

Supporting Information for

Towards green chemicals and edible coatings from barks and peels with near critical extraction of suberin

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This PDF file includes:

Supporting text
Figures S1 to S13
Tables S1 to S6

Supporting Information Text

Life Cycle Assessment of Suberin production for coating

We performed an LCA study, using the data as shown in the process model in Figure S13. The process model has been used as the base to build the inventory table for the LCA. The software SIMAPRO 9.4.0.2 was used to implement the LCA model. All background data are calculated using the database Ecoinvent 3.8. The CO₂ emissions from the combustion of the residual bark are considered biogenic emissions. The environmental impacts are calculated using the Environmental Footprint 3.0 methodology, which is the LCA impact assessment method suggested by the European commission to measure the life cycle environmental performance of products (EU Commission Recommendation 2021/2279).

LCA hotspot analysis for suberin production

The results of the hotspot analysis for the suberin production process are shown in figure 5A, normalized to the percentage of the total result for each environmental impact. The results in absolute values of the hotspot analysis are also listed in table S4. From the results of the hotspot analysis, it can be concluded that the use of electricity for the distillation process, and the production of the heat through natural gas are the two main environmental hotspots of the suberin production process.

Comparative LCA Suberin vs LDPE

To understand the environmental performances of suberin compared to a fossil-based plastic, we performed a comparative LCA between suberin and LDPE (Low Density PolyEthylene), assuming that both materials are produced to be used as coating of a medium size fruit (e.g. a cucumber or a melon). It is calculated that the amount of suberin required is 0.35 g, while 1.5 g of LDPE is required for the same application. The end-of-life of LDPE is also included, considering two possible treatments: incineration (with no energy recovery) and recycling (including the sorting process, to produce a clean fraction that can be sent to the plastic recycling facilities). The LDPE production and both end-of-life scenarios are modelled using the data available in the Ecoinvent 3.8 database. No end-of-life treatment is considered for suberin, since it is an edible material and it is supposed to be removed with the peel or consumed during the use phase. The results of the comparative LCA of suberin and LDPE are shown in Figure 5B, normalized to the total result for LDPE+incineration (set as 100%). Non-normalized results are reported in table S5. The comparative LCA results reveals that suberin coating exhibits slightly higher impacts in most environmental categories compared to LDPE + incineration. However, in the cases of “ozone depletion”, “ionizing radiation”, and “eutrophication, freshwater”, suberin coating demonstrates considerably higher impacts compared to LDPE. This significant difference between suberin and LDPE in these three categories can be attributed to the fact that these categories highly depend on the electricity and energy production processes. For eutrophication freshwater, the contribution of electricity production is 95%. For ionizing radiation the contribution of electricity is 97.8%. For ozone depletion the contribution of electricity is 23%, and heat is 49%. Our analysis, combined with data from the Ecoinvent database, highlights a substantial difference in electricity usage between the suberin and LDPE production processes. Specifically, the electricity demand for LDPE production ranges from 5 to 10 MJ per kg of LDPE produced^{1,2}. In contrast, according to our calculation at the early stages of process development, suberin coating production necessitates 150.6 MJ per kg of suberin produced. Consequently, this difference in electricity usage between suberin and LDPE production processes emerges as a key factor behind the significant impact variations observed across these specific environmental categories.

Only for the categories “particulate matter”, “water use”, and “resource use” suberin perform better than LDPE + incineration. Combining these results with the hotspot analysis, we concluded that the suberin production process need still further optimization, especially in the use of electricity and heat, if we want to achieve an environmental profile that can be competitive with the alternative,

fossil-based plastics available today in the market. However, further upscaling of lab scale processes will lead to a more optimized used of energy, that will improve the environmental profile of the process³. Also, in the case of suberin production, we concluded that the use of a cleaner electricity mix and heat recovery are the most effective strategies to improve the environmental profile of the process.

Sensitivity analysis

To corroborate our conclusion that a change in the electricity mix would lead to different environmental profiles of the suberin production process, we performed a sensitivity analysis on the LCA model, by substituting the US electricity mix with the one of Indonesia, that has a large availability of cassava peels but relies mostly on fossil-based energy, and Norway, that presents an electricity mix where $\approx 90\%$ is hydroelectric. The results of the sensitivity analysis are shown in Figure 5C, and in table S6. The results of the sensitivity analysis confirms that suberin can have a better environmental profile in all aspects except ozone depletion compared to LDPE if a clean electricity mix is used.

- 1 S. Cascone, C. Ingraio, F. Valenti and S. M. C. Porto, *J Environ Manage*, 2020, **254**, 109796.
- 2 L. Leppäkoski, G. Lopez, V. Uusitalo, H. Nieminen, N. Järviö, A. Kosonen, T. Koiranen, A. Laari, C. Breyer and J. Ahola, *Science of The Total Environment*, 2023, **882**, 163628.
- 3 F. Piccinno, R. Hischier, S. Seeger and C. Som, *J Clean Prod*, 2016, **135**, 1085–1097.

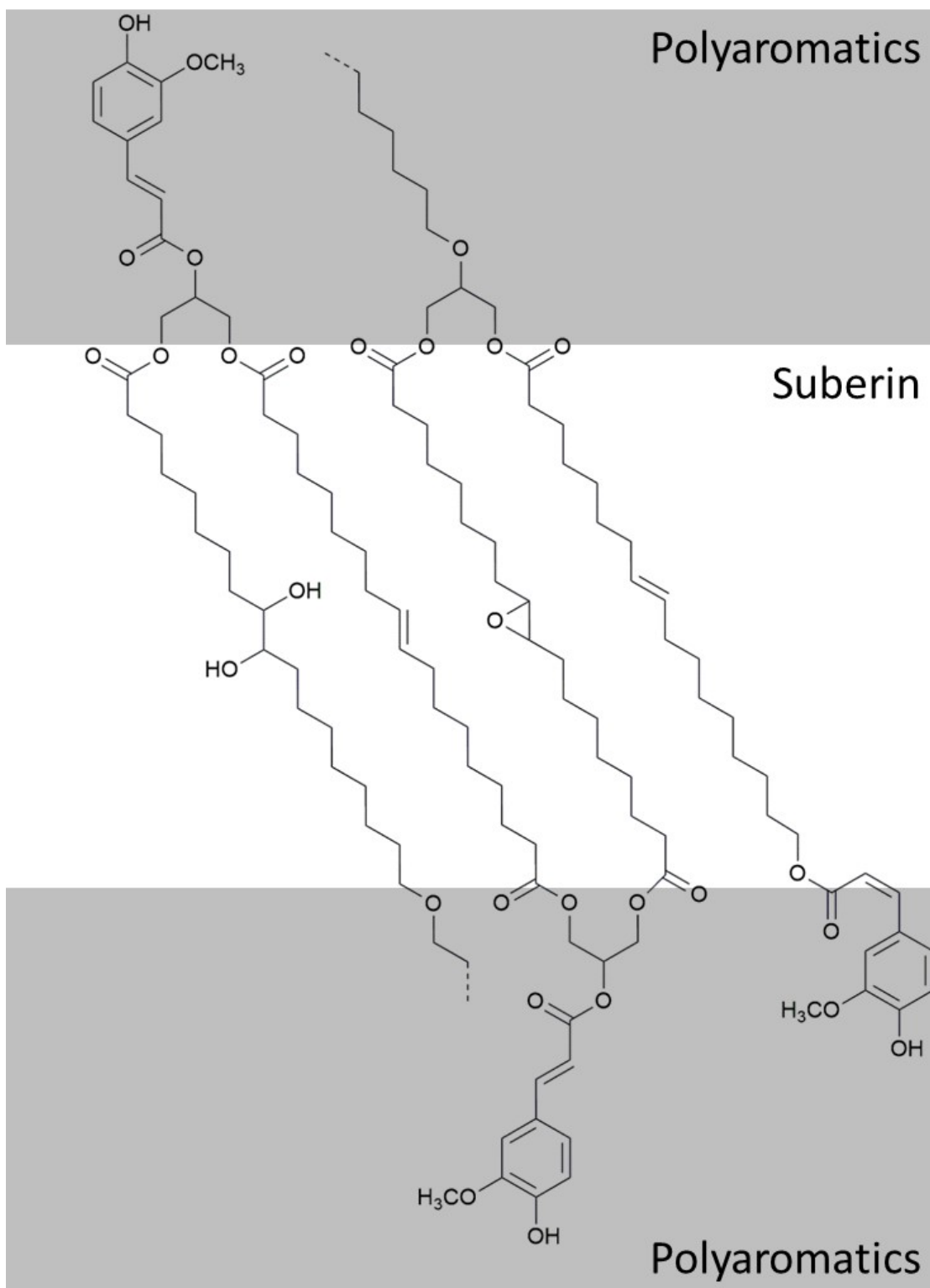


Fig. S1. Hypothetical structure of native suberin in the cell wall. Poly(acylglycerol) (suberin) is positioned between two layers of lignin-like polyaromatics. Chain lengths and intermediate functions may vary.

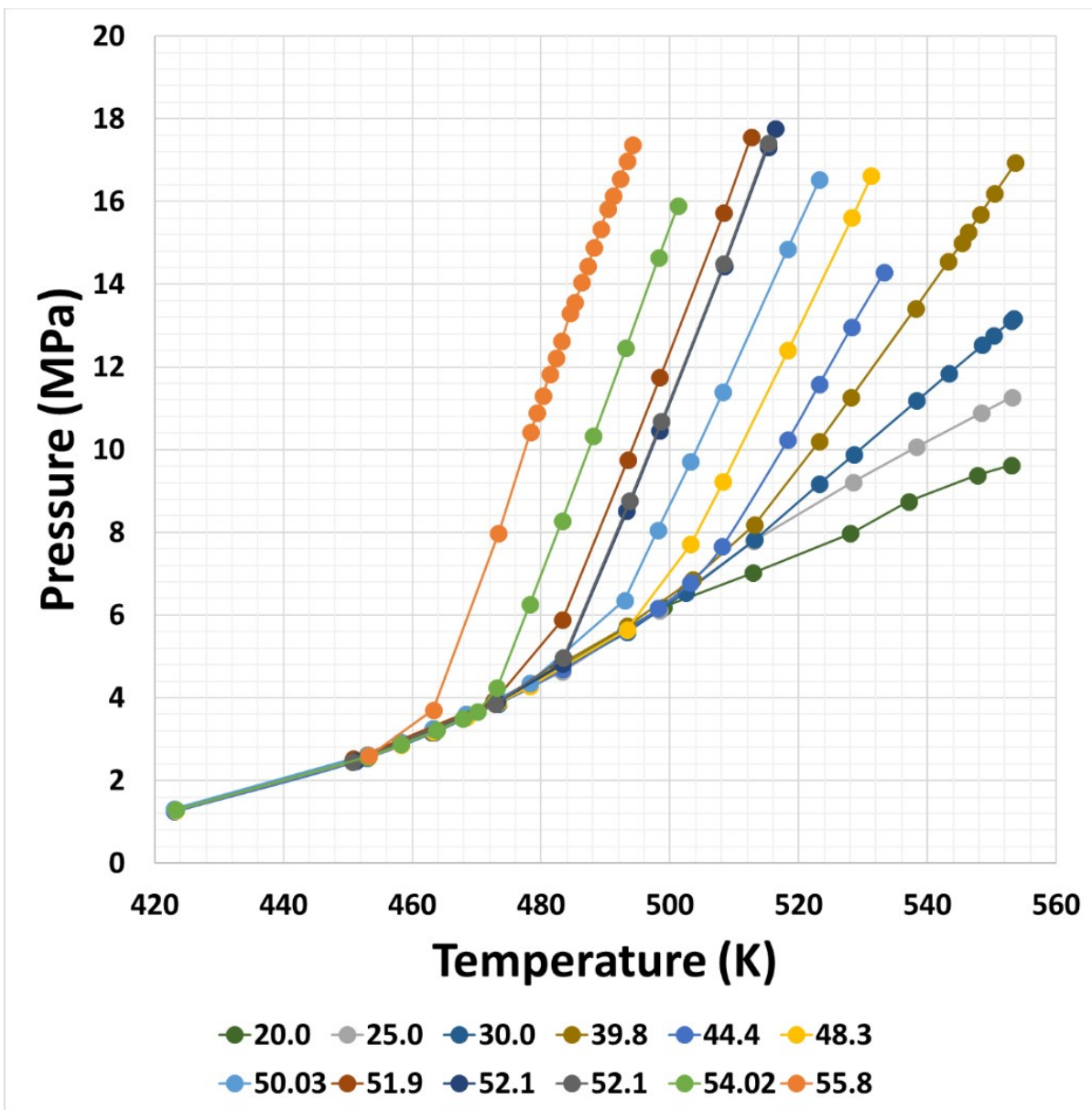


Fig. S2. Range of temperature and pressure achievable in 75 mL Parr series 5000 reactor system (Parr Instrument Co, Illinois, USA) in function of the mass of methanol inside (in g).

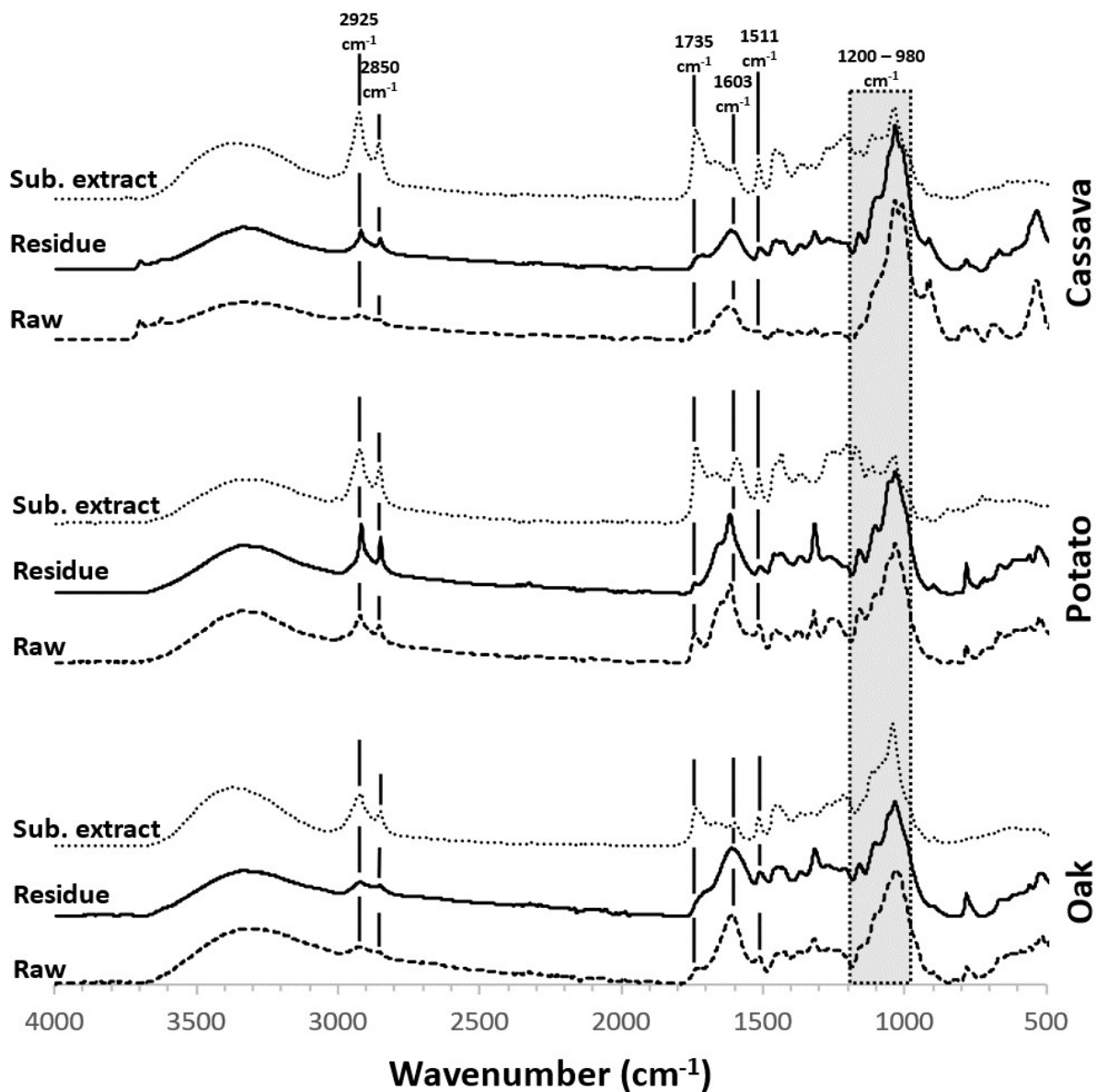


Fig. S3. ATR-FTIR spectra of SBM before treatment (Raw), after SC conditions at 518K 60 min 8.3MPa (Residue) and corresponding suberinic extract (Sub. Extract). 2925 cm^{-1} and 2850 cm^{-1} are attribute to aliphatic chain (C-H stretching and C-H, CH₃ stretching); 1735 cm^{-1} is attribute to suberin (C=O stretching); 1603 cm^{-1} is attribute to lignin (aromatic stretching); 1511 cm^{-1} is attribute to lignin (aromatic C=C stretching); 1200 - 980 cm^{-1} area is attribute to polysaccharides. Spectra are presented in absorbance.

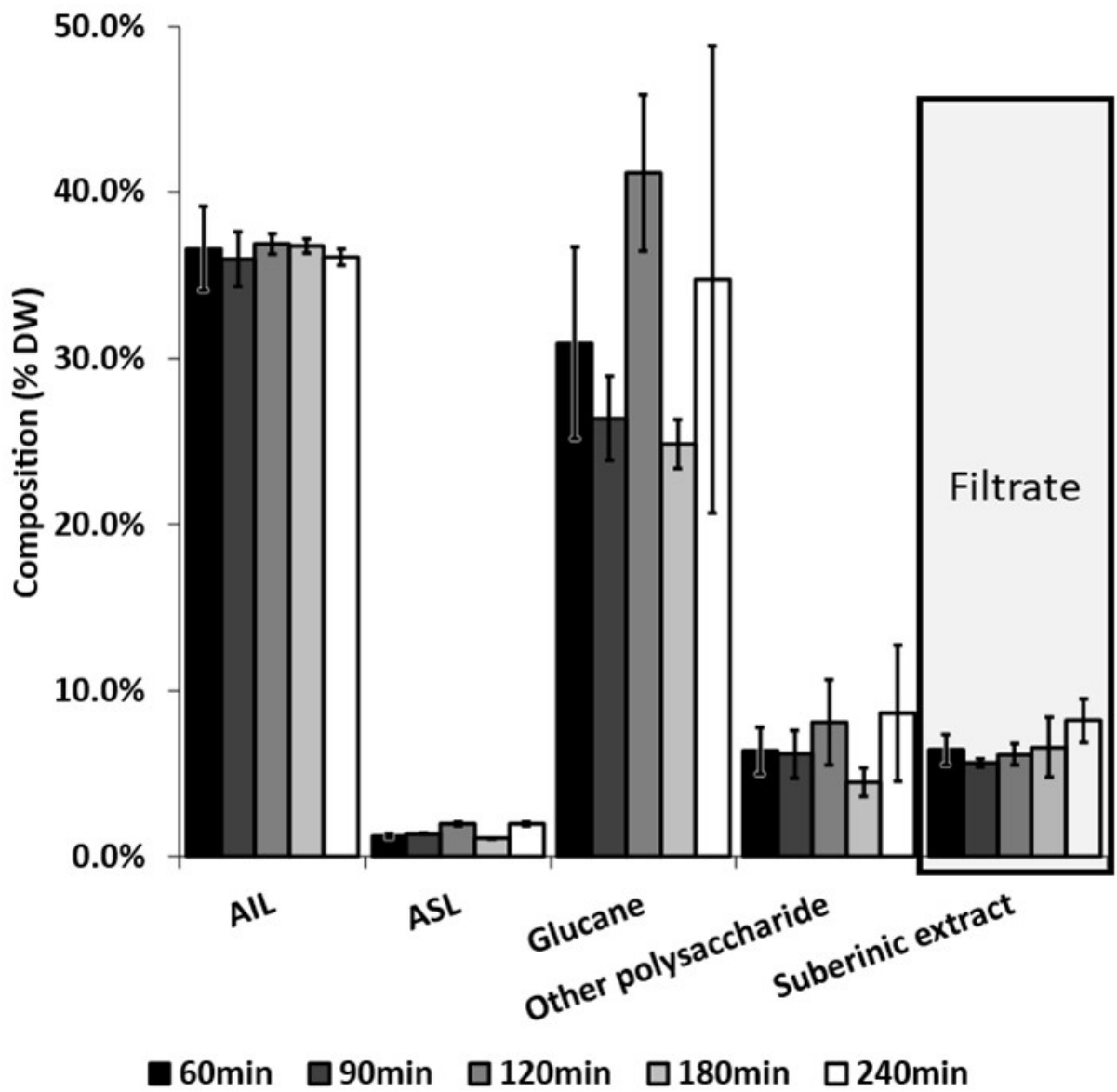


Fig. S4. Effect of SC conditions at 518K 8.3MPa 60-240 min on SBM component and suberin extract mass yield of cassava peels expressed as w% of treated dried peels. AIL = Acid Insoluble lignin and ASL = Acid soluble lignin. Absence of letters means no statistically significant differences were noticed inside each component ($P \leq 0.05$, Tukey HSD, $n=3$).

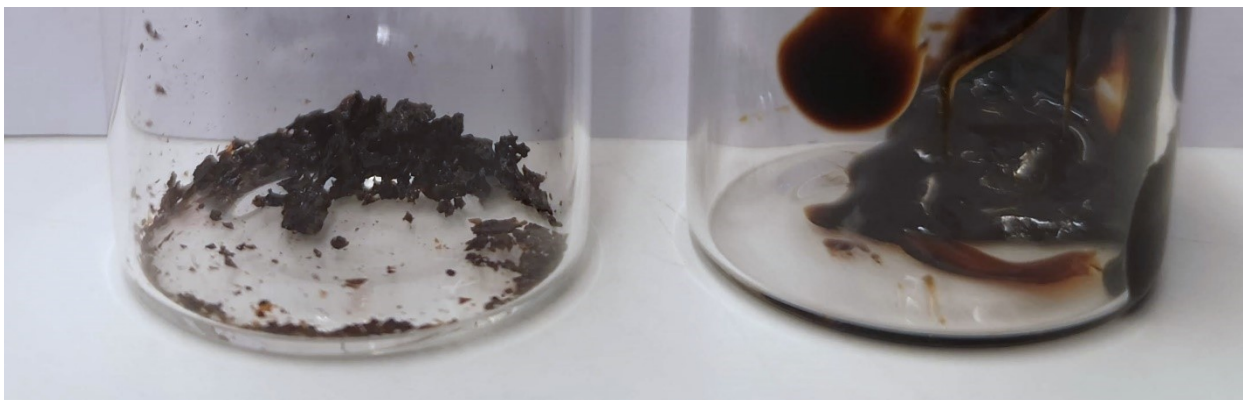


Fig. S5. Extracted suberinic material from oak bark (*Quercus robur*). (left: mild condition; right: strong condition).



Fig. S6. Extracted suberinic material from cassava peel (*Manihot esculenta*) mild condition.

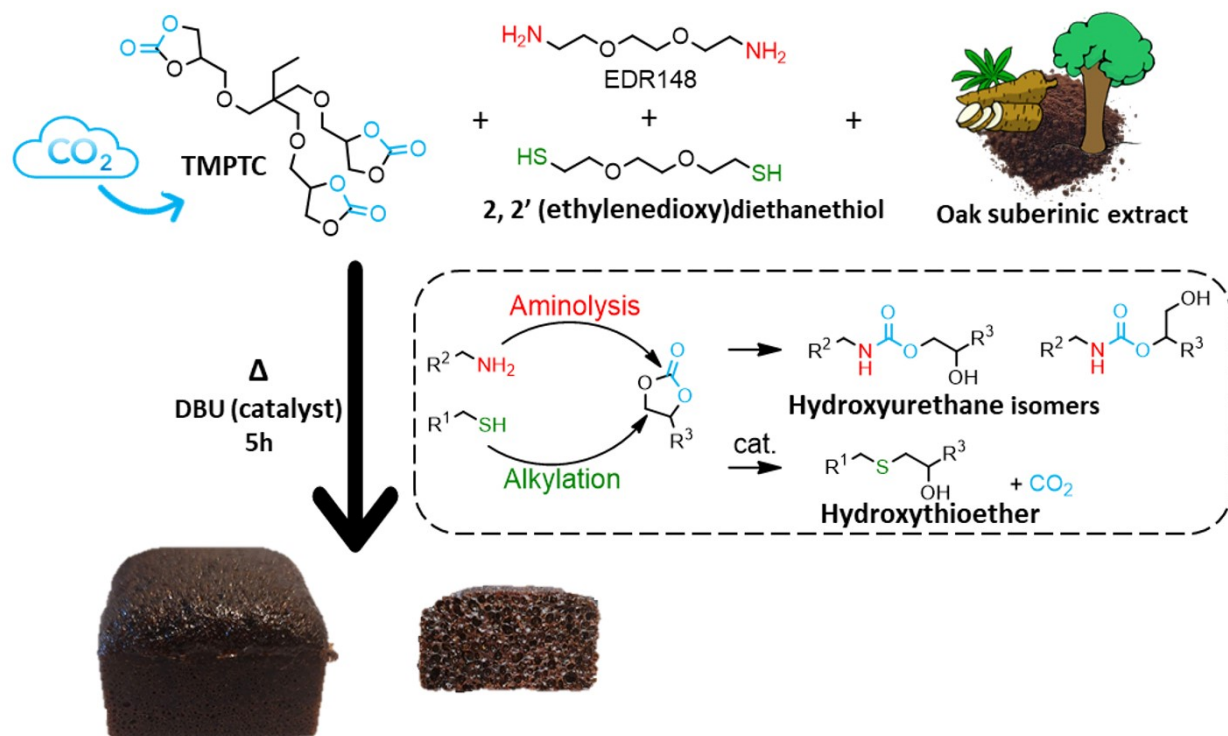


Fig. S7. NIPU formulation loaded or not by suberinic extract with associated reactions (urethane linkages and blowing agent formations).

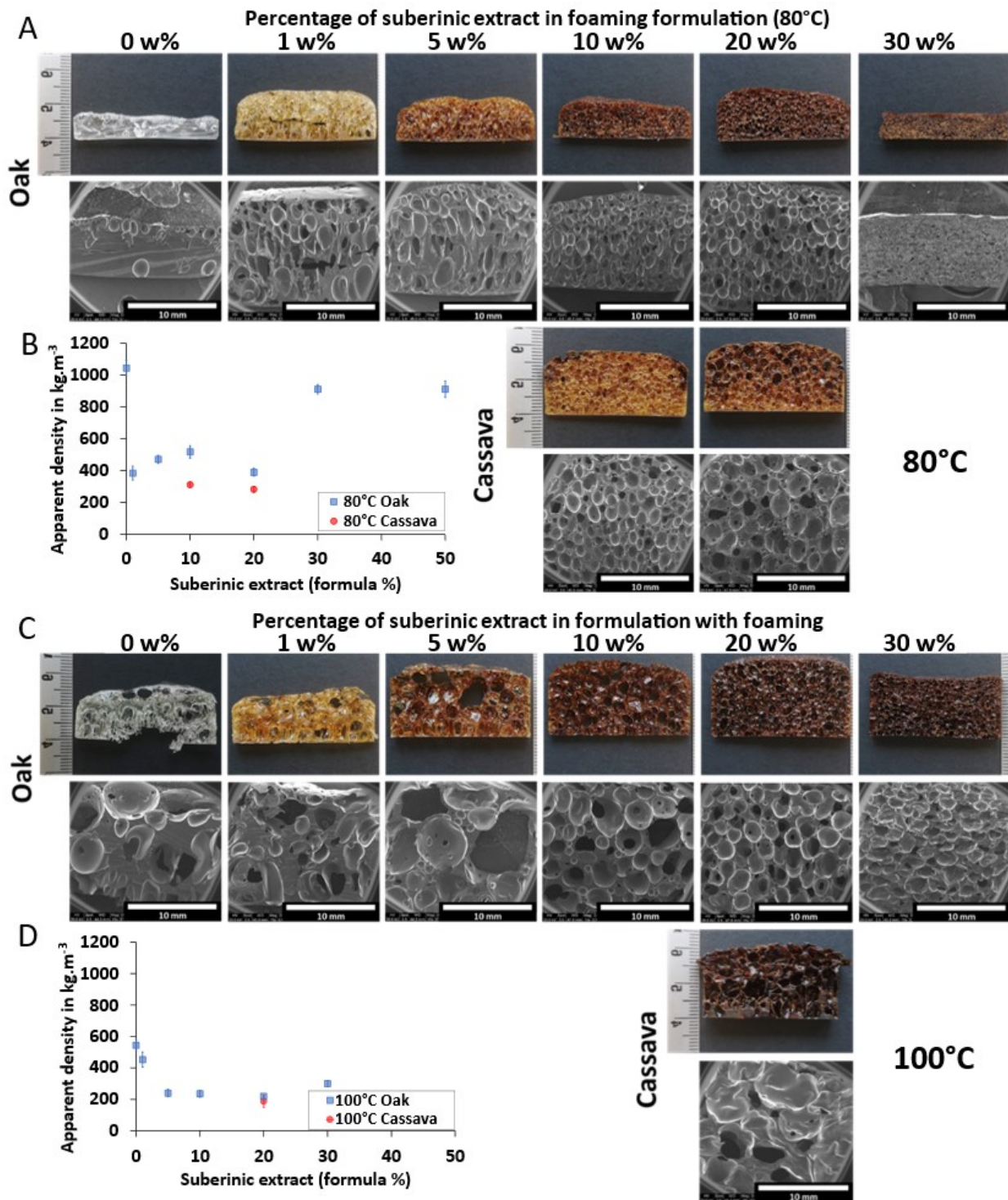


Fig. S8. Homogeneity and density of foams with and without suberinic extract loadings. (A) NIPU foams prepared from different suberinic extract loadings at 80°C, (B) Foam density vs the suberinic extract loadings for the foams prepared at 80°C. (C) NIPU foams prepared from different suberinic extract loadings at 100°C. (D) Foam density vs the suberinic extract loadings for the foams prepared at 100°C.

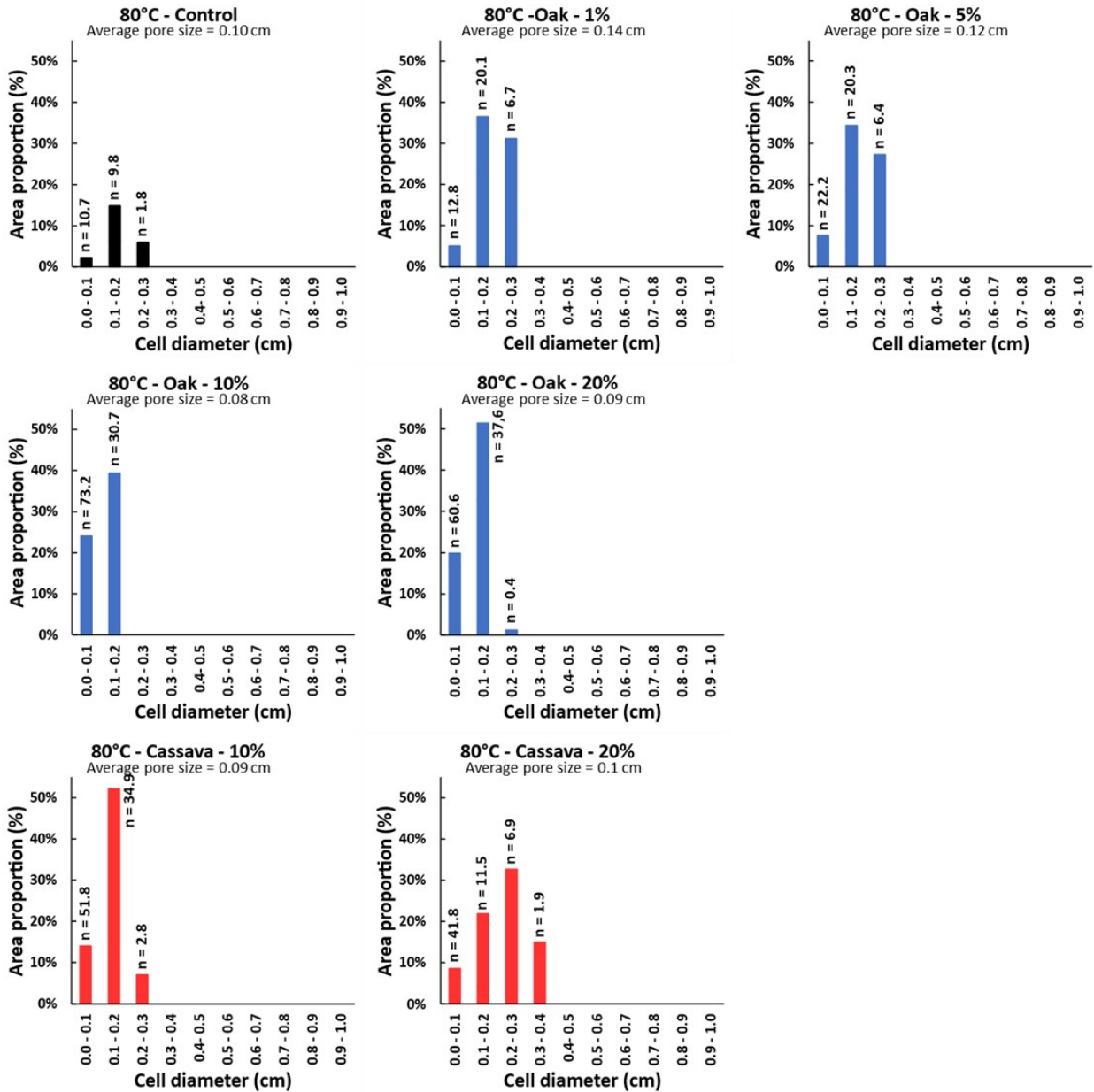


Fig. S9. pore size distribution in function of suberinic extract loadings for a foaming temperature of 80°C. n = number of cells in 1cm².

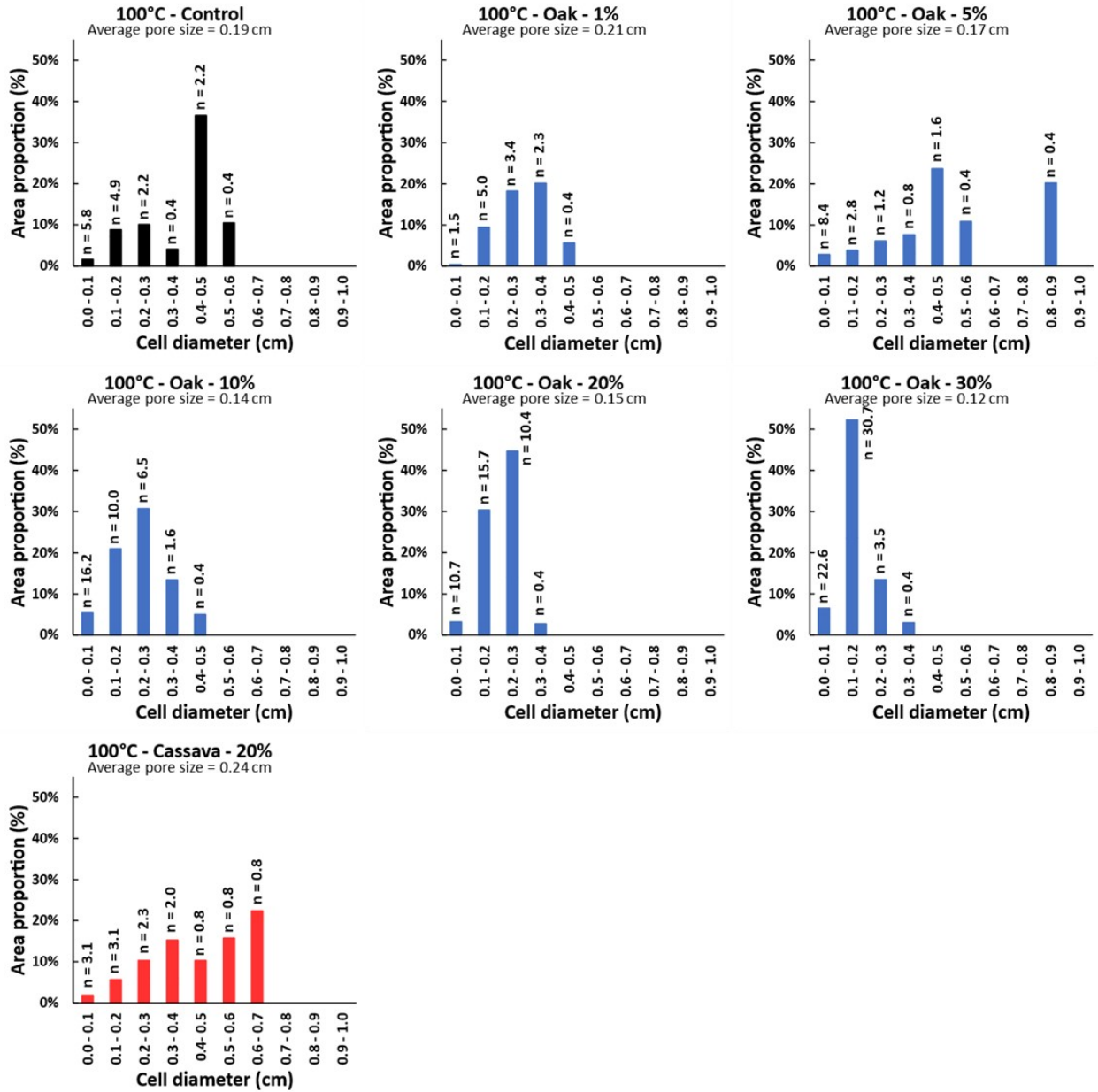


Fig. S10. pore size distribution in function of suberinic extract loadings a foaming temperature of 100°C. n = number of cells in 1cm².

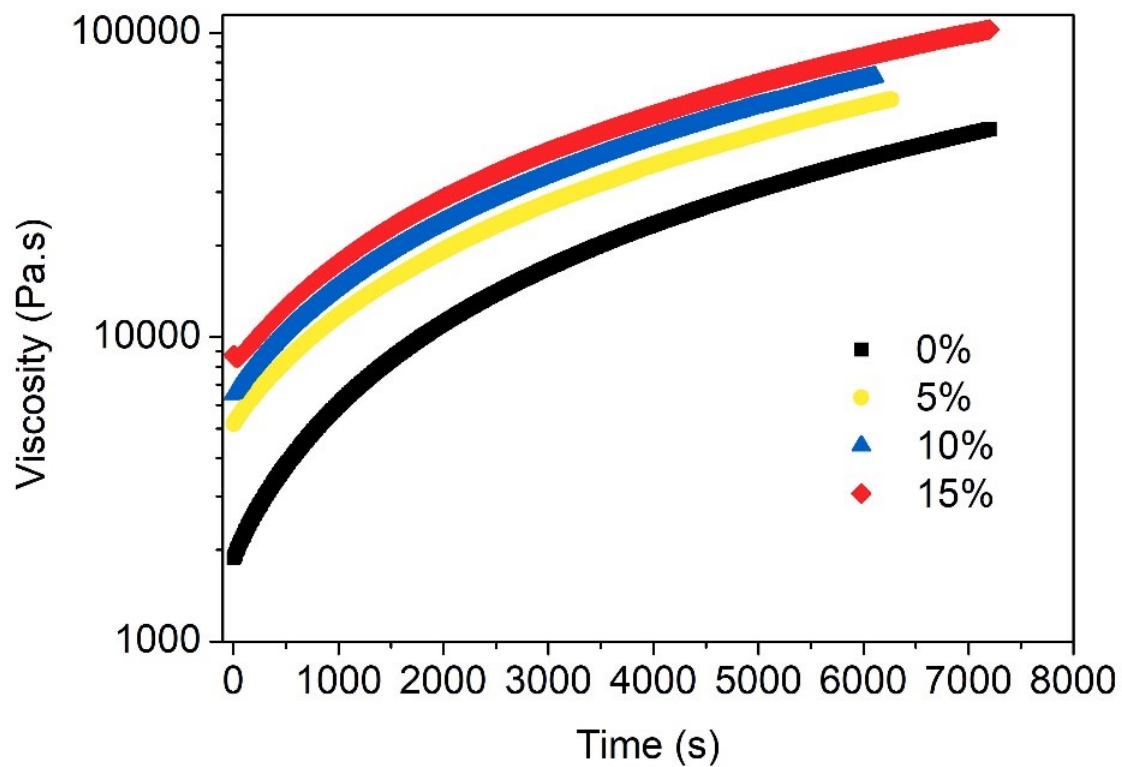


Fig. S11. Rheology measurement of reactive mix in function of oak suberinic extract loading at room temperature.

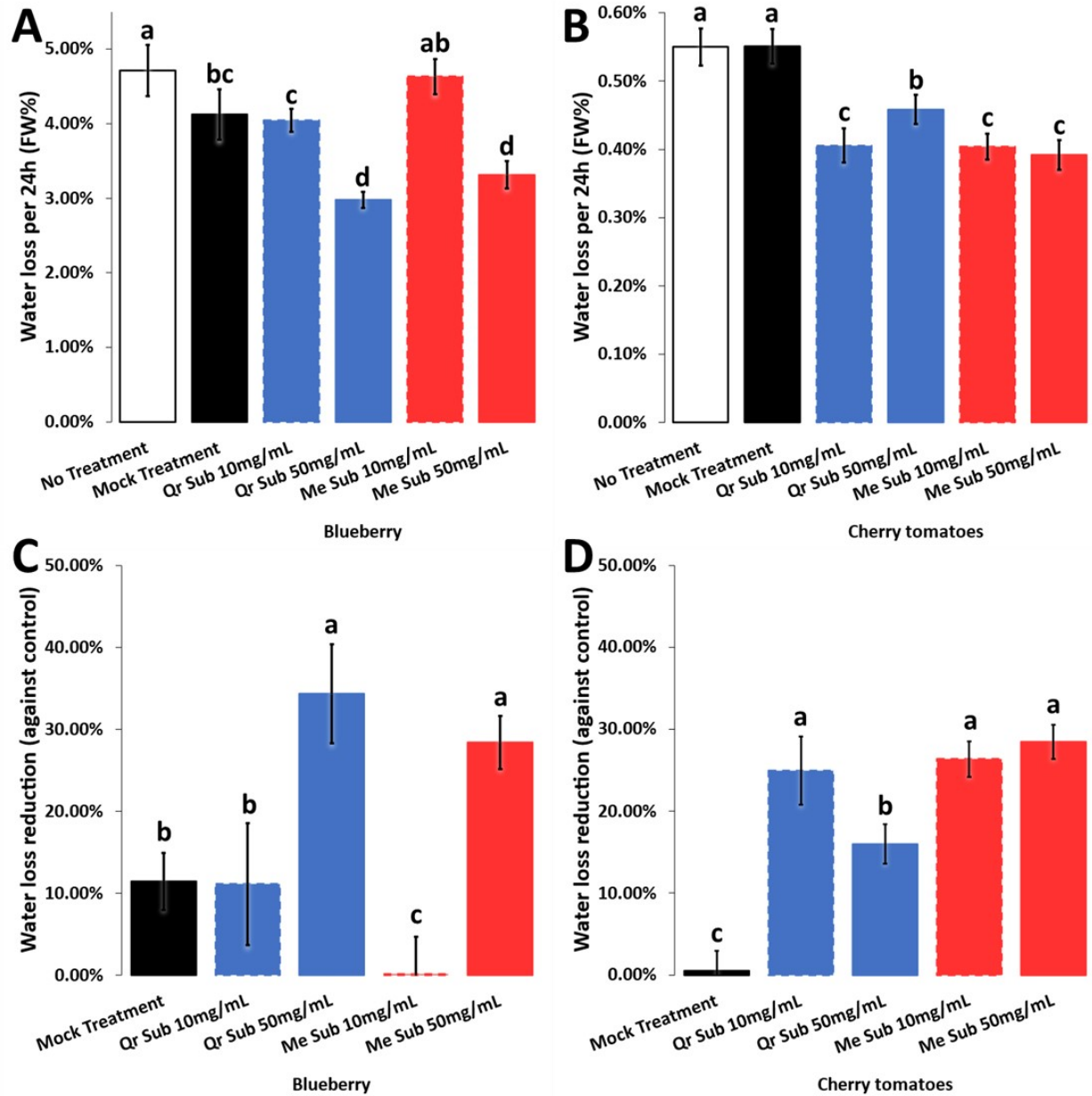


Fig. S12. Effect of sprayed suberinic extract coating on fruits. Average water loss per 24h for blueberries (**A**) and cherry tomatoes (**B**) and its reduction compared to control (**C** and **D**) with and without coatings of suberinic extract. Qr = oak ; Me = cassava ; Sub = suberinic extract at 493K 0 min 9MPa. Different letters indicate statistically significant differences ($P \leq 0.05$, Tukey HSD ($n=5$; i.e: average water loss per 24h of 15 blueberries or 10 cherry tomatoes after 35h 58h 82h 130h 202h)).

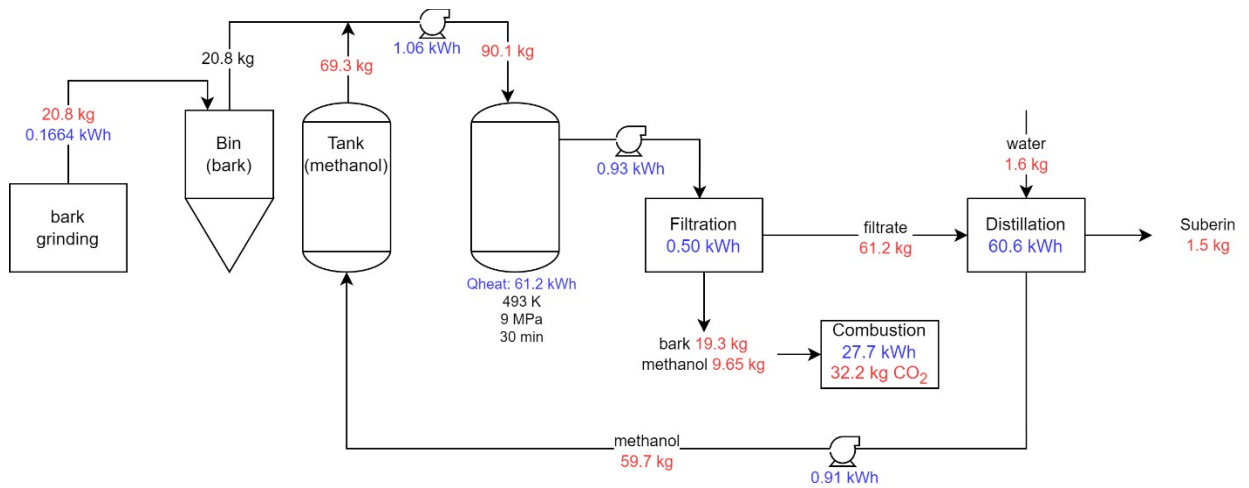


Fig. S13. Process model flowsheet for suberin production. The process model used as the inventory for the LCA is built based on a laboratory procedure and is upscaled according to the method described by Piccinno et al. (53).

Table S1. Effect of temperature (T in K), pressure (P in MPa), duration (min) and physical state of solvent (PSS; L for liquid, CL for compressible liquid, G for gaseous, SCF for supercritical fluid) on oak bark suberin extraction and depolymerization using methanol. Different letters indicate statistically significant differences ($P \leq 0.05$, Tukey HSD, $n=3$).

T - P - Dur. - PSS					Suberinic Extract (%)	Glycerol (‰)	COOH/Glycerol molar ratio
1	418	[<7.0]	0	L	0.0 ± 0.0^a	0 ± 0^a	-
2	473	[7.0-8.0]	0	L	5.0 ± 0.1^b	0 ± 0.01^{ab}	5501 ± 2009^d
3	493	[8.1-10.0]	0	CL	7.2 ± 0.5^{cd}	0.05 ± 0.01^{ac}	2755 ± 584^c
4	493	[>14.5]	0	CL	7.6 ± 0.5^{cd}	0.06 ± 0^{ac}	1601 ± 1003^b
5	493	[8.1-10.0]	60	CL	10.0 ± 0.1^{fg}	0.24 ± 0.04^{cd}	817 ± 129^{ab}
6	493	[>14.5]	60	CL	10.4 ± 0.3^{fg}	0.2 ± 0.02^{cd}	640 ± 377^{ab}
7	518	[7.0-8.0]	0	G	5.4 ± 0.1^{bc}	0.17 ± 0.03^{ad}	1037 ± 220^{ab}
8	518	[8.1-10.0]	0	SCF	9.1 ± 0.3^{df}	0.13 ± 0.02^{bcd}	1154 ± 407^{ab}
9	518	[7.0-8.0]	60	G	4.6 ± 0.2^b	1.07 ± 0.03^g	176 ± 13^a
10	518	[8.1-10.0]	60	SCF	9.8 ± 0.0^{efg}	0.58 ± 0.02^f	262 ± 81^a
11	543	[10.1-13.4]	0	SCF	7.5 ± 0.1^{cde}	0.48 ± 0.02^{ef}	262 ± 110^a
12	543	[13.4-14.5]	0	SCF	11.3 ± 0.8^g	0.36 ± 0.01^{de}	518 ± 84^{ab}
13	553	[8.1-10.0]	0	SCF	3.8 ± 0.2^b	0.98 ± 0.02^g	157 ± 55^a

Table S2. Effect of temperature (T in K), pressure (P in MPa), duration (min) and physical state of solvent (PSS; CL for compressible liquid, G for gaseous) on oak bark (E-Qr) and cassava peels (E-Me) suberin extraction and depolymerization using methanol. Different letters indicate statistically significant differences ($P \leq 0.05$, Tukey HSD, $n=3$).

Biomass - T° - P° - Dur. - PSS					Sub. ext.(%)	Glycerol (mg/g)	COOH/Gly. molar ratio
E-Qr	493	[81-100]	0	CL	7.2 ± 0.5^b	0.05 ± 0.01^a	2755 ± 584^b
E-Qr	518	[70-80]	60	G	4.6 ± 0.2^a	1.07 ± 0.03^b	176 ± 13^a
E-Me	493	[81-100]	0	CL	10.3 ± 0.2^c	0.2 ± 0.06^a	281 ± 129^a
E-Me	518	[70-80]	60	G	15.7 ± 2.4^d	1.1 ± 0.03^b	65 ± 7^a

Table S3. Main molecules identified in the suberinic extract by GC-MS. *Identification performed using NIST17 database; ** tentative identification. Results are given in peak area percentage over the total peak area.

	Oak		Cassava	Retention index
	518K 60min 7.5MPa	493K 0min 9MPa	493K 0min 9MPa	
Triacylglycerol (TAG)	3.1	11.6	1.5	
Gly-1,2,3-C(8:0)*	/	1.9	/	2954
Gly-2-C(10:0)-1,3-C(8:0)*	1.4	5.0	1.0	3135
Gly-2-C(8:0)-1,3-C(10:0)*	1.7	4.6	0.4	3542
Monoacylglycerol (MAG)	3.7	0.6	52.0	
Gly-2-C(16:0)-1,3-diOH*	/	/	1.2	2570
Gly-2,3-diOH-1-C(16:0)*	1.3	0.6	31.9	2606
Gly-2-C(18:0)-1,3-diOH*	Trace	Trace	Trace	2765
Gly-2,3-diOH-1-C(18:0)*	2.4	Trace	18.9	2802
α, ω-dicarboxylic acids (DCA)	1.1	Trace	Trace	
9,10-epoxy-C(18:0)**	1.1	Trace	Trace	2765
ω-Hydroxyfatty acids (HFA)	12.5	Trace	4.7	
12,18-OH-C(18:1)**	/	/	4.7	2228
18-OH-C(18:1)*	12.5	/	/	2228
18-OH-9,10-diOH-C(18:0)*	Trace	Trace	Trace	2782
Fatty Acids (FA)	25.9	20.1	10.9	
C(16:0)*	9.4	4.9	4.6	2054
C(18:0)*	8.8	4.0	4.0	2253
C(19:0)*	7.7	11.2	2.4	2347

Table S4. Results of the LCA hotspot analysis to produce 1.5 kg of suberin, using the process model in Figure S11

Product:		1,5 kg Suberin								
Method:		EF 3.0 Method (adapted) V1.03 / EF 3.0 normalization and weighting set								
Impact category	Unit	Total	Process-direct emissions	Methanol	Water	Electricity {US} grinding	Electricity {US} pumping	Electricity {US} distillation	Heat_process	Heat_waste combustion
Climate change	kg CO2 eq	6,35E+01	0	6,408789	0,000541	0,08356	1,456275	30,43113	17,3016	7,845089
Ozone depletion	kg CFC11 eq	7,81E-06	0	2,15E-06	3,43E-11	4,72E-09	8,23E-08	1,72E-06	2,66E-06	1,20E-06
Ionising radiation	kBq U-235 eq	11,89828	0	0,139951	0,00012	0,030407	0,529938	11,07387	0,085312	0,038683
Photochemical ozone formation	kg NMVOC eq	8,96E-02	0	1,89E-02	1,25E-06	1,22E-04	2,13E-03	4,46E-02	1,64E-02	7,44E-03
Particulate matter	disease inc.	7,26E-07	0	8,88E-08	1,98E-11	1,40E-09	2,44E-08	5,10E-07	6,99E-08	3,17E-08
Human toxicity, non-cancer	CTUh	3,52E-07	8,58E-08	4,09E-08	7,76E-12	4,83E-10	8,42E-09	1,76E-07	2,78E-08	1,26E-08
Human toxicity, cancer	CTUh	1,25E-08	0	1,85E-09	3,45E-13	1,98E-11	3,44E-10	7,19E-09	2,10E-09	9,53E-10
Acidification	mol H+ eq	1,47E-01	0,00E+00	2,24E-02	2,68E-06	2,64E-04	4,59E-03	9,60E-02	1,66E-02	7,51E-03
Eutrophication, freshwater	kg P eq	2,50E-02	0	5,42E-04	3,25E-07	6,24E-05	1,09E-03	2,27E-02	3,84E-04	1,74E-04
Eutrophication, marine	kg N eq	2,85E-02	0	3,82E-03	4,52E-07	4,97E-05	8,66E-04	1,81E-02	3,92E-03	1,78E-03
Eutrophication, terrestrial	mol N eq	2,59E-01	0	4,06E-02	4,34E-06	4,09E-04	7,13E-03	1,49E-01	4,24E-02	1,92E-02
Ecotoxicity, freshwater	CTUe	619,8742	13,29191	120,8896	0,010083	1,145159	19,9577	417,047	32,7038	14,82893
Land use	Pt	1,07E+02	0	1,08E+01	1,94E-03	2,28E-01	3,97E+00	8,29E+01	6,43E+00	2,91E+00
Water use	m3 depriv.	8,187863	0	1,651181	6,91E-02	0,016187	0,282111	5,89515	0,188584	0,08551
Resource use, fossils	MJ	1229,653	0	299,6151	0,007852	1,40733	24,52679	512,5252	269,4113	122,1595

Table S5: Results of the comparative LCA of suberin vs LDPE

Impact category	Unit	Suberin production	LDPE + Recycling	LDPE + Incineration
Climate change	kg CO2 eq	0,014823	0,003965	0,009015
Ozone depletion	kg CFC11 eq	1,82E-09	7,91E-11	1,22E-10
Ionising radiation	kBq U-235 eq	0,002776	0,00039	0,000421
Photochemical ozone formation	kg NMVOC eq	2,09E-05	1,64E-05	1,86E-05
Particulate matter	disease inc.	1,69E-10	1,40E-10	1,77E-10
Human toxicity, non-cancer	CTUh	8,21E-11	2,95E-11	3,95E-11
Human toxicity, cancer	CTUh	2,91E-12	9,46E-13	2,16E-12
Acidification	mol H+ eq	3,44E-05	1,77E-05	1,98E-05
Eutrophication, freshwater	kg P eq	5,83E-06	1,18E-06	1,26E-06
Eutrophication, marine	kg N eq	6,66E-06	3,21E-06	4,06E-06
Eutrophication, terrestrial	mol N eq	6,04E-05	3,41E-05	4,15E-05
Ecotoxicity, freshwater	CTUe	0,144637	0,046026	0,052541
Land use	Pt	0,02502	0,012125	0,016507
Water use	m3 depriv.	0,001911	0,003415	0,003535
Resource use, fossils	MJ	0,286919	0,121673	0,127343
Resource use, minerals and metals	kg Sb eq	1,74E-08	2,13E-08	2,42E-08

Table S6: Results of the sensitivity analysis of the suberin production process

Impact category	Unit	Suberin(Indonesia)	LDPE + Incineration	Suberin(Norway)	Suberin(US)
Climate change	kg CO2 eq	0,024013	0,009015	0,007649	0,014823
Ozone depletion	kg CFC11 eq	1,79E-09	1,22E-10	1,41E-09	1,82E-09
Ionising radiation	kBq U-235 eq	0,000148	0,000421	0,000318	0,002776
Photochemical ozone formation	kg NMVOC eq	5,85E-05	1,86E-05	1,06E-05	2,09E-05
Particulate matter	disease inc.	1,28E-09	1,77E-10	5,82E-11	1,69E-10
Human toxicity, non-cancer	CTUh	1,76E-10	3,95E-11	4,21E-11	8,21E-11
Human toxicity, cancer	CTUh	3,72E-12	2,16E-12	1,49E-12	2,91E-12
Acidification	mol H+ eq	9,57E-05	1,98E-05	1,18E-05	3,44E-05
Eutrophication, freshwater	kg P eq	2,98E-05	1,26E-06	3,62E-07	5,83E-06
Eutrophication, marine	kg N eq	2,52E-05	4,06E-06	2,46E-06	6,66E-06
Eutrophication, terrestrial	mol N eq	2,10E-04	4,15E-05	2,64E-05	6,04E-05
Ecotoxicity, freshwater	CTUe	0,089079	0,052541	0,04707	0,144637
Land use	Pt	0,010927	0,016507	0,008625	0,02502
Water use	m3 depriv.	0,002663	0,003535	0,000801	0,001911
Resource use, fossils	MJ	0,326781	0,127343	0,166791	0,286919
Resource use, minerals and metals	kg Sb eq	1,81E-08	2,42E-08	1,42E-08	1,74E-08