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Supporting Information

Hydrophobic Silsesquioxane Modified Lignin Incorporated Polyurethane Film

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Number of tables: 1 (S1)

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Number of equations: 1(S1)

Preparation of KL-WAPMSS (WL) Polymer. KL (1 g, 5.5 mmol) was dispersed in deionized water (40 mL) in a three-neck flask to make a 25 gL^{-1} lignin suspension in deionized water. The suspension was kept stirring for 1 h. Then, the WAPMSS solution, 20% in water (9 mL, 5.5 mmol), in a 1:1 molar ratio with WL, was added to the reaction medium. The reaction was initiated by transferring the three-neck flask to a preheated water bath at 60 °C, mixing at 250 rpm. Upon completion of the reaction (after 48 hours), the reaction medium was cooled to room temperature. The product was centrifuged and washed three times with toluene to remove any remaining unreacted chemicals. The supernatant, i.e., copolymerized lignin, was resuspended in water, and the suspension was neutralized with 1 M HCl, followed by dialysis for 24 hours, and then dried in a standard oven at 60 °C for 48 hours.

Preparation of Sulfoethylated Lignin (SL). To synthesize sulfoethylated lignin, KL (1.5 g, 5.5 mmol) was dispersed in a mixture of isopropyl alcohol (45 mL) and NaOH (12 mL, 30 wt.%) at room temperature and stirred (250 rpm) for 30 min in a three-neck flask. Then, a sulfoethylation reagent (1:0.6 mmol ratio of KL: sodium 2-bromoethanesulfonate) was added to the mixture and refluxed in continuous cold water at 80 °C for 2 h. Afterward, the reaction product was washed several times with an ethanol/water mixture (40:10 vol/vol) and recovered by centrifugation at 3000 rpm for 5 min. The precipitates were dissolved in deionized water (50 mL) and purified using dialysis for 2 days. After purification, the collected products were dried in a conventional oven at 60 °C until a constant weight was obtained.

Synthesis of polyurethane (PU) emulsion. Initially, PTMG (20 g) and IPDI (11.04 g) were introduced into a desiccated three-neck flask. Subsequently, the flask was immersed in an oil bath and subjected to mechanical stirring at 200 rpm. At 85 °C, acetone (5 mL), DMBA (2.03 mL), and DBTDL (20 µL) were added to the flask, and the system was maintained for 1 h. Subsequently, 1,4-butanediol (BDO) (1.42 g) was introduced to the system, and the mixture was stirred at 200 rpm using a mechanical stirrer for 3 h. Every hour, acetone (5 mL) was introduced to the reaction system to maintain the system's viscosity low. Subsequently, the mixture was cooled until it reached a temperature of 60 °C. Afterward, a quantity of triethylamine (1.38 g) was added to the flask, and the reaction proceeded for 0.5 h. After the reaction, the mixture was emulsified by adding deionized water at a concentration of 40 g/L and agitating it with a magnetic stirrer at 250 rpm for 4 hours.

Reaction yield. The reaction yield was calculated by measuring the reaction product before and after the silanization and sulfoethylation lignin modifications (Equation S1).

$$\% \, Yield = \frac{dry\ mass\ of\ A}{dry\ mass\ of\ SKL + B} \times 100 \text{--} (S1)$$

"A" stands for either WL or SL. "B" refers to WAPMSS (3-(triethoxysilyl)propyl methacrylate) for the process of silanization or sodium 2-bromoethanesulfonate for sulfoethylation. According to the equation, the results for WL were 80%, and for SL, the reaction yield was 75%.

Nuclear magnetic resonance (NMR). For H-NMR and HSQC, 60-70 mg of oven-dried WL sample were dissolved in 1 mL of D_2O and 2 µL of 40% NaOD, while 60-70 mg of KL and SL were mixed in 1 mL of DMSO–d_6 at room temperature for 12 hours. ^{1}H NMR test parameters were 16 scans, a 3.28-second acquisition time, a 1-second relaxation delay, and a 90° pulse at room temperature. Bruker pulse prog "hsqcetgpsisp2.3 software was utilized for the HSQC analysis using 13 ppm spectra width in the F2 (^{1}H) dimension with 2048 data points (155 ms acquisition time), 165 ppm in the F1 (^{13}C) dimension with 256 data points (6.2 ms acquisition time), a 1.5 s pulse delay, and sixteen scans at room temperature. As previously established, P-NMR was used to quantify the phenolic, aliphatic, and carboxylic hydroxyl groups of KL, WL, and SLs. To proceed, 50-60 mg of oven-dried samples were dissolved in 1 mL of chloroform-d ($CDCl_3$) and pyridine (1:1.6 vol/vol) at 60°C. Then, 52 µL (5 g/L) of the relaxing agent (chromium(III) acetylacetonate) was added to the mixture, and the mixture was stirred at 120 rpm for 12 hours. After adding 200 µL of phosphorylating reagent (TMDP) to the sample solutions, the mixture was agitated at 120 rpm for 1 h. Afterward, 50 µL of internal standard (cyclohexanol, 20 g/L) was added to the system, and the system was stirred for an additional 30 min. After that, the solutions were placed in NMR tubes and analyzed under the set-up conditions of 1024 scans per sample, a 90° pulse width, and a 5-second relaxation delay.

Molecular weight analysis. The molecular weight (MW) of KL, WL, SL, and KLT (lignin treated in the same manner as SL without the reagent) was measured using the static light scattering (SLS) technique. This method utilized laser light scattering equipment attached to a goniometer (BI-200SM, Brookhaven Instruments Corporation, NY, USA) to analyze the molecular weight (MW) of polymers in solution at 35 mW and 637 nm at ambient temperature. The molecular weight (MW) of the samples was calculated by measuring the scattered light intensity at scattering angles ranging from 20 ° to 155 °. Five concentrations of each copolymer (0.2, 0.6, 1.2, 1.6, and 2.1 mg/mL) were mixed in 15% NaOH for 24 hours at room temperature. The equipment analyzed samples using Brookhaven Zimm plot software after filtering with 0.45 µm nylon filters. A BI-DNDC differential refractometer (Brookhaven Instruments Corporation, NY, USA) was used to measure the refractive index increment (dn/dc) of the polymers in solution at 620 nm.

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) was used to analyze the structure of the samples. In this set of experiments, 60-80 mg of dried, crushed lignin derivatives were deposited on the Total Reflectance (ATR) crystal of Bruker Tensor 37 (Bruker, Germany) with a PIKE MIRacle Diamond Attenuated FTIR instrument. Then, 32 scans were conducted for each sample, with a resolution of 4 cm-1, at a wavenumber range of 500-4000 cm^{-1}.

Solubility and charge density

The charge quantity of lignin samples was measured using a Particle Charge Detector (Mutek, PCD 04, Germany) with a poly(diallyldimethylammonium chloride) (PDADMAC) (0.005 M) as a standard cationic solution.

Fourier-transform infrared spectroscopy (FTIR)

The FTIR spectra of KL, SL, and WL are shown in **Figure S1**. The transmittances at 1600, 1510, and 1425 cm^{-1} are distinctive peaks of aromatic ring vibrations for KL. These distinctive peaks are present in both SL and WL, aligned with ^{1}H NMR and HSQC analyses. The transmittance peak at 3340 cm^{-1} is attributed to the aliphatic and phenolic OH stretching of KL. A reduction in the intensity of the phenolic hydroxyl group peak is noticed for KL and WL. This information can be used to support P-NMR results, as it confirms that sulfoethyl groups occupied phenolic OH groups of lignin for SL. According to P-NMR, silanol groups occupied all of the hydroxyl groups in WL. The signal at 1080 cm^{-1} in the SL FTIR spectra refers to the symmetric stretching vibration of the SO_3H group. Hence, the observed decrease in the peak corresponding to the phenolic hydroxyl group and the emergence of the SO_3H stretching vibrational group confirm the sulfoethylation of SL, as indicated by both FTIR and XPS analyses. The WL spectra indicated transmittance at 3750 cm^{-1}, corresponding to free silanol (Si-OH) groups in organosilicon compounds. The transmittance at 3005 cm^{-1} corresponds to sp^2, which is the contribution of C-H associated with silicon.

Additionally, the high transmittance at 835 and 785 cm-1 is a characteristic of $Si-CH_3$. The siloxanes (Si-O-Si) had more intense infrared bands between 1008 and 1000 cm^{-1}. The presence of the mentioned transmittance signals on WL, aligned with the H-NMR, HSQC, and XPS analyses, confirmed the successful silanization of lignin.

Solubility, charge density, molecular weight (M_W), and thermal properties

The solubility and charge density of KL and SL are listed in **Table S1**. This study aimed to investigate the effects of sulfoethylation and silanization on the properties of the resulting polymers. However, because of the complete insolubility of the WL in aqueous solutions, it was not possible to quantify its charge density. In contrast, the process of sulfoethylation resulted in the formation of water-soluble SL. The solubility was enhanced by 6 g/L, and the charge density increased by 1.3 mmol/g when sulfoethylation was applied to KL. The enhanced solubility and charge density of sulfonated lignin (SL) can be ascribed to the presence of the sulfonate group covalently bonded to the phenolic group of lignin.

Additionally, the molecular weight (MW) of SL and WL was higher than that of KL. The increase in the molecular weight (MW) is attributed to the grafting of the sulfoethyl group in the case of SL and the grafting of WAPMSS molecules to the KL structure for WL. The significantly higher Mw of WL is attributed to the amine group from WAPMSS, which can induce further side reactions on the lignin backbone. 2 These reactions include condensation crosslinking, as confirmed by NMR, FTIR, and XPS analyses.

In addition, the thermal treatment response of the polymers was analyzed using TGA and DSC, and the results are presented in **Table S1**. The onset temperature (T_o), the temperature at which 50% weight loss ($T_{50\%}$) occurs, and the maximum decomposition temperature (DTGmax) were used to characterize the thermal sensitivity of the samples. KL displayed a rapid weight loss at approximately 291 °C, with a 50% weight loss at approximately 510 °C. Due to the intricacy of lignin biomacromolecules, its complete breakdown occurred between 510 and 520 °C. [3] The decomposition of the SL sample started at a lower temperature of 200 °C, and 50% weight loss was observed at 100 °C lower than that of KL. Also, the complete decomposition of the sample occurred at 415 °C. This decrease in the thermal stability of the copolymer can be attributed to the destabilization of the polymer chain in the presence of the sulfonic acid group.[4] The desulfonation process for sulfonated materials includes a thermal desulfonation step that takes place at temperatures ranging from 200 to 400 °C. This step mostly involves the release of SO_2. [5] WL displayed a more distinctive decomposition behavior than KL. The decomposition of WL began at higher temperatures, i.e., approximately 336 °C, and a 50% weight loss was observed at a temperature higher than 600 °C. The enhancement in the decomposition temperature of the WL was observed due to the condensation or crosslinking reaction of WAPMSS within KL macromolecules, as evidenced by NMR, XPS, and FTIR analyses. Furthermore, the integration of Si into the WL macromolecular structure can be the reason for the rise in the maximum degradation temperature from 520 °C to 669 °C and the increase in char residue from 2% to 40% for KL and WL, correspondingly.[6]

The glass transition temperatures, Tg, of KL, SL, and WL are listed in **Table S1**. T_g is strongly reliant on the molecular structure and crosslinking density of a polymer.[7] The T_g of the SL polymer was not significantly higher than that of KL. The T_g decrease was also observed for KLT, which could be due to the removal of specific lost segments from the lignin macromolecular structure or the presence of active deprotonated sites in the lignin structure during the pretreatment with NaOH and isopropanol. This potentially creates additional space within the molecular structure, allowing for increased molecular movement and ultimately leading to a decrease in the T_g.

However, the T_g of WL was significantly higher than that of KL due to the silanization of KL. In this case, the crosslinking of WAPMSS and KL through copolymerization resulted in the formation of a crosslinked structure, effectively decreasing the available space for chain movement. This reduction in chain mobility resulted in an elevated glass transition temperature (Tg). Consequently, the enhancement in the T_g can be attributed to the rise in molecular weight (as shown in **Table S1**) and the presence of a rigid silsesquioxane structure in the material, as well as the possible formation of a crosslinking network due to a chain reaction induced by the amine group from the oligomer.

Mechanical properties analysis. Samples were cut from composite sheets using a dog-bone-shaped die, measuring 27 cm in length, 3.12 cm in width (ASTM D638 type V), and 0.5–1 mm in thickness. Three specimens from each film were evaluated at a speed of 50 mm/min and room temperature; the average values, along with error bars, are reported.

Thermogravimetric analysis (TGA). The instrument was loaded with 10-10.36 mg of dried samples in a Tzero® aluminum pan. The analysis was conducted in a nitrogen environment with a flow rate of 10 mL/min and a heating rate of 10 °C/min from 25 °C to 800 °C.

Differential scanning calorimetry (DSC). A 3-4 mg sample was placed in a Tzero pan (T 140829, Switzerland), sealed with a Tzero lid (T 140826, Switzerland), and fed to the instrument. The sample was then heated from 20 °C to 200 °C in three heating cycles. The last heating cycle was used to find the T_g and T_m.

Liquid water contact angle. The sessile liquid droplet approach from one attention program was utilized for the static contact angle analysis. The test involved placing a 6-10 µL liquid droplet on the PU films, coated wood, metal, and paper surfaces, and measuring the contact angle visually using a camera for 50 s. A tilting stage test was conducted to determine the water sliding angle on the surfaces. The test involved placing a water droplet (6-10 µL) on the surfaces at 180° on the tilting stage and slowly tilting it until the droplet started to slide. The measurement was repeated three times and reported as a mean with the standard deviation.

Smoke Density. The coated samples (42 mm × 42 mm × 4 mm) were placed in the instrument and subjected to a propane gas pressure of 0.14 MPa for 250 seconds after ignition. The light absorption curves and smoke density ratings (SDRs) of the samples were analyzed and reported.

Limiting oxygen index (LOI). The films and coated wood samples were tested using this method. The glass column's center was burned in a controlled environment of nitrogen and oxygen. Sample dimensions were 140 mm × 20 mm × 10 mm for wood and 120 mm × 35 mm × 2.5 mm for films, and the test was conducted in five replicates.

Vertical burning test. Samples measuring 100 mm × 10 mm × 0.2 mm were subjected to propane gas exposure, and the combustion behavior of the materials was visually assessed. Photographs were used to evaluate the samples' flame retardancy in accordance with the standard.

Sample	Solubility, gL^{-1}	Charge density, mmol g^{-1}	$Mw\times10^5$, g mol^{-1}	To, °C	$T_{50\%}$ °C	DTGmax, °C	T_g, °C
SL	10	2.1 ± 0.05	(1.87±0.64)	200	410	415	153
KL	4	0.8±0.02	(1.75±0.15)	291	510	520	158
WL	ND	ND	(2.14 ± 0.23)	336	600	669	185
KLT	9	1.5±0.04	(1.51±0.24)	311	398	372	123

Table S1. Quantify the proportions of aliphatic, aromatic, and carboxylate hydroxyl groups in the samples.

ND: not determined.
± standard deviation

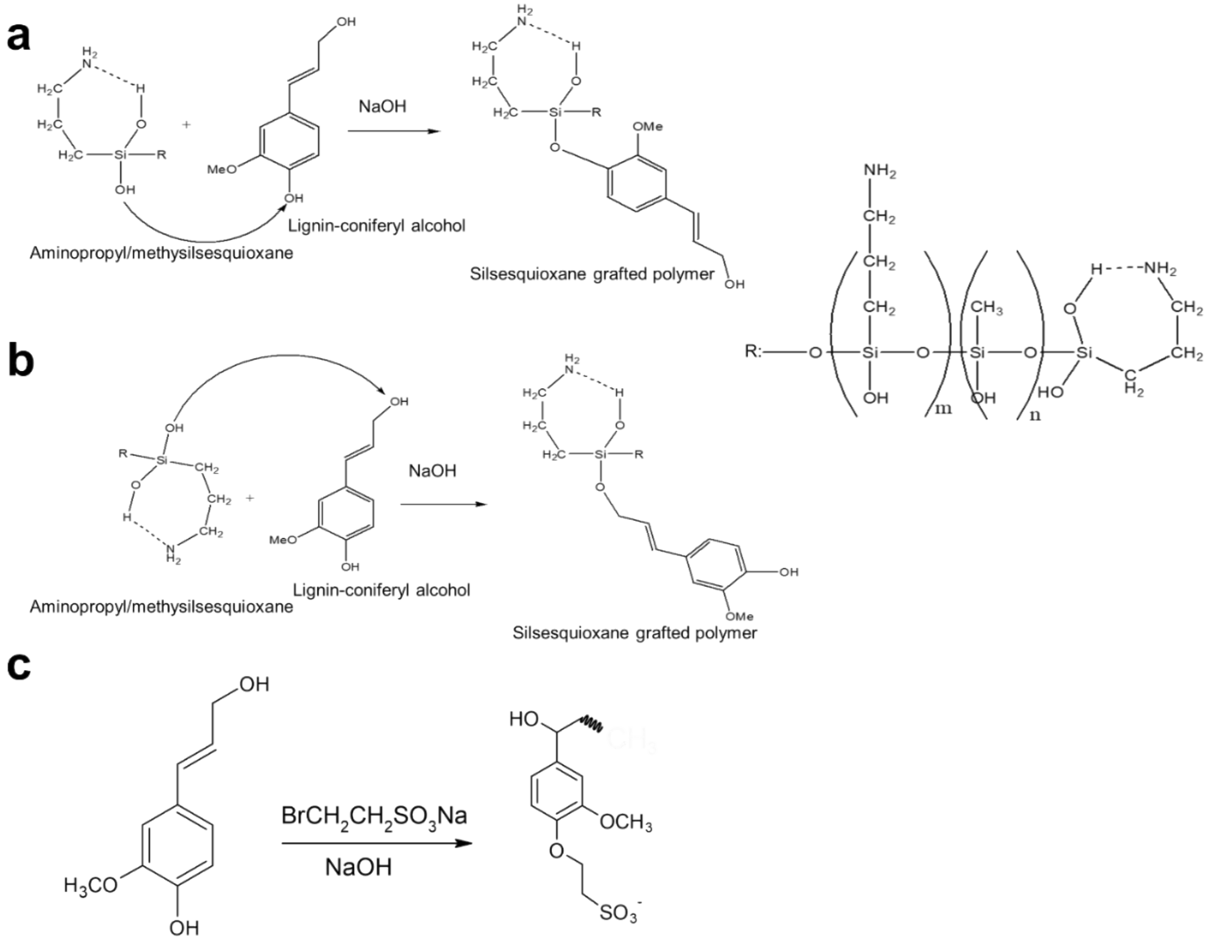

Fig. S1. Reaction pathway of KL and WAPMSS (a and b) and sulfoethylation reaction pathway (c)

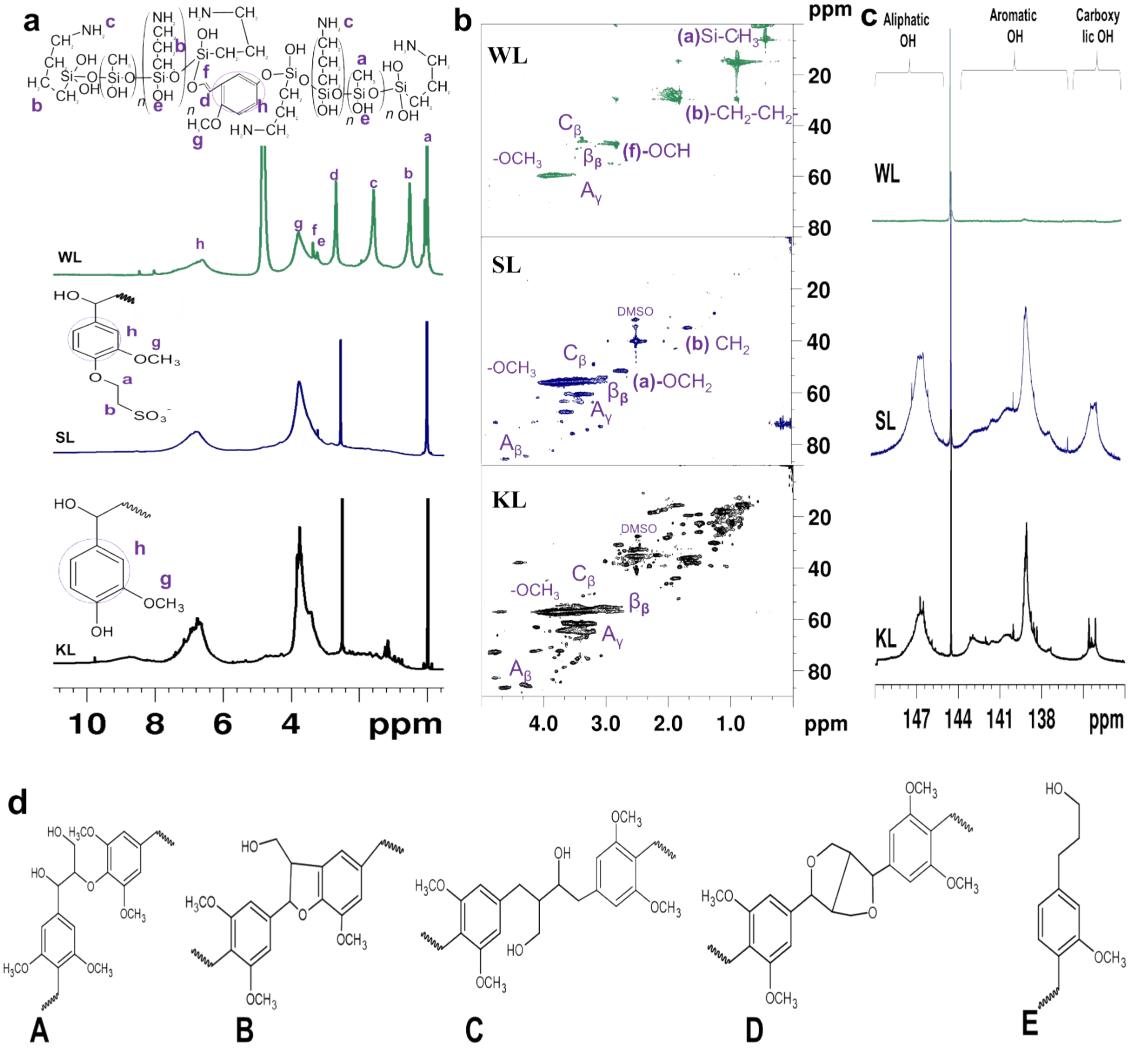

Fig. S2. H-NMR (a), HSQC (b), ^{31}P-NMR (concentration of hydroxyl groups is mmol/g) (c) of Structure of KL, SL, and WL and major linkages (c) (A) β-aryl ether (β-O-4) linkages: (B) phenyl-coumaran structure (β-5′/α-O-4′); (C) secoisolariciresinol substructure; (D) resinol substructure (β-β); (E) guaiacyl propanol unit.

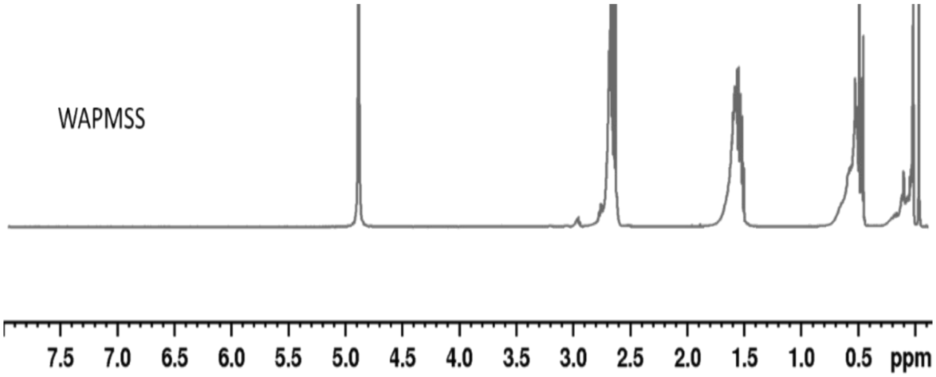

Fig. S3. H-NMR for Aminopropyl/methyl silsesquioxane (WAPMSS) oligomer in D_2O and NaOD

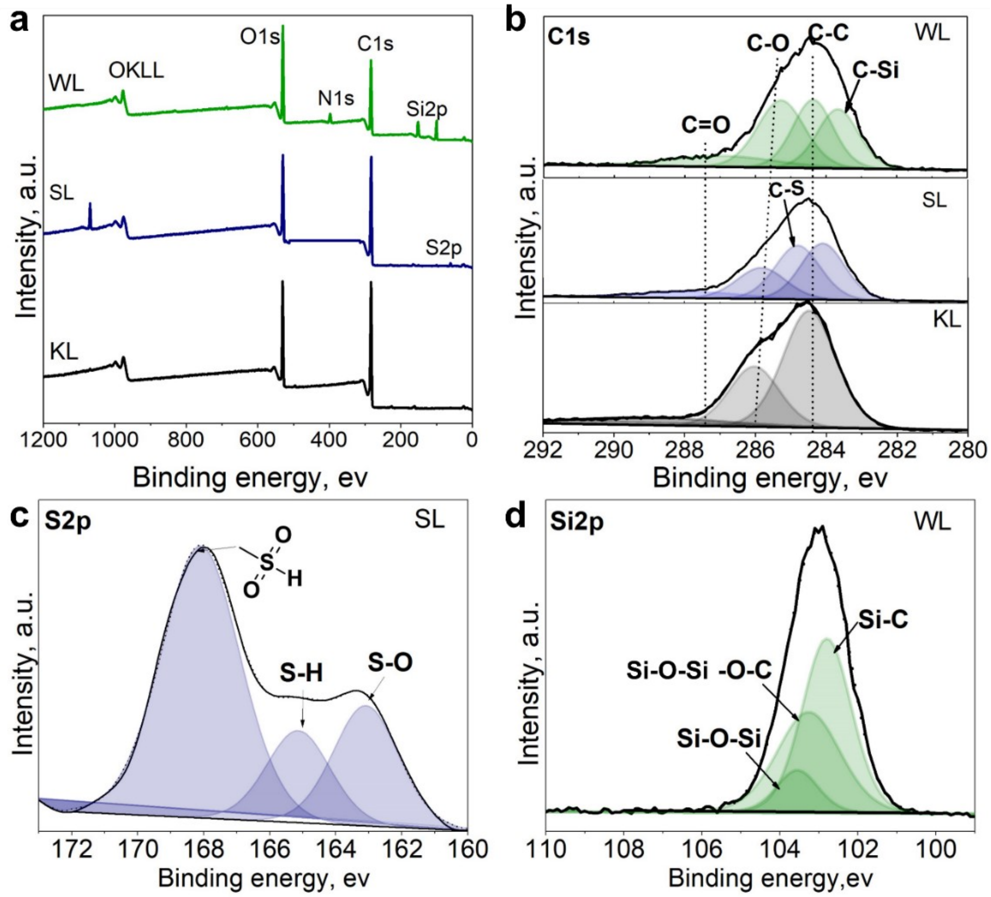

Fig. S4. XPS wide spectra (a), C1s peaks deconvolution for KL, SL, and WL (b), S2p peaks deconvolution for SL (c), and Si 2p peaks deconvolution for WL (d).

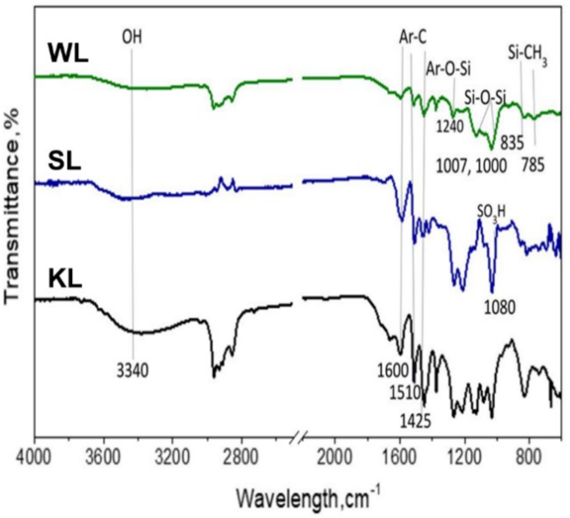

Fig. S5. FTIR spectra for KL, SL, and WL

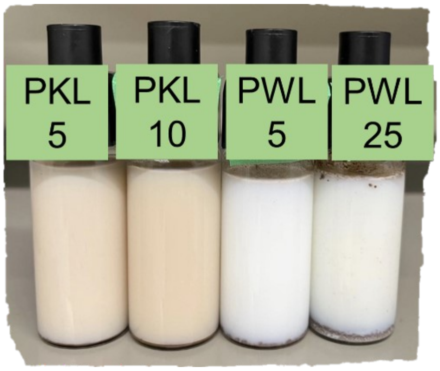

Fig. S6. Visual appearance of Coating formulations.

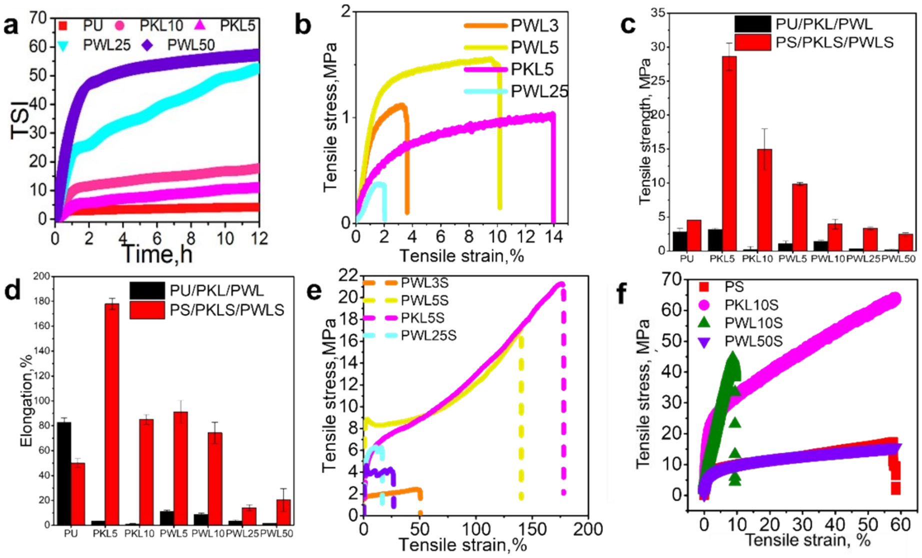

Fig. S7. TSI (a), stress-strain of films (b), tensile strength (c), elongation at break (d), stress-strain after introduction of SL(S) of films (e), and stress-strain after recycling (f).

Fig. S8. The appearance of PKL15 film without SL and with SL

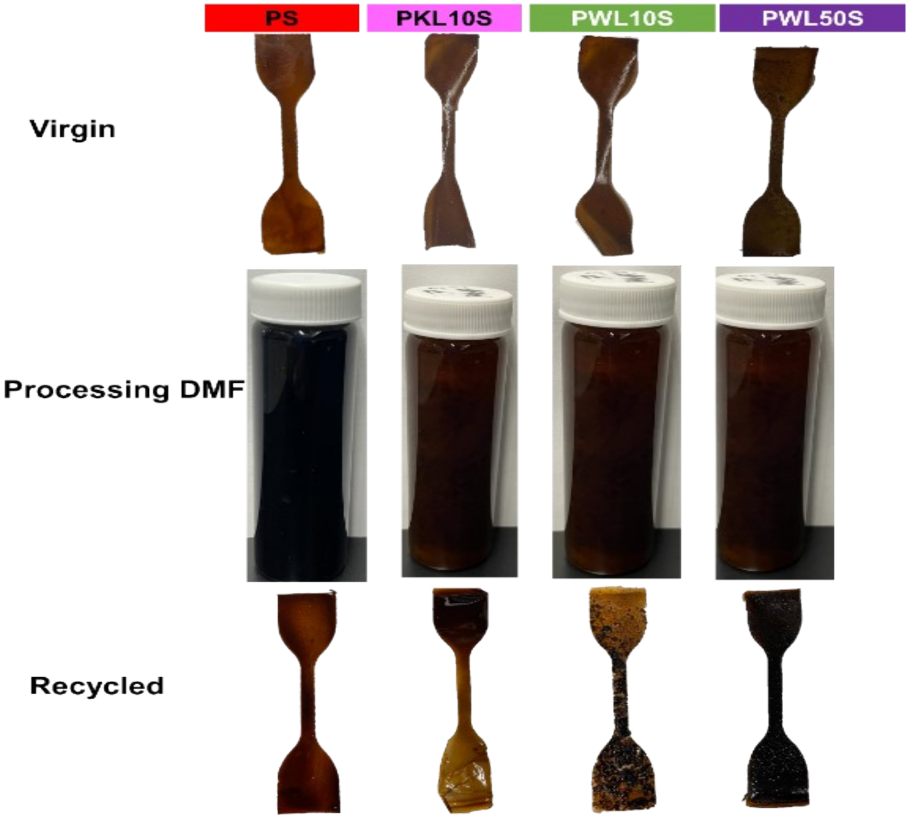

Fig. S9. Recyclable behavior of PU films via solution casting DMF as a solvent.

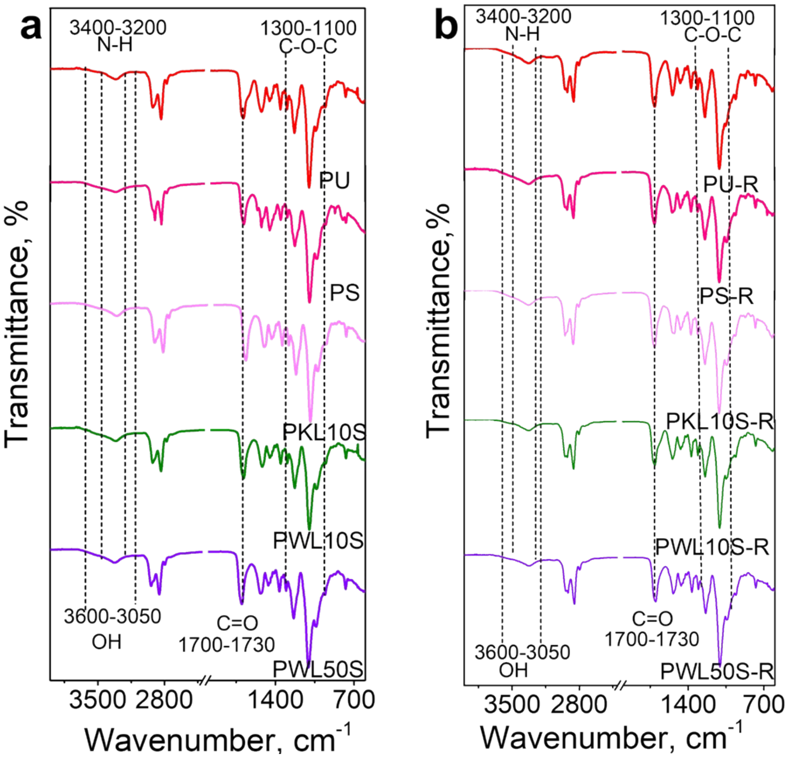

Fig. S10. FTIR spectra of PU films as prepared (a) and after recycling (b)

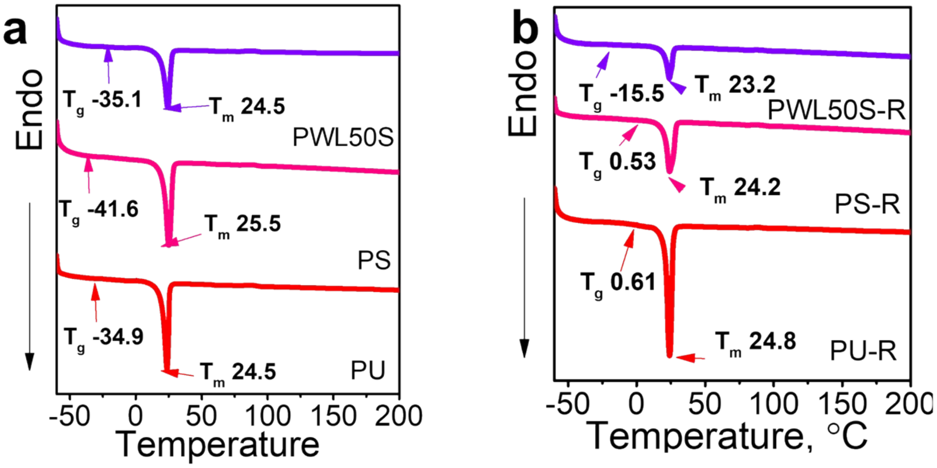

Fig. S11. DSC graph showing melt temperature (Tm) and glass transition (Tg)temperatures for as-prepared (a) and reprocessed PU films (b).

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