Supplementary Information

Why does wood not get contact charged? Lignin as an antistatic additive for common polymers.

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1. Experimental Procedures & Results

1.1.Preparation of Lignin-Free Wood and Doping of the Lignin-Free Wood with Lignin

Lignin was removed from limba wood (Terminalia superba) through a two-step extraction process. First, 2.5 M NaOH and 0.4 M Na_2SO_3 solutions were prepared by dissolving each substance in 500 mL distilled water. The solutions were mixed and taken into a flask, wood pieces were placed in the final solution and the mixture was refluxed at 120°C overnight. Then, brownish-red solution of lignin was poured off and the wood was washed 3 times with distilled water. Second, wood sample was boiled and bleached with H_2O_2 solution (500 mL) for 3 hours in order to remove the residual lignin and finally obtain a white solid. The lignin-free wood sample was washed 3 times with distilled water and dried at 60°C under vacuum. (During these treatments hemicelluloses are also removed.) The complete removal of lignin was proven by FTIR-ATR spectra (see below). Lignin extracted from pine bark was doped into lignin-free wood sample by cryomilling the sample with lignin obtained through the procedure described in Fig. S4, Section 1.2.2.

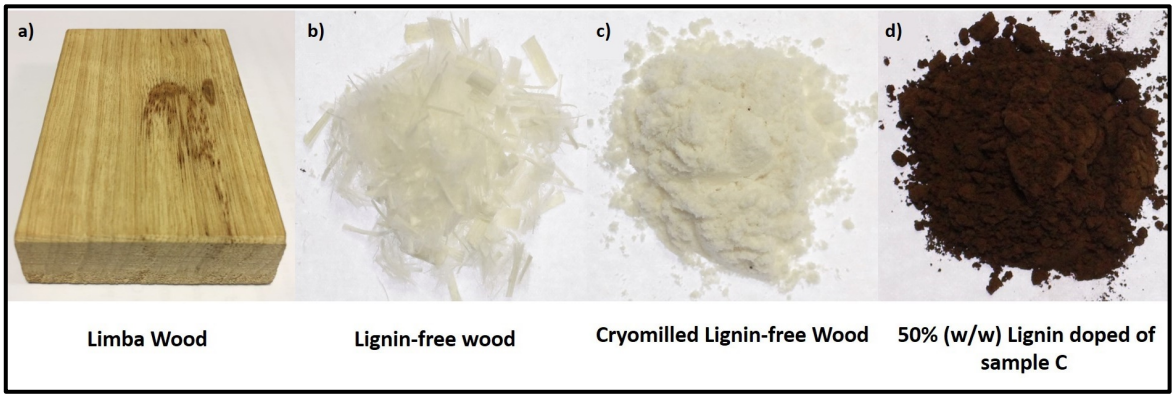


Figure S1. a) Limba wood used to obtain lignin-free wood. **b)** Lignin-free wood (See Section 1.2.1 for the lignin extraction procedure). **c)** cryomilled lignin-free wood (See Section 1.2.2 for experimental details, here shown a sample cryomilled for 5 min). **d)** 50% w/w lignin doped sample. 2.5 g of sample in (c) is mixed with 2.5 g of lignin and cryomilled for 5 min to obtain a homogeneous mixing.

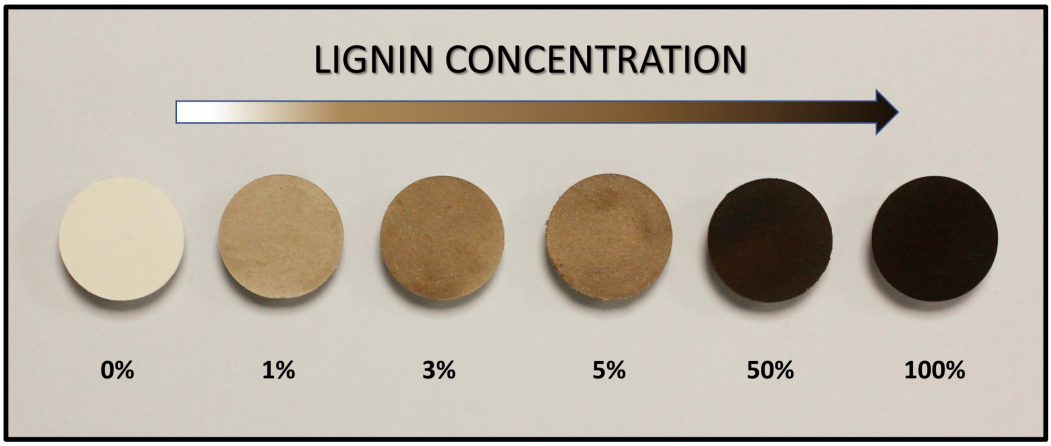


Figure S2. Lignin (here shown, lignin obtained from pine bark, section 1.2.2) doping to lignin-free wood (section 1.2.1) to obtain samples with lignin concentrations of 1 % to 50 % (w/w). The lignin-free wood is cryomilled for 5 min with lignin and then shaped as pellets (diameter: 1.4 cm) under 5000 bar using hydraulic pellet press.

1.2. Lignin Extraction and Particle Size Reduction

Lignin was obtained from hard and soft wood samples of pine, maple, birch barks, and nutshell through a stepwise process as shown in Fig. S4. The particle sizes of the samples were determined by zeta-sizer measurements.

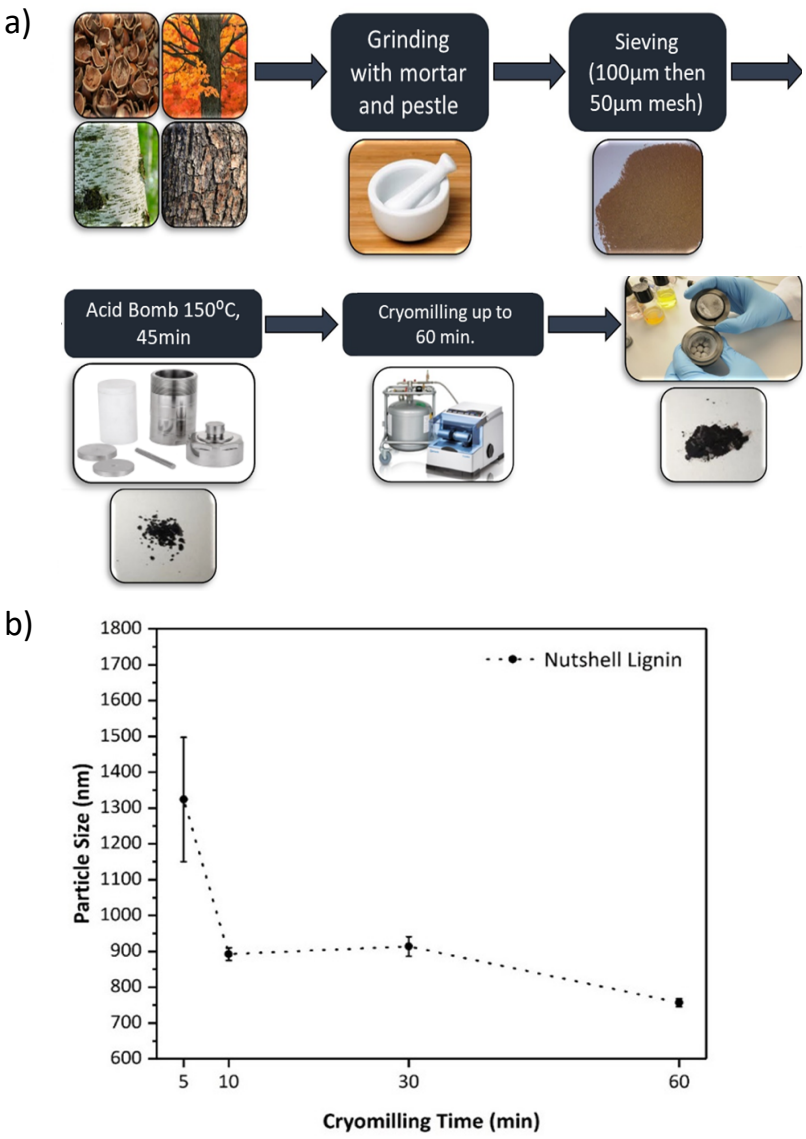


Figure S3. a) Extraction and particle size reduction flow-chart of the various natural sources of lignin. Samples from maple, birch, pine tree barks, and nutshell were grinded with mortar and pestle, then were sieved using 100 µm and 50 µm molecular test sieves respectively. 5.0 g of sieved sample was taken into the autoclave reactor and 10 mL of 72% H_2SO_4 (diluted from stock solution 95-97%) solution was added. The reactor was placed in an oven, and kept at 150 °C for 45 minutes. The extracted material was washed with distilled water several times and the solid lignin was collected by suction filtration. A pinch of extracted lignin was dissolved in 1,4-dioxane to measure the pH of the solution, which should be around 4-5. Extracted material was dried overnight at 40 °C under vacuum. Lignin samples were then cryomilled for 5-60 min to reduce the particle size. **b)** Lignin particle size reduces with increasing cryomilling time. Error bars were calculated based on at least 3 measurements for each sample.

Partial Lignin Removal from Limba Wood (Terminalia Superba)

The lignin was partially removed from the Limba wood samples with removal treatments (section 1.1) performed for 1, 3, 10, 20, 60, and 120 minutes.

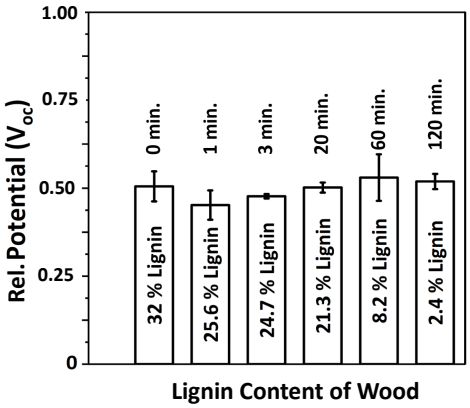


Figure S4. The effect of partial lignin extraction from limba wood (32% lignin). Lignin was extracted partially with the procedure (section 1.1). The duration of extraction to obtain the designated amount of lignin is given above the data bar for each sample. The relative open circuit voltages were measured using the measurement setup shown in Figure S18b. Partial removal of lignin from wood does not decrease the V_{oc}. Error bars correspond to standard deviations determined from at least three independent experiments. (RH : 35-40%).

1.3. Acylation of the Lignin

Extracted, cryomilled and ultrasonicated lignin samples are not soluble in any solvent. They are only slightly soluble in pyridine. Their poor solubility prevents further characterization (e.g. by UV-Vis, GPC) so that solubility could be increased. Lignin samples were acylated with trimethylacetylchloride and the detailed procedure is given below.

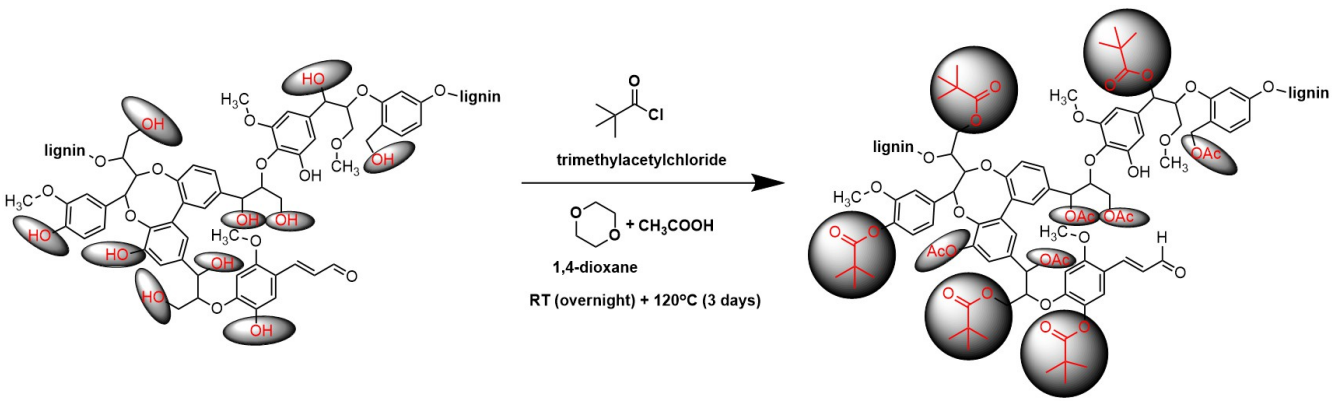


Figure S5. Acylation of lignin with trimethylacetylchloride.

20 mg of cryomilled lignin was dissolved in 20 mL of 1,4-dioxane then 5 mL acetic acid was added dropwise while mixing. The mixture was stirred overnight at room temperature in order to dissolve the lignin. Excess amount of trimethylacetylchloride (10 mL) was added and the mixture was refluxed for 3 days at 120 ^{o}C. Acetic acid and excess of trimethylacetylchloride were evaporated at vacuum and the acylated samples were dried at 40 ^{o}C, at vacuum for 24 hours. The acylated samples were used without further purification. For doping of the acylated lignin into PDMS, the samples were cryomilled again to reduce the lignin particle size.

1.4. Characterization of the Lignin-free wood, Lignin, Cryomilled Lignin, and Acylated Lignin

FTIR-ATR Spectroscopy

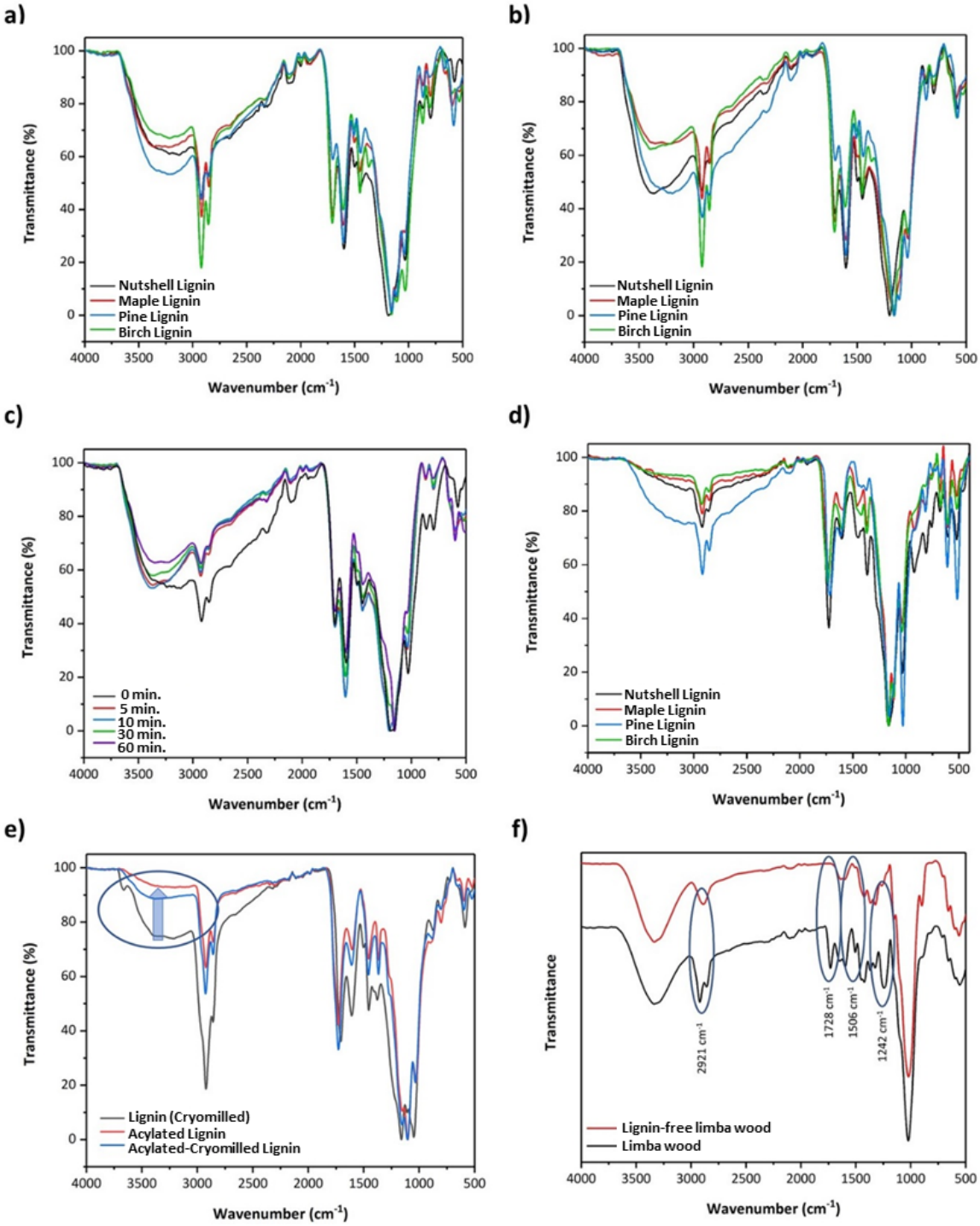


Figure S6. FTIR-ATR spectra of the lignins, acylated lignins, and lignin-free wood. Lignin (5.0 g) extracted from birch, pine, maple barks and nutshell, **a)** before and **b)** after cryomilling for 60 min. **c)** Lignin from nutshell cryomilled for the given milling times (Section 1.2.2). Cryomilling shifts the OH

stretching to higher wavenumbers (3400 cm^{-1}), which displays an increase in number of free OH) **d)** and **e)** Transmittance of the OH-band (3400 cm^{-1} indicated as blue arrow) increases after acylation of lignin (Section 1.2.3) and decreases slightly upon cryomilling of the acylated lignin. Shown in (e), the spectra for birch lignin. **f)** Lignin-free wood and Limba wood (Section 1.2.1). 2921 cm^{-1}, 1728 cm^{-1}, 1506 cm^{-1} and 1242 cm^{-1} for aromatic C-H stretching in lignin dissappear after removal of lignin from wood.

Lignin-free limba wood. Lignin-free limba wood does not have peaks at 2921 cm^{-1}, 1728 cm^{-1}, 1506 cm^{-1} and 1242 cm^{-1} for aromatic C-H stretching, carbonyl (C=O) stretching, guaiacyl and syringyl aromatic skeletal vibrations and guaiacyl ring and C=O stretching, respectively. It is shown that lignin removal from the wood kept the OH band at 3400 cm^{-1} due to OH groups on cellulose and hemicellulose structures in lignin-free wood, while peaks originating from aromatic groups (aromatic skeleton vibrations, C-H stretches, guaiacyl (G), and syringyl (S) unit vibrations) dissappeared (Fig. S6f).

Lignin and Cryomilled lignin. The lignin samples obtained by the extraction process described in 1.2.2 are identified through the aromatic skeleton (vibrations at 1600 cm^{-1}, 1510 cm^{-1}, and 1450 cm^{-1}), methylene and methyl groups (sp^2 and sp^3 vibrations at 2921 cm^{-1} and 2852 cm^{-1}, respectively), and the aliphatic and aromatic hydroxyl groups in the structure (ca. 3200 cm^{-1}) (Fig. S6a). The comparison of FTIR-ATR spectra of the lignin before and after cryomilling (Fig. S6a and S6b) shows no change in the former groups in the lignin structure upon cryomilling. However, -OH band centered at ca. 3200 cm^{-1} shifts towards ca. 3400 cm^{-1} due to breaking of phenyl ether linkages on the polymer backbone and the increase in the number of free OH's. Even with 5 min of cryomilling the shift is significant, showing that the mechanochemical bond breakages are significant even at this milling time (Fig. S6c). (The phenyl ether bond breakage is the dominant mechanochemical breakage of the structure upon cryomilling, as also evident from the ESR spectroscopy, displaying no other type of radicals produced upon milling (Fig. S6).

Acylation of lignin. Figure S6d and S6e proved that the acylation reaction (Section 1.2.3) converted the phenolic OH groups to acetates, which significantly decreases the OH peak intensity at 3400 cm^{-1} of the cryomilled lignin precursor. In the acylated product, the intensity of the carbonyl peak on aromatic structures (at 1708 cm^{-1}) also increased and the band shifted to 1728 cm^{-1} due to esterification reaction[1,2].

ESR Spectroscopy

The extracted (non-cryomilled) and cryomilled lignin samples were analyzed by ESR spectroscopy to identify the chemical nature of the radicals present in these samples. Both before and after cryomilling, the lignin samples have only phenoxy type radicals as evident by the g-value (~2.003) of their corresponding ESR signals (Fig. S7). This is attributed to the fact that the mechanochemical breakages happen dominantly at the phenyl ether positions in the lignin structure[3].

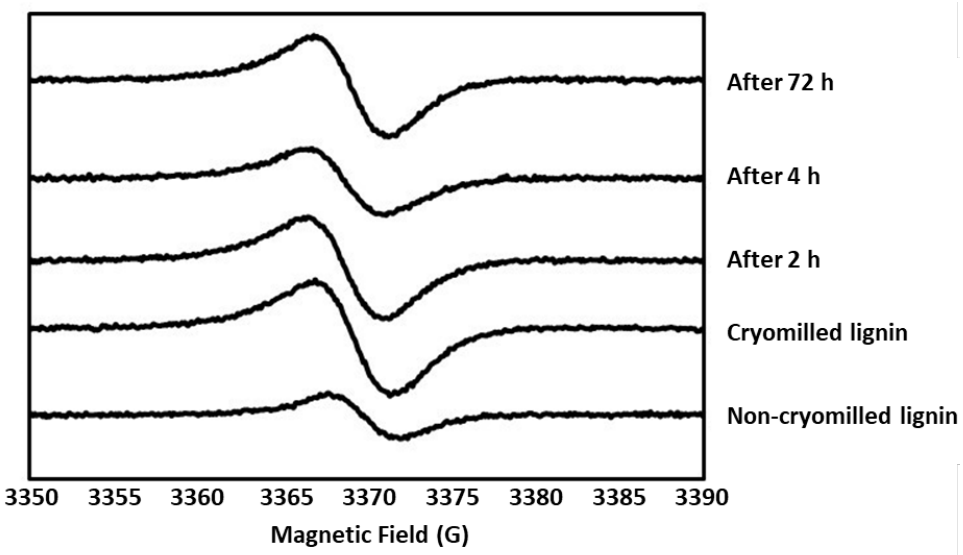


Figure S7. ESR spectra of non-cryomilled lignin, 10 min. cryomilled lignin waited for 2, 4, and 72 hours under ambient atmosphere. Before and after cryomilling, the lignin samples have only phenoxy type radicals as evident by the g-value (2.003) of their corresponding ESR signals.

Prussian Blue Method for Total Phenol Content (TPC) Determination

Reagents

- 0.02 M $FeCl_3$ Solution in 0.10 M HCl

  8.3 mL of the concentrated HCl was diluted to 1 L with distilled water and 3.24 g anhydrous ferric chloride was dissolved in 1 L of the 0.10 M HCl solution. The solution has a pale-yellow color.
- 0.016 M $K_3Fe(CN)_6$ Solution

5.26 g of potassium ferricyanide was dissolved in 1 L of distilled water. The solution has a yellow color.

- Stabilizer Solution

  1.0 g gum arabic was dissolved in 80 mL of distilled water by boiling for 25 minutes. The solution was filtered, and filtrate was diluted to 100 mL. 10 mL 85% H_3PO_4 and 10 mL 1% gum arabic were mixed and diluted to 50 mL with distilled water. The stabilizer solution was refrigerated. (Stable for 1 week.)

Procedure

Exactly 5.00 mg of cryomilled lignin (polyphenol) sample was suspended in 0.1 mL of 1,4-dioxane. 3.00 mL deionized water was added and the solution was vortexed. (Poor quality water, particularly iron-containing water may give unacceptable results) 1.00 mL of freshly prepared $FeCl_3$ solution was added to the mixture, followed by 1.00 mL of freshly prepared $K_3Fe(CN)_6$ solution, just 1 minute after the addition of the $FeCl_3$ solution. The mixture was stirred for 24 hours for a complete reaction (stable color). 5.00 mL of stabilizer (gum arabic solution) was added to terminate the reaction. After 10 times dilution of the final solution, its absorbance at the absobance maximum of Prussian blue ($Fe_4[Fe(CN)_6]_3$) at 700 nm was recorded. 5 identical preparations for each lignin sample were made and their absorbances were measured using the same procedure[4]. The absorbance values of the lignin-Prussian Blue samples were then used to calculate the concentration of the Prussian Blue formed, which was used to calculate the methyl gallate equivalent, using the result from methyl gallate test described below.

For obtaining the standard values of the phenol content, methyl gallate (methyl-3,4,5-trihydroxybenzoate) standard was prepared by weighing exactly 5.00 mg of methyl gallate. The standard was tested for its phenol content through the procedure described above except that this time only 30 minutes was enough to acquire stable blue color for the standard samples. After 30 minutes the reaction was stopped by addition of 5.00 mL of stabilizer solution, then the absorbance of the formed Prussian Blue ($Fe_4[Fe(CN)_6]_3$) at 700 nm was measured after 10-times dilution of the sample. Standard deviations were calculated based on 5 independent measurements (Fig. S8).

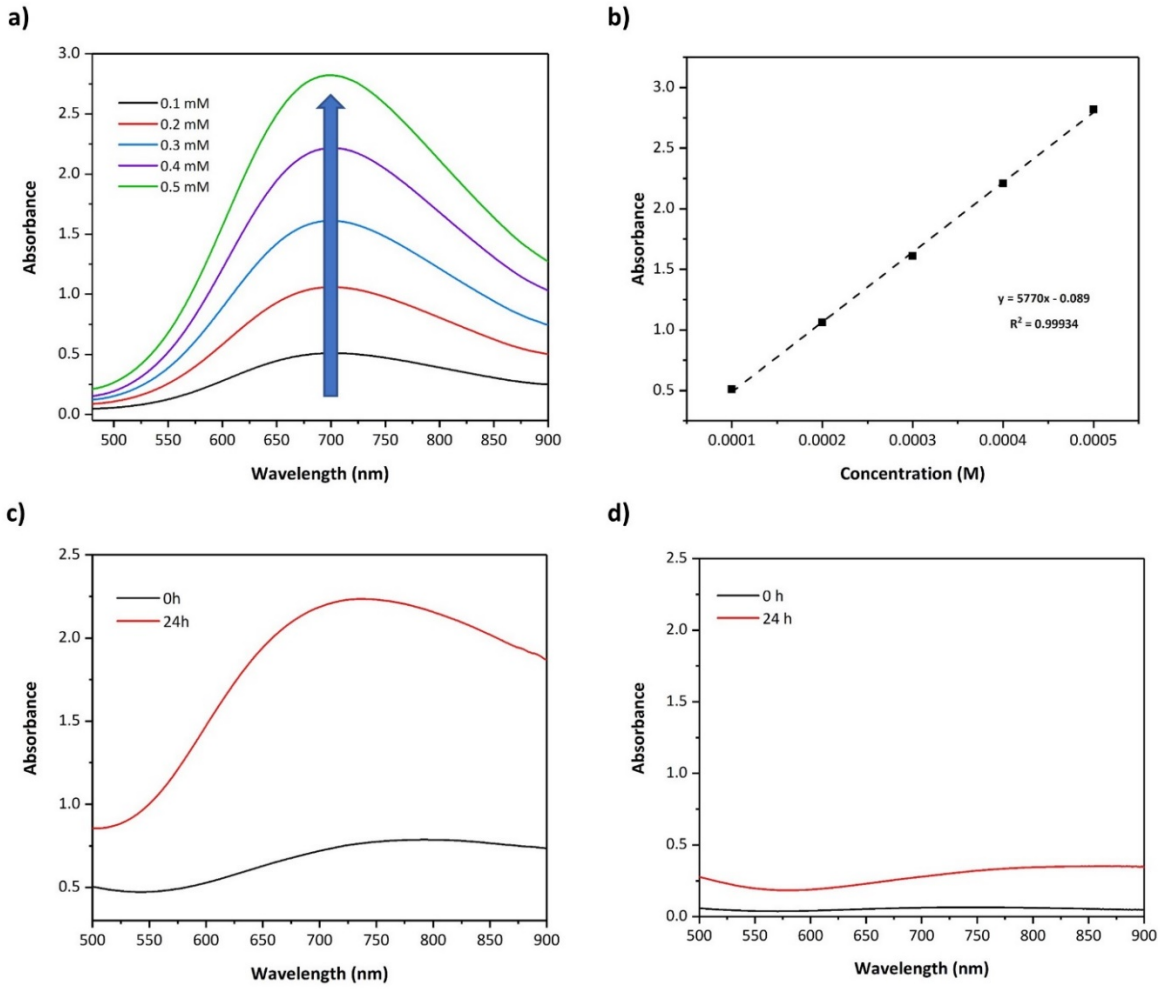


Figure S8. **a)** UV-Vis spectra of Methyl Gallate (MG) standard solutions (0.1 mM – 0.5 mM) used in Prussian blue test for polyphenols showing an intensity increase (indicated as blue arrow) of the absorption band at 700 nm (the absorption maximum for Prussian blue that forms upon oxidation of polyphenols); **b)** the calibration curve for MG standard; **c)** UV absorption changes of Prussian blue reaction of nutshell lignin as an example. **d)** control sample (lignin-free) solution at 0 hour and after 24 hours.

Table S1. Total phenol content of the lignin samples.

Sample	Absorbance Mean at (700 nm)	MG[b] Equivalent Mean (mg/5 mg lignin)	MG Equivalent Mean (mmol/g lignin)
Nutshell Lignin	2.04	3.39 ± 0.23[a]	3.68 ± 0.25
Pine Lignin	2.25	3.74 ± 0.38	4.06 ± 0.41
Maple Lignin	1.90	3.17 ± 0.29	3.44 ± 0.31
Birch Lignin	1.83	3.07 ± 0.25	3.33 ± 0.27

[a] Standard deviations and mean values were calculated from 5 different samples prepared by using same procedure. [b] Methyl gallate standard.

Gel Permeation Chromatography

Since lignin is insoluble in all common solvents, the lignin samples were made soluble by acylation (Section 1.2.3). Acylated lignin samples from different lignin sources were then dissolved in THF (HPLC grade, without stabilizer) to have 1 mg/mL solutions for the analyses. Sample solutions were filtered using a PTFE syringe filter (0.45 µm pore size) prior to injection into the system. Table S2 shows the molecular weights and polydispersity index of the lignin samples.

Table S2. Molecular weights of acylated polymers.

Lignin	M_w (g/mol)	M_n (g/mol)	M_z (g/mol)	PDI*
Acylated Nutshell	1110	746	1562	1.48
Acylated Pine	1121	848	1425	1.32
Acylated Maple	1127	846	1448	1.33
Acylated Birch	988	680	1401	1.45

*Polydispersity index.

^{13}C-CP/MAS NMR

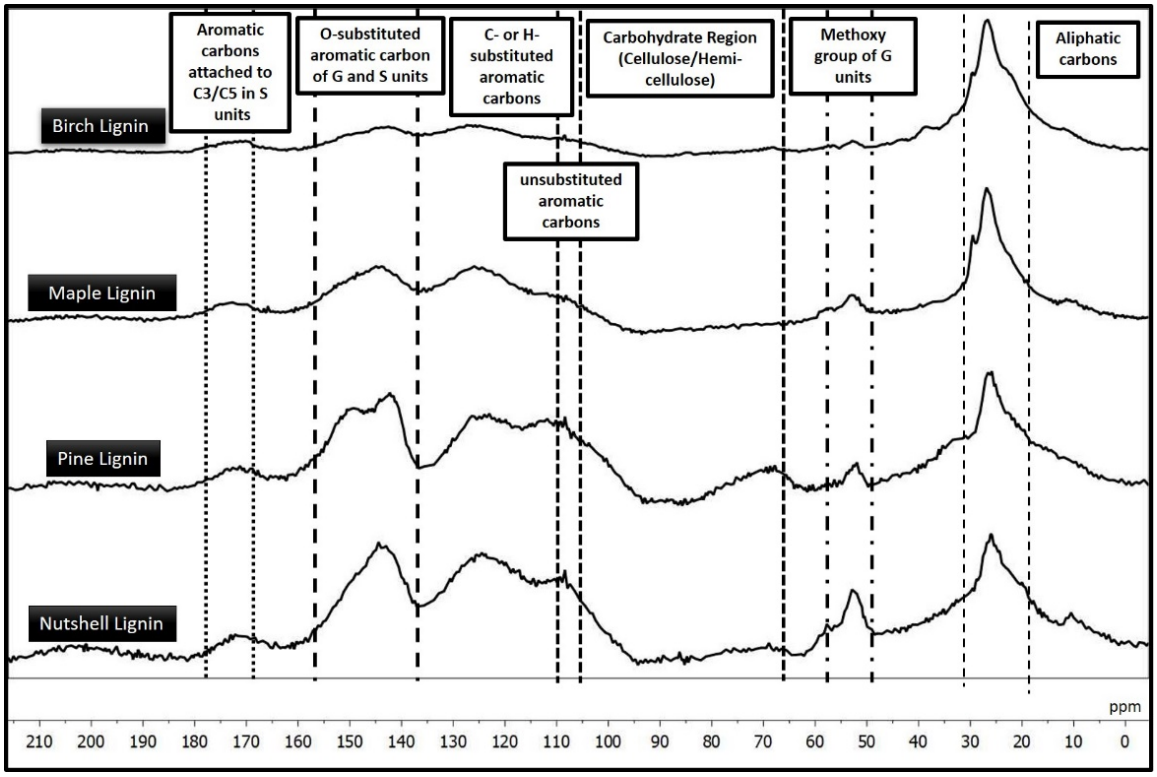


Figure S9. ^{13}C-CP/MAS (Cross-coupling/Magic angle spinning) NMR spectra of the cryomilled nutshell, pine, maple, and birch lignin (from bottom to top). Due to the low solubility of lignin in many organic solvents (e.g. $CDCl_3$), solid state ^{13}C-NMR was performed.

The chemical shifts of the aromatic and aliphatic peaks in the ^{13}C-CP/MAS NMR of the samples were found to be in agreeement with the ones given in previous reports[5–7]. Although quantitative analysis is not possible, one can qualitatively compare the peak intensities of the syringyl (S), guaiacyl (G) and p-hydroxyphenyl (H) sub-units present in the lignins obtained from different sources.

Nutshell Lignin: ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 143.9, 124.4, 109.0, 57.1, 52.4, 26.2, 10.5 ppm.

Maple Lignin: ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 143.9, 124.8, 112.7, 57.5, 53.0, 27.1, 11.7 ppm.

Pine Lignin: ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5, 148.4, 141.7, 123.1, 110.6, 68.1, 52.0, 31.9, 25.9 ppm.

Birch Lignin: ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1, 142.7, 126.3, 109.2, 84.7, 68.6, 52.9, 38.4, 27.1, 12.9 ppm.

Thermal Stability of Lignin

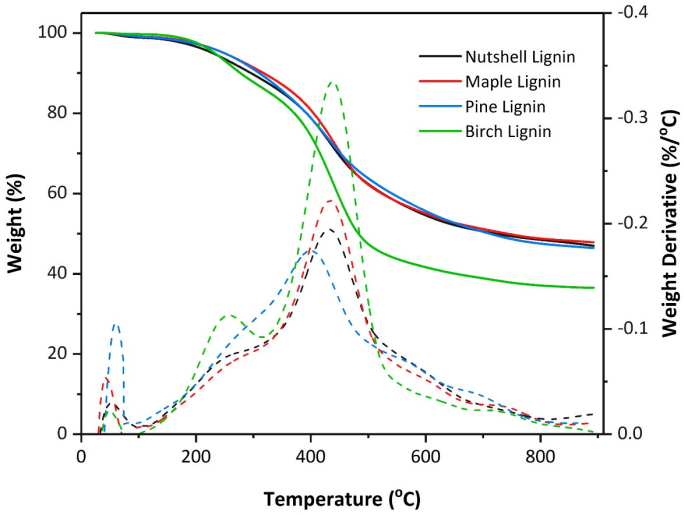


Figure S10. Thermogravimetric Analysis (TGA/DTG). 5-8 mg of samples were scanned from 25 °C to 900 °C. All lignin have thermal stability up to 200 °C (also in agreement with the literature[8]), which is higher than the temperature used during the doping of thermoplastics (100 °C – 150 °C) (section 1.2.5).

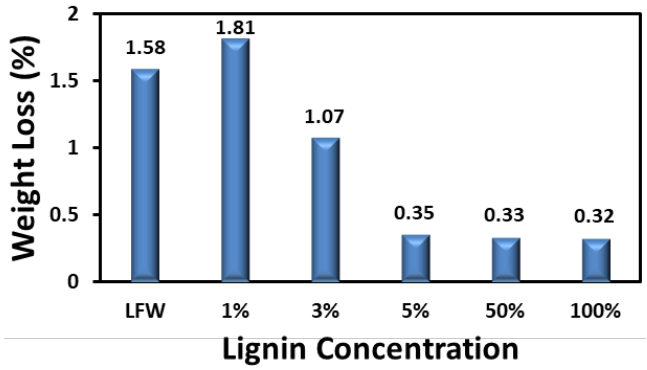


Figure S11. Determination of the moisture content of lignin-free wood (LFW), 1-50% w/w lignin doped lignin-free wood and lignin samples using TGA. The samples are heated at 50 °C under N_2 gas, while the weight of the samples (initial masses of 6.0 mg) are tracked by TGA.

1.5. Lignin Doping to Polymers

After extraction of the lignin samples, the samples were cryomilled in order to reduce the particle size and increase the surface area. Thermoplastics (PE, PP, PS, PLA) and an elastomer (Polydimethylsiloxane, PDMS) were doped with cryomilled lignin. Thermoplastics were chosen among the most common engineering polymers, and as an example of an elastomer, PDMS was preferred due to formation of smooth surfaces on molds upon curing.

Lignin Doping to PDMS

PDMS (Sylgard 184) was prepared by mixing the base and the curing agent in 10:1 ratio and cryomilled lignin (up to 5% w/w) was added to this mixture by vigorous mixing. Then the mixture (thickness: 0.2 cm) was poured in a petri dish and cured in oven for 4 hours at 60^{o}C. Then, additional 0.4 cm undoped PDMS layer was cured onto lignin-doped PDMS in order to obtain thicker samples that are easily handled upon electrical measurements. Cured lignin-doped PDMS (L-PDMS) (thickness: 0.6 cm) was cut into 1x1 cm pieces. In contact electrification tests, the smooth, lignin doped side of L-PDMS touching with petri dish was used. Cryomilling of lignin ensured homogeneous dispersion of lignin in the sample, thus the samples doped with cryomilled lignin were used in all experiments (Fig. S12).

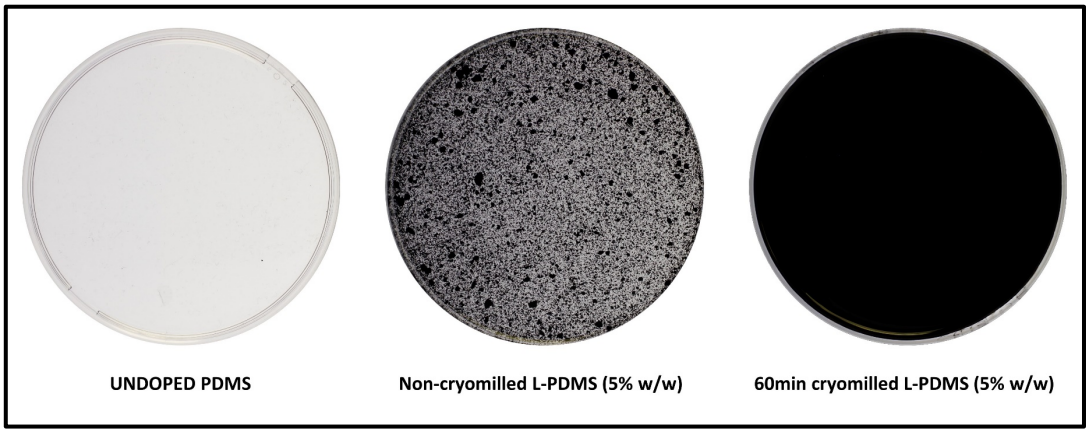


Figure S12. Images of undoped PDMS, lignin (non-cryomilled) doped L-PDMS and lignin (60 min. cryomilled) doped L-PDMS.

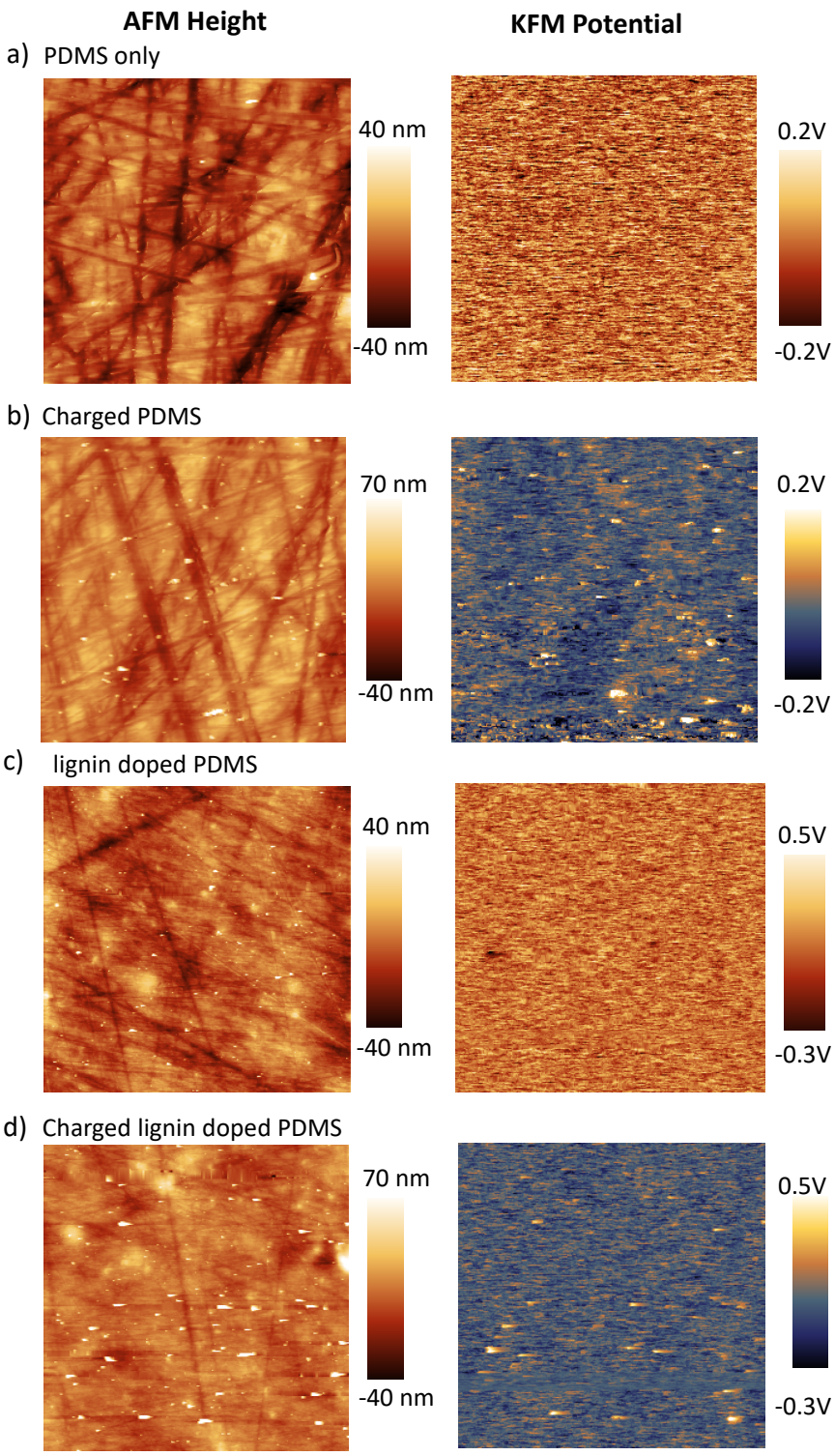


Figure S13. AFM Height (left) and KFM Potential (right) images of PDMS and 5% lignin (from nutshell) doped L-PDMS. Samples were peeled off after curing on petri dishes. The samples in b and d are tapped for 20 mins at the tapping device before AFM imaging. Their corresponding charge decay times at the time of imaging are 1 hour and 10 mins, respectively. Image size=50 mm.

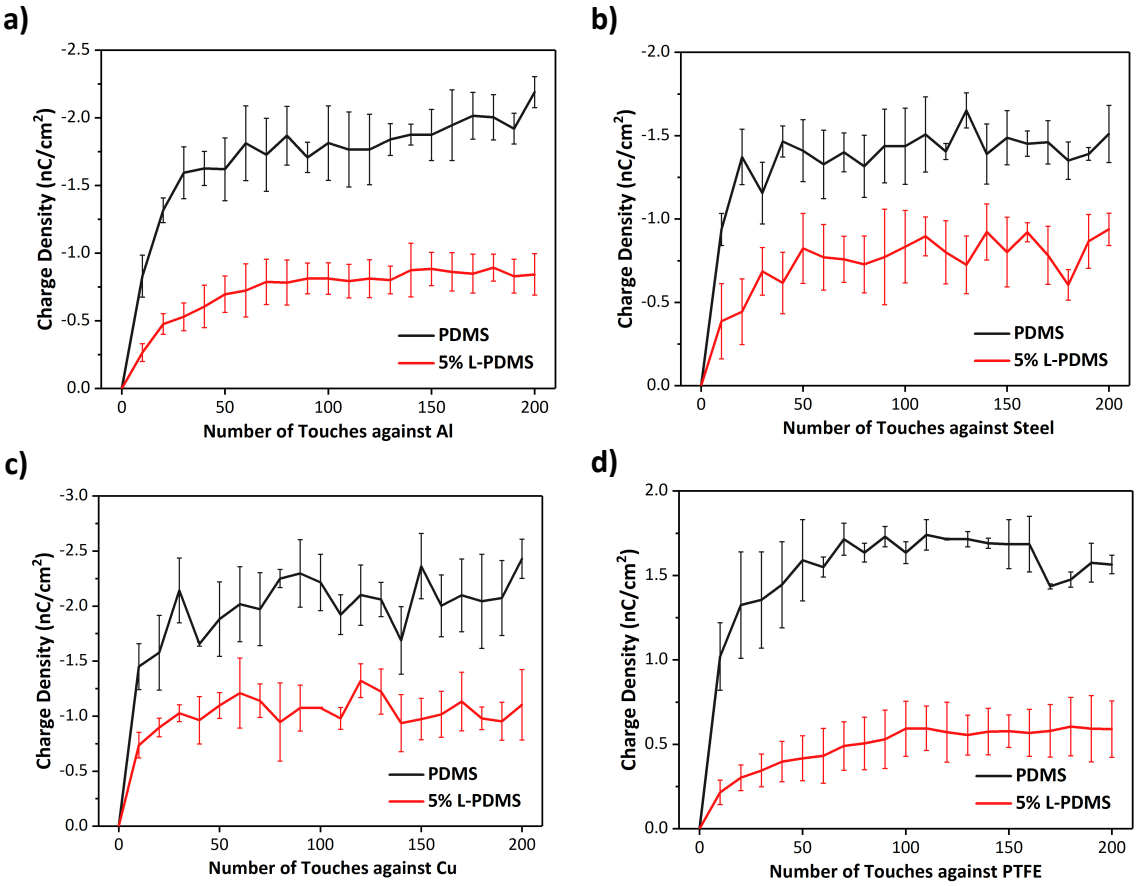


Figure S14. Contact charge density of PDMS and L-PDMS (lignin 5%, w/w) touched against **a)** Aluminum **b)** Steel **c)** Copper, and **d)** PTFE.

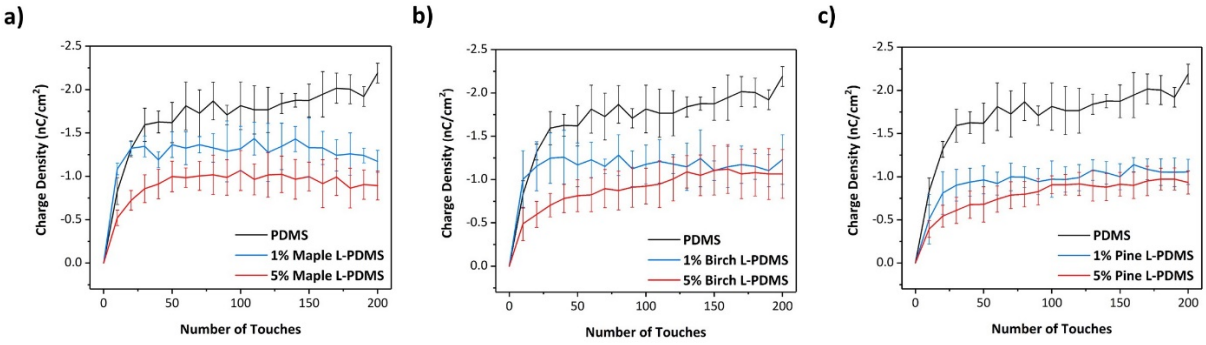


Figure S15. Contact charging of PDMS doped with cryomilled lignin (1% and 5% w/w) extracted from different sources **a)** maple, **b)** pine **c)** birch lignin.

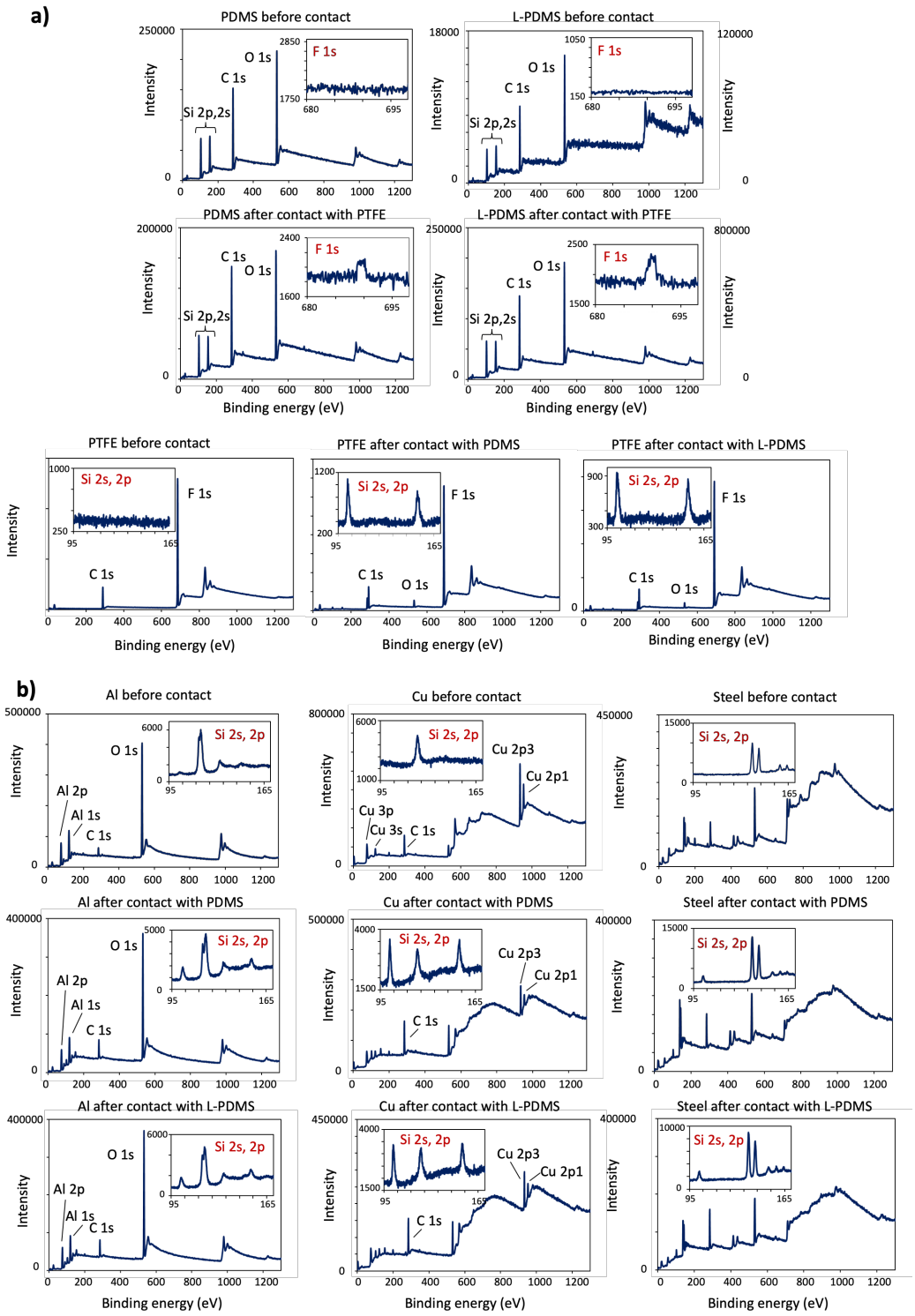


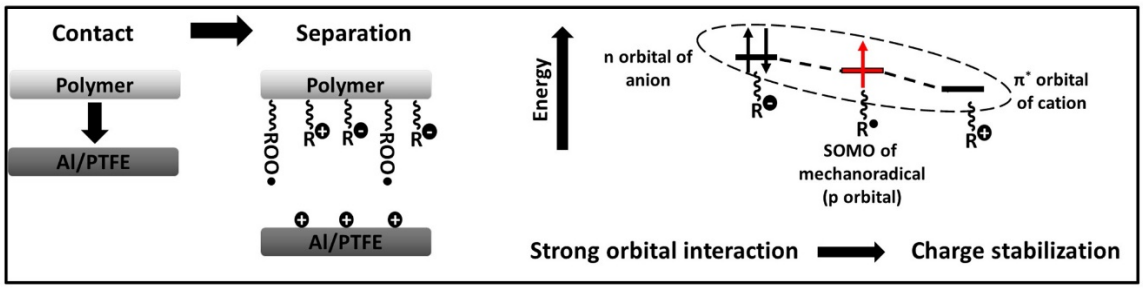
Figure S16. **a)** Survey XPS, Si 2s and 2p, F1s HIRES XPS (as insets) spectra of PDMS and L-PDMS, lignin 5% w/w contacted to PTFE before and after contact, **b)** Survey XPS, Si 2s and 2p HIRES XPS (as insets) spectra of metals contacted to PDMS and L-PDMS, lignin 5% w/w before and after contact. In all cases the appearance of the new signals that correspond to the atoms in the counter polymer material (PDMS or PTFE) is the evidence of the material transfer and hence the bond-breaking of the polymers during the contact.

Lignin Doping of Thermoplastics (PE, PP, PS, PLA)

Polyethylene, polypropylene, polystyrene, and polylactic acid were melted on the hot-plate and pressed with a thick Teflon plate in order to achieve undoped samples with flat surfaces necessary for maintaining reproduciblity in the contact electrification experiments. To obtain the doped samples; lignin (5% w/w) was doped into the melted thermoplastic by vigorous mixing and the melt was poured between two Teflon plates and was pressed to a thickness of 0.4 mm. The doped and undoped sample were let to solidify at room temperature. The lignin-doped thermoplastics were cut by a laser-cutter into circular pieces of 1.2 cm diameter, which were then mounted onto the Al stubs connected to electrodes of the electrometer.

1.6. The Proposed Mechanisms of Antistatic Action of Lignin in Common Polymers

a)



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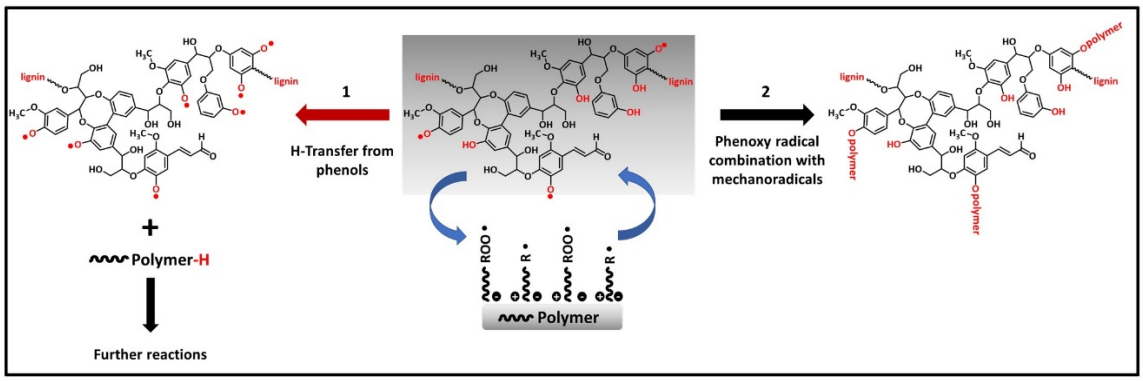

Figure S17. a) The mechanism of contact charge formation and stabilization on the surface of an undoped polymer (main text ref. 32). Mechanical breakages of the polymer backbone create polymer mechanoions (charges) and polymer mechanoradicals on the surface. These species coexist and polymer mechanoradicals stabilize the polymer mechanoions (charges) by orbital interaction. The

chemical removal of mechanoradicals were shown to increase the charge destabilization and fast charge dissipation and thus yielding in an antistatic action in the polymer. **b)** In presence of lignin as an additive in the polymer, the polymer mechanoradicals can be removed and the charges can be destabilized through two mechanisms: 1) H-atom transfer from phenyl groups of lignin to the polymer mechanoradicals or 2) removal of polymer mechanoradicals via radical combination with lignin radicals. Further discussion on the proposed mechanism is provided in the main text.

1.7. Electrical Measurements

a)

b)

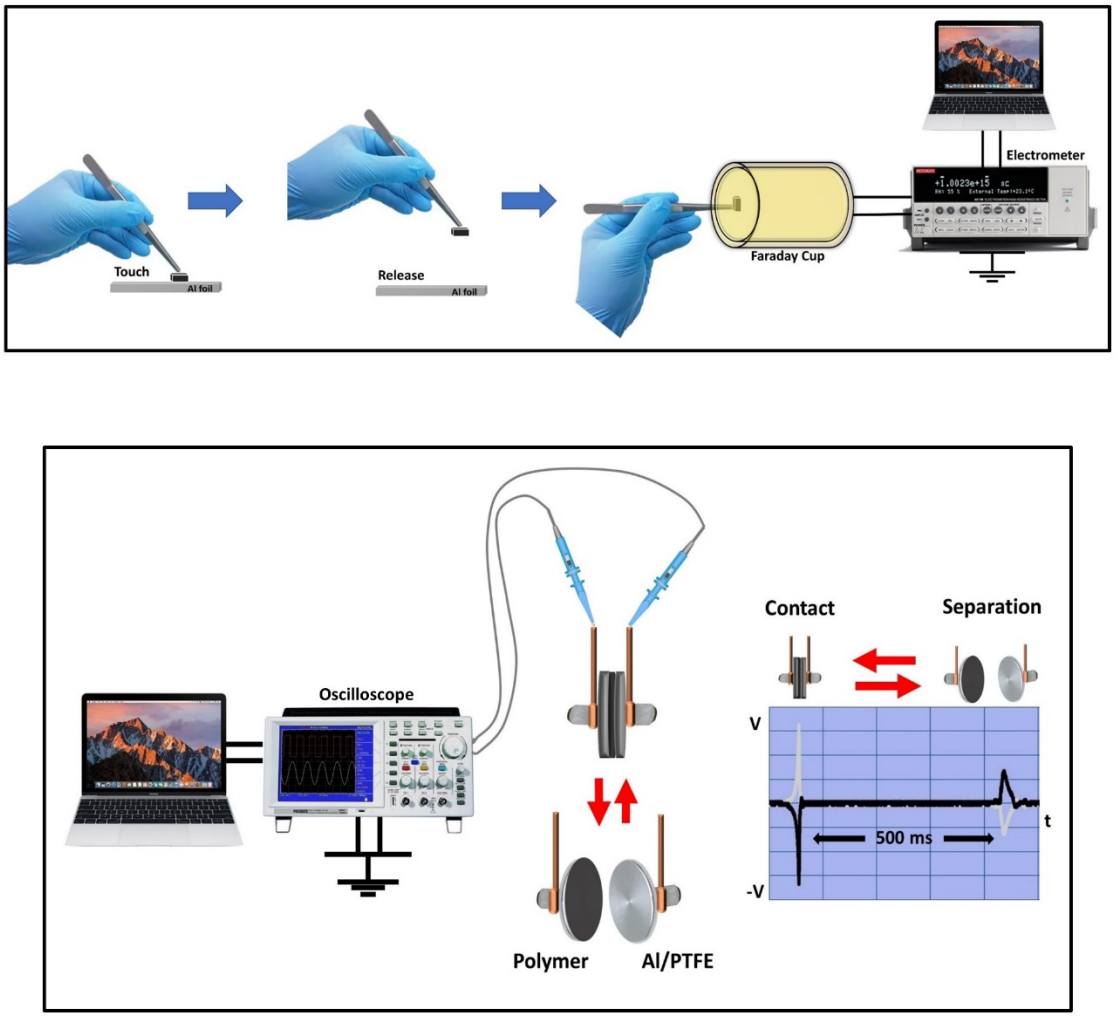

Figure S18. Illustration of **a)** contact electrification setup of PDMS and L-PDMS (gloves and tweezers were washed with ethanol prior to the experiments and polymer samples were handled cautiously not to interfere the readings) **b)** homemade tapping device used to record open-circuit potentials of the contact-charged surfaces of thermoplastics and wood. Typical signals obtained from contact and separation events for each electrode.

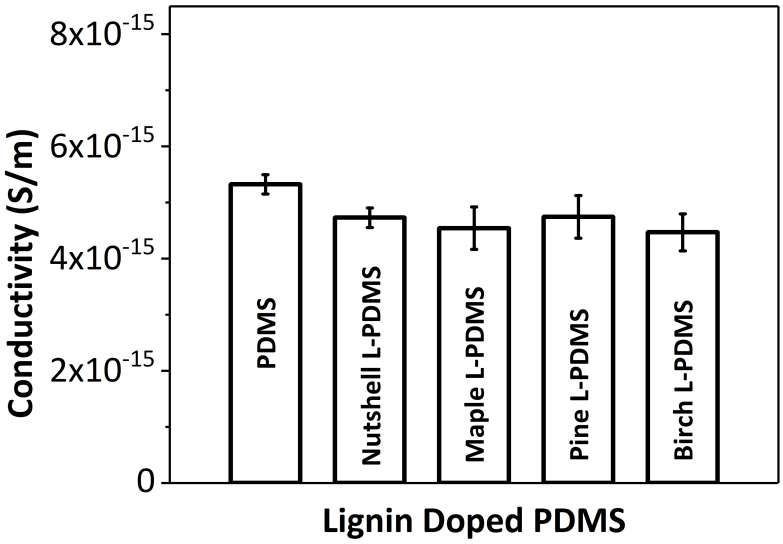

Figure S19. The charge dissipation mechanism is not based on the conductivity increase unlike the conventional methods. Conductivities of all samples were measured using two-probe method described in SI and 5% maximum doping concentration was used for comparison.

2. References

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