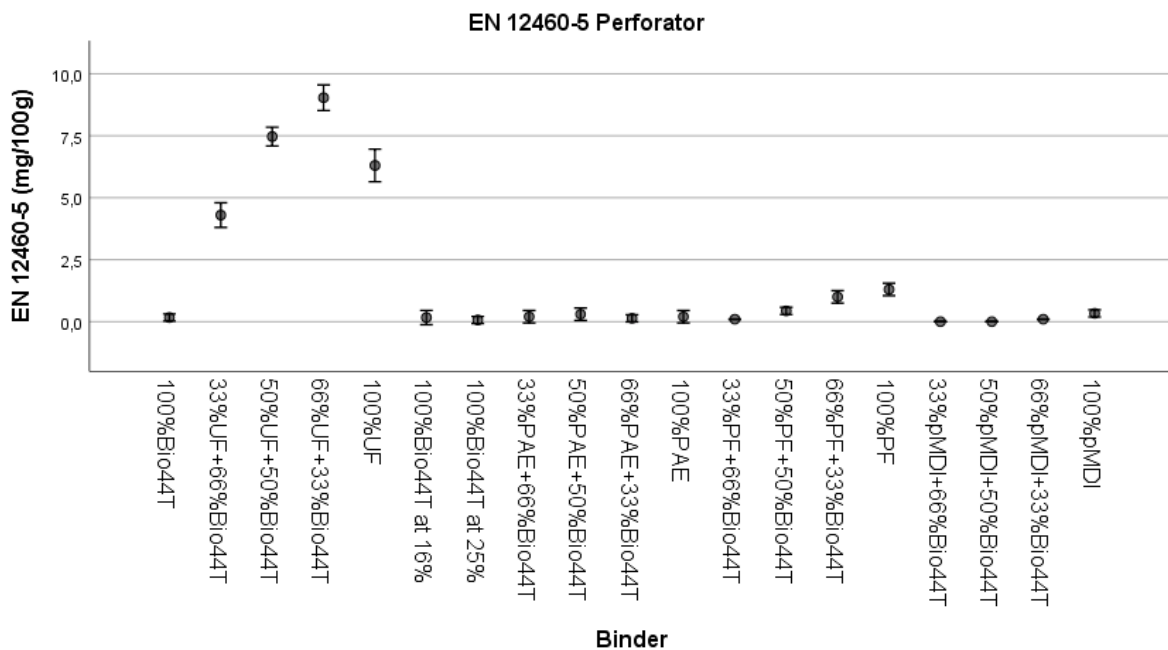


Fig. 42. Formaldehyde content of particleboards produced with combinations of the natural adhesive (Bio44T) and synthetic resins (UF,PAE, PF and pMDI).

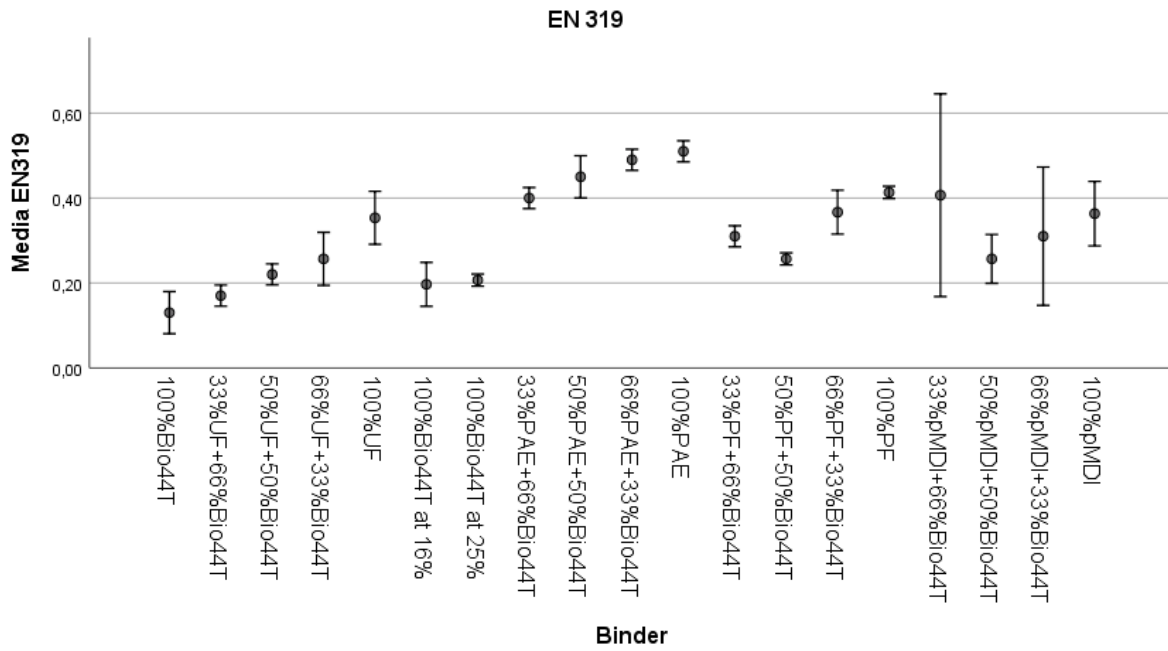


Fig. 43. Internal bond strength of particleboards produced with combinations of the natural adhesive (Bio44T) and synthetic resins (UF,PAE, PF and pMDI).

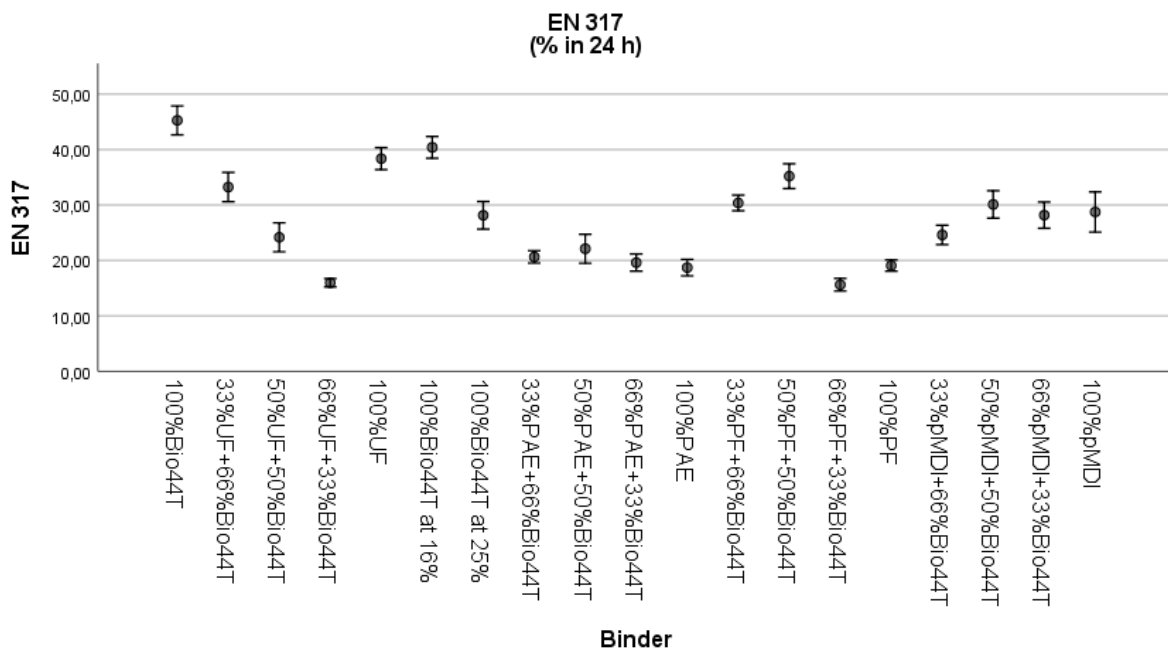


Fig. 44. Thickness swelling of particleboards produced with combinations of the natural adhesive (Bio44T) and synthetic resins (UF,PAE, PF and pMDI).

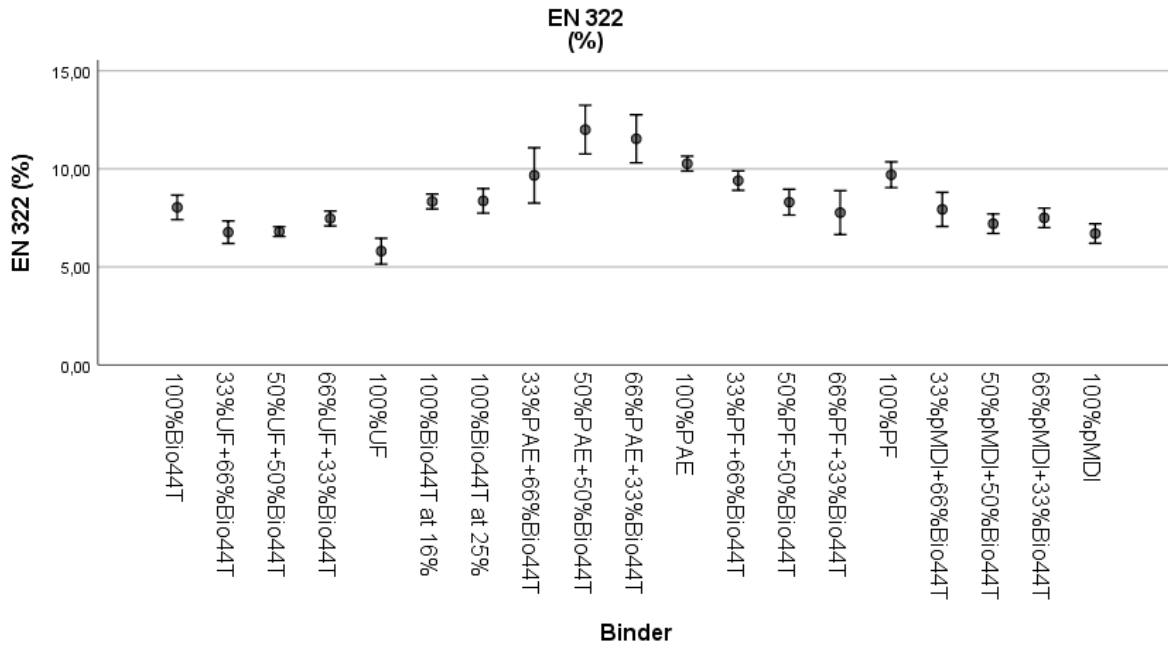


Fig. 45. Moisture content of particleboards produced with combinations of the natural adhesive (Bio44T) and synthetic resins (UF,PAE, PF and pMDI).

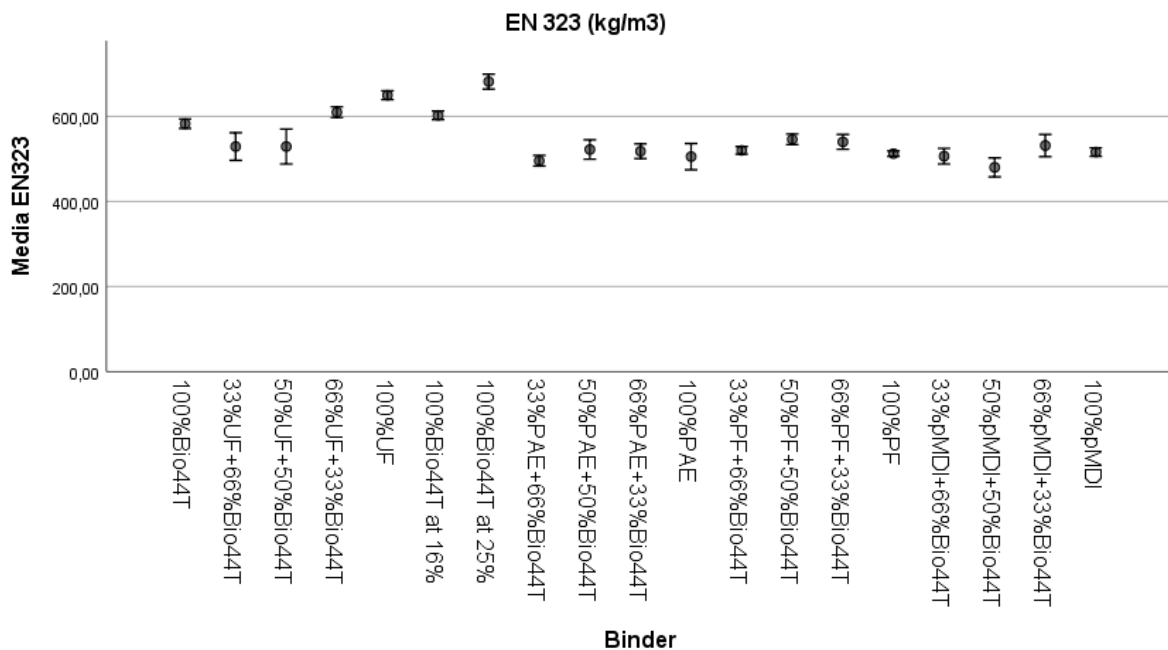


Fig. 46. Density of particleboards produced with combinations of the natural adhesive (Bio44T) and synthetic resins (UF,PAE, PF and pMDI).

Comments about the tests on the particleboards made with hybrid resins at NIS Lab:

- BIO44T adhesive has a lower internal bond (IB) strength (test performed according to EN 319) and higher humidity (test performed according to EN 322) if compared to other samples; on the other hand, there is almost no formaldehyde (reference test EN 12460-5, the perforator method).
- Regarding the presence of formaldehyde, a clear deterioration of the values occurs when the BIO44T was added to 33%; while when the BIO44T was added to 67% a lowering of the formaldehyde value was obtained compared to 100% UF.
- Increasing the amount of natural adhesive (sample 6 and 7) from 16% to 25% didn't improved the IB;
- The intrinsic adhesive properties of the natural adhesive without added PAE were found to be much inferior to UF (reference industry resin) in terms of internal bond (IB) strength (Fig. 47). IB improved significantly with the addition of PAE, and differences were statistically different with UF for each tested PAE load level (ANOVA, P = 5 %). These results imply that PAE is necessary to impart adequate bond properties to the natural adhesive. A PAE-natural adhesive ratio of 33:67 % is sufficient in that respect. PAE resins bond well to wood, and thus PAE alone provided the highest IB. The enhanced protein content of the natural adhesive offered by the plant-derived enzymatic hydrolysate should have contributed to a better interaction with PAE and wood.

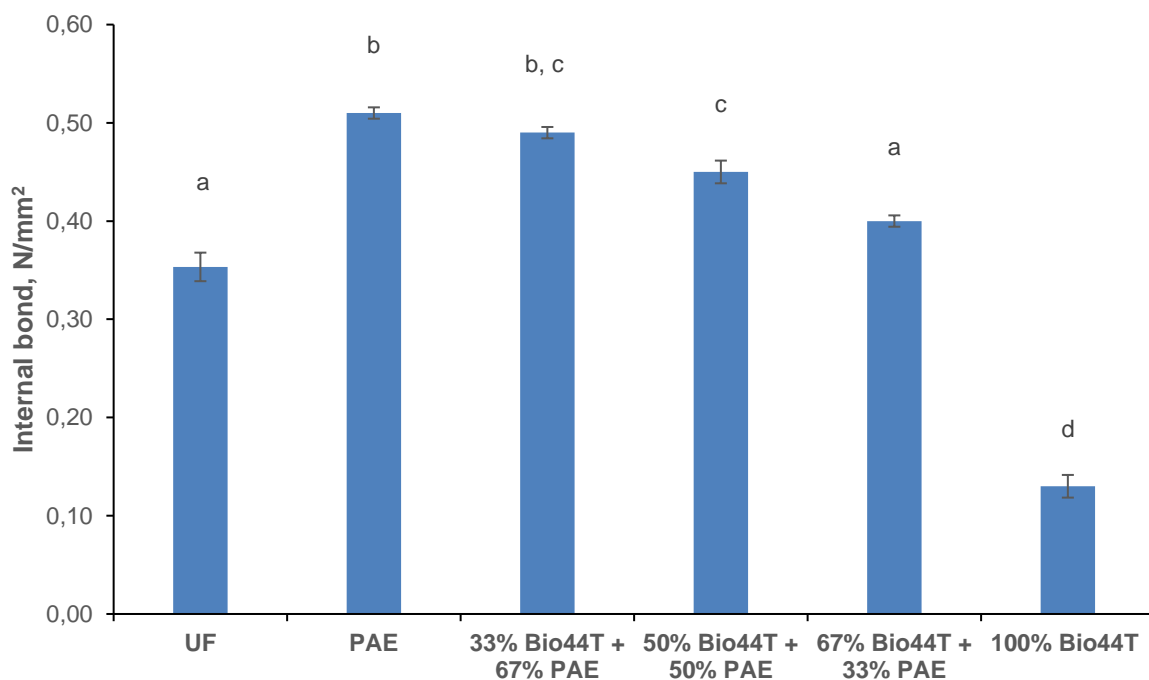


Fig. 47. Internal bond strength of particleboards produced with combinations of the natural adhesive (Bio44T) and PAE. UF-bonded boards served as additional reference. Error bars represent standard errors with 95% confidence interval for means. Values labelled with different letters are statistically different according to ANOVA and Tukey's HSD test for P = 5 %).

- The poor water resistance of soy protein adhesives is a known problem that limits their application (Gao et al. 2011¹²⁸; Chen et al. 2015¹²⁹). The swelling results of the particleboards with the natural adhesive alone underscored as compared to the UF-bonded boards (Fig. 48). Plywood panels bonded with a soy flour-MgO adhesive at weight ratios ranging from 10:1 to 1:1 were reported to pass successfully a three cycle soak test, which is the industrial water-resistant requirement for interior plywood (Jang and Li 2015¹³⁰). It was shown that close interactions between MgO and soy proteins instead of soy carbohydrates were responsible for the high water resistance of the soy flour-MgO adhesive. It is evident that the low amount of MgO (2.8 % wt) in the natural adhesive is not enough to fully provide the necessary water-resistance. As expected, a significant improvement in water resistance occurred when PAE was used, already at the lower percentage of 33 %. Swelling values were more or less similar for all natural adhesive-PAE combinations, and significantly lower than those of UF (ANOVA, P = 5 %).

¹²⁸ Gao, Q., Shi, S. Q., Li, J., Liang, K., and Zhang, X. (2011). "Soybean meal-based wood adhesives enhanced by modified polyacrylic acid solution," *BioResources*, 7, 1, 946-956.

¹²⁹ Chen, M., Chen, Y., Zhou, X., Lu, B., He, M., Sun, S., and Ling, X. (2015). "Improving water resistance of soy-protein wood Adhesive by using hydrophilic additives," *BioResources*, 10, 1, 41-54.

¹³⁰ Jang, Y., and Li, K. (2015). "An all- natural adhesive for bonding wood," *J. Am. Oil Chem. Soc.*, 92, 431-438.

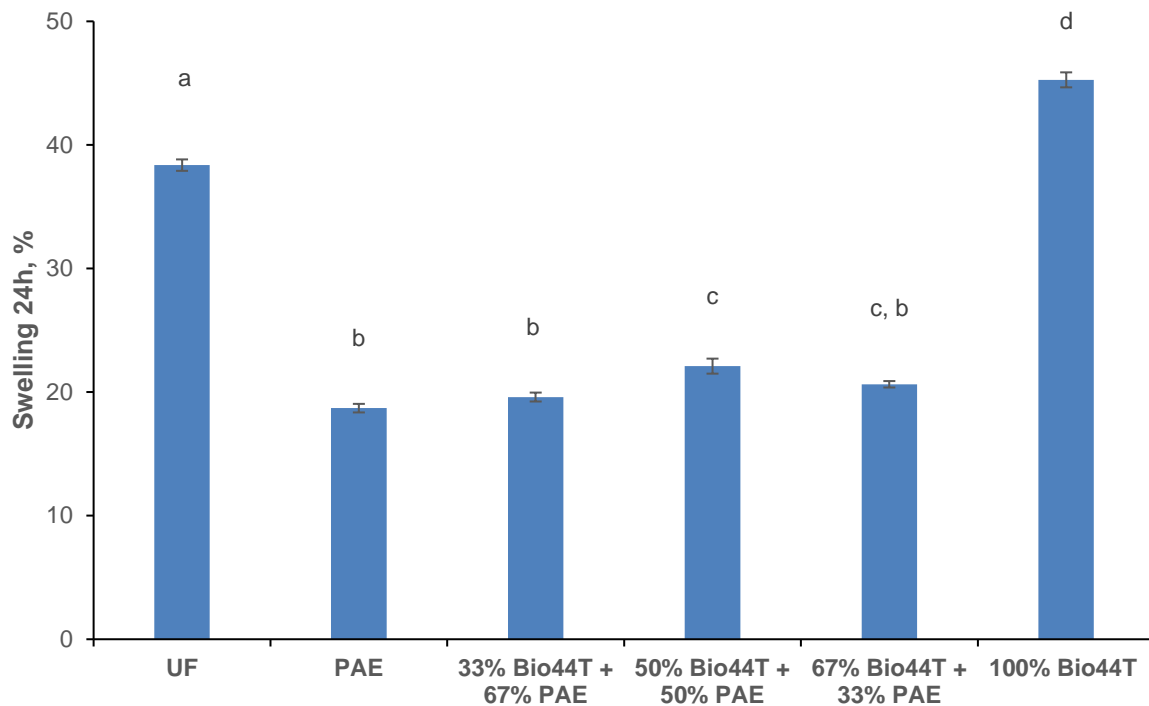


Fig. 48. Thickness swelling of particleboards produced with combinations of the natural adhesive (Bio44T) and PAE. UF-bonded boards served as additional reference. Error bars represent standard errors with 95% confidence interval for means. Values labelled with different letters are statistically different according to ANOVA and Tukey's HSD test for P = 5 %).

- The particleboards with the natural adhesive and its combinations with PAE had significantly less formaldehyde content than the UF-bonded boards (Fig. 49). Formaldehyde-free wood particleboards with soybean protein adhesives have also been reported by others (Ferguson et al. 2014¹³¹). The low detectable levels of formaldehyde associated with the natural adhesive/ PAE-based particleboards are within natural wood levels (Hemmilä et al. 2019a¹³²).
- The overall results suggest that the combination of the natural materials soy flour, MgO and plant-derived enzymatic hydrolysate show good potential for developing formaldehyde-free adhesives for particleboards. Further work on such formulations should focus on optimum

¹³¹ Ferguson, C. R., Mendon, S. K., Rawlins, J. W., and S. F. Thames. (2014). "Formaldehyde-free wood composites from soybean protein adhesive," *J. Renew. Mater.*, 2, 3, 166-172.

¹³² Hemmilä, V., Meyer, B., Larsen, A., Schwab, H., and Adamopoulos, S. (2019a). "Influencing factors, repeatability and correlation of chamber methods in measuring formaldehyde emissions from fiber- and particleboards," *Int. J. Adhes. Adhes.*, 94, 102420.

levels of PAE as a crosslinker, appropriate solids content and viscosity, and reduced press times.

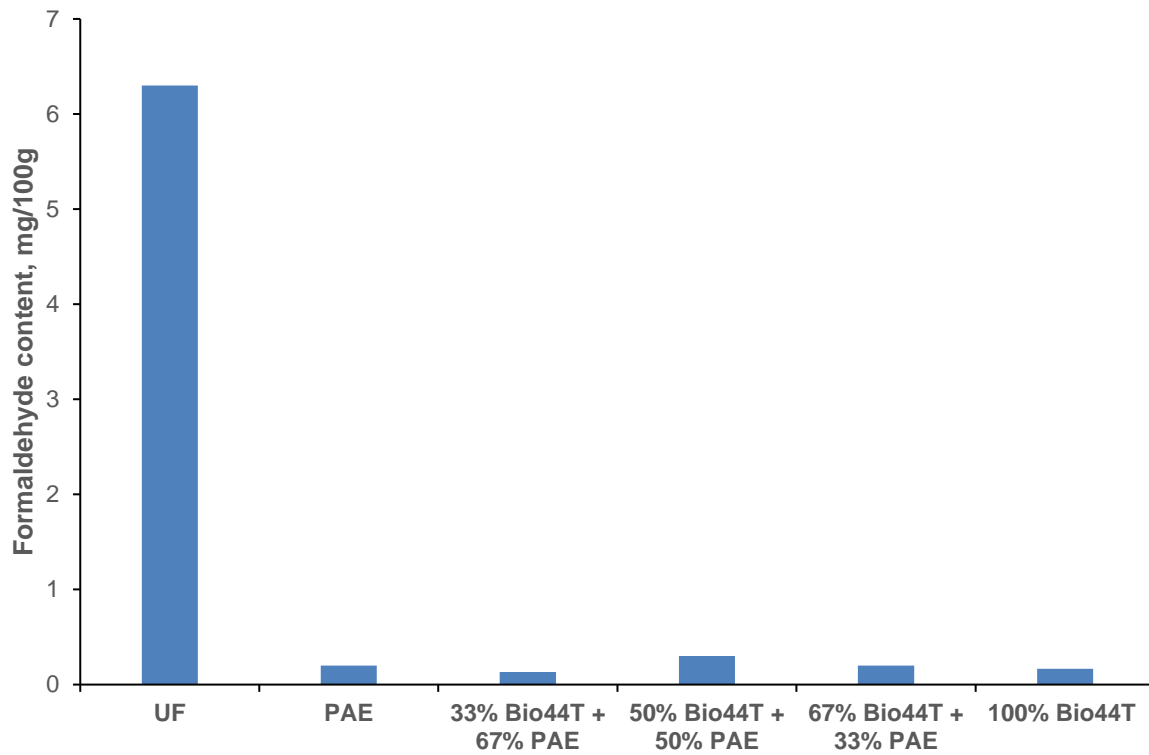


Fig. 49. Formaldehyde content of particleboards produced with combinations of the natural adhesive (Bio44T) and PAE according to EN 12460-5 standard (perforator method). UF-bonded boards served as additional reference.

5. CONCLUSIONS

5.1 PREMISE

The furniture sector is strongly demanding for wood-based panels made with bio-based adhesives without formaldehyde.

So far, the wood panel industry uses almost exclusively synthetic, petroleum-derived thermosetting adhesives, which are mainly based on the reaction of formaldehyde with urea, melamine, phenol, or co-condensates¹³³.

But in the 2004 the International Agency for Research on Cancer (IARC)¹³⁴ had reclassified formaldehyde from “probable human carcinogen” to “known human carcinogen”; thus in the last years changes in both formaldehyde legislations (i.e. United States of America with EPA TSCA Title¹³⁵ VI regulation, new limits foreseen for 2020 in Germany¹³⁶ with the halving of the European E1 class, GPP criteria) that limit emissions from furniture and building products has persuaded the panel manufacturers to reduce or better to eliminate the content of formaldehyde.

Furthermore, the wood-furniture sector is facing the challenge of the circular economy in order to have a positive impact on people and planet. Nowadays one of the tendencies is to reduce the use of fossil-based materials, with bio-based materials. (Pizzi 2006¹³⁷; Ferdosian et al. 2017¹³⁸; Hemmilä et al. 2017¹³⁹; Heinrich 2019¹⁴⁰; Solt et al. 2019¹⁴¹)

This study proposed a renewable bio-adhesive for plywood (in particular curved) and particleboards based on soy flour, MgO and a liquid enzymatic hydrolysate of an agricultural crop.

It was hypothesized a good solubility and interaction of proteins from the soy flour and the plant

¹³³ Pizzi, A. (2016). Wood products and green chemistry. *Annals of forest science*, 73(1), 185-203.

¹³⁴ IARC. (2004). IARC Classifies Formaldehyde as Carcinogenic to Humans, International Agency for Research on Cancer (IARC), Lyon, France, Press Release June 15, No. 153.

¹³⁵ EPA. (2017). Code of Federal Regulations (CFR) 40 CFR § 770 on Formaldehyde Standards for Composite Wood Products Act, Title VI to the Toxic Substances Control Act, TSCA; US Environmental Protection Agency.

¹³⁶ Bundesministerium für Umwelt Naturschutz und nukleare Sicherheit. (2018). Bekanntmachung analytischer Verfahren für Probenahmen und Untersuchung für die in Anlage 1 der Chemikalien-Verbotsverordnung genannten Stoffe und Stoffgruppen, Bundesanzeiger, BAnz, AT 26.11.2018 B2.

¹³⁷ Pizzi, A. (2006), “Recent developments in eco-efficient bio-based adhesives for wood bonding: Opportunities and issues,” *J. Adhes. Sci. Technol.*, 20(8), 829-846.

¹³⁸ Ferdosian, F., Pan, Z., Gao, G., and Zhao, B. (2017). “Bio-based adhesives and evaluation for wood composites application,” *Polymers*, 9(2), 70.

¹³⁹ Hemmilä, V., Adamopoulos, S., Karlsson, O., and Kumar, A. (2017). “Development of sustainable bio-adhesives for engineered wood panels—A Review,” *RSC Adv.*, 7, 38604-38630.

¹⁴⁰ Heinrich, L. A. (2019). “Future opportunities for bio-based adhesives – advantages beyond renewability,” *Green Chem.*, 21, 1866-1888.

¹⁴¹ Solt, P., Konnerth, J., Gindl-Altmutter, W., Kantner, W., Moser, J., Mitter, R., and van Herwijnen, H.W.G. (2019). Technological performance of formaldehyde-free adhesive alternatives for particleboard industry,” *Int. J. Adhes. Adhes.*, 94, 99-131.

hydrolysate under basic conditions offered by MgO in water. By grinding the mixtures, it was prepared an adhesive with 44 % solids.

5.2 RESULTS

- The natural adhesive showed the typical non-Newtonian behaviour of soy protein adhesives in terms of its viscosity as a function of rotation speed, and appropriate operability for wood-based panels. (Zhang et al. 2005¹⁴²; Frihart and Satori 2013¹⁴³; Feng et al. 2018¹⁴⁴).
- The latter finding was also supported by the thermal analysis results: the natural adhesive appeared to be thermal stable in the temperature range 130 to 240 °C with unchanged mass (TGA) and no major signals in the DSC and DTA curves (Wu et al. 2016¹⁴⁵; Ghahri and Pizzi 2018¹⁴⁶; Ghahri et al. 2018¹⁴⁷).
- No dangerous volatile substances were released from the natural adhesive according to headspace GC-MS. The detected cyclotetrasiloxane and cyclopentasiloxane are cyclic dimethyl polysiloxane compounds and are commonly used in cosmetics. The Cosmetic Ingredient Review Expert Panel has concluded that these ingredients are safe in the present practices of use and concentration. In detail, available data on these compounds did not suggest skin irritation or sensitization potential, and it is not likely that dermal exposure would cause systemic exposure (Johnson, Jr. et al. 2011¹⁴⁸).
- SEM analysis revealed a less coarse surface morphology of cured samples when the adhesive mixture was grinded.
- The natural adhesive requires a synthetic crosslinker such as PAE, at one third of the final formulation, for effective internal bond strength and swelling of particleboards. All

¹⁴² Zhang, J. T., Yang, X. Q., and Huang, L. X. (2005). "Changes of viscosity during preparation of soy protein isolate adhesives and their adhesive properties," *China Oils Fats* 30, 68-70.

¹⁴³ Frihart, C. R., and Satori, H. (2013). "Soy flour dispersibility and performance as wood adhesive," *J. Adhes. Sci. Technol.* 27(18-19), 2043-2052. DOI: 10.1080/01694243.2012.696948

¹⁴⁴ Feng, C., Wang, F., Xu, Z., Sui, H., Fang, Y., Tang, X., and Shen, X. (2018). "Characterization of soybean protein adhesives modified by xanthan gum," *Coatings* 8(10). DOI: 10.3390/coatings8100342

¹⁴⁵ Wu, Z., Lei, H., Cao, M., Xi, X., Liang, J., and Du, G. (2016). "Soy-based adhesive cross-linked by melamine-glyoxal and epoxy resin," *J. Adhes. Sci. Technol.* 30(19), 2120-2129. DOI: 10.1080/01694243.2016.1175247

¹⁴⁶ Ghahri, S. and Pizzi, A. (2018). "Improving soy-based adhesives for wood particleboard by tannins addition," *Wood Sci. Technol.* 52, 261-279. DOI: 10.1007/s00226-017-0957-y

¹⁴⁷ Ghahri, S., Pizzi, A., Mohebbi, B., Mirshokraie, A., and Mansouri, H. R. (2018). "Soy-based, tannin-modified plywood adhesives," *J. Adhes.* 94(3), 218-237. DOI: 10.1080/00218464.2016.1258310

¹⁴⁸ Johnson, Jr., W., Bergfeld, W. F., Belsito, D. V., Hill, R. A., Klaassen, C. D., Liebler, D. C., Marks, Jr., J. G., Shank, R. C., Slaga, T. J., Snyder, P. W., et al. (2011). "Safety assessment of cyclomethicone, cyclotetrasiloxane, cyclopentasiloxane, cyclohexasiloxane, and cycloheptasiloxane," *Int. J. Toxicol.* 30, 149S-227S. DOI: 10.1177/1091581811428184

particleboards manufactured with various combinations of natural adhesive and PAE showed very low formaldehyde content (Wescott et al. 2006¹⁴⁹; Zhong et al. 2007¹⁵⁰).

¹⁴⁹ Wescott, J.M., Frihart, C.R., Traska, A.E. (2006) "High-soy-containing water-durable adhesives *Journal of Adhesion Science and Technology*", 20 (8), pp. 859-873. doi: 10.1163/156856106777638734

¹⁵⁰ Zhong, Z., Sun, X. S., and Wang, D. (2007). "Isoelectric pH of polyamide–epichlorohydrin modified soy protein improved water resistance and adhesion properties," *J. Appl. Polym. Sci.* 103(4), 2261-2270. DOI: 10.1002/app.25388

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- Circular Economy Action Plan published on the 4th March 2019 (<http://ec.europa.eu/environment/circular-economy/>)
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