

Supplementary Information:

Fast Relaxing Lignin-derived Fully Biobased Vitrimeric Elastomer

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Materials:

Epoxidized Natural Rubber with 25mol% epoxy groups (ENR-25) was purchased from Sanyo Corporation of America. Softwood lignin was obtained from Kruger Wayagamack, Inc. Zinc acetylacetonate hydrate ($\text{Zn}(\text{acac})_2$) (99.995%) was purchased from Sigma Aldrich and used as received. Acetonitrile (ACN) and tetrahydrofuran (THF) were purchased from Sigma Aldrich and used without further purification.

Instrumentation:

- FTIR was used to confirm the chemical composition of all the vitrimer samples. The spectra and measurements were recorded in attenuated total reflection (ATR) mode with 16scans on a PerkinElmer Frontier instrument.
- The thermal stability experiments on all the vitrimer samples were carried on a Q500 from TA Instruments, at a ramp rate of 10°C/min between 25°C and 700°C.
- The DSC analysis on Lignin-ENR vitrimers was performed using a heat/cool/heat thermal cycle on a Q2000 from TA instruments, between -80°C and 200°C, with a heating and cooling rate of 10°C/min.
- The dynamic mechanical properties for each vitrimer were analyzed on a Q800 from TA Instruments in tension mode. A strain rate of 0.1 %, a frequency of 1Hz, and a heating rate

of 3°C/min was employed over a temperature range of -80°C to 250°C. Each specimen had a dimension of 20mm × 4mm which was cut from the pressed vitrimer sheets. Additionally, the frequency sweep experiment was performed on each vitrimer sample at 25°C from 0.01Hz to 100Hz at a strain rate of 0.02 %.

- To identify the viscoelastic region of the vitrimers at each temperature before conducting the stress relaxation experiment, a strain sweep experiment was performed. Samples underwent a 5-minute conditioning at a specific temperature, with an angular frequency of 10 rad/sec. Subsequently, a logarithmic oscillation strain sweep ranging from 0.0001 % to 50 % was carried out. The storage and loss moduli were recorded as a function of oscillation strain during this process.
- The stress relaxation experiments were performed at different temperatures on each vitrimer sample to examine dynamic properties. A DHR-3 rotational rheometer from TA instruments using ETC parallel plate geometry with 8mm sample disks was used for these experiments. A constant axial force of 5N and a constant strain of 0.667 % was applied for the stress relaxation experiments. The relaxation modulus was recorded over time at constant temperature.
- Creep recovery experiments were conducted on all vitrimer and control samples at various temperatures utilizing a DHR-3 rotational rheometer from TA Instruments, employing ETC parallel plate geometry with 8mm sample disks. Initially, each sample underwent pre-heating at a specific temperature for 5 minutes. Subsequently, a consistent force of 2000 Pa was applied to the sample for a duration of 1000 seconds. Following this period, the force was removed, allowing the material to recover for an additional 1000 seconds.
- Uniaxial Tensile Testing: The tensile strength experiments were performed on an MTS Criterion model 42 using dogbone-shaped specimens. These specimens were cut from the pressed sheets using an ASTM D-638-5 standard die. The gauge and thickness dimension were measured for each specimen prior to testing and a minimum of four samples were tested for each vitrimer sample. The tensile measurements were performed using a 2000 N load cell at a strain rate of 50 mm/min. The mechanical properties of the reprocessed samples were also performed using same conditions.
- Atomic force microscopy measurements were carried out on a NanoIR2 platform (Bruker) with a pulsed tunable infrared quantum cascade laser (Daylight MIRCAt). All measurements were carried out with a FORTGG cantilever (AppNano). Topography images were acquired in tapping mode using the first resonance of the cantilever ~60 kHz. The force curves were acquired in contact mode, before and during illumination of the vitrimer. Given the varying temperature of the cantilever throughout, the force curve measurements are presented in Deflection vs. Z, corresponding to the raw data.
- The nanoscale infrared spectra were acquired by engaging the cantilever in contact with the sample surface and tuning the pulse frequency of the infrared laser to the contact resonance of the cantilever in the 280-320 kHz range. The contact resonance was optimized before each spectrum acquisition to accommodate with the variations in mechanical properties of the material under the tip of the cantilever. At fixed illumination wavelengths, the power output was calculated using the laser background data acquired for each measurement, which provides the power in mW for each wavelength. For spectral data, the power is

referred to in % for clarity. All nanoscale infrared spectra were smoothed (Savitzky-Golay, 3 pts for Fig. S8 and 8 pts for Fig. S9) and normalized for comparison of the peak position.

- The dynamics of soft and rigid components of a representative vitrimer at various temperature range was investigated by low-field NMR spectroscopy. ^1H time domain NMR was collected on the vitrimer containing 60 phr lignin and its corresponding control without use of catalyst using a Minispec MQ20 Bruker Corp system operating at 20 MHz ^1H frequency. The free induction decays were collected using a single 90° excitation pulse of $3\ \mu\text{s}$ and an instrument dead time of $\sim 9\ \mu\text{s}$. Variable temperature was measured over a wide range from ambient to $200\ ^\circ\text{C}$, depending on the sample using a BVT3000. ^1H signals were fit following the method outlined in V. Rantzsch et al ¹.

A two-component fit was applied using the equation below:

$$FID = A_g \times \exp\left(\left(t/T2_g\right)^b\right) + A_m \times \exp\left(\left(t/T2_m\right)^c\right)$$

where A_g the rigid and A_m the mobile component. The shape factors b and c were initially left free but the b factor showed a random pattern around 1 and so was fixed to $b=1$ for more stable fits while c was left free and varied between 0.7 and 1.1. Furthermore, Akaike and Bayesian information criterion were compared between different cases of shape parameters and were found to be lowest for this model. In this case, the rigid component is dominated by the lignin phase and mobile component represents soft rubbery phase. It is important to emphasize that this technique only ‘counts’ protons, so making mass conversion calculations is only possible with homogeneous structures or if the molecular weights of the molecules used are precisely known for each phase. It does nevertheless quantitatively reflect all protons, their phase behavior and dynamics in the system.

Experimental:

Lignin Fractionation:

As received softwood lignin was fractionated with acetonitrile (ACN). 1000mL of ACN was added to 1 L glass jar containing 100g of as-received softwood lignin. The mixture was stirred for 24 h and then centrifuged to remove the insoluble part of lignin; the remaining residue-free lignin solution was collected in a 1000 mL glass beaker. ACN fractionated lignin (ACN-lignin) was obtained by removal and recovery of ACN by a rotary evaporator. The collected ACN-Lignin was further dried for 24h at room temperature in a vacuum hood. The yield of ACN-Lignin was roughly 25 % per batch.

Synthesis of ACN-Lignin/ENR25 vitrimeric elastomers: Solvent-free high temperature shear mixing

The Lignin-ENR25 vitrimer with different weight ratios of ACN-Lignin (40, 50, 60 phr) was synthesized using a Brabender Plasticorder (C.W. Brabender Instruments, NJ) melt mixer. The mixing was done in two stages. In the first mixing cycle, ENR-25, ACN-Lignin, $\text{Zn}(\text{acac})_2$ were

homogenously mixed at 78°C for 40 min at a rotor speed of 60 rpm. This was followed by a second mixing step at 180°C for 10 min with a rotor speed of 60 rpm. The resulting homogenous Lignin-ENR mixture was further cured and hot-pressed into sheets of a thickness of roughly 0.5 mm in a Carver Hydraulic Laboratory hot press at a temperature of 180°C and a pressure of 900 psi for 2 h.

Reprocessing of Vitrimer:

The tensile tested broken dogbone samples of the vitrimer were further broken into smaller pieces (<3 mm) and casted into a sheet of thickness of 0.2 mm in a hot press at 180°C for 30 min. An ASTM D-638-5 standard die was further used to cut dogbone samples from these reprocessed sheets.

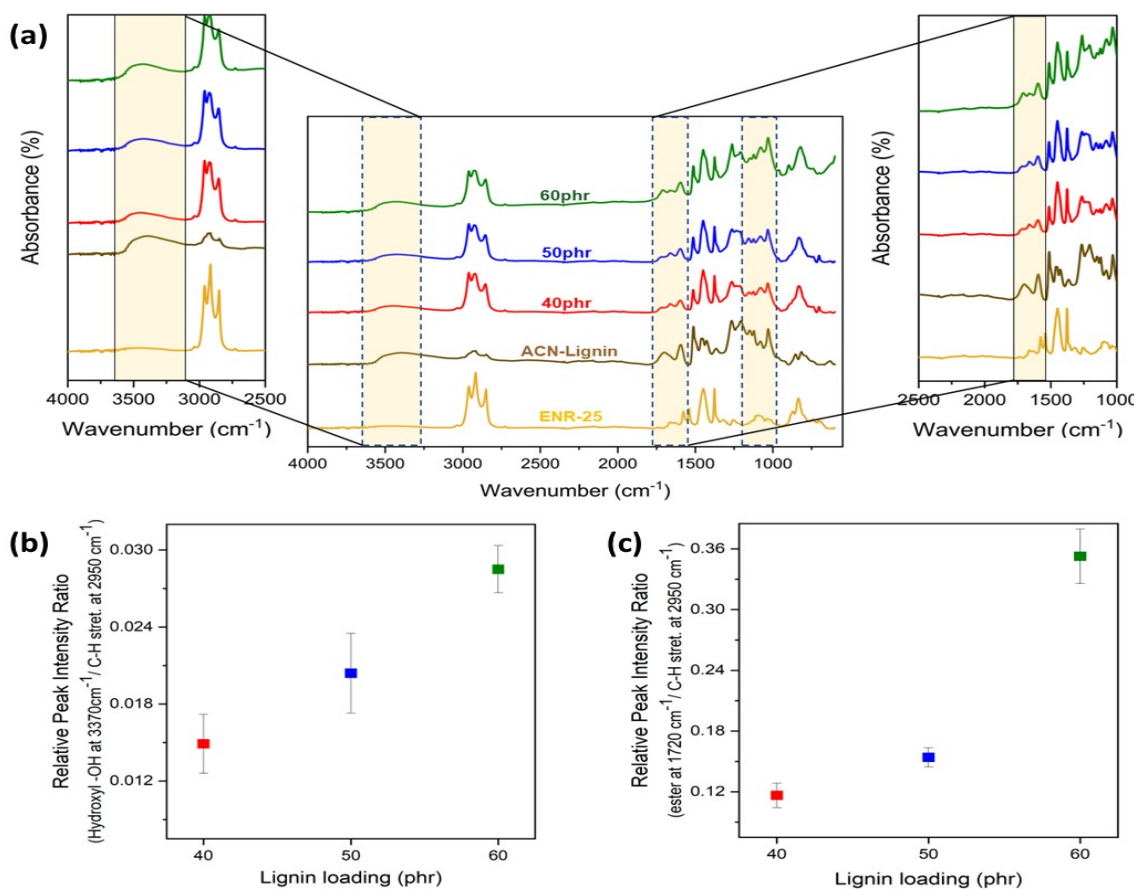


Fig. S1. (a) FTIR spectra of ENR25, ACN Lignin, Lignin-ENR25 vitrimer with different lignin content. Peak intensity ratio of (b) Hydroxy group at 3370 cm⁻¹ to C-H stretching at 2950 cm⁻¹, (c) ester group at 1720 cm⁻¹ to C-H stretching at 2950 cm⁻¹ as a function of lignin content.

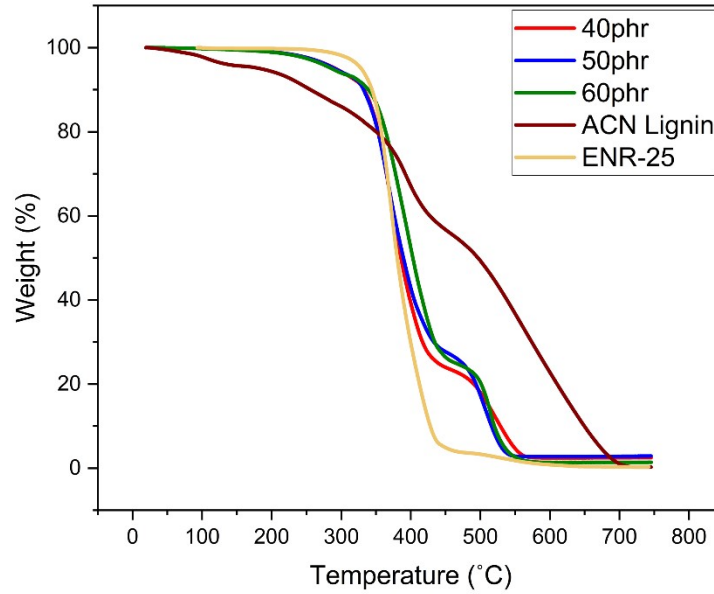


Fig. S2. TGA thermogram of ENR25, can Lignin, Lignin-ENR25 vitrimer with different lignin content.

Calculation of static heat resistant temperature: ²

$$A1 = T_s = 0.49 \times [T_{d5\%} + 0.6 \times (T_{d30\%} - T_{d5\%})]$$

where T_s is Static heat resistant temperature and $T_{d5\%}$, $T_{d30\%}$ are temperature corresponding to 5 % and 30 % mass loss respectively.

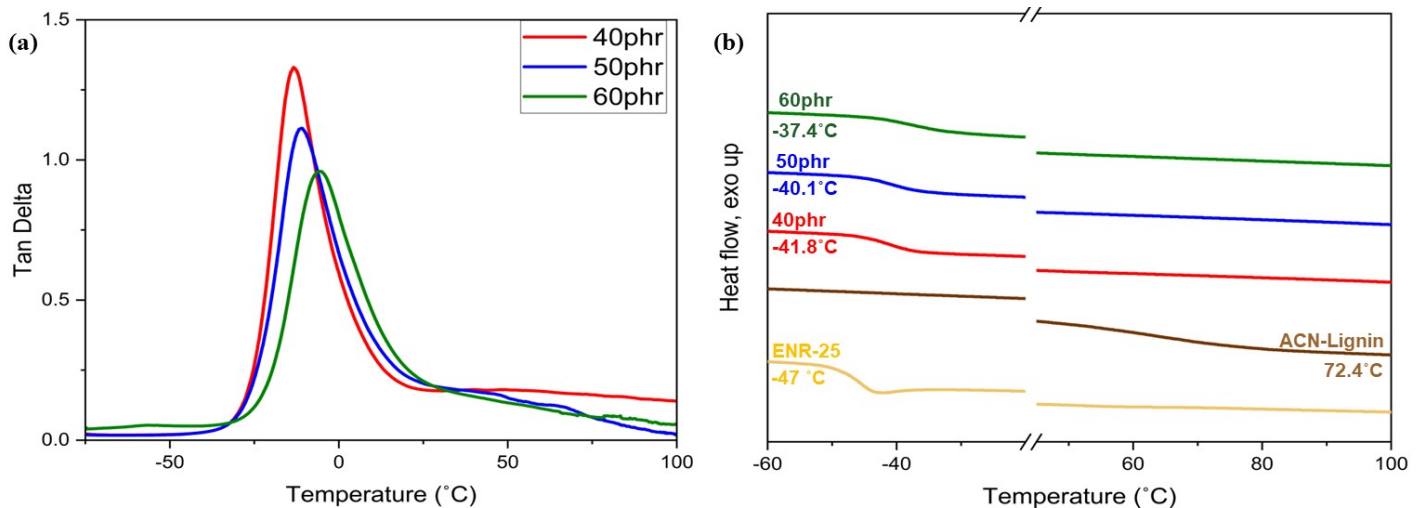


Fig. S3. (a) Tan Delta and (b) DSC thermogram of Lignin-ENR25 vitrimer with different lignin content.

Swelling Ratio, Gel Content and Soluble Fraction ³:

The swelling ratio and gel content of the ACN Lignin-ENR25 vitrimers were determined by solvent extraction method [1]. A pre-weighed dry sample of ~50 mg of each vitrimer sample was immersed in 10 mL of THF for 48 h at 25°C.

$$\bullet \text{ Swelling Ratio (\%)} = \frac{M_s - M_i}{M_i} \times 100 \%$$

$$\bullet \text{ Gel Fraction (\%)} = \frac{M_d}{M_i} \times 100 \%$$

$$\bullet \text{ Soluble Fraction (\%)} = \frac{M_i - M_d}{M_i} \times 100 \%$$

where, M_i , M_s and M_d correspond to the initial, swollen and dry masses of each vitrimer sample, respectively.

Rheology:

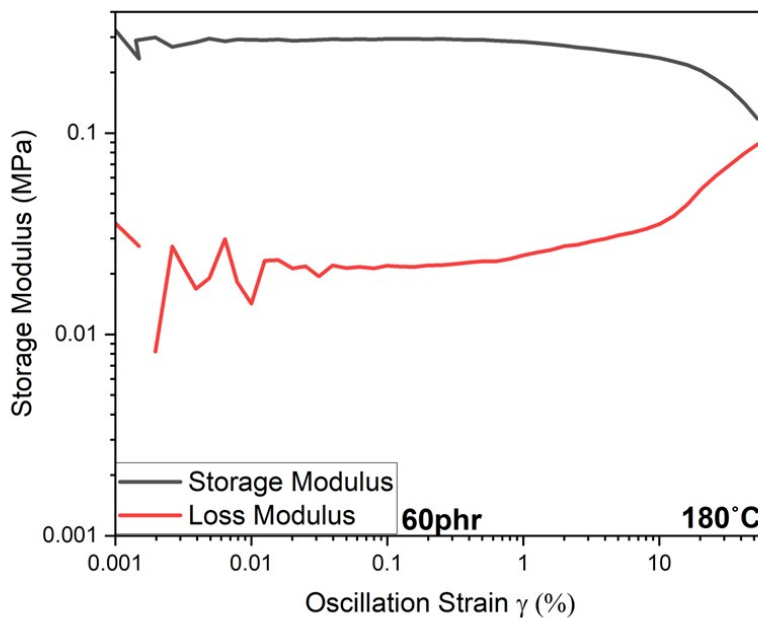


Fig. S4. Oscillation Strain sweep experiment for 60 phr ACN Lignin/ENR vitrimer carried out at 180°C.

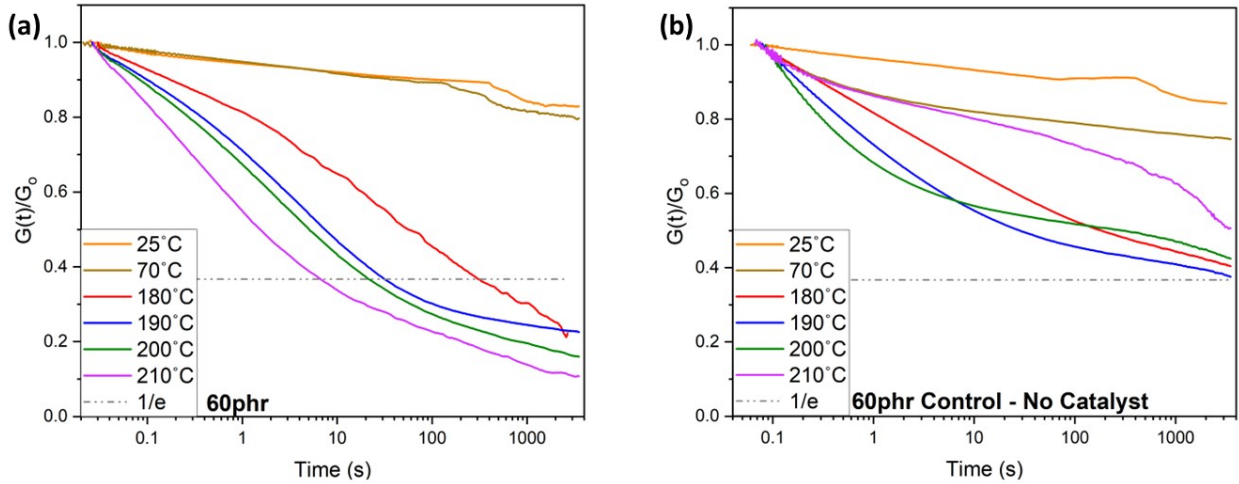


Fig. S5. Stress relaxation curves for 60 phr ACN Lignin-ENR25 (a) vitrimer formed with catalyst showing rapid decay of normalized stress at elevated temperature and (b) control blend without catalyst exhibiting insignificant stress relaxation patterns (without any rapid decay in stress) even at very high temperature.

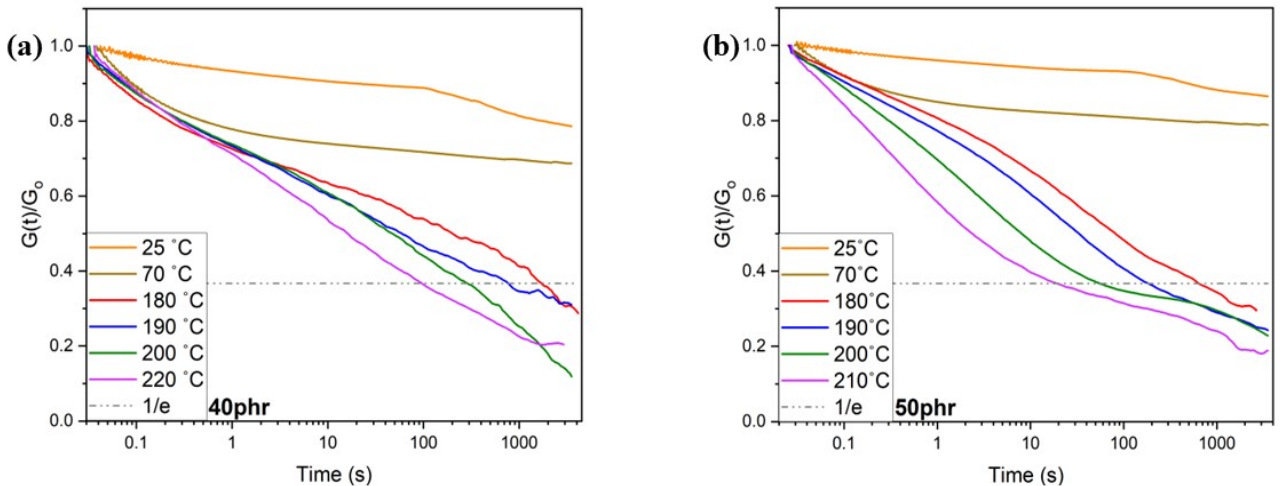


Fig. S6. Stress relaxation curves for (a) 40 phr and (b) 50 phr ACN Lignin-ENR25 samples at different temperatures.

Calculation of activation energy derived from stress relaxation experiment ³:

- For 40 phr ACN Lignin-ENR25 vitrimer:
 Equation obtained from Arrhenius Law: $25.286x - 47.840$
 Arrhenius Law related to activation energy is: $t^* = t_0 \exp(E_a/RT)$ where $R=8.314$
 Which corresponds to: $\ln(t^*) = 25.286 \cdot 1000/T - 47.840$
 Where, $\ln(t^*) = \ln(t_0) + E_a/RT$
 Thus, $E_a/R = 25.286 \cdot 1000$
 Hence, $E_a = 25.286 \cdot 1000 \cdot 8.314 = \mathbf{210.22 \text{ kJ/mol}}$

- For 50phr ACN Lignin-ENR25 vitrimer
Equation obtained from Arrhenius Law: $23.869x - 46.419$
Which corresponds to: $\ln(t^*) = 23.869 \cdot 1000/T - 46.419$
Where, $\ln(t^*) = \ln(t_0) + E_a/RT$
Thus, $E_a/R = 23.869 \cdot 1000$
Hence, $E_a = 23.869 \cdot 1000 \cdot 8.314 = \mathbf{198.44 \text{ kJ/mol}}$
- For 60phr ACN Lignin-ENR25 vitrimer:
Equation obtained from Arrhenius Law: $20.363x - 40.193$
Which corresponds to: $\ln(t^*) = 20.363 \cdot 1000/T - 40.193$
Where, $\ln(t^*) = \ln(t_0) + E_a/RT$
Thus, $E_a/R = 20.363 \cdot 1000$
Hence, $E_a = 20.363 \cdot 1000 \cdot 8.314 = \mathbf{169.30 \text{ kJ/mol}}$

Calculation for theoretical topology freezing temperature (T_v) using Arrhenius equation from stress relaxation ³:

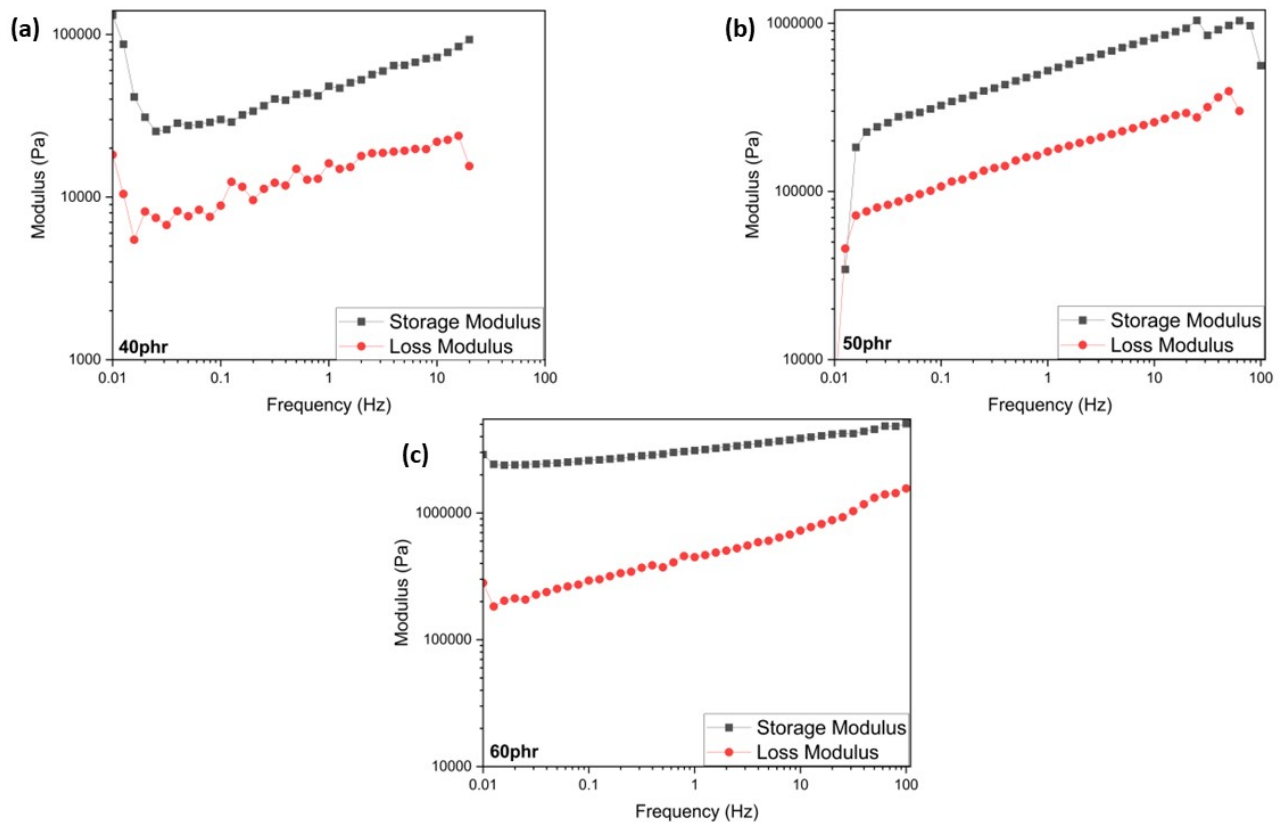


Fig. S7. Storage modulus and loss modulus for (a) 40phr, (b) 50phr, (c) 60phr Lignin-ENR25 vitrimer samples at room temperature.

- For 40phr ACN Lignin-ENR25 vitrimer:
Equation obtained from Arrhenius Law: $25.286x - 47.840$
The following Maxwell equation is used for calculation of T_v by utilizing an arbitrary value of viscosity as $\eta = 10^{12}$

$$\eta = G \times \tau^*$$

$$\text{Where } G^2 = G'^2 + G''^2$$

The value for G' and G'' is extracted from frequency sweep DMA experiment at room temperature. The value for G' and G'' is taken from rubbery plateau at 1Hz (Fig S6).

For 40phr sample, $G = 0.05$ MPa, thus $\tau^* = 10^{12}/0.05 \times 10^6 = 20 \times 10^6$

$$\ln(20 \times 10^6) = 16.811$$

Using the Stress Relaxation equation: $x = 1000/T = (\ln(\tau^*) + 47.840)/25.286 = 2.55$

$$\text{Now, } T_v = 1000/x = 1000/2.55 = 392.15\text{K} = \mathbf{119} \text{ }^\circ\text{C}$$

- For 50phr ACN Lignin-ENR25 vitrimer:
Equation obtained from Arrhenius Law: $23.869x - 46.419$
For 50phr sample, $G = 0.549$ MPa, thus $\tau^* = 10^{12}/0.549 \times 10^6 = 1.69 \times 10^6$

$$\ln(1.69 \times 10^6) = 14.34$$

Using the Stress Relaxation equation: $x = 1000/T = (\ln(\tau^*) + 46.419)/23.869 = 2.54$

$$\text{Now, } T_v = 1000/x = 1000/2.54 = 393.70\text{K} = \mathbf{120.5} \text{ }^\circ\text{C}$$

- For 60phr ACN Lignin-ENR25 vitrimer:
Equation obtained from Arrhenius Law: $20.363x - 40.193$
For 60phr sample, $G = 3.11$ MPa, thus $\tau^* = 10^{12}/3.11 \times 10^6 = 0.32 \times 10^6$

$$\ln(0.32 \times 10^6) = 12.68$$

Using the Stress Relaxation equation: $x = 1000/T = (\ln(\tau^*) + 40.193)/20.363 = 2.59$

$$\text{Now, } T_v = 1000/x = 1000/2.59 = 386.10\text{K} = \mathbf{112.9} \text{ }^\circ\text{C}$$

Atomic Force Microscopy (AFM) coupled with nano-FTIR analysis for localized structure analysis of Lignin/ENR compositions.

The effect of heat on the nanoscale morphology of the films was evaluated by atomic force microscopy (AFM). To reach temperatures approaching the transition of the lignin-based vitrimer, we developed a protocol exploiting the heat generated in the material by the infrared laser illumination, which retains the overall integrity of the film except in the focal region of the laser underneath the AFM tip, making imaging and nanoscale functional measurements more stable than heating the entire film.

We studied the effect of laser power on the temperature of an absorbing polymer using polycarbonate, with a $T_g = 150^\circ\text{C}$, which is in the range of the expected transition of the vitrimer. The contact resonance of the cantilever (Fig. S8) and AFM force curves (Fig. S9) allowed us to determine the laser power at which a softening of the material occurs. As can be seen optically

(inset in Figure S8(b)), softening of polycarbonate was observed at an illumination power of ~ 130 mW (47.62×272.5 mW) at 1728 cm^{-1} , which corresponds to the wavenumber (energy) exciting the C=O stretch mode of polycarbonate. The laser pulse rate was tuned to match the cantilever contact resonance at laser power output up to 130 mW. The pulse width was set at 200 ns for this measurement. As can be seen in Figure S1, the contact resonance of the cantilever engaged with the surface of the polycarbonate substrate observed a downward shift with increasing laser power, with a plateau of the resonance at ~ 277 kHz above 65 mW. While the shift to lower frequency is indicative of a softening of the material, the plateau between 65 and 130 mW suggests that the material reaches its T_g in this range, with visual confirmation only at 130 mW. The amplitude and width of the resonance peak was also found to increase, suggesting that the photothermal expansion of the polymer resulted from the infrared illumination until softening of the film.

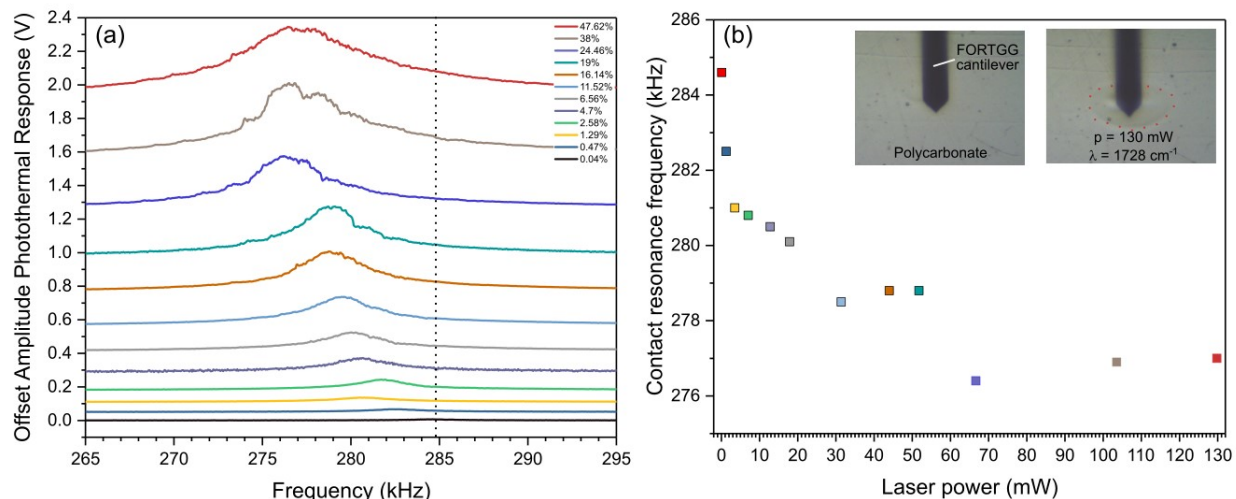


Fig. S8. Evaluation of the effect of power of the infrared illumination on absorbing polycarbonate. (a) AFM cantilever contact resonance acquired at increasing laser power. (b) Position of the contact resonance as a function of laser power. The optical view in inset indicates the region softened by laser illumination at ~ 130 mW at 1728 cm^{-1} , which corresponds to the wavenumber (energy) exciting the C=O stretch mode of polycarbonate.

Force curves between the cantilever tip and the polycarbonate surface were acquired before and during illumination and show that reaching the temperature at which the polycarbonate softens to the point of the deformation observed in the optical image in Figure S8b results in an increase in the indentation depth of the cantilever when approaching the surface, and a different profile of the adhesion upon pulling the tip away from the surface to jump out of contact with the surface.

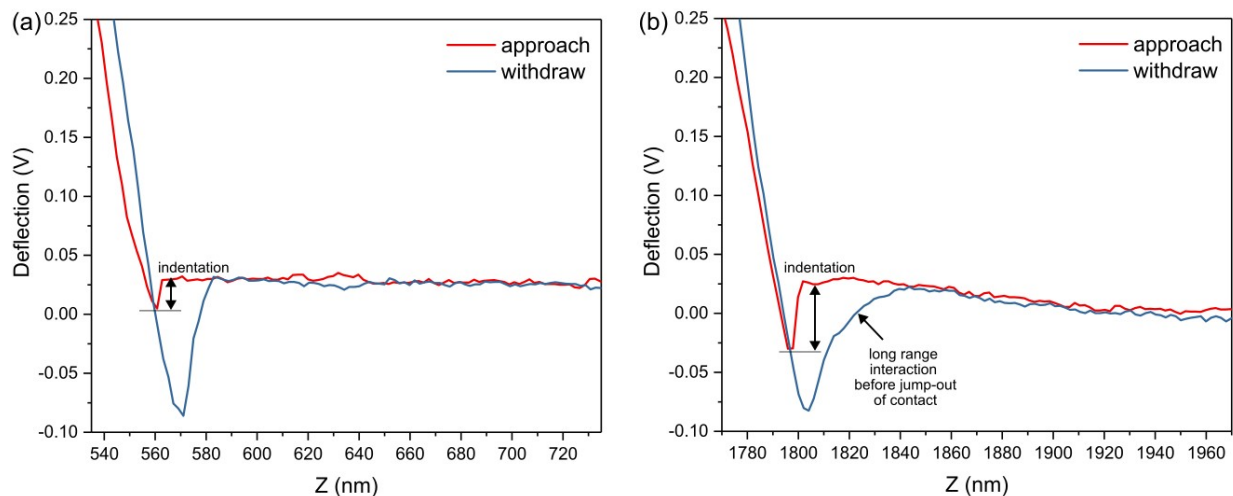


Fig. S9. AFM force curves describing the AFM tip-polycarbonate interaction at room temperature (before infrared illumination) and when the polycarbonate is illuminated with infrared light with power ~ 130 mW, corresponding to the softening of the material. The deflection and displacement of the sample are displayed as a qualitative comparison of the force curves.

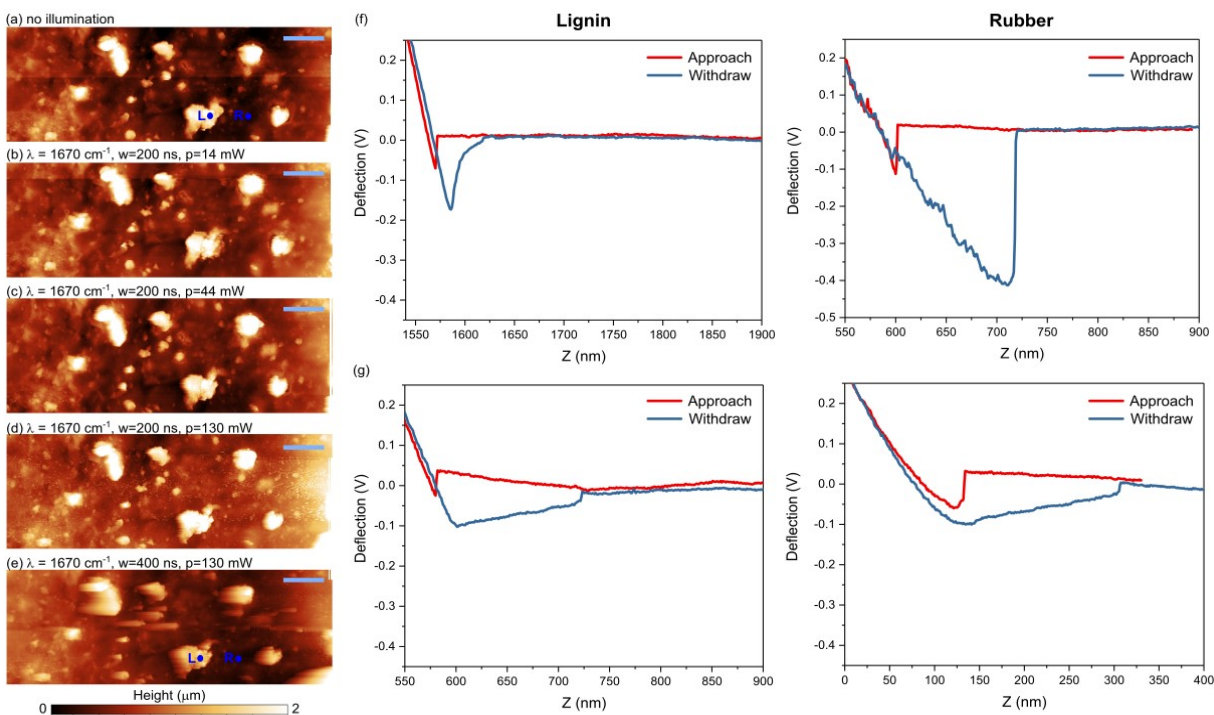


Fig. S10. AFM topography image of the lignin-ENR25 50 phr film under infrared illumination at 1670 cm^{-1} at different laser power. (a) before illumination, (b) at power of 14 mW, (c) at power of 44 mW, (d-e) at power of 130 mW. The pulse width was set at 200 ns for (b-d) and increased to 400 ns for (e). (f-g) AFM force curve measurements of the lignin features and rubber matrix before illumination (f) and at 130 mW (g).

References:

1. V. Röntsch, M. Haas, M. B. Özen, K.-F. Rätzsch, K. Riazi, S. Kauffmann-Weiss, J. K. Palacios, A. J. Müller, I. Vittorias, G. Gisela and M. Wilhelm, *Polymer*, 2018, **145**, 162-173.
2. A. Moreno, M. Morsali and M. H. Sipponen, *ACS applied materials & interfaces*, 2021, **13**, 57952-57961.
3. S. Dhers, G. Vantomme and L. Avérous, *Green Chemistry*, 2019, **21**, 1596-1601.