

SUPPLEMENTARY INFORMATION

Acidic Wood Extractives Accelerate the Curing Process of Emulsion Polymer Isocyanate (EPI) Adhesives

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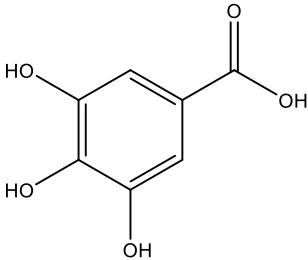
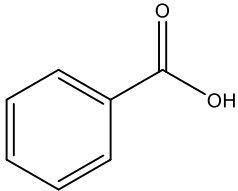
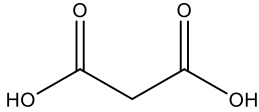
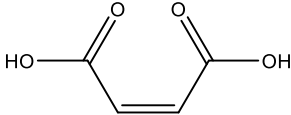
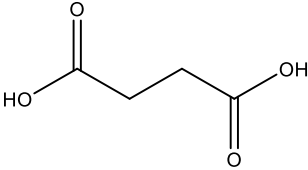
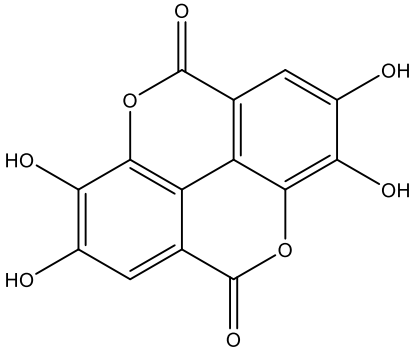
Supplementary Tables

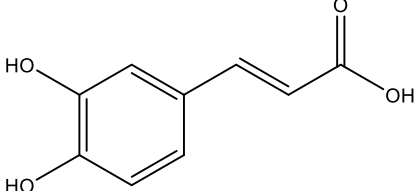
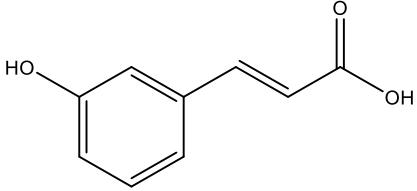
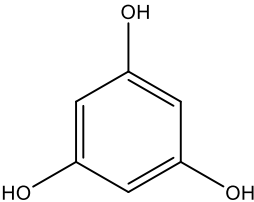
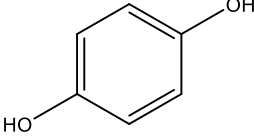
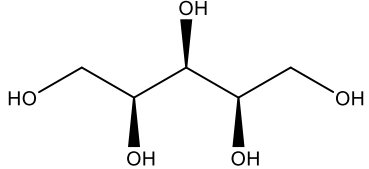
Table SI-1 Spectral changes related to EPI-curing

FTIR band (cm ⁻¹)	Assignment	The relative changes		
		EPI-Ref	EPI-Ch	EPI-Oa
3100-3500	N-H str. Due to the formation of the amine (N-H), urea (NHCON-H), and urethane (OCON-H) moieties, but partly overlaps with OH str.	+28%	+48%	-12%
2270	NCO str. Isocyanate stretching from the hardener	-31%	-47%	-37%
1730	CO str. free urethane moiety together with the acetyl moiety	-21%	-5%	-15%
1645	CO str.	+44%	+70%	-2%

	carbonyl stretching of H-bonded urea motifs (NHCONH) and partly overlapped with scissoring band of water			
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Table SI-2. pK_a values for the compounds used in the mixtures with EPI-adhesive.

Acidic Compounds		pK_a^*
Gallic acid		3.94
Benzoic acid		4.08
Malonic acid		2.43
Maleic acid		1.83
Succinic acid		3.55
Ellagic acid		5.54

Caffeic acid		3.14
m-Coumaric acid		4
Phenolic compounds		
Phloroglucinol		9.13
Hydroquinone		9.68
Sugar alcohol		
Xylitol		12.76

* Based on the values in ChemAxon.

Table SI-3. Storage shear modulus (G'), segmental molecular weight (M_c) and crosslinking density (v_c) for the samples EPI-Ref, EPI-Ch and EPI-Oa after 36 h of curing.

Sample	G' (MPa)	M_c (g/mol)	v_c (mol/m ³)*
EPI-Ref	6.26	466	2568
EPI-Ch	7.23	403	2966
EPI-Oa	5.61	520	2302

*The density for the cured EPI-adhesive was estimated to be 1.20 g/cm³ at 20 °C.

Supplementary Figures

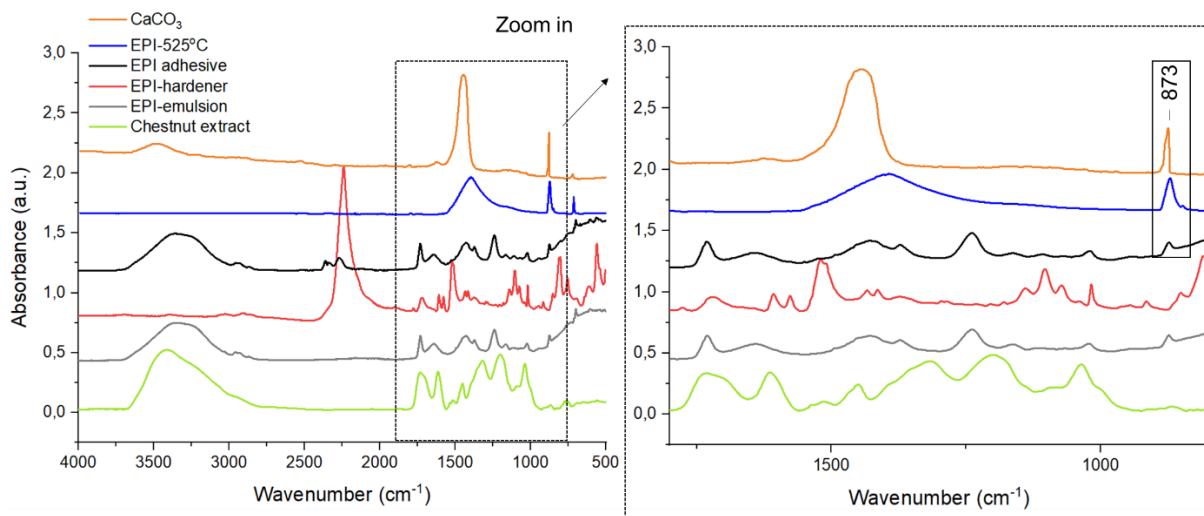


FIGURE SI-1 FTIR spectra comparison: water-based EPI-adhesive components: chestnut extract (green), EPI-emulsion part (grey), EPI-isocyanate based hardener (red), EPI-adhesive (emulsion+hardener at the beginning of rheology measurements, t=0 min) (black), cured EPI-adhesive after ashing at 525 °C for 90 min (blue), and precipitated CaCO₃ (orange, NIST database).

a)



b)

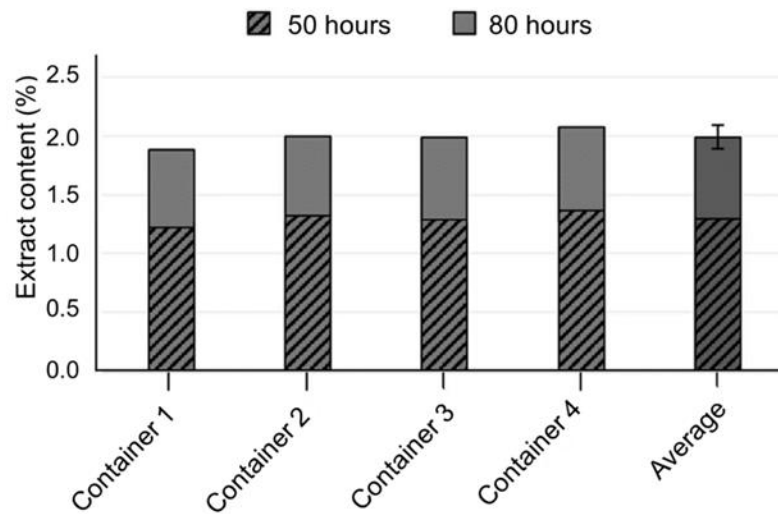


FIGURE SI-2 a) The water extraction set-up at room temperature. b) The extracted content after 50 and 80 h of extraction on the chestnut wood panels from which the tensile shear test specimens were prepared.

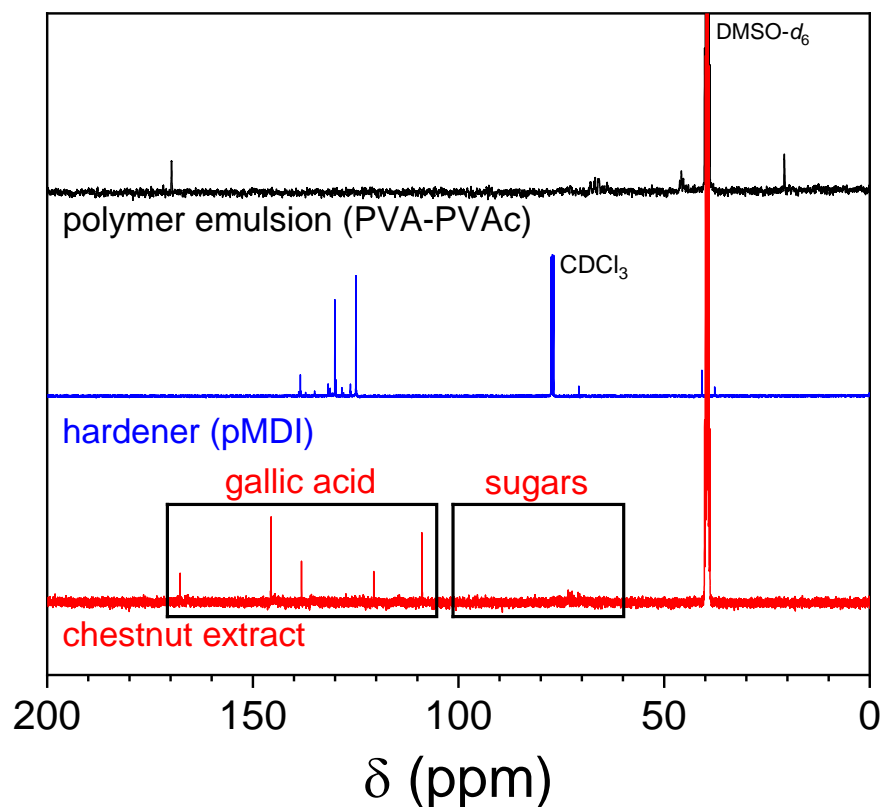


FIGURE SI-3 Liquid ^{13}C NMR spectra of the polymer EPI-emulsion component (PVA-PVAc, black), the EPI-hardener (pMDI, blue), and the chestnut extract (gallic acid and sugar molecules, red).

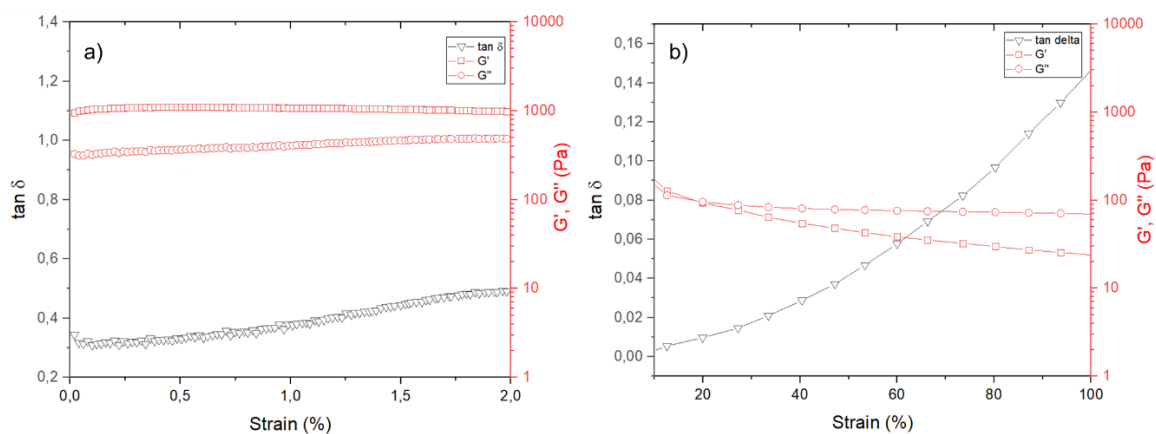


FIGURE SI-4 Strain-sweep tests at 1 Hz frequency and 20 °C on the EPI-Ref sample a) at lower strain % values (for the determination of the LVR Region), and b) at higher strain % values (indicating a shear thinning behavior).

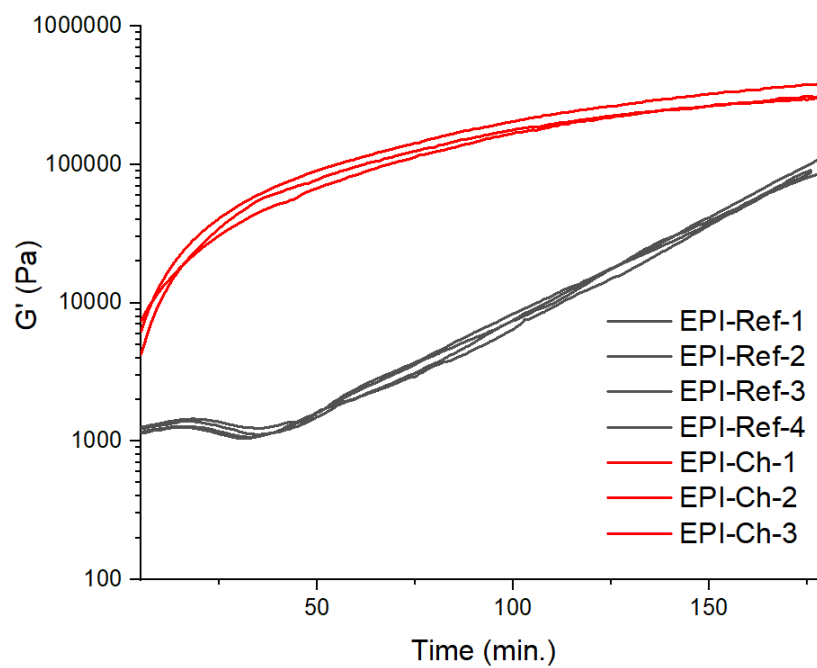


FIGURE SI-5 Example of technical variabilities in G' curves within the sample groups.

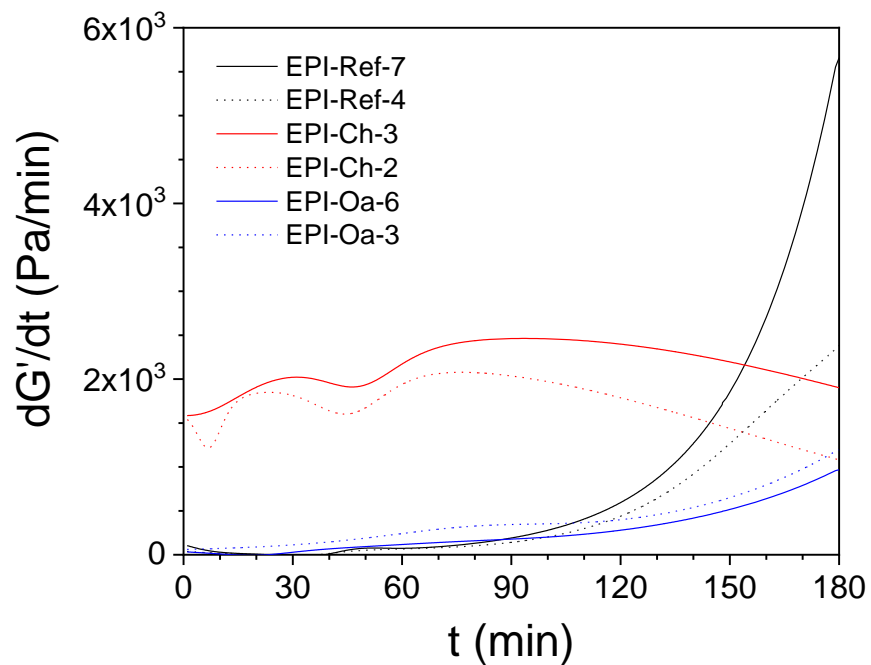


FIGURE SI-6 Derivative curves, dG'/dt , as a function of time for the samples EPI-Ref (black), EPI-Ch (red) and EPI-Oa (blue) showing the different reaction kinetics for 3 h of measurement.

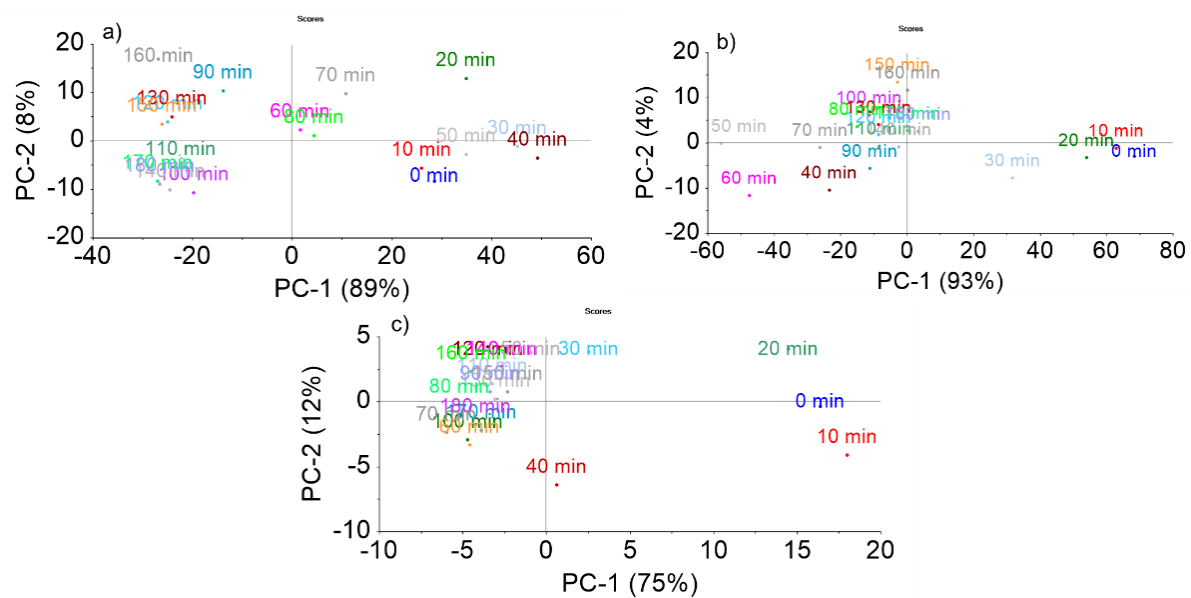


FIGURE SI-7 PCA scores from the FTIR spectra for the a) EPI-Ref, b) EPI-Ch and EPI-Oa samples

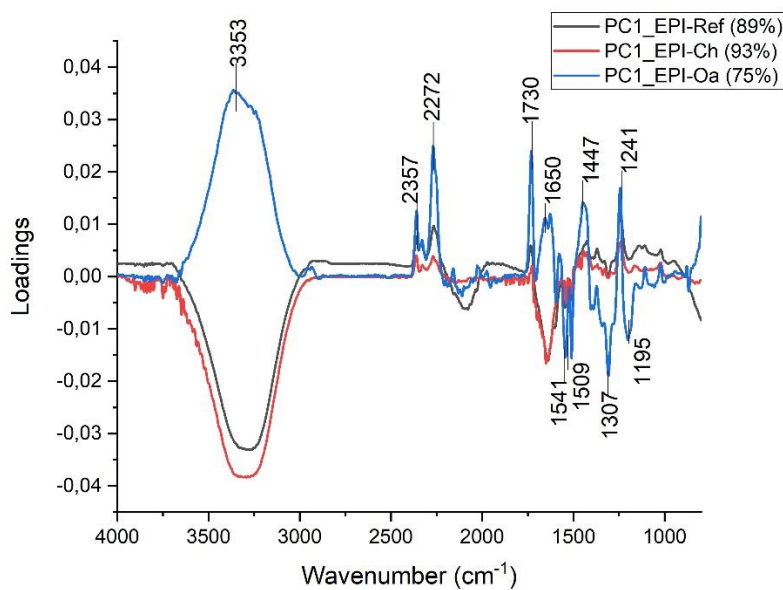


FIGURE SI-8 Loading PC1 comparison for the EPI-Ref, EPI-Ch and EPI-Oa

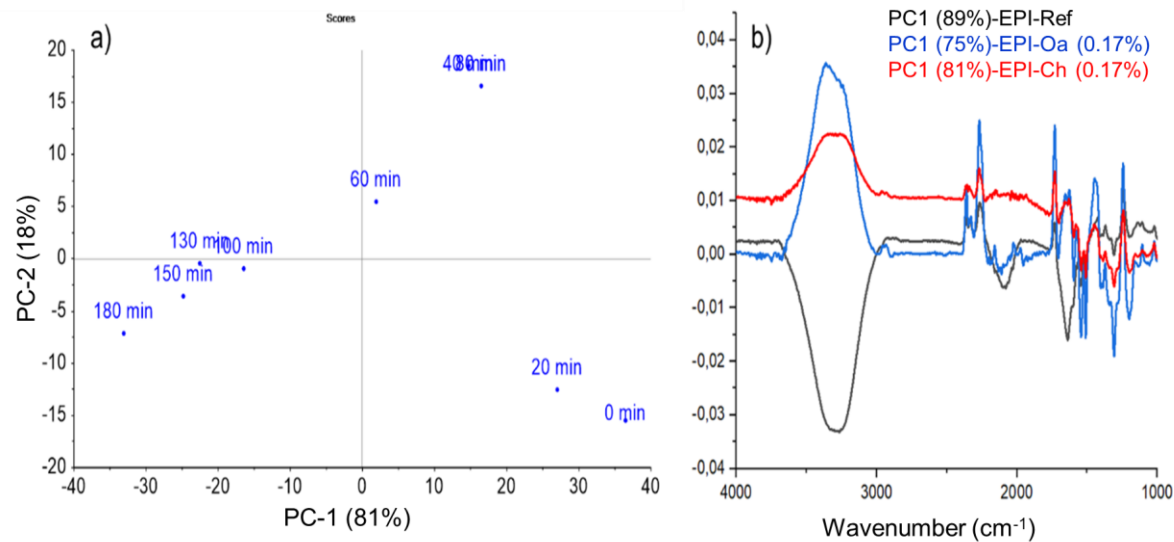


FIGURE SI-9 PCA Results from the FTIR spectra: a) PC scores of EPI-Ch with 0.17 % extract addition, b) the comparison of the loadings PC1 between the samples.

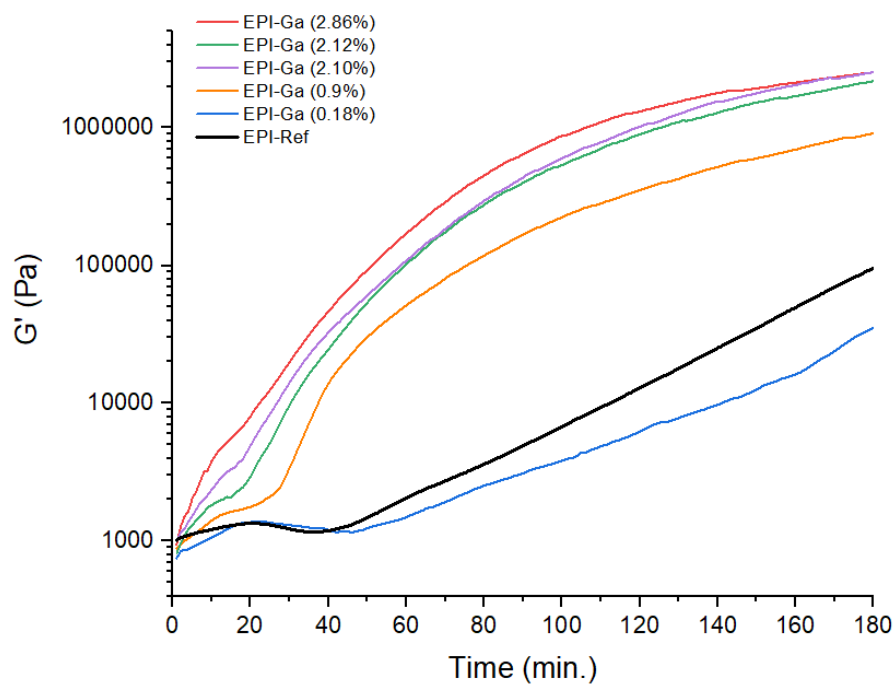


FIGURE SI-10 Storage shear modulus G' as a function of time and for different amounts of gallic acid.

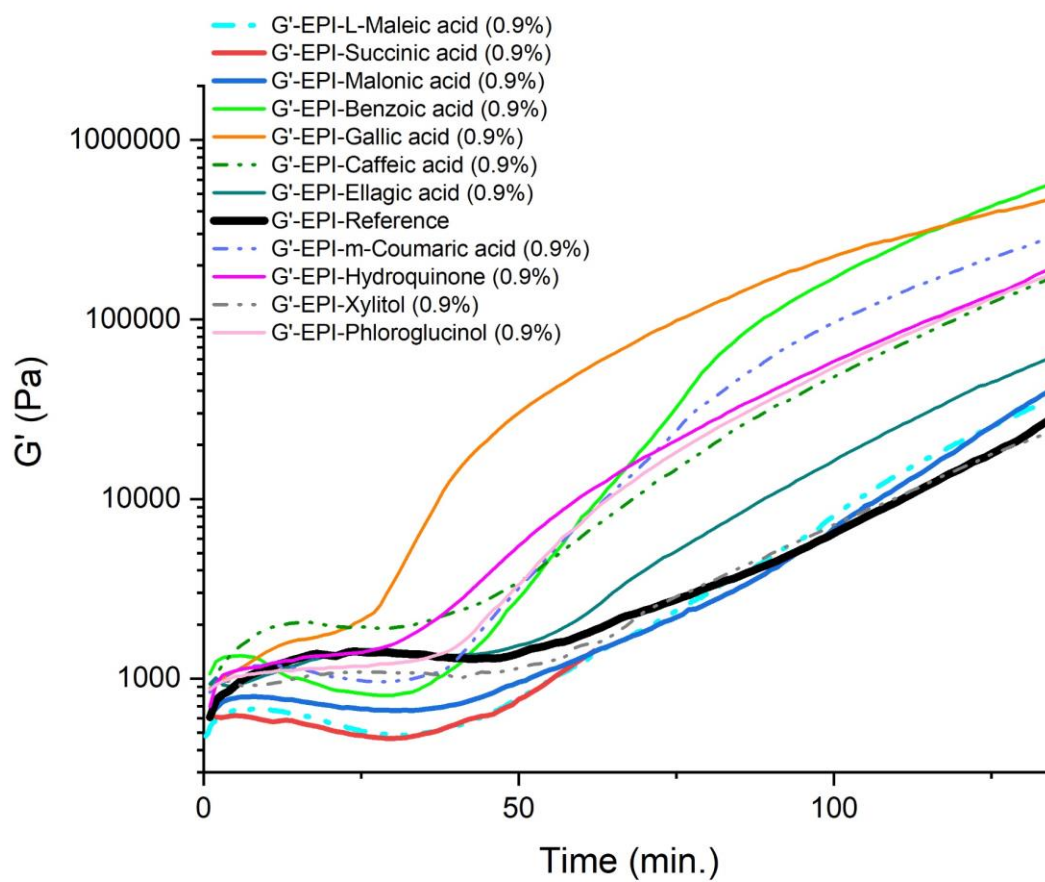


FIGURE SI-11 Storage shear modulus G' as a function of time for some EPI-mixtures with different organic compounds.

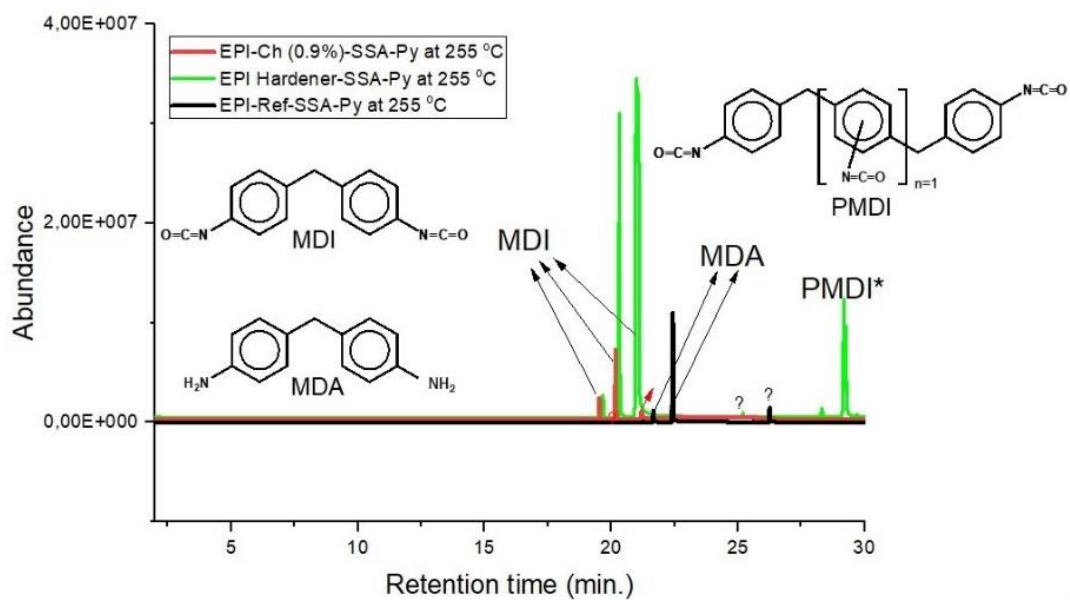


FIGURE SI-12 Single Shot Analysis (SSA)-pyrolysis products of the EPI-Ref, EPI-Ch samples and the hardener (at 255 °C).

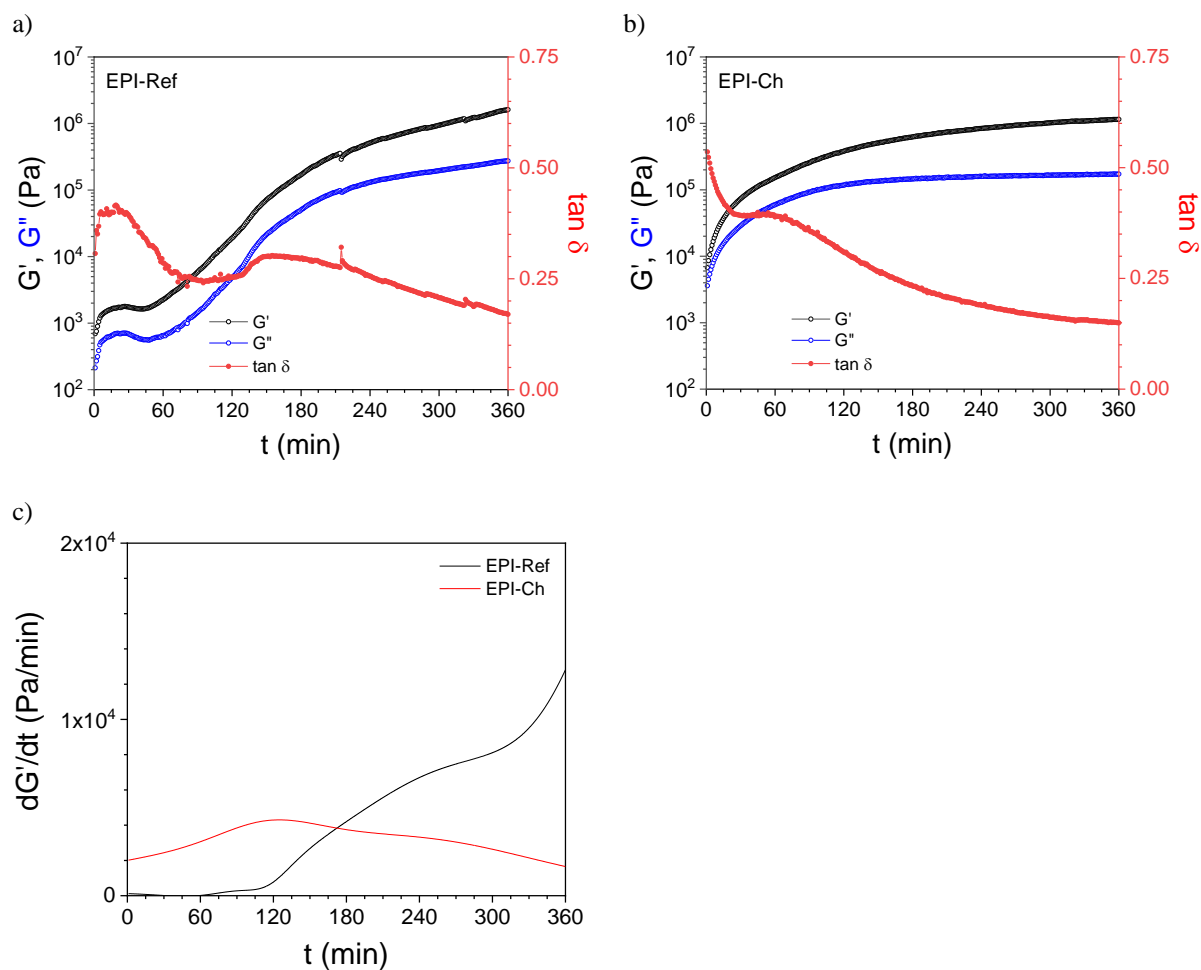


FIGURE SI-13 Storage shear modulus, G' , loss shear modulus, G'' , and loss factor, $\tan \delta$, evolution for 6 h for the samples a) EPI-Ref, b) EPI-Ch and c) Derivative curves, dG'/dt , as a function of time for 6 h of measurement.

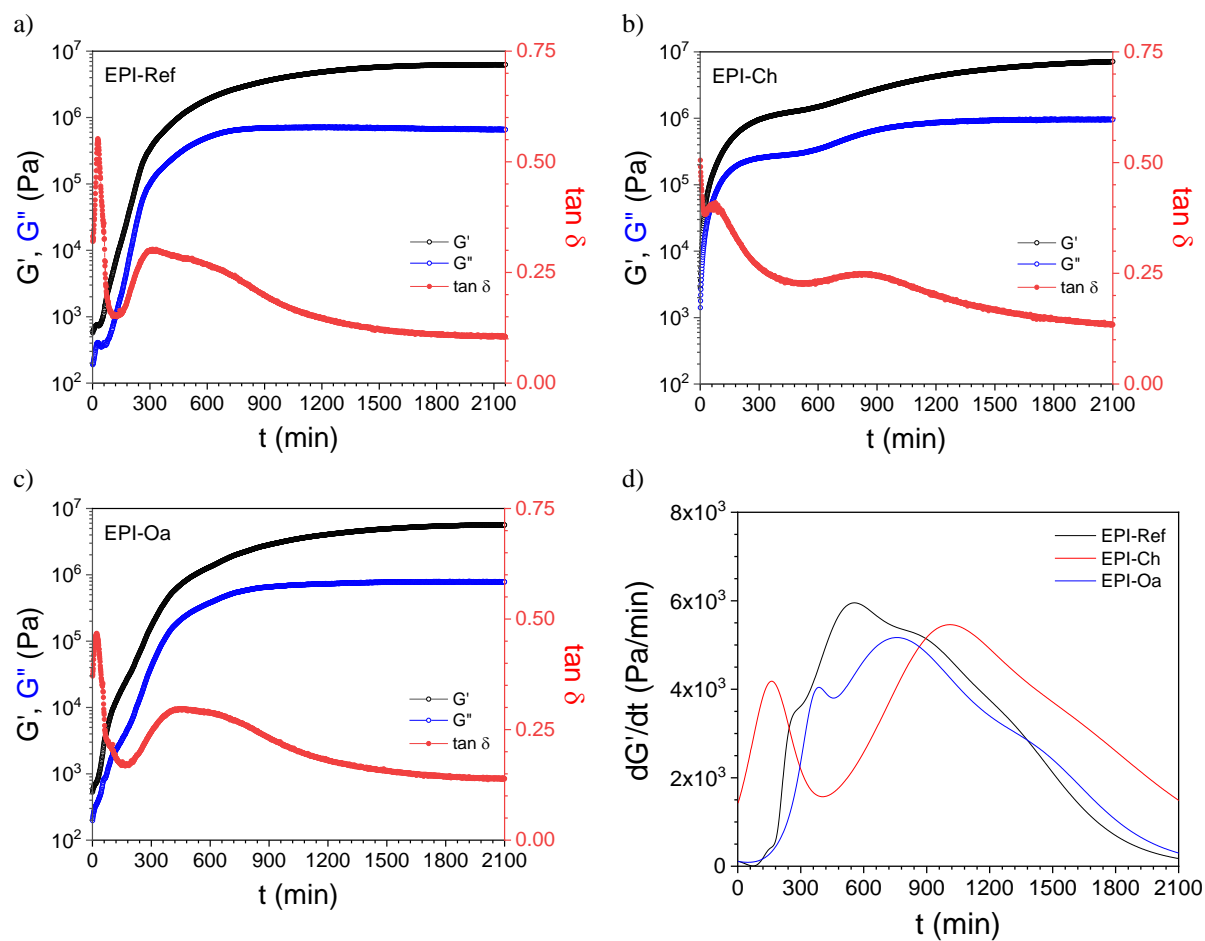


FIGURE SI-14 Storage shear modulus, G' , loss shear modulus, G'' , and loss factor, $\tan \delta$, evolution for 35 h for the samples a) EPI-Ref, b) EPI-Ch and c) EPI-Oa, and d) Derivative curves, dG'/dt , as a function of time for 35 h of measurement.

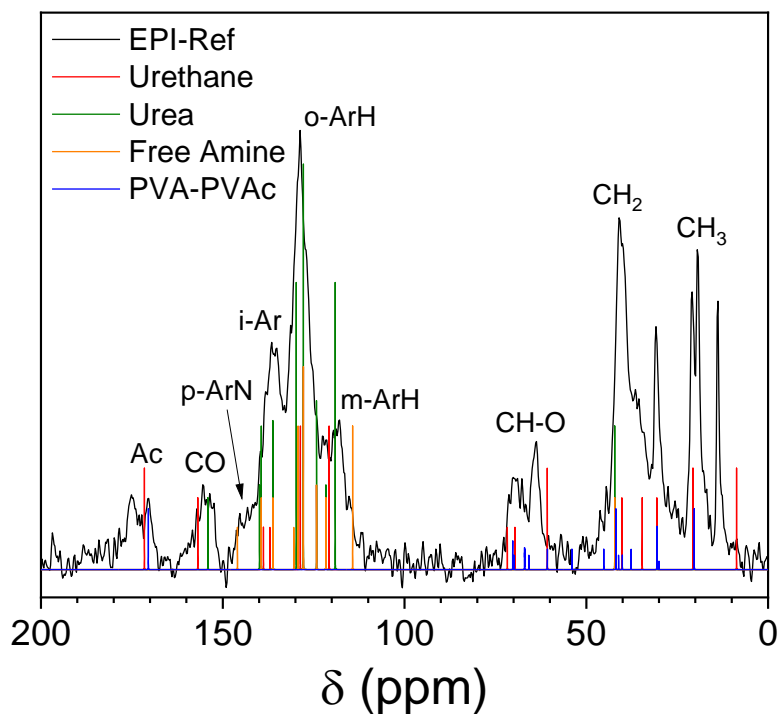


FIGURE SI-15 Solid-state ^{13}C NMR of the EPI-Ref sample (black), and the simulated peaks of the urethane (red), urea (green) and free amine (orange) formed during the curing process, and the PVA-PVAc polymer in the EPI-emulsion (blue).

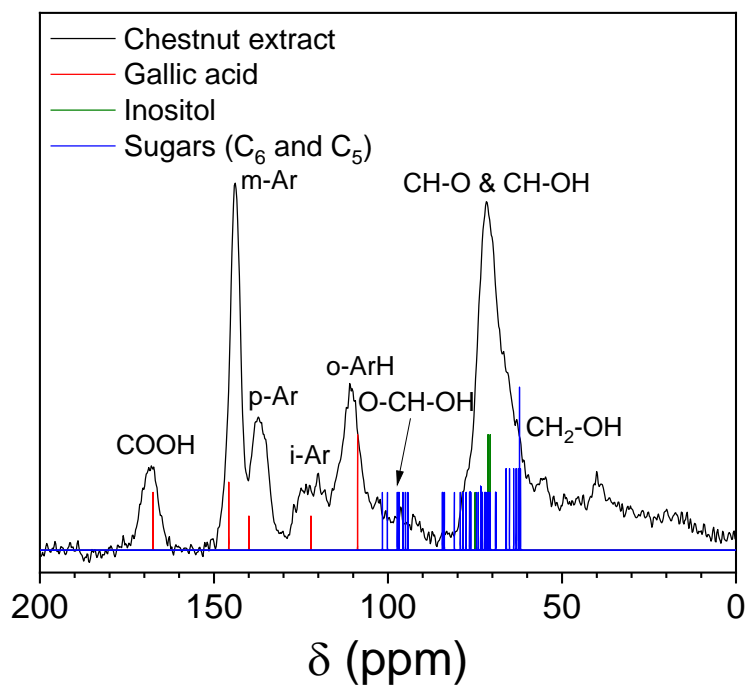


FIGURE SI-16 Solid-state ^{13}C NMR of the chestnut extract (black), and the simulated peaks of gallic acid (red), inositol (green), and sugars (C₆ and C₅, blue).

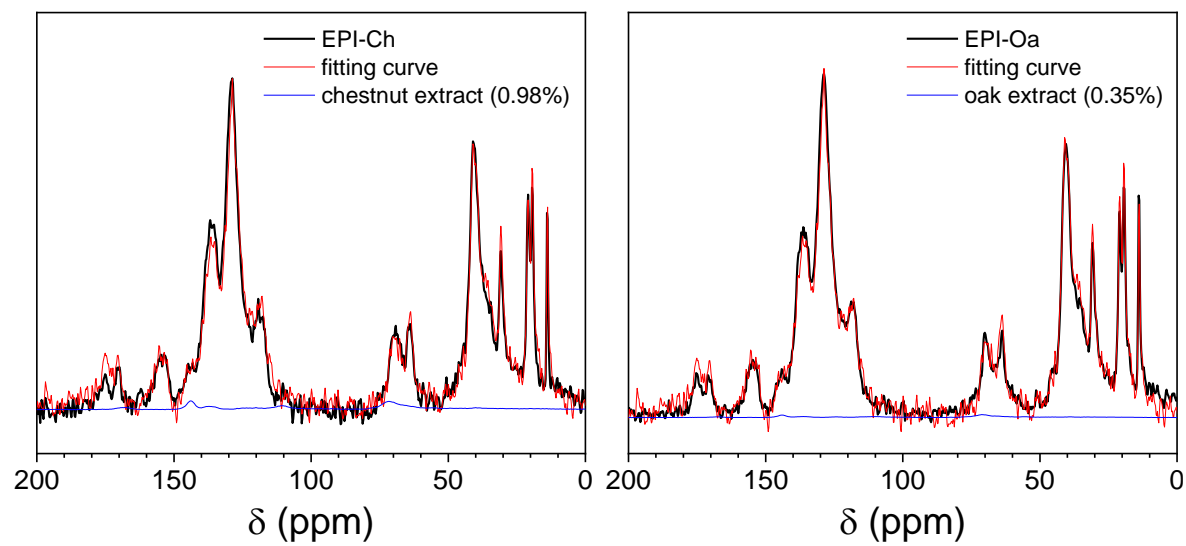


FIGURE SI-17 Solid-state ^{13}C NMR spectra for the a) EPI-Ch (0.93%) and b) EPI-Oa (0.17%). The fitting curves (red) and the corresponding extract (blue) are evaluated from the deconvolution process. The results indicate 0.98% and 0.35% of extractives for the EPI-Ch and EPI-Oa samples, respectively.