

## *Electronic Supplementary Information*

# Fully Biomass-based Biodegradable Polymers from Lignin and Raw Castor oil: Lignin-graft-castor oil

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Table S1. Comparison of expected and calculated mole ratios of synthesized modified lignins

Entry	Input % of acetic acid <sup>a)</sup>	Input % of acetic acid per carboxylic acid <sup>b)</sup>	Acetyl in modified lignin <sup>c)</sup>	Sample code <sup>d)</sup>
1	25 %	14 %	8 %	8CL
2	50 %	33 %	27 %	27CL
3	75 %	60 %	35 %	35CL
4	83%	71 %	59 %	59CL

<sup>a)</sup> Mole ratio, [acetic acid]/ ([acetic acid] + [succinic acid]), <sup>b)</sup> [acetic acid]/([acetic acid] + 2 x [succinic acid]), <sup>c)</sup> Determined by <sup>1</sup>H NMR signals in Figure 1 near 1.92 and 1.98 ppm (carboxyl) and 2.44 ppm (acetyl). <sup>d)</sup> Sample codes are defined as follows: numbers represent the ratio of acetic acid.

### FT-IR spectrum of lignin-graft-castor oil

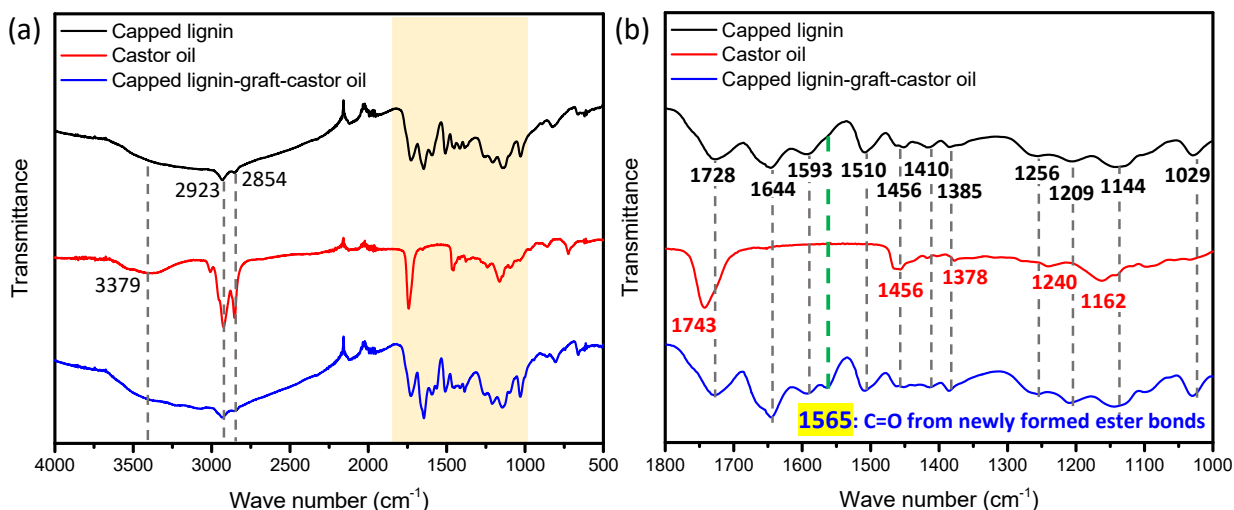


Figure S 1 a) FT-IR spectra of capped lignin (black line), castor oil (red line), and lignin-graft-castor oil (blue line), (b) FT-IR spectra focused on the region between 1000-1800 cm<sup>-1</sup> in Figure S 1a yellow region. The peak at 1565 cm<sup>-1</sup> indicates newly synthesized ester bond between lignin and castor oil

Figure S1 shows FT-IR spectra of capped lignin, castor oil, and lignin-graft-castor oil. The capped lignin (Figure S1 a black line) shows a broad peak at 3600 -2400  $\text{cm}^{-1}$  attributed to the O-H stretching vibration of a carboxylic acid. Two peaks at 2923  $\text{cm}^{-1}$  and 2854  $\text{cm}^{-1}$  originate from C-H stretching in aromatic methoxy and methyl groups and methylene groups of side chains on lignin (Figure S 1a black line). The broad peaks at 3379  $\text{cm}^{-1}$  are assigned to O-H stretching vibration in the hydroxyl group on castor oil. (Figure S 1a red line). Also, the same peaks at 2923  $\text{cm}^{-1}$  and 2854  $\text{cm}^{-1}$  are also observed from C-H stretching in alkyl chains of castor oil. In Figure S 1a blue line, a broad peak at 3600 - 2400  $\text{cm}^{-1}$  from O-H stretching of the unreacted carboxylic acid group is observed. Peaks at 2923  $\text{cm}^{-1}$  and 2854  $\text{cm}^{-1}$  indicate C-H stretching from aromatic methoxy groups, methyl and methylene groups of lignin, and alkyl chain on castor oil.

Figure S 1b shows narrow range at 1000-1800  $\text{cm}^{-1}$  which is yellow region in Figure S 1a. As shown in Figure S 1b black line, the large peak is found at 1728  $\text{cm}^{-1}$ , originating from unconjugated C=O stretching from the carboxylic acid, and the peak at 1644  $\text{cm}^{-1}$  is associated with C=O stretching from ester linkages (R-COO-R').<sup>1</sup> The peaks at 1593, 1510, and 1410  $\text{cm}^{-1}$  are assigned aromatic skeleton vibrations, and the peak at 1456  $\text{cm}^{-1}$  and 1385  $\text{cm}^{-1}$  are the results of the asymmetric and symmetric deformation vibration of  $-\text{CH}_3$ .<sup>2</sup> The C-O stretching, C=O stretching, and C-H stretching for the guaiacyl unit appear at 1256, 1209, and 1144  $\text{cm}^{-1}$ , respectively. <sup>2,3</sup> The peak at 1029  $\text{cm}^{-1}$  results from the aromatic C-H deformation. <sup>2</sup> Castor oil shows five main peaks at 1743, 1456, 1378, 1240, and 1162  $\text{cm}^{-1}$  (Figure S 1b red line). The peak at 1743  $\text{cm}^{-1}$  is assigned to the C=O stretching from the ester bond, and the peaks are found at 1456 and 1378  $\text{cm}^{-1}$ , originating from asymmetric and symmetric deformation vibration of  $-\text{CH}_3$ . Also, the peaks at 1240 and 1162  $\text{cm}^{-1}$  are associated with the stretching vibration for C-O in the ester bond.<sup>4</sup> The Figure S 1b blue line showed the FT-IR spectrum of lignin-graft-castor oil. The spectrum showed all main peaks from capped lignin and castor oil, and there is an additional peak at 1565  $\text{cm}^{-1}$  associated with C=O stretching from newly formed ester linkages between lignin and castor oil.

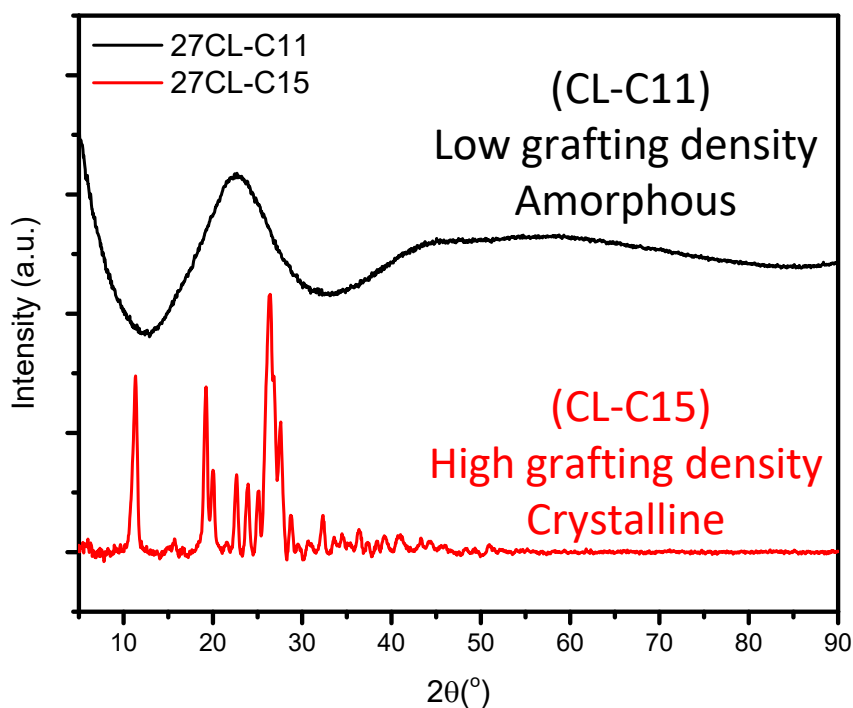


Figure S 2 PXR D patterns of 27CL-C11 (low grafting density) and 27CL-C15 (high grafting density)

### Effect of grafting density of mechanical properties

The effect of the weight ratio of castor oil on mechanical properties is shown in f. A sample 27CL-C11 (Figure S 3 black line, entry 2 in Table 2) demonstrated higher Young's modulus and maximum tensile strength than 27CL-C15 (Figure S 3 red line, entry 5 in Table 2). On the contrary, the strain at break of 27CL-C15 is larger than that of 27CL-C11. In the lignin-graft-castor oil, capped lignin serves as the hard domain and castor oil serves as the soft domain of these

copolymers. Thus, an increase in the hard domain (lignin) would be expected to increase the toughness of the copolymers themselves.<sup>5</sup>

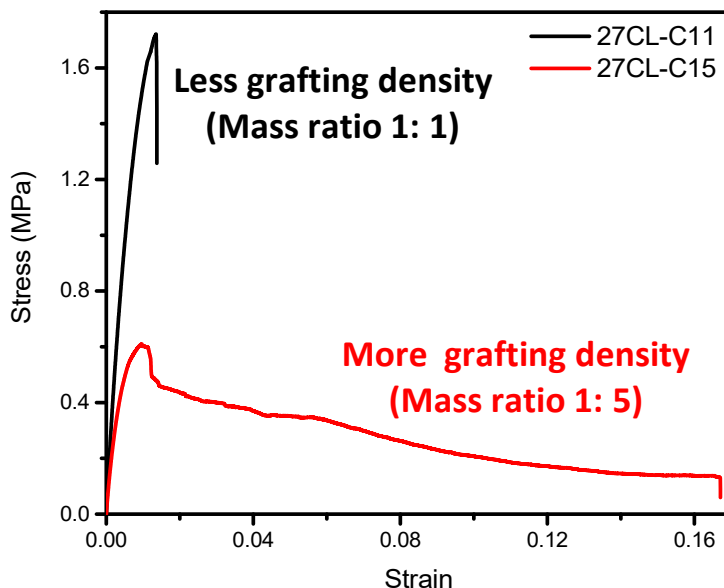


Figure S 3 Strain-Stress curves of 27CL-C11 (black line) and 27CL-C15 (red line)

**Calculation of modified lignin and lignin-graft-castor oil molecular weight:** The molecular measurement of modified lignin was reported previously.<sup>1,5-9</sup> Briefly, the determined molecular weight of natural lignin is 24,000 g/mol and the number of grafting sites for each lignin molecule is 86. Based on the number of grafting sites per lignin molecule and the molecular weight of natural lignin, we added the molecular weight of succinic acid and acetic acid, 118.09, 60.05 g/mole, respectively, following the ratio of acetic acid. Then, we added the molecular weight of castor oil 927 g/ mole following the mass ratio. The calculated the molecular weight of the reported modified lignin of 27CL-C11 was 62,334 g/mol.

## References

- 1 S. Kim and H. Chung, *ACS Sustain. Chem. Eng.*, 2021, **9**, 14766–14776.
- 2 C. G. Boeriu, D. Bravo, R. J. A. Gosselink and J. E. G. Van Dam, *Ind. Crops Prod.*, 2004, **20**, 205–218.
- 3 R. J. Sammons, D. P. Harper, N. Labbé, J. J. Bozell, T. Elder and T. G. Rials, *BioResources*, 2013, **8**, 2752–2767.
- 4 H. Li, S. Niu and C. Lu, *Procedia Eng.*, 2017, **205**, 3705–3710.
- 5 H. Liu and H. Chung, *Macromolecules*, 2016, **49**, 7246–7256.
- 6 S. Kim and H. Chung, *ACS Sustain. Chem. Eng.*, 2023, **11**, 1709–1719.
- 7 H. Liu, L. Mulderrig, D. Hallinan and H. Chung, *Macromol. Rapid Commun.*, 2021, **42**, 2000428.
- 8 H. Liu and H. Chung, *ACS Sustain. Chem. Eng.*, 2017, **5**, 9160–9168.
- 9 H. Liu, N. Mohsin, S. Kim and H. Chung, *J. Polym. Sci. Part A Polym. Chem.*, 2019, **57**, 2121–2130.