

Original polyols based on organosolv lignin and fatty acids: new bio-based building blocks for polyurethanes synthesis

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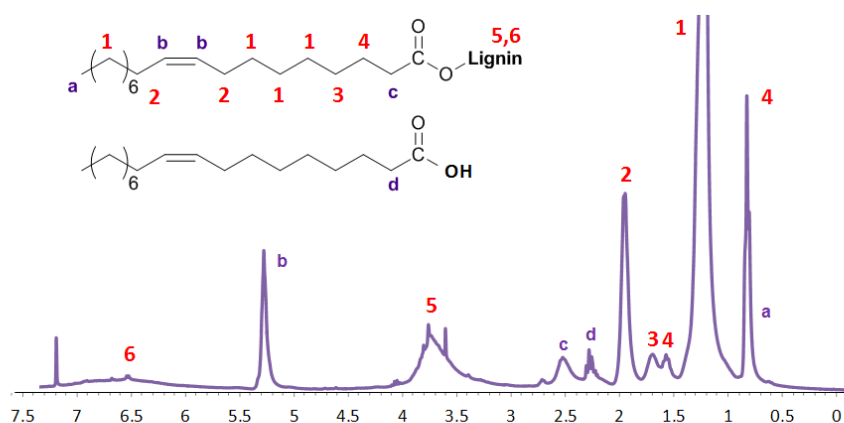
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Supplementary information

1) NMR assignments



Signal	δ ppm	Assignment
a	0.88	3H,t, CH_3
b	5.32-5.38	vinylc protons
c	2.54	2H,t, CH_2 -COOCH ₃
d	2.29	2H,t, CH_2 -COO-lignin
1	1.27	2H, CH_2 from the aliphatic chain of oleic acid
2	1.9	2H,t, CH_2 -CH=CH
3	1.63	2H,t, CH_2
4	1.4	2H,t, CH_2
5	3.88	3H, OCH ₃ , lignin methoxy protons
6	6.3-7.2	Aromatic protons from lignin

Table S1. NMR assignments for EL and oleic acid.

It is important to notice that all the assignments for lignin molecule (Signals 5 and 6) are also present in NMR spectra of ELO and LOAP molecules. The signal between 1 and 1.5ppm can also be attributed to the CH₂ and CH₃ groups in aliphatic chains of lignin molecule.

2) Hydroxyl Index determination

The hydroxyl index of polyol has been determined and expressed as milligrams of potassium hydroxide equivalent for one gram of the sample (mg KOH.g⁻¹). The method used for hydroxyl index determination was adapted from the standard ASTM 4274-99 method. It is particularly recommended for polyester and polyether polyols containing primary and secondary hydroxyl groups. This method is based on the reaction of hydroxyl terminal groups with organic acids (acetic anhydride or phthalic anhydride). Two solutions were previously prepared, reactive solution (phthalic anhydride in pyridine-1mol.L⁻¹) and titration solution (sodium hydroxide in water-1mol.L⁻¹). 2g of polyol were introduced in Erlenmeyer with 20 mL of phthalic anhydride solution and stirred magnetically until complete dissolution. The reactive mixture was then heated under reflux at 130°C for 45 min. After the reflux, the flask was left to cool at room temperature before adding 30 mL of pyridine and 30 mL of deionized water. The acid carboxylic groups resulting from the excess of phthalic anhydride were then titrated by a pHmetric method with a solution of sodium hydroxide. Titration was carried out 2 times and one blank was also performed. Hydroxyl index (I_{OH}) in mg of KOH.g⁻¹, was determined according to equation (1):

$$(1) \quad I_{OH} = \frac{(V_{blank} - V_p) \times C \times 56.1}{W_p}$$

Where V_{blank} (mL) is the NaOH volume required for blank titration, V_p (mL) is the NaOH volume required for polyol sample titration, C (mol.L⁻¹) is the NaOH concentration and W_p (g) is the polyol weight.

3) Cross-linking density determination

The cross-linking density (v_e) was calculated by Equation (3) derived from the theory of rubber elasticity:

$$(1) \quad v_e = \frac{E'}{3 RT}$$

Equation 3 establishes the relationship between crosslink density and Young's Modulus (E) of polymers above T_g . Since the storage modulus (E') obtained from DMTA can be associated to the elastic modulus (E) at temperature above T_g (in the rubbery region at $T_g + 40^\circ\text{C}$), E' can be substituted in Equation (3) to determine v_e . R is the gas constant ($8,31 \text{ J.mol}^{-1}.\text{K}^{-1}$) and T is the temperature in Kelvin.

4) *Supplementary syntheses*

To illustrate the influence of lignin-fatty acid based polyol (LOAP) on the PU network, three blank syntheses have been performed in the presence of Poly(Propylene) Glycol and 4,4' MDI. So far, three polyurethanes have been synthesized by varying the diol (PPG) molar mass (425 , 1000 and 2000 g.mol^{-1}) while the molar ratio of isocyanate and hydroxyl groups remains constant, i.e $\text{NCO:OH} = 1.03$.

Polymer synthesis procedure

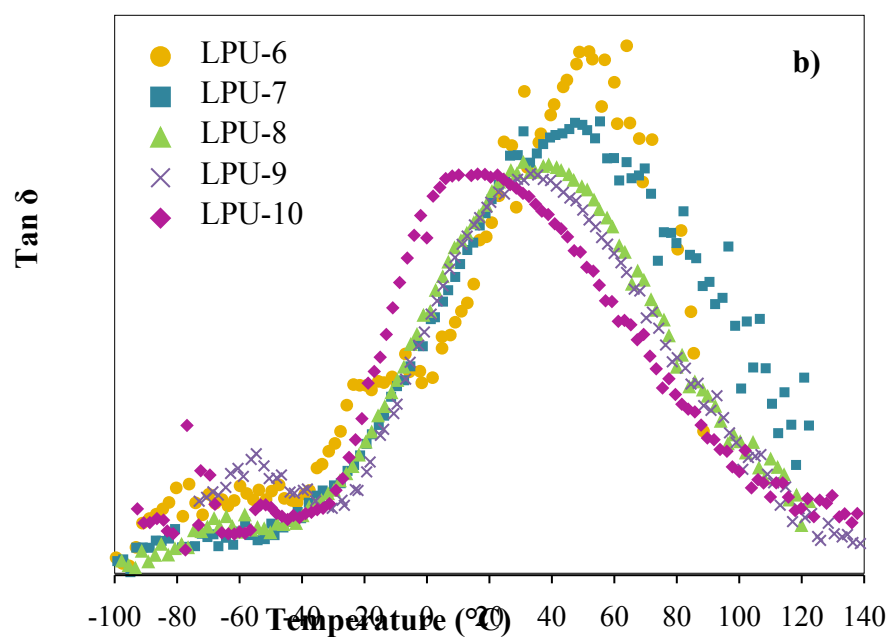
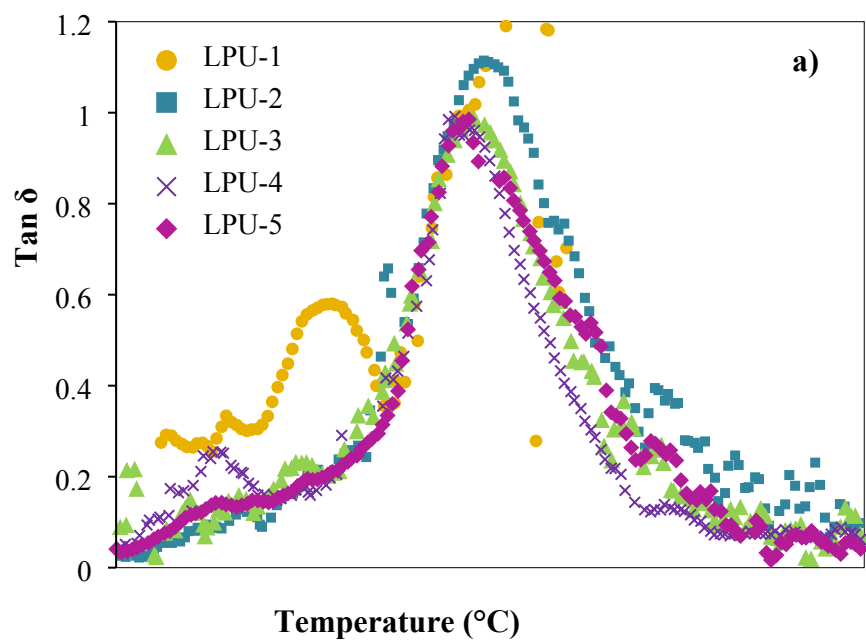
A 250mL round-bottomed flask was fitted with a nitrogen inlet tube and a mechanical stirrer. Poly(Propylene Glycol) and 4,4' MDI ($f=2$) were added into the flask and stirred at 70°C during 5 hours to yield PUs. The ensuing PUs were coded as BPU_{425} , BPU_{1000} and BPU_{2000} for blank syntheses with PPG with molecular weights of 425 , 1000 and 2000 g.mol^{-1} , respectively.

Characterization of BPUs

The ensuing BPUs were analyzed by FT-IR and DSC according the procedure described in the publication.

Samples	T_g ($^\circ\text{C}$)
BPU₄₂₅	33
BPU₁₀₀₀	-27
BPU₂₀₀₀	-57

Table S2. T_g data obtained from DSC experiments for blank PUs.



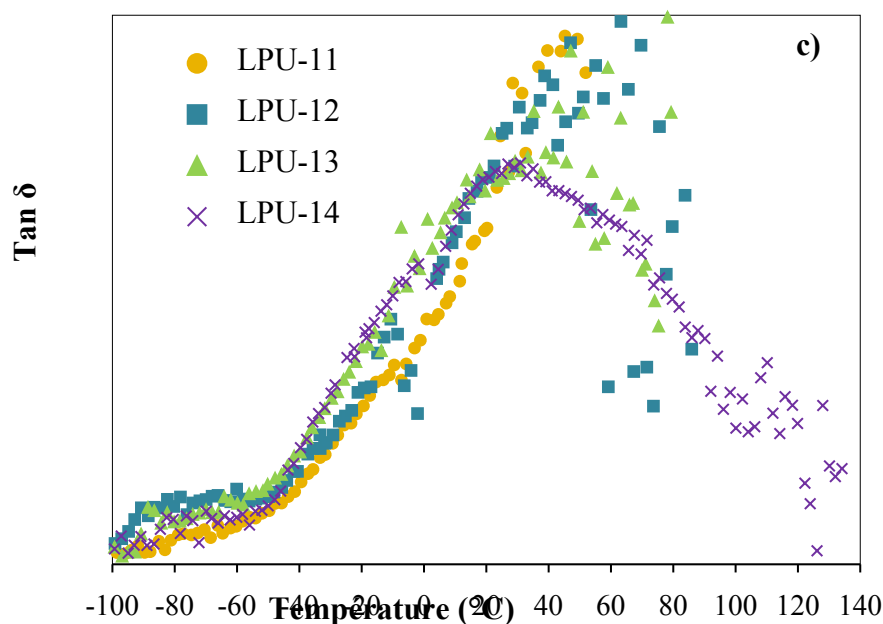
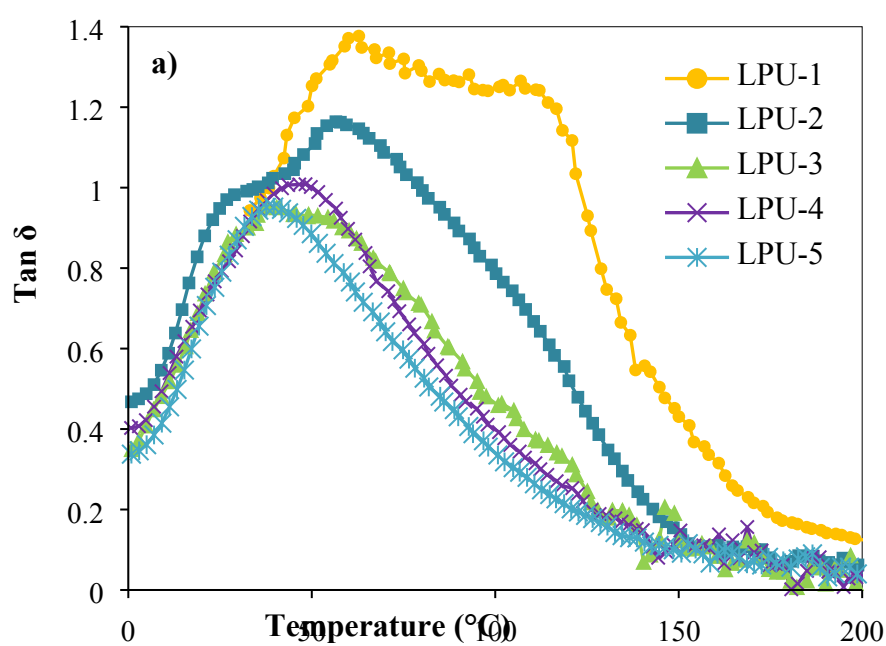


Figure S1. Changes in the position and intensity of the relaxation transition ($\tan \delta$) on the stoichiometric ratio of the component. (a: $\tan \delta$ of PU based on P_{425} systems; b: $\tan \delta$ of PU based on P_{1000} systems; c: $\tan \delta$ of PU based on P_{2000} systems)

The following figure S2 display the dependence of $\tan \delta$ for the LPU's samples on temperature.

Analyses have been performed by DRA (Dynamic rheological analyses) at a heating rate of $2^{\circ}\text{C}.\text{min}^{-1}$



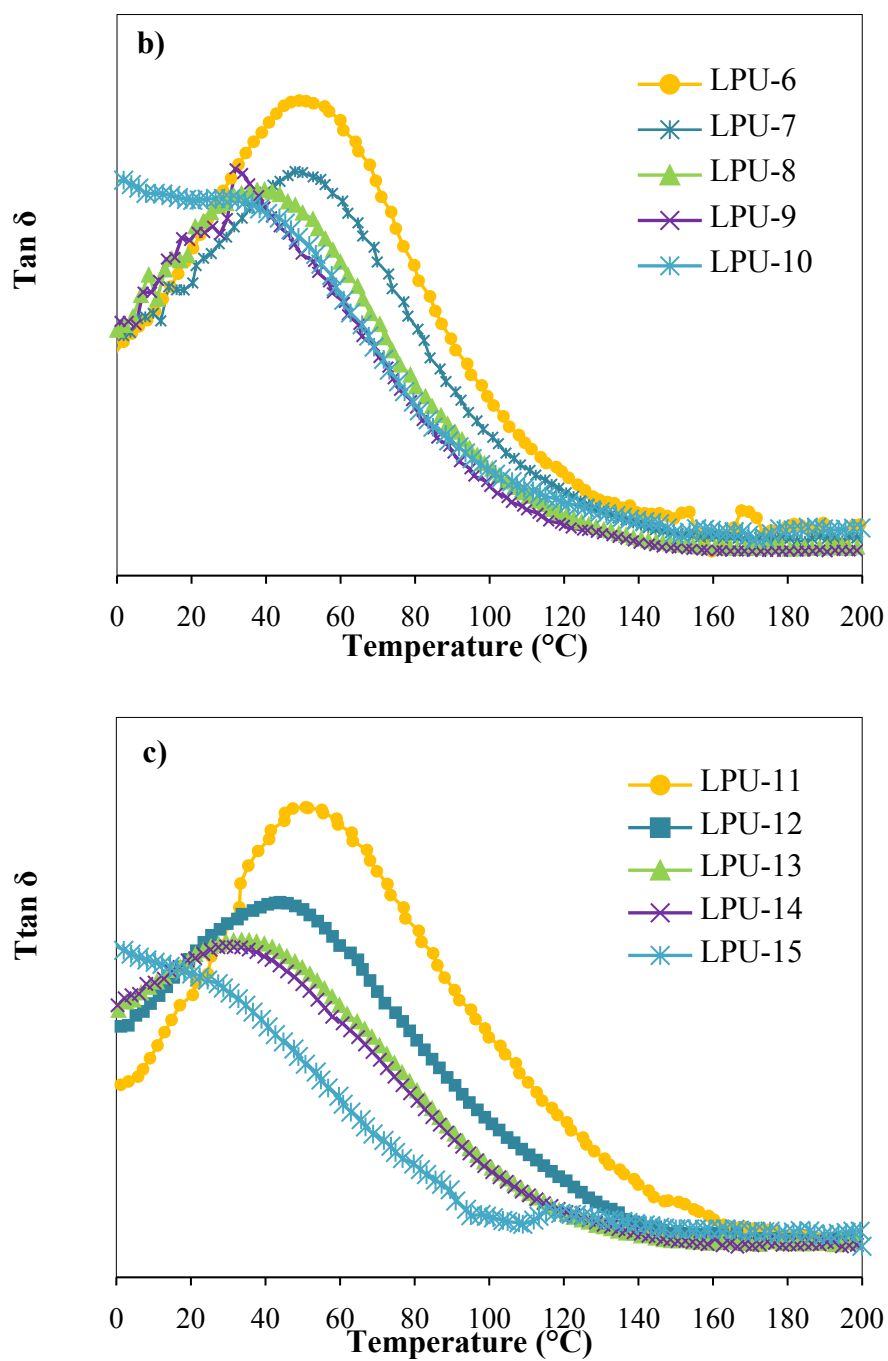


Figure S2. Temperature sweep of loss tangent ($\tan \delta$) for synthesized PU performed by using a strain-controlled rheometer with parallel-plate geometry (a: $\tan \delta$ of PU based on P_{425} systems; b: $\tan \delta$ of PU based on P_{1000} systems; c: $\tan \delta$ of PU based on P_{2000} systems)

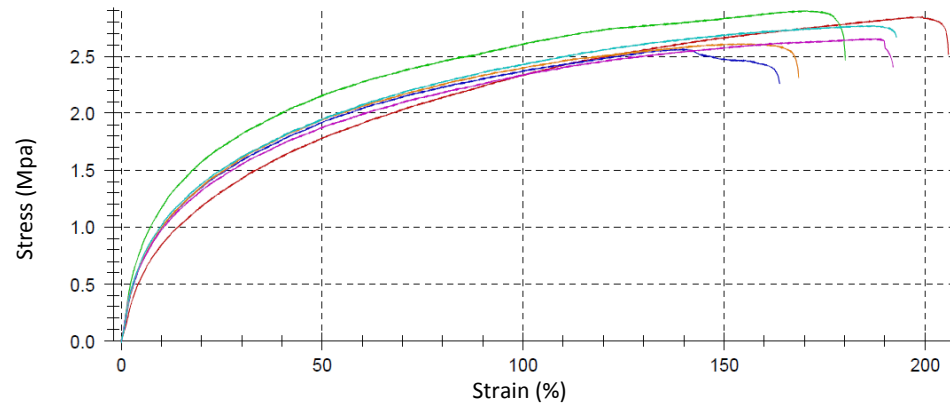
Samples	$T_{g\text{ ss}} (^{\circ}\text{C})$		$T_{g\text{ HS}} - \tan \delta \text{ maximum } (^{\circ}\text{C})$	
	By DSC	By DMTA (max E'')	By DMTA	By DRA
LPU-1	-7	-18	53	63
LPU-2	-7	-11	49	57
LPU-3	-10	-	42	46
LPU-4	-7	11	42	47
LPU-5	-6	-7	41	40
LPU-6	-27	-54	51	49
LPU-7	-19	-35	44	58
LPU-8	-24	-38	31	38
LPU-9	-19	-	29	32
LPU-10	-15	-	22	-
LPU-11	-36	-48	51	51
LPU-12	-39	-60	50	44
LPU-13	-42	-64	38	34
LPU-14	-41	-44	34	29
LPU-15	-42	-	30	-

Table S3. Glass transitions of soft and hard segments in lignin-based polyurethanes. Comparison of data obtained by DSC, DMTA and DRA experiments.

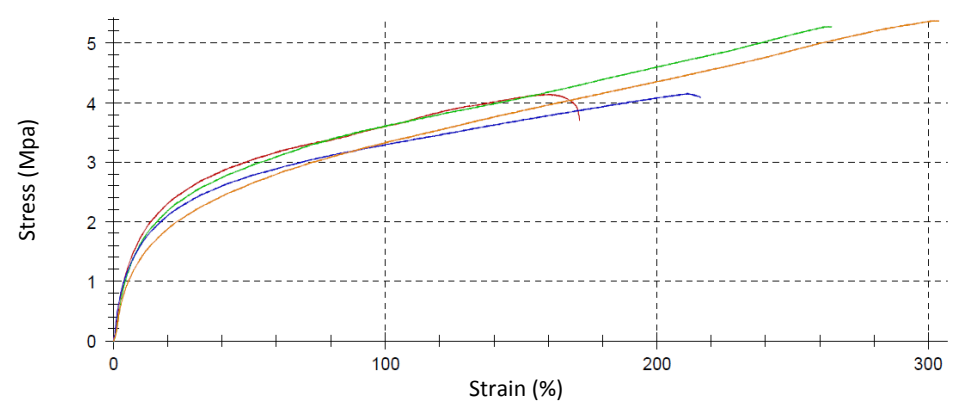
Table S3 displays results obtained by means of DSC, DMTA and DRA. As can be seen, these results confirmed the previous comments. The difference observed between $T_{g\text{ ss}}$ obtained from DSC and DMTA tests is caused by the nature of these two methods. DSC measures the change in heat capacity from frozen to unfrozen chains, while DMTA measures the change in the mechanical response of the polymer chains. However, these results seem to corroborate the phase separation behavior of LPU samples with two different T_g attributed to soft segments and hard segments, respectively.

5) Stress-strain curves

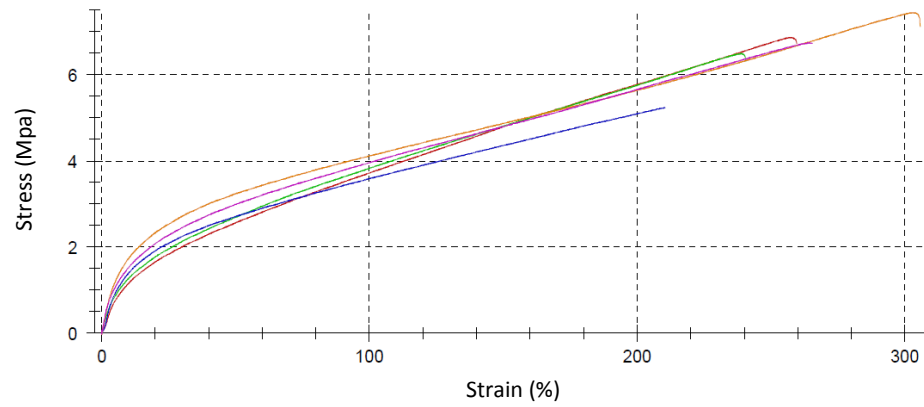
LPU-1



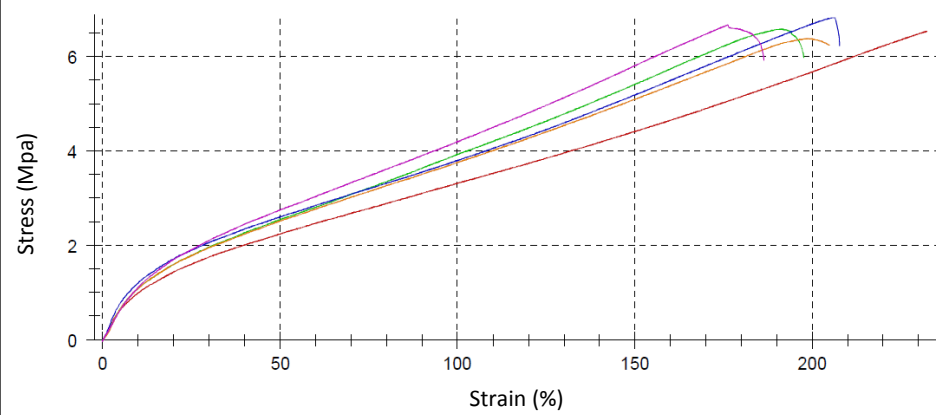
LPU-2



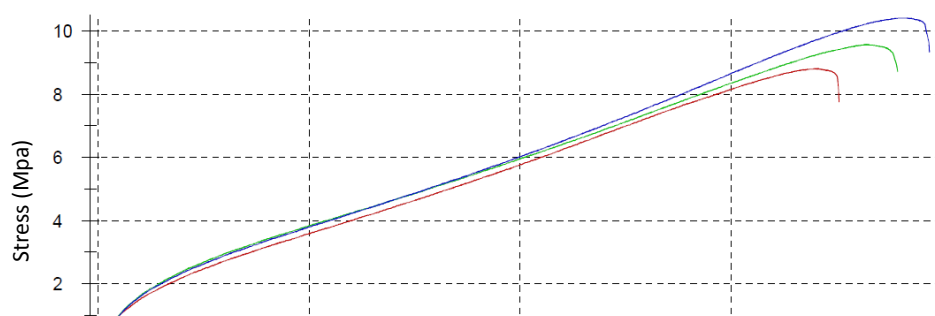
LPU-3



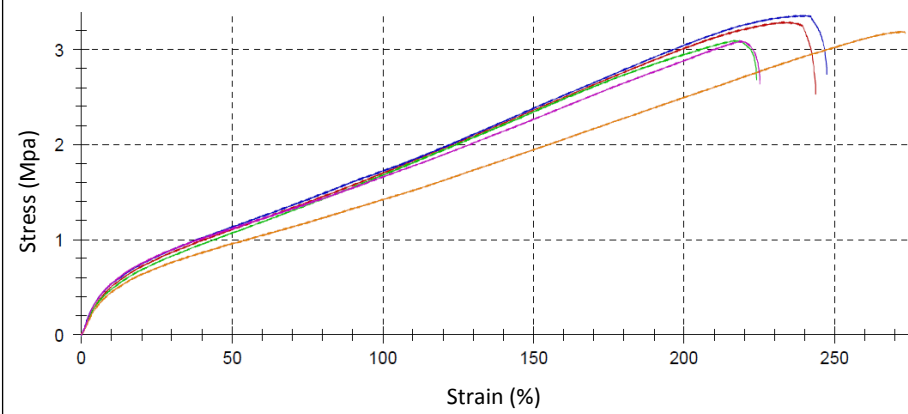
LPU-4



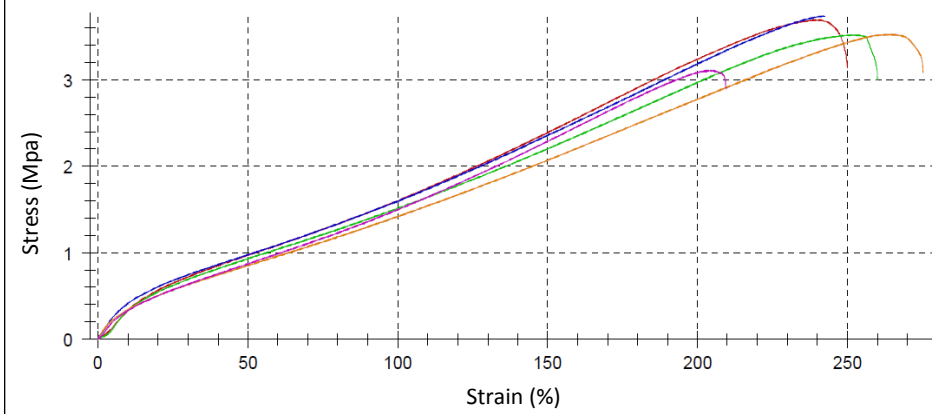
LPU-5

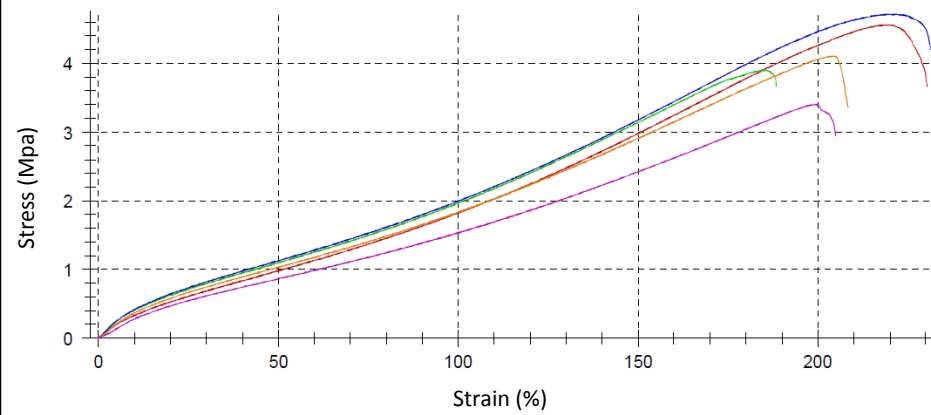
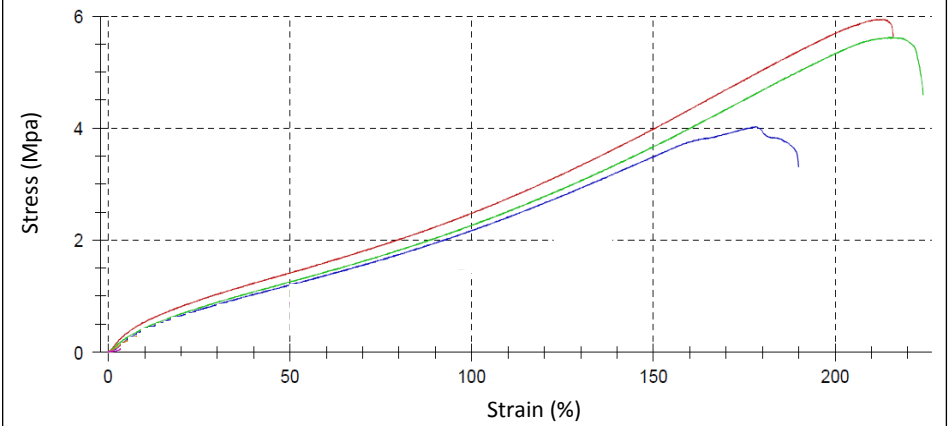
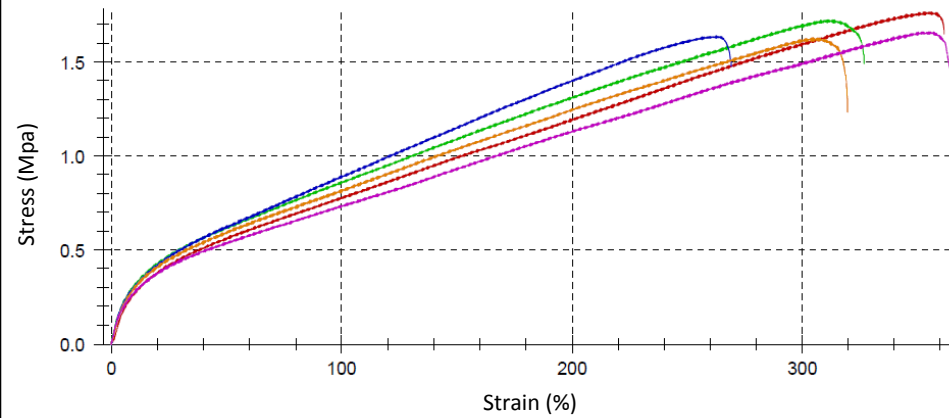
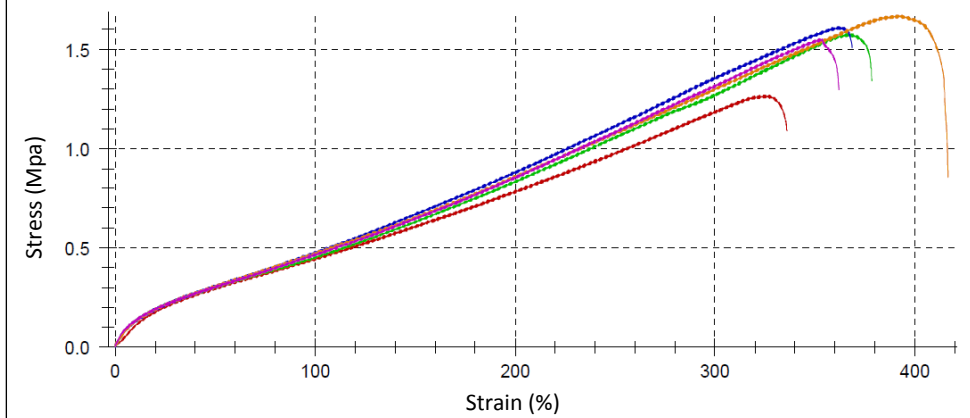


LPU-6

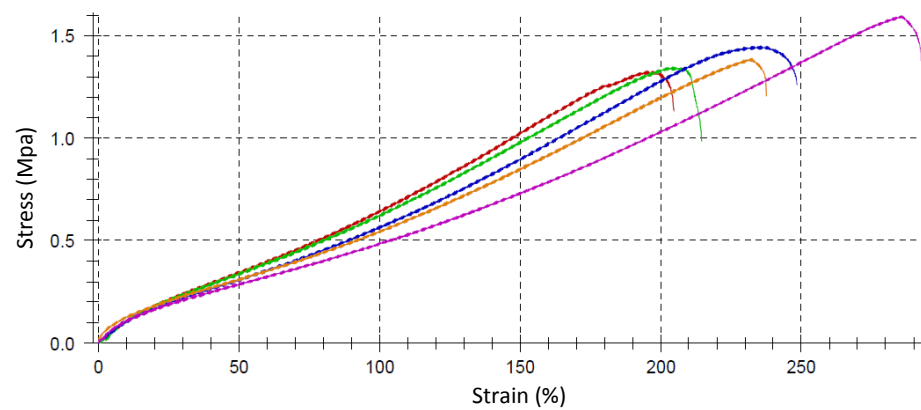


LPU-7



LPU-8**LPU-9****LPU-11****LPU-12**

LPU-13



LPU-14

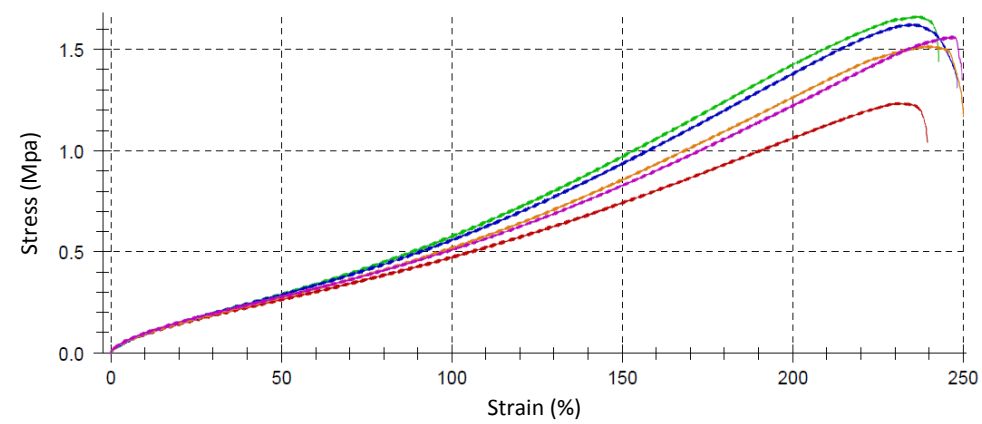


Figure S3. Stress strain curves of LPU polymers.