Journal of Environmental Chemical Engineering 10 (2022) 107053

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Sustainable non-isocyanate polyurethanes bio-adhesives for engineered wood panels are revealed as promising candidates to move from formaldehyde-based alternatives

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ARTICLE INFO

Editor: Apostolos Giannis

Keywords:
Lignocellulosic waste streams valorization
Bio-adhesives
Life Cycle Assessment
Wood bio-adhesives
Agro-industrial streams valorization

ABSTRACT

The main driving forces on the development of eco-friendly wood adhesives are based on environmental sustainability, costs savings, recyclability, reusability and health benefits, in comparison with synthetic resins. Lignin, tannin, proteins and carbohydrates are the main renewable raw materials being studied. Taking as a premise the technical performance of different bio-based alternatives, in comparison with formaldehyde-based resins, it is necessary to evaluate the environmental profile of such products in order to assess the pros and cons. In this regard, this manuscript addresses the industrial-scale design and environmental evaluation, through the Life Cycle Assessment methodology, of four formaldehyde-free bio-adhesives. For this purpose, the use of renewable resources such as Organosolv (OSL) and kraft (KL) lignins, soy (SPI) and tannins (MT)), crosslinked and hardened with NIPU (non-isocyanate polyurethanes) were considered. The impact results obtained showed that OSL-NIPU bio-adhesive, with a single environmental score of 35.27 mPa, has the best environmental profile, followed by SPI-NIPU, with a value of 63.36 mPa. Therefore, both could be considered as potential substitutes for synthetic resins. On the other hand, it has been identified that hexamethylenediamine (HDMA), used as crosslinking agent for the formulation of the bio-adhesives, is one of the main hotspots of the environmental profiles of OSL, KL and MT NIPU bio-adhesives. In the case of SPI-NIPU adhesives, it is the soy protein isolation process that leads to a higher environmental contribution. Thus, future research should focus on trying to reduce the dose of HMDA and on improving the soy protein isolation process.

1. Introduction

The depletion of fossil resources and environmental awareness are the main drivers for modifying industrial production patterns, based on the linearity of manufacturing, towards a circular economy model that encourages the use of renewable resources and the valorization of by-products and waste within the framework of the EU Bioeconomy Strategy and the Climate Change Mitigation Strategy 2050. Wood panel industry is one of the sectors considered strategic to meet the challenges proposed by the United Nations Sustainable Development Goals, specifically those included in SDGs 1, 2, 3, 6, 7, 13, 14 and 15. The integration of biotechnological approaches in forestry activities is essential to promote the use and industrialization of wood resources, processes that must take into account environmental protection and the conservation of natural heritage, thus developing alternatives that promote a sustainable use of natural resources. In this way, an ideal and sustainable coexistence between forestry and industrialization would be possible [26].

The global market of wood-based panels has continuously expanded since 2014, reaching production of 400 million cubic meters in 2018 [11]. The synthetic resins used in the wood-based panel industry mainly belong to formaldehyde-based types: phenol-formaldehyde (PF), urea-formaldehyde (UF) and melamine-urea-formaldehyde (MUF). Their widespread use is based on the fact that these adhesives exhibit versatile properties such as flexibility, low cost, high thermal stability, water and chemical resistance. However, formaldehyde emissions during their production and use associated with their fossil-based formulation have raised interest in environmentally sustainable and safe alternatives [22,30].

Therefore, the development of formaldehyde-free bio-adhesives, and derived from waste streams and non-usable resources, is considered an innovative option with a high market presence [14]. However, the formulation of bio-based adhesives for the wood-based panel industry is

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https://doi.org/10.1016/j.jece.2021.107053
Received 14 October 2021; Received in revised form 2 December 2021; Accepted 20 December 2021
Available online 23 December 2021

Nomenclature

DC	Damage Category
DMC	Dimethyl Carbonate
EQ	Ecosystem Quality
FE	Freshwater Eutrophication
FET	Freshwater Ecotoxicity
FRS	Fossil Resource Scarcity
GDE	Glycerol Glycidyl Ether
GW	Global Warming
HCT	Human Carcinogenic Toxicity
HH	Human Health
HMDA	Hexamethylenediamine
HNCT	Human Non-Carcinogenic Toxicity
KL	Kraft Lignin
KL-NIPU	Kraft Lignin Non-Isocyanate Polyurethane adhesive
LCA	Life Cycle Assessment
ME	Marine Eutrophication
MET	Marine Ecotoxicity
MT-NIPU	Mimosa Tannin Non-Isocyanate Polyurethane adhesive
MUF	Melamine-Urea-Formaldehyde resin
NIPU	Non-Isocyanate Polyurethane
OSL	Organosolv Lignin
OSL-NIPU	Organosolv Lignin Non-Isocyanate Polyurethane adhesive
PF	Phenol-Formaldehyde resin
SC	Source Scarcity
UF	Urea-formaldehyde resin
WC	Water Consumption

at an early stage of development, mainly at laboratory scale [7,13,19], so scale-up to a larger production capacity is required to evaluate and compare the potential of the bio-adhesives in the wood-based panel market. Accordingly, process modeling in the SuperPro Designer tool has been considered to develop the conceptual design of the manufacture processes. Alternatives based on the use of by-products or residues from the wood and agri-food industries have been selected, two of which are based on Organosolv and Kraft lignins, one based on tannins and the last one based on soy protein. Prior to the use of these raw materials in the formulation of bio-adhesives, it is necessary to carry out a series of steps to functionalize them, in order to accomplish the mechanical properties required by the standards. This process of functionalization and production of bio-adhesives is mainly divided into two different stages, a first carbonation stage based on the use of dimethyl carbonate (DMC) [16], which will allow the formation of carboxyl bonds that, in a second stage, will react with hexamethylene diamine (HMDA). This process causes the formation of high hardness urethane bonds, which result in non-isocyanate polyurethane resins (NIPU), which exhibit mechanical properties suitable for application in the panel gluing stage.

Once the bio-adhesive production processes have been designed and input and output flows estimated, the Life Cycle Assessment methodology will be applied to evaluate the environmental profiles associated with each of the proposed alternatives, in order to identify which of the NIPU bio-adhesives has the best environmental performance, i.e., the one with the lowest environmental impact.

2. Materials and methods

2.1. Goal and scope

The main objective of this manuscript is to evaluate the environmental profile associated with different formulations of bio-based NIPU adhesives for the wood-based panel industry to replace commonly used petrochemical options. To this end, process modeling has been addressed, with the objective of reaching a production capacity of 24 tons/day [10,20,21]. The use of SuperPro Designer® software allows modeling the process, identifying the composition of the streams, the chemical and energy requirements, and the design of the equipment for the bio-adhesive formulation stage. The assessment of the environmental profile associated with the production of bio-adhesives was performed according to the Life Cycle Assessment (LCA) methodology (ISO 14040, 2006), as it allows the evaluation of the environmental analysis and the identification of the main hotspots related to the manufacturing process [1,4,15,18].

Regarding the data source, the Ecoinvent database of the SimaPro v9.0 software was used for the analysis of the life cycle inventories of each proposed alternative considering a cradle-to-gate perspective. The ReCiPe 2016 Hierarchist Midpoint method v1.03 World (2010) was used to calculate the environmental impacts associated with the three proposed alternatives. The impact categories selected for the study were Global warming (GW), Stratospheric Ozone Depletion (SOD), Terrestrial Acidification (TA), Freshwater Eutrophication (FE), Marine Eutrophication (ME), Terrestrial Ecotoxicity (TET), Freshwater Ecotoxicity (FET), Marine Ecotoxicity (MET), Human Carcinogenic Toxicity (HCT), Human Non-Carcinogenic Toxicity (HNCT), Fossil Resource Scarcity (FRS) and Water Consumption (WC).

On the other hand, to perform a comparative analysis of the NIPU bio-adhesive alternatives, the calculation methodology selected was ReCiPe 2016 Hierarchist Endpoint method v1.03 World (2010), as it allows obtaining a single environmental score that encompasses three damage categories: Ecosystem Quality, Human Health and Source Scarcity.

2.2. Description of the process

In the development of NIPU bio-adhesives, two main steps could be differentiated along the large-scale production process. To perform the activation/functionalization of the bio-resources structures, it is required to develop a carbonation reaction, which is considered an effective method since it leads to an improvement in thermal stability, mechanical properties and increased affinity of the bio-adhesive polymer blend [10,12,25,28].

Accordingly, dimethyl carbonate (DMC), the simplest non-cyclic aliphatic carbonate, is used. It is considered as a green carboxymethylating agent that develops an acyl cleavage nucleophilic substitution [24,27]. Furthermore, it is important to take into account the reaction temperature, since DMC is able to undergo different reaction mechanisms depending on the temperature at which the reaction takes place. This mechanism is based on the reaction with the phenolic (-OH) groups present in the molecular structure of the lignocellulosics and vegetable proteins, leading to the release of methanol [16,25].

The second step requires the addition of a diamine compound, concretely hexamethylene diamine (HMDA), in which the amino group reacts with the intermediate, forming urethane linkages [19] and releasing methanol from the methoxy group (-OCH_3) of the intermediate and the hydrogen atom (-H) of the HMDA molecule.

Figs. 1 and 2 represents a simple mechanism for the formulation of the SPI-NIPU and lignin-based NIPU bio-adhesives.

Moreover, in the case of tannin-NIPU bioadhesives, a third step is required, since the addition of DMC and HMDA is not enough to obtain an adhesive suitable for their application since it requires such a high curing temperature that cannot be used as wood resins [6]. This drawback could be solved by the addition of glycerol diglycidyl ether (GDE), a reaction enhancer that attacks the amino group (-NH_2) of the HMDA

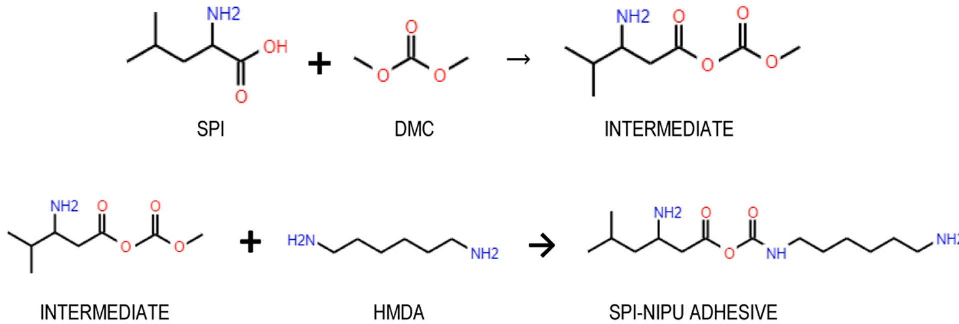


Fig. 1. Representation of a simple mechanism for the formulation of the SPI-NIPU bio-adhesives.

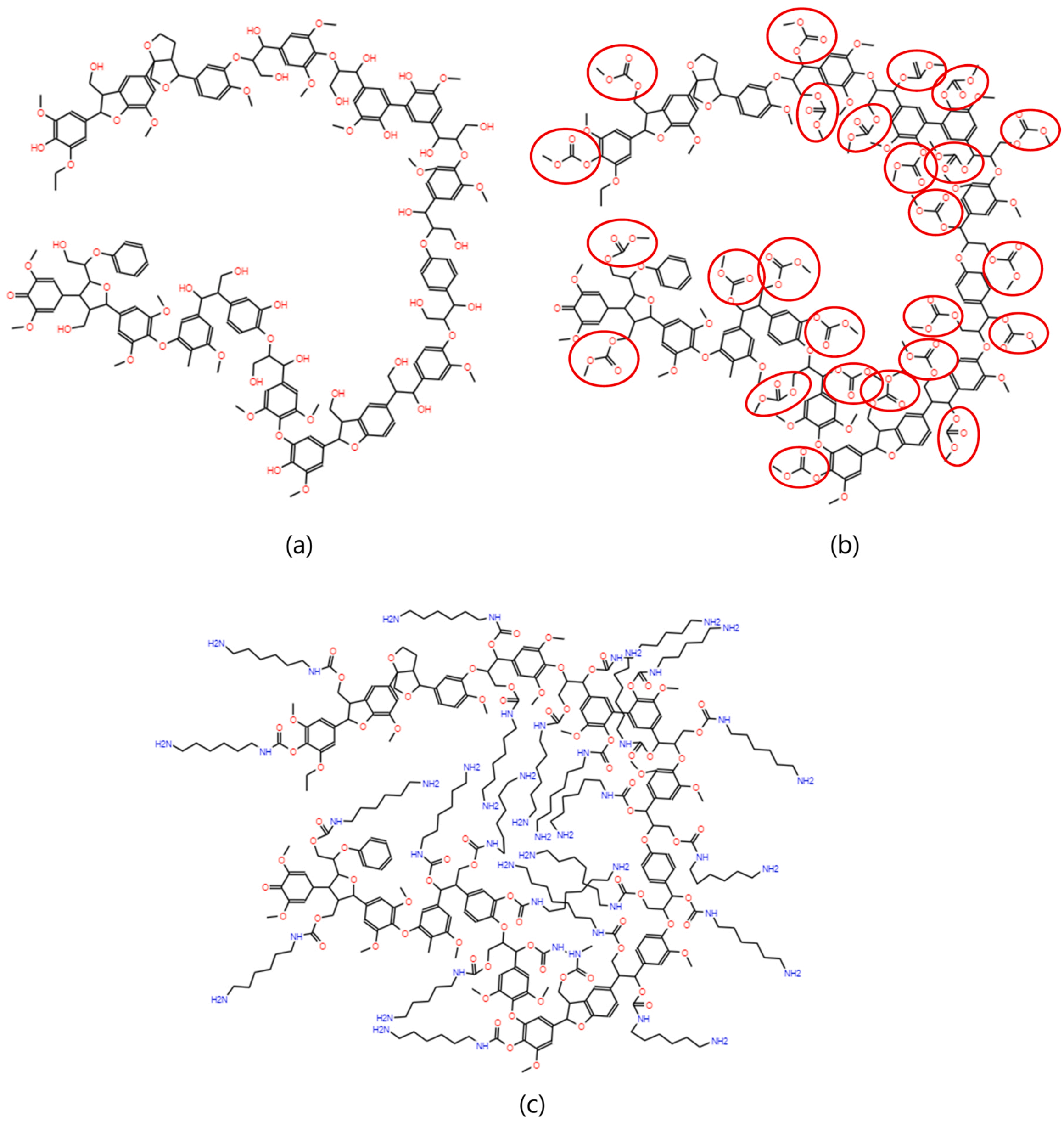


Fig. 2. Representation of a simple mechanism for the formulation of the OSL-NIPU bio-adhesives.

through ring opening and proton transfer mechanism (Fig. 3). This enhancement promotes low temperature adhesive curing, stronger adhesive bonds, high thermal stability, wet and shear resistance. Fig. 4 depicts a simple mechanism for the formulation of the MT-NIPU bio-adhesive.Fig. 5.

On the other hand, it is important to mention that, when selecting these bio-adhesives, in addition to their formulation process, their mechanical properties have also been considered, of which the most

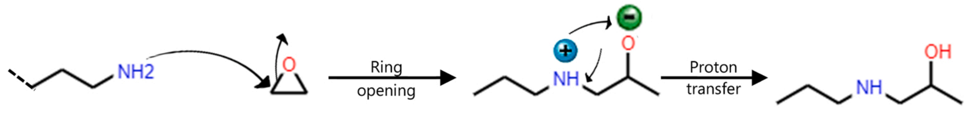


Fig. 3. Ring opening and proton transfer mechanism between amino group and GDE.

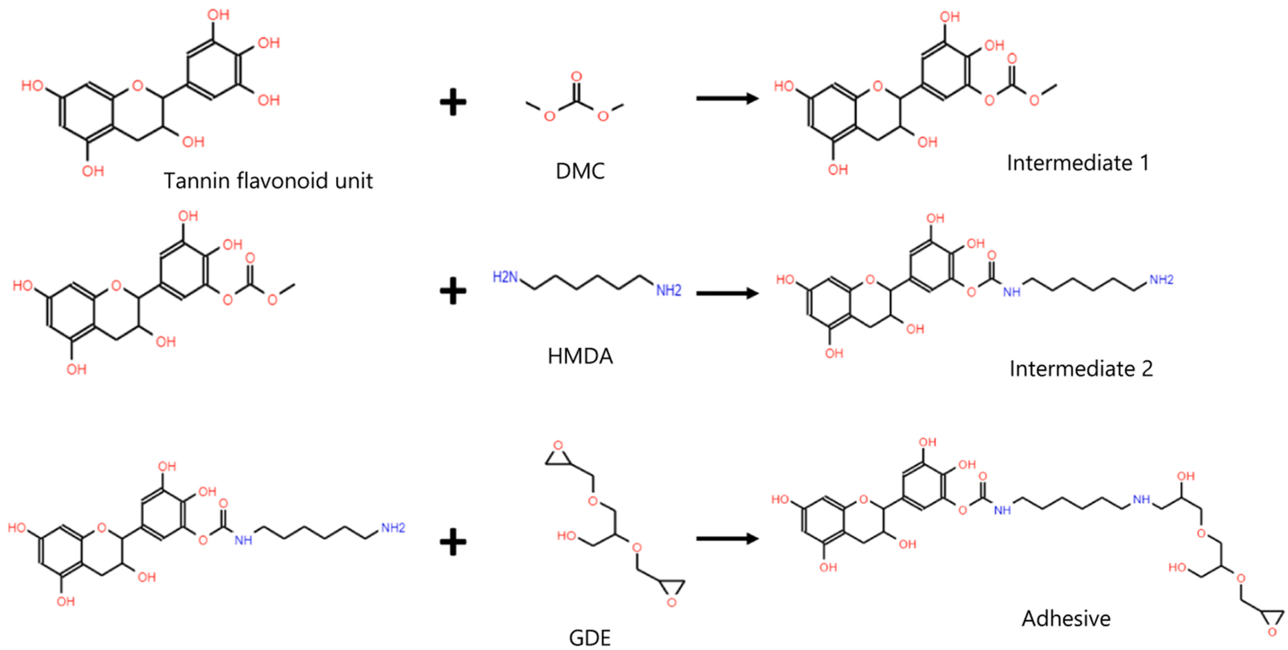


Fig. 4. Representation of a simple mechanism for the formulation of the MT-NIPU bio-adhesives.

significant is shear strength. For this reason, Table 1 includes a brief description of the values of this measurement parameter for each of the NIPU bio-adhesives proposed for the development of the LCA methodology.

2.3. Description of system boundaries and process inventories for LCA

In accordance with the system boundaries, a "cradle-to-gate" approach has been considered for the collection of inventory data (Fig. 4), i.e., stages from the extraction of materials and resources to the factory gate were considered. This approach is in line with the requirements of environmental product declarations [5]. Production and maintenance of infrastructure and transportation activities were left out of the system boundaries, as their contribution to the overall process environmental loads are not significant [2,29].

2.3.1. Description of process inventories for LCA

Once the system boundaries are defined, life cycle inventories are calculated, considering all inputs and outputs corresponding to the foreground systems of bio-based NIPU adhesives, considering the production of 1 kg of wood bio-based NIPU adhesive as the functional unit. The life cycle inventories for each of the alternatives are show from Tables 2 to 5.

In addition, the Ecoinvent® database was used as the main source of data (Table 6). Given that not all the components necessary for the formulation of bio-adhesives are available in the database, certain proxies had to be made. Ethylenediamine has been considered as an analogous product to HDMA, since its production process is similar to a large extent and, therefore, it is foreseeable that their environmental burdens will be analogous. In the case of GDE, bisphenol has been assumed as both products are considered to be widely used for the formulation of epoxy resins.

In the case of DMC and other bio-based, water and energy resources, inventory data are available for the development of its environmental assessment. As for electricity, it has been considered to be medium voltage, as it is sufficient for the energy requirements needed for the bio-adhesive formulation process.

3. Results

In order to evaluate the best procedure for the NIPU bio-based adhesives formulation, it is necessary to perform a comparative environmental analysis. ReCipe Midpoint V1.03 has been the selected methodology to determine the environmental impact values for each of the proposed alternatives (Table 7). But, at the same time, it is important to develop a more exhaustive study for each of the proposed processes to analyze the contribution of each input and output included within the system boundaries. These analyses are included in Sections 3.1 to 3.2. On the other hand, a comparative evaluation of the NIPU bio-adhesives alternatives has also been included in Section 3.4.

3.1. Environmental profile of the SPI-NIPU bio-adhesive

The characterization results of the SPI-NIPU bio-adhesive applying Recipe MidPoint methodology show two main hotspots (Fig. 6): soy protein isolate and HMDA, with the former being more remarckable in the SOD, FE, FET, MET and HNCT impact categories, while HMDA in the others. The high environmental contribution of SPI is the result of the energetic and chemical requirements needed to perform the protein isolation process [1]. It is based on the sequence of 7 differentiated stages in which three products are obtained: soy protein, soy flour and whey, according to [3]. Therefore, since the product of interest is soy protein, a mass allocation has been performed to identify only the environmental contribution associated with the production of soy

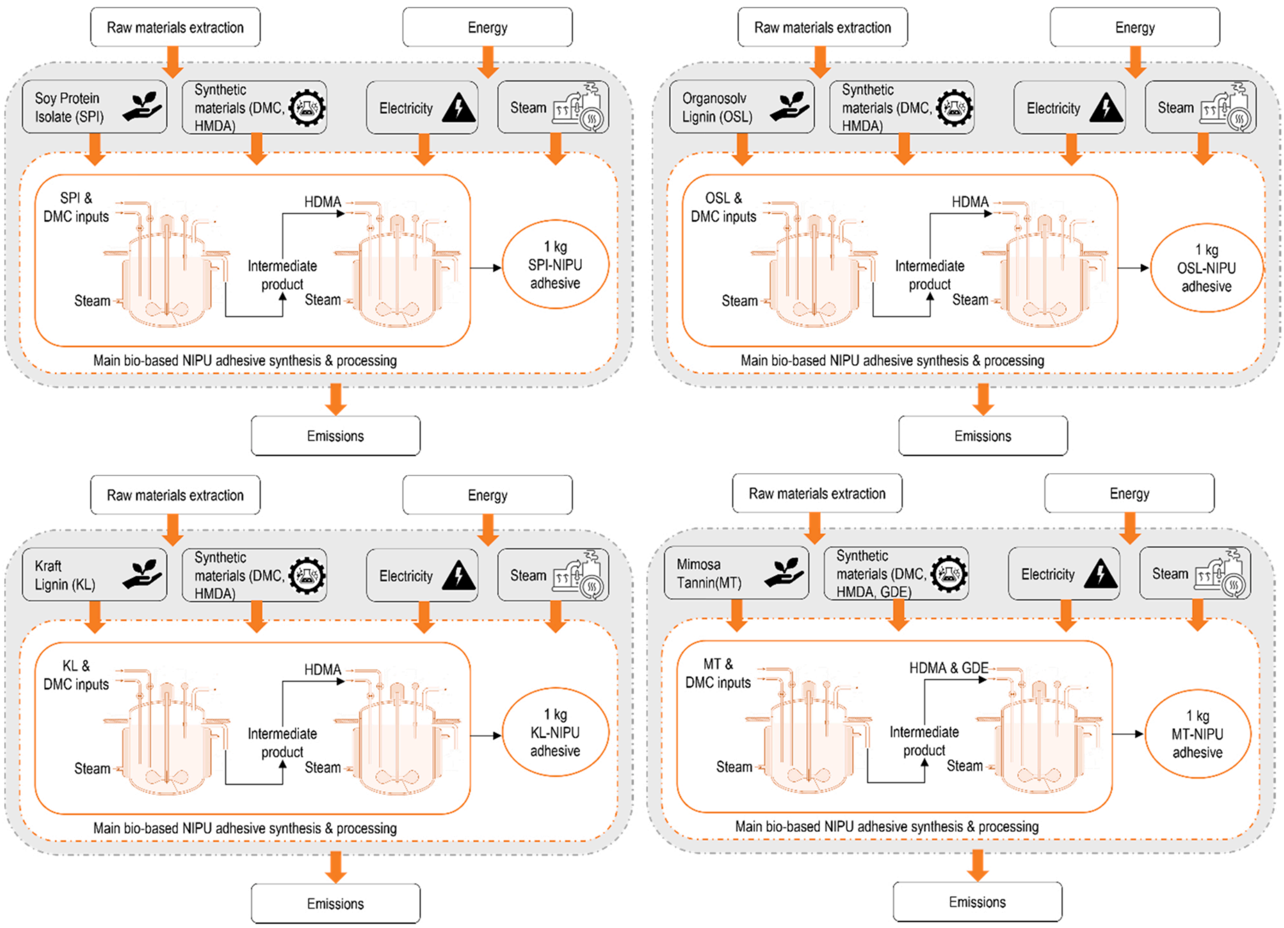


Fig. 5. System boundaries considered for the bio-based NIPU wood adhesives.

Table 1
Main strength properties of NIPU bio-adhesives alternatives.

SPI-NIPU		OSL-NIPU			KL-NIPU	MT-NIPU	
DBS[1] (MPa)		*SR[2] (N/mm^2)*			*DBS[1] (N/mm^2)*	*DBS[1] (MPa)*	
63 °C 3h	**Cold water 24 h**	**180 °C**	**200 °C**	**230 °C**	**200 °C**	**6 min**	**9 min**
		7.00	6.00	4.00	**10 min**	0.92	1.05
		DBS[1] (MPa)			**1 MPa**	*WBS[3] (3h, hot water, MPa)*	
0.28	0.34	**180 °C**		**230 °C**	3.00	**6 min**	**9 min**
		0.22		0.77		0.27	0.52

[1]DBS: Dry Bond Strength, [2]SR: ShearStrength, [3]WBS: Wet Bond Strength.
Data source:(Chen et al. [6], Pizzi et al. [20], Santiago-Medina et al. [23], Xi et al. [27])

Table 2
Main inputs and outputs values considered to perform the life cycle inventory of the SPI-NIPU adhesive.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
SPI	0.22	kg	**Adhesive**	1	kg
DMC	0.15	kg			
HMDA	0.28	kg			
H_2O	1.08	kg			
Electricity/heat			*Emissions to air*		
Steam	1.85	kg	**Water, vapor**	0.61	kg
Power	0.59	kWh	**Methanol**	0.11	kg

Table 3
Main inputs and outputs values considered for performing the life cycle inventory for OSL-NIPU adhesive.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
OSL	0.18	kg	**Adhesive**	1	kg
DMC	0.12	kg			
HMDA	0.25	kg			
H_2O	0.68	kg			
Electricity/heat			*Emissions to air*		
Steam	0.41	kg	**Water, vapor**	0.13	kg
Power	0.54	kWh	**Methanol**	0.11	kg

Table 4
Main inputs and outputs values considered for performing the life cycle inventory for KL-NIPU adhesive.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
KL	0.19	kg	**Adhesive**	1	kg
DMC	0.13	kg			
HMDA	0.26	kg			
H_2O	0.60	kg			
Electricity/heat			*Emissions to air*		
Steam	1.06	kg	**Water, vapor**	0.03	kg
Power	3.81	kWh	**Methanol**	0.12	kg

protein, for which, among others, NaOH and HCl, as pH regulating agents are added. In addition, the temperature required for the protein extraction process has been identified as the main hot spot of the process [3]. Therefore, these are the reasons identified to explain the significant environmental contribution of SPI in the profile obtained for the

Table 5
Main inputs and outputs values considered for performing the life cycle inventory for MT-NIPU adhesive.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
MT	0.24	kg	**Adhesive**	1	kg
DMC	0.16	kg			
HMDA	0.47	kg			
H_2O	0.20	kg			
GDE	0.10	kg			
Electricity/heat			*Emissions to air*		
Steam	0.43	kg	**Methanol**	0.19	kg
Power	2.48	kWh			

Table 6
Main data required for developing the LCA using Ecoinvent database®.

Materials	SimaPro Database
Hexamethylenediamine (HMDA)	Ethylenediamine {RER}| market for ethylenediamine | Cut-off, U
Dimethyl carbonate (DMC)	Dimethyl carbonate {GLO}| market for dimethyl carbonate | Cut-off, U
Water (H_2O)	Tap water {Europe without Switzerland}| market for | Cut-off, U
GDE	Bisphenol A, powder {GLO}| market for | Cut-off, U
Electricity/heat	
Steam	Steam, in chemical industry {RER}| market for steam, in chemical industry | Cut-off, U
Power	Electricity, medium voltage {Europe without Switzerland}| market group for | Cut-off, U

Table 7
Characterization results of the NIPU bio-based adhesives alternatives considering ReCipe Midpoint V1.03 as the calculation methodology.

Impact category	Unit	SPI-NIPU	OSL-NIPU	KL-NIPU	T-NIPU
GW	kg CO_2 eq	3.55	1.98	3.63	5.70
SOD	mg CFC_{11} eq	4.34	0.92	1.66	3.24
TA	g SO_2 eq	9.42	5.48	11.19	20.27
FE	g P eq	1.48	0.61	1.99	2.13
ME	g N eq	1.9	0.93	1.06	1.83
TET	kg 1.4-DCB	4.43	3.13	4.09	7.05
FET	kg 1.4-DCB	0.04	0.02	0.06	0.07
MET	kg 1.4-DCB	0.06	0.03	0.08	0.09
HCT	kg 1.4-DCB	0.09	0.05	0.12	0.14
HNCT	kg 1.4-DCB	2.06	0.86	2.54	3.10
FRS	kg oil eq	1.16	0.80	1.26	2.15
WC	m^3	0.05	0.03	0.06	0.11

SPI-NIPU bio-adhesive. As for the impact of the use of HMDA, it is the result of the background activities of its production process, which is characterized by being highly energy demanding and using chemical agents that also carry a significant environmental contribution.

On the other hand, energy requirements are also identified as impact contributors to the environmental profile obtained, with steam being the most noticeable in the GW, TA, TET and FRS impact categories, while the contribution of electricity is higher in the remaining categories. Aiming the reduction of the environmental impacts involved in the formulation of this bio-adhesive, the use of renewable resources could be considered as an alternative to supply energy requirements, since both are the main hotspots in the environmental profile of SPI and HDMA.

Regarding the results obtained after the application of the EndPoint methodology (Fig. 7), a certain analogy with the previous ones is perceived, since HDMA is the main contributor in the CS category and, in the two remaining damage categories, it is equivalent to the SPI, with contribution values around 34%. On the other hand, in terms of energy requirements, steam accounts for the highest impacts, being more noticeable in the SC category.

3.2. Environmental profile of the OSL-NIPU bio-adhesive

Two main hotspots associated with the bio-adhesive production procedure can be identified (Fig. 6): the use of hexamethylenediamine (HMDA), used as a crosslinking agent for the adhesive formulation, to favour the urethane bonds, and the energy required for agitation and maintenance of the temperature st 50ºC for the carbonation process, and 90ºC for bonding between the amino group of HMDA and the carbonated intermediate product. In addition, some energy is also required to increase the solids content of the bio-adhesive up to 46%. In this case, unlike the previous one, the environmental contribution of HMDA is significantly higher and stands out compared to the other components of the life cycle inventory. The reason for this higher contribution is based on the fact that in the case of OSL it is used directly for the formulation of the bio-adhesive, i.e., it does not require a previous treatment process for its use as a resource for the formulation of the adhesive.

In contrast, in the case of soy, a first stage of the protein separation (leucine) is required. Therefore, the use of the resource greatly favors its reduced environmental impact, in comparison, thus avoiding not only the consumption of non-renewable resources, i.e. the chemicals needed for its extraction and energy requirements, but also avoiding the associated emissions. Therefore, although the amount of HDMA used in the formulation of the bio-adhesive, in percentage terms, is similar, its impact is not, since the fact that the OSL has a lower environmental

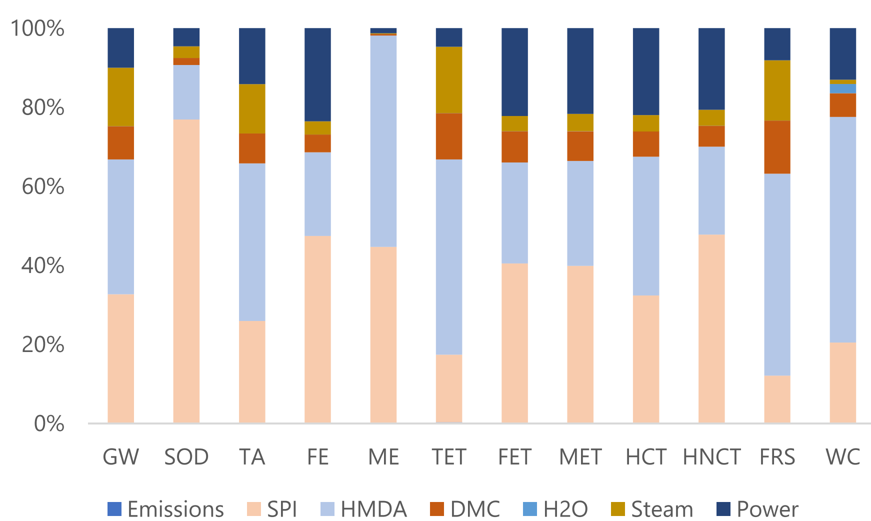
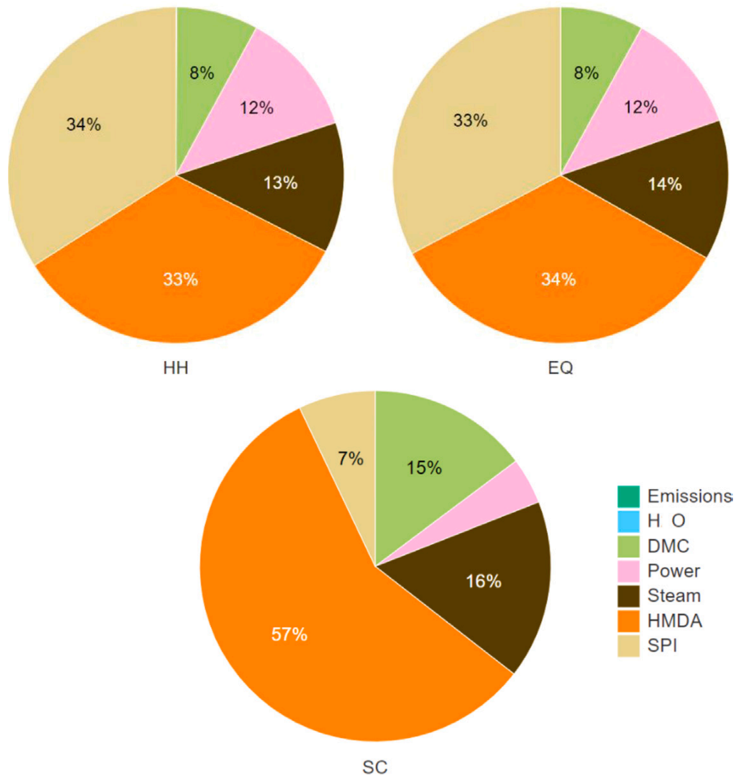


Fig. 6. Environmental profile and individual contributions of SPI-NIPU adhesive obtained by applying Recipe Midpoint methodology.



DC	Emissions	SPI	HMDA	DMC	H2O	Steam	Power	*Total*
HH (mPt)	0.01	17.71	17.42	4.10	0.03	6.54	6.24	*52.04*
EQ (mPt)	-	2.38	2.48	0.58	-	0.98	0.85	*7.27*
SC (mPt)	-	0.29	2.33	0.60	-	0.67	0.17	*4.05*
Total (mPt)	*0.01*	*20.37*	*22.22*	*5.28*	*0.03*	*8.19*	*7.26*	*63.36*

Fig. 7. Recipe Endpoint-Single Score values for SPI-NIPU adhesive.

contribution entails a more notable environmental contribution from the rest of the components.Fig. 8.

On the other hand, the evaluation of this NIPU bio-adhesive alternative considering the Endpoint calculation methodology also shows the important and significant contribution of HMDA in all damage categories, with the HH category being the most affected (Fig. 9). A certain impact of DMC is also noted, especially in the SC category. The reason for its relatively high impact is based on the energy requirements of its production process, which are non-renewable based and therefore contribute to the depletion of fossil resources.

3.3. Environmental profile of the KL-NIPU bio-adhesive

Although the operating conditions are analogous to those of the OSL-

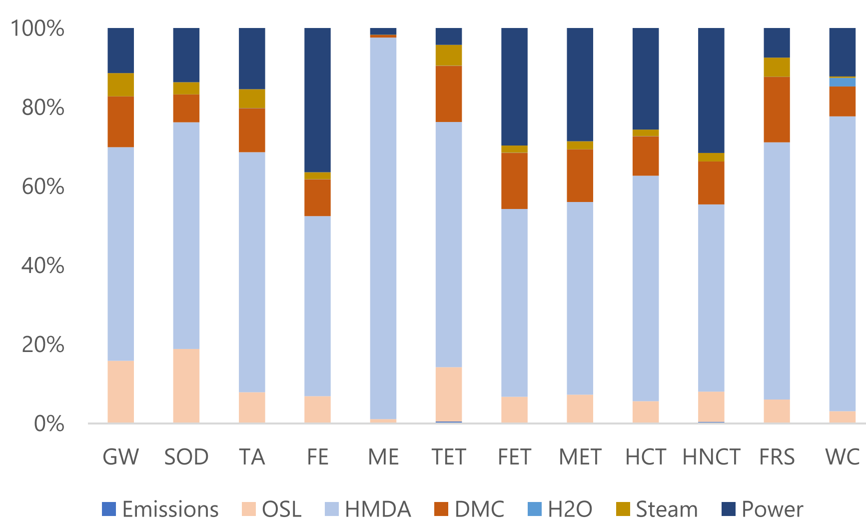
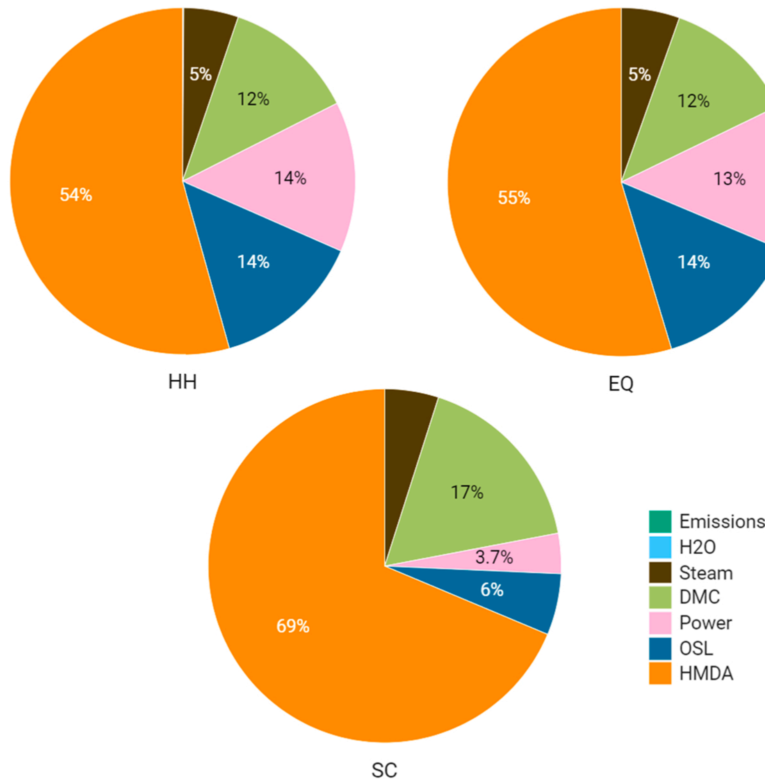


Fig. 8. Environmental profile and individual contributions of the OSL-NIPU adhesive considering the Recipe Midpoint methodology.



DC	Emissions	OSL	HMDA	DMC	H_2O	Steam	Power	*Total*
HH (mPt)	0.01	3.99	15.42	3.51	0.02	1.45	3.97	*28.36*
EQ (mPt)	-	0.56	2.19	0.50	-	0.22	0.54	*4.01*
SC (mPt)	-	0.17	2.06	0.51	-	0.15	0.11	*3.00*
Total (mPt)	*0.01*	*4.72*	*19.67*	*4.51*	*0.02*	*1.82*	*4.62*	*35.37*

Fig. 9. Recipe Endpoint-Single Score values for OSL-NIPU adhesive.

NIPU bioadhesive, the contribution of energy requirements in the environmental profile of the KL-NIPU bio-adhesive is greater than the previous option presented above. This increase in the electricity consumption of the process could already be observed in the inventories of both alternatives, where in the case of OSL a total of 0.54 kWh/kg of bioadhesive is required, this value is almost eight times higher for the KL-based adhesive, amounting to 3.81 kWh/kg of bio-adhesive. The reason behind this increase is based on the different molecular weights of the lignins. While in the case of OSL, its average molecular weight is around 4689 g/mol, in the case of KL its value rises to 7916 g/mol. A higher molecular weight implies a greater difficulty in maintaining the homogeneity of the crosslinking reaction medium between the components contributing to the bio-adhesive formulation, i.e., a greater need for stirring power, since mass is directly proportional to density and, in turn, to stirring power. Therefore, the greater the molecular mass, most difficulty of homogenization and higher requirements of stirring power

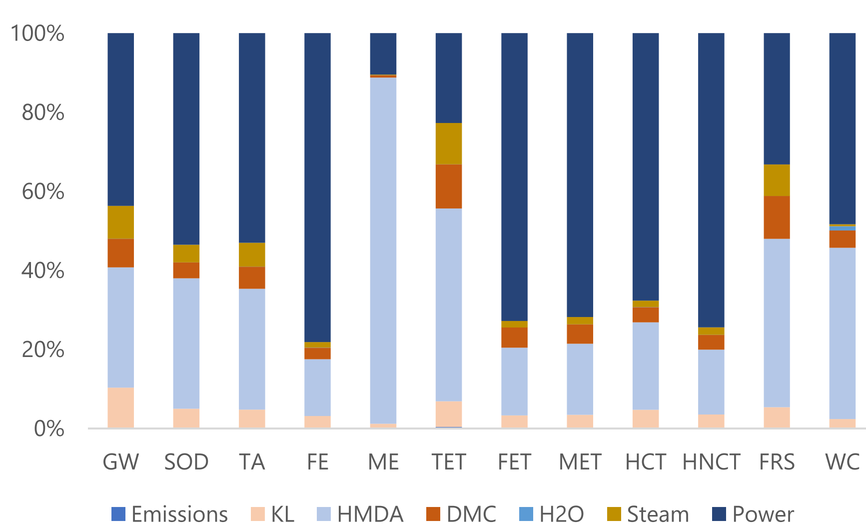


Fig. 10. Environmental profile and individual contributions of the KL-NIPU adhesive considering the Recipe Midpoint methodology.

which, consequently, will need a higher energy demand, leading to a greater contribution to the environmental profile (Fig. 10). Finally, it is worth mentioning that the contribution of HDMA to the bio-adhesive profile remains high, as was the case for the two NIPU bio-adhesive alternatives studied previously.

Regarding the results obtained after the application of the Endpoint methodology (Fig. 11), as expected, for the KL-NIPU bio-adhesive the contribution of electrical requirements on the damage categories is notably higher compared to the previous scenarios, amounting to a percentage contribution of approximately 50%. This result is associated with the consumption of non-renewable fossil resources, which affects, not only the depletion of resources, but also the quality of the environment, given the emissions involved in the extraction and production process, which in turn has a negative impact on the quality of human health. In addition, a significant contribution from HMDA is still perceived, the reasons being analogous to those given for energy requirements: the production processes of this compound, i.e., the background activities, contribute significantly to the consumption of non-renewable resources.

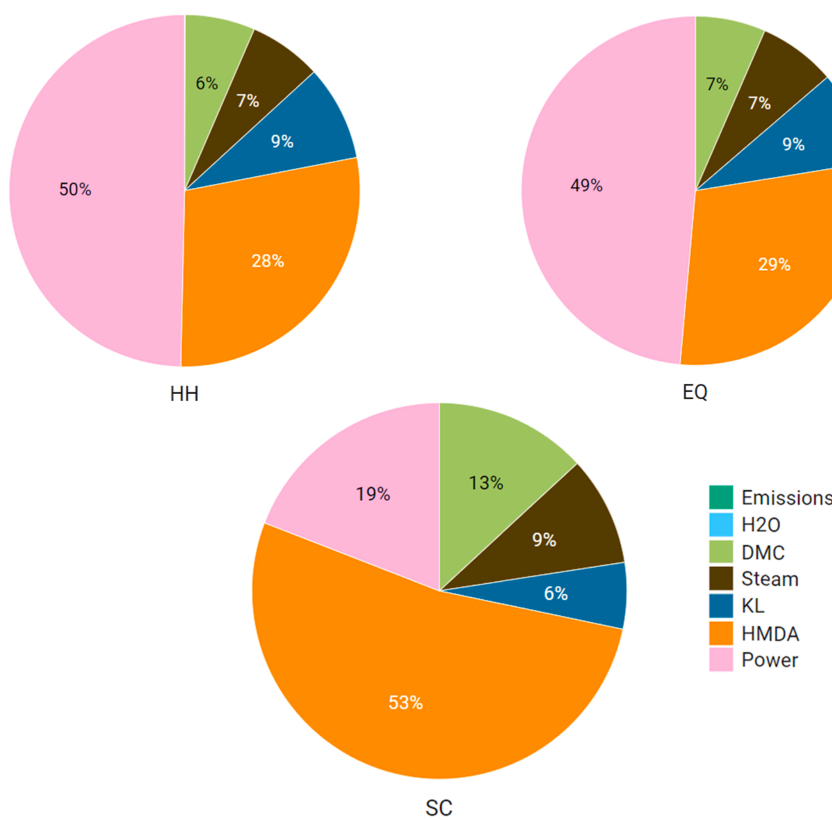
3.4. Environmental profile of the MT-NIPU bio-adhesive

The NIPU bio-adhesive formulated from tannins is the one that has the most significant difference in its formulation, compared to the other three alternatives developed, since it requires the addition of GDE, an aliphatic monomer epoxy that improves its thermo-mechanical properties, thus favoring a lower curing temperature and increasing its applicability in the wood panel forming industry. This fact also implies a certain contribution of the GDE in the environmental profile, although it is not very significant (Fig. 12). On the other hand, the background activities associated with tannins do contribute significantly to the environmental profile obtained, together with HMDA and electrical energy requirements. In the case of steam, its contribution is lower compared to the other scenarios because, for the formulation of the MT-NIPU bio-adhesive, the temperature is 50ºC, much lower if compared to that of the SPI/KL/OSL-NIPU bio-adhesives, which require 90 ºC.

Regarding the results of EndPoint (Fig. 13), the trend of the environmental contribution of HMDA is analogous to the previous profiles, although a certain impact of the use of GDE in the formulation of the bio-adhesive could be observed. Its most significant contribution is observed in the SC category, with a percentage value of damage that amounts to 9%, because of the background activities associated to its production process, which uses fossil resources to fulfill the energy requirements of the process.

3.5. Comparison between NIPU bio-adhesives considering EndPoint values

The different NIPU bio-adhesives have been ranked according to the single score values of EndPoint methodology. The bio-adhesive formulated with Organosolv lignin was the best from an environmental point of view, as its single score value is 25 points lower than the second and third alternatives: SPI-NIPU (63.36 mPt) and KL-NIPU (67.75 mPt). The main difference is observed in the HH damage category, although the



DC	Emissions	KL	HMDA	DMC	H_2O	Steam	Power	*Total*
HH (mPt)	0.01	4.90	15.87	3.61	0.02	3.75	27.77	*55.93*
EQ (mPt)	-	0.68	2.26	0.51	-	0.56	3.79	*7.79*
SC (mPt)	-	0.23	2.12	0.53	-	0.38	0.77	*4.03*
Total (mPt)	*0.01*	*5.81*	*20.24*	*4.65*	*0.02*	*4.69*	*32.33*	*67.75*

Fig. 11. Recipe Endpoint-Single Score values for KL-NIPU adhesive.

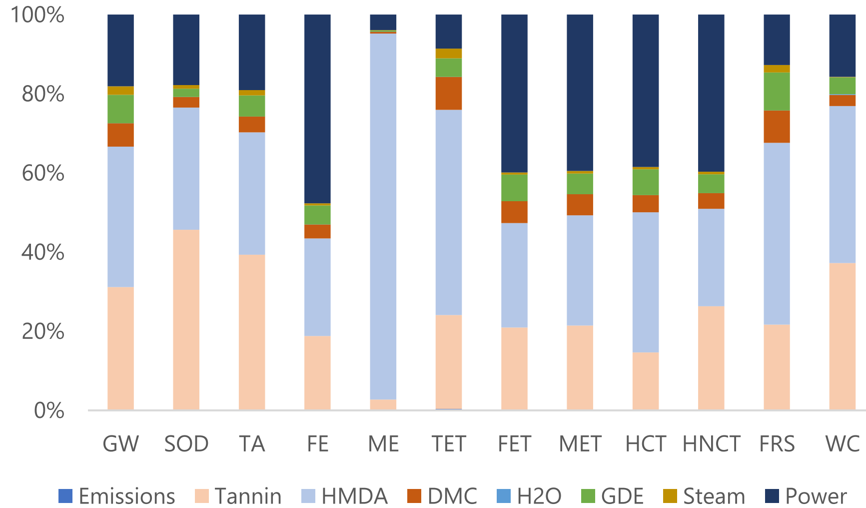
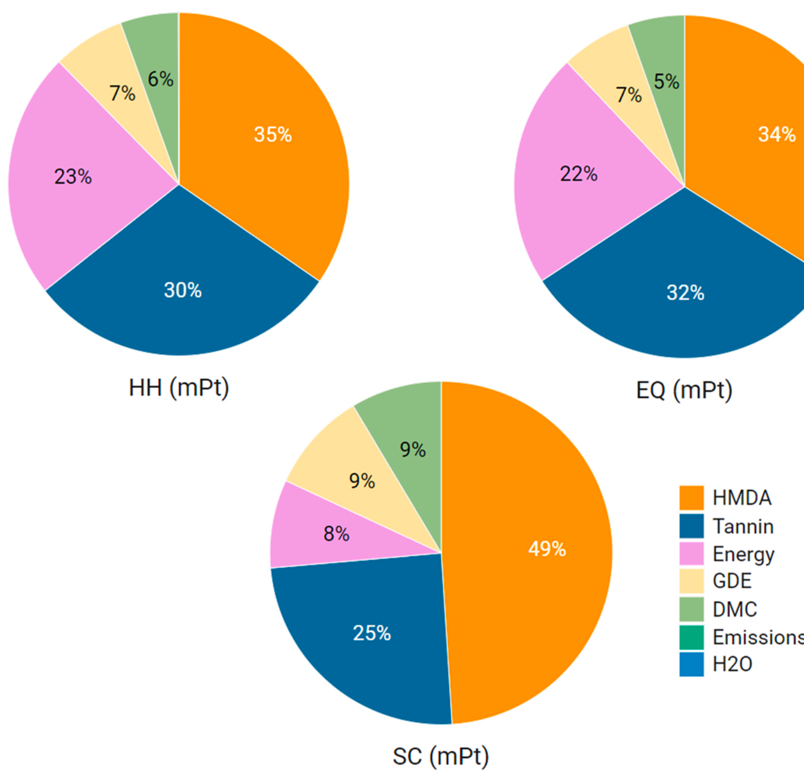


Fig. 12. Environmental profile and individual contributions of the MT-NIPU adhesive considering the Recipe Midpoint methodology.



DC	Emissions	Tannin	HMDA	DMC	H_2O	GDE	Steam	Power	*Total*
HH (mPt)	0.02	25.04	29.08	4.63	0.01	5.73	1.52	18.08	*84.10*
EQ (mPt)	-	3.88	4.13	0.66	-	0.81	0.23	2.47	*12.18*
SC (mPt)	-	1.95	3.88	0.68	-	0.75	0.16	0.50	*7.92*
Total (mPt)	*0.02*	*30.87*	*37.10*	*5.96*	*0.01*	*7.29*	*1.91*	*21.05*	*104.20*

Fig. 13. Recipe Endpoint-Single Score values for MT-NIPU adhesive.

variation of values in the EQ category is also significant. On the contrary, the MT-NIPU alternative is the one that leads to the worst result from the environmental point of view, reaching a damage value of 104 mPt. Therefore, it is in this bio-adhesive where further improvement and optimization work of the production process is required, given that tannins are considered as a raw material with high potential for the development of bio-adhesives for wood boards.

3.6. *Comparison with synthetic wood adhesives*

When new bio-based processes are developed to provide innovative alternatives that promote the rules of circular economy, through the valorization of waste streams from industrial processes, it is important to carefully evaluate their properties and characteristics in order to compare them with their synthetic-based analogues, i.e. those that are widely developed and implemented in wood-based panel production processes and in the market. In this way, it will be possible to obtain a global vision of their market opportunities, their improvement ranges, potentialities and deficiencies. When talking about bio-based products, it is important to bear in mind a fundamental aspect: bio-based products do not necessarily have to be environmentally friendly. They are two concepts that seem to go hand in hand, but they are not necessarily linked. While the recovery of residual resources is a plus, as it leads to avoiding the depletion of fossil resources and favoring the reduction of waste to landfill (for example), the processes associated for the functionalization of the raw materials in the formulation of bio-adhesives involve the use of chemical agents and energy, two aspects that can significantly affect the environment. Therefore, a detailed analysis of these new bio-based NIPU adhesives is important, as well as their comparison with synthetic resins, since the main objective is the search for a bio-adhesive that allows the reduction of the environmental impacts involved in the use of fossil-based adhesives and has the properties that allow the potential to replace them. Fig. 14.

Thus, in order to perform the comparative evaluation between bio-adhesives and synthetic resins, single score values obtained by applying the Recipe EndPoint calculation methodology were used. In the previous section, NIPU bio-adhesives were compared according to this same methodology, considering the damage categories separately, concluding that OSL-NIPU and SPI-NIPU are the ones with the best environmental profiles, as they cause less environmental damage both on human health and on ecosystem quality and resource scarcity.

The single score depicted in Fig. 15 show that both SPI and lignin-based bio-adhesive have the potential to replace synthetic resins, as they have a lower damage score than PF resin. But it is the OSL-NIPU bio-adhesive that has a better profile, from an environmental and human health point of view, as it has a single score value only three points above MUF resin and 3 ½ points below UF resin.

3.7. How could the environmental profiles of the bio-based NIPU adhesives be improved? Brainstorming of the proposals

Once all the environmental profiles of the proposed bio-based NIPU wood adhesive alternatives have been evaluated, as well as the relative contribution of each of the inventory components required for their formulation, with the objective of reducing the impact values obtained for each of the categories studied, a set of possible improvement actions is presented. Such proposals could be useful for researchers and stakeholders to identify where to focus on the study of bio-based wood adhesives. Throughout this report, two main hot spots have been identified in the environmental profiles, on the one hand the use of HMDA as a crosslinking agent and, on the other hand, the energy consumption, with the electrical requirements being the most detrimental.

Regarding the use of HMDA as crosslinking agent, its substitution by another crosslinking agent with less environmental impact could lead to a reduction in the efficiency of adhesion and in the quality of the wood panels obtained. But, although this substitution alternative could be considered as a "structural disadvantage", the optimization of the HMDA dosage used can be a key point for the environmental improvement of NIPU-based bio-adhesives. It should be recalled that the evaluation presented in this report has been developed based on laboratory-scale data, where the optimization of the resources used for adhesive formulation is not as relevant as the search for maximum adhesive quality. Therefore, it is common to overestimate the use, sometimes in excess, of the components that make up the molecular structure of the bio-adhesive to ensure its functionality.

In terms of energy consumption, the options for improvement are more extensive. The first option, and perhaps the most obvious and preferable, would be to opt for the use of renewable energies or the use of biomass in a cogeneration system, from which heat and electricity could be obtained. Furthermore, given that the ideal in the development of large-scale production of NIPU bio-adhesive would be to include it as an additional stage of the wood-based panel production facility, or as a downstream recovery stage of the pulp production process (in the case of KL and OSL NIPU bio-adhesives), other streams of the production process, which are in different temperature ranges, could be used as heat transfer agents in the jacketed CSTRs used for the formulation of NIPU bio-adhesives, thus reducing the consumption of steam and, therefore, of non-renewable fossil resources. In addition, another important aspect is the choice of the right equipment, from the point of view of energy efficiency. In addition, special emphasis must be placed on the correct insulation of the equipment, thus avoiding heat losses that would lead to an increase in the consumption of energy resources. On the other hand, another aspect that greatly affects the consumption of electrical energy and heating is the time spent in the bio-adhesive formulation reactors. In general, the production process takes about 3–4 h, so future research studies should perhaps focus their efforts on the search for production systems capable of obtaining bio-adhesives in a shorter time.

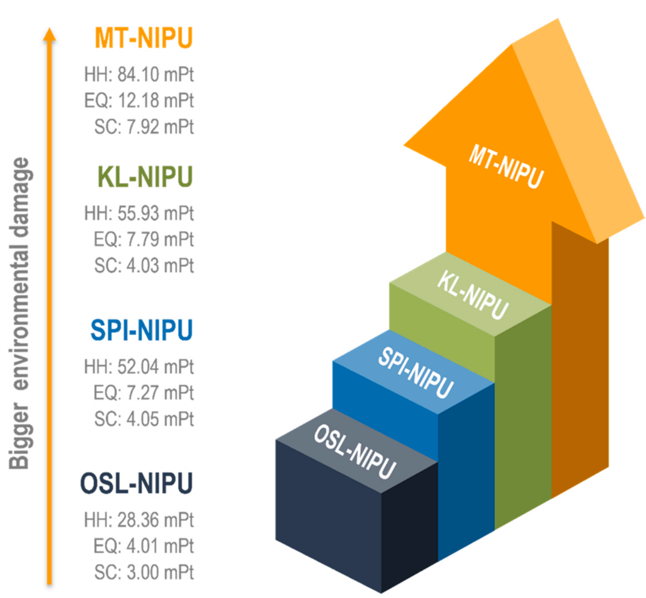


Fig. 14. Comparison between the bio-based NIPU adhesives considering the damage categories of ReCipe EndPoint methodology: HH, EQ, SC.

4. Discussion and conclusions

This report has addressed the environmental profile of four different wood bio-adhesive alternatives. Significant environmental achievements have been identified by developing an industrial scale-up simulation based on the approximation of bio-adhesive performance at laboratory scale and by applying the LCA methodology as a tool to assess the environmental impacts associated with the production processes. Thus, the results obtained have shown that it is the OSL-NIPU bio-adhesive alternative that allows the most environmentally friendly profile, reaching similar or even better values than synthetic adhesives, whose production process is fully optimized. Moreover, also the bio-adhesives KL-NIPU and SPI-NIPU have achieved interesting results to consider them as potential alternatives to replace formaldehyde-based resins. On the other hand, taking into account the contribution of the components/stages evaluated in the production process, the use of HMDA and the energy requirements contribute significantly to the environmental profiles obtained for each alternative studied. Thus, certain improvement strategies need to be implemented to obtain even better results for these NIPU bio-based wood adhesives.

In the search for new bio-adhesives alternatives for wood, given the good results obtained for soy protein, it would be interesting to apply an analogous production method using other proteins of vegetable origin. In fact, there are already some studies in which, for example, cottonseed protein is used as raw material to produce bio-adhesives for wood [8,9,

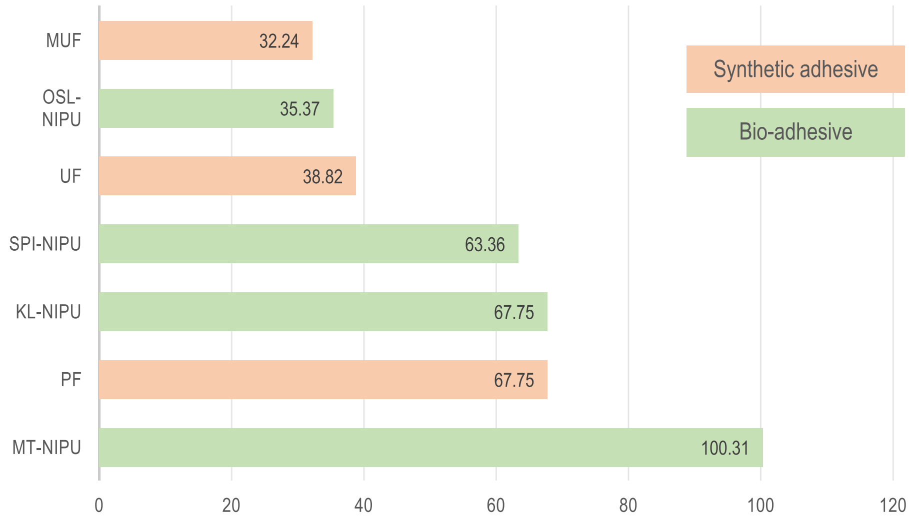


Fig. 15. Comparison between the bio-based NIPU adhesives and synthetic resins considering Single Score values.

17]. Therefore, future studies should focus on the environmental assessment and development of plant protein-based bio-adhesives, not only because of their environmental benefits, but also because they have demonstrated the ability to provide a bio-adhesive with mechanical properties suitable for the gluing of wood panels.

CRediT authorship contribution statement

Ana Arias: Methodology, Formal analysis, Investigation, Writing – original draft. **Eduardo Entrena-Barbero:** Methodology, Writing – original draft. **Gumersindo Feijoo:** Writing – review & editing. **Maria Teresa Moreira:** Conceptualization, Supervision, Writing – review & editing.

Acknowledgements

This research has been financially supported by ERA-CoBIOTECH project (PCI2018–092866) Programación Conjunta Internacional 2018-WOODBADH project. The authors belong to the Galician Competitive Research Group (GRC ED431C 2017/29) and to the Cross-disciplinary Research in Environmental Technologies (CRETUS Research Center, ED431E 2018/01).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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