

The concentration and origins of carboxylic acid groups in oil paint

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FTIR spectrum polymerised LO

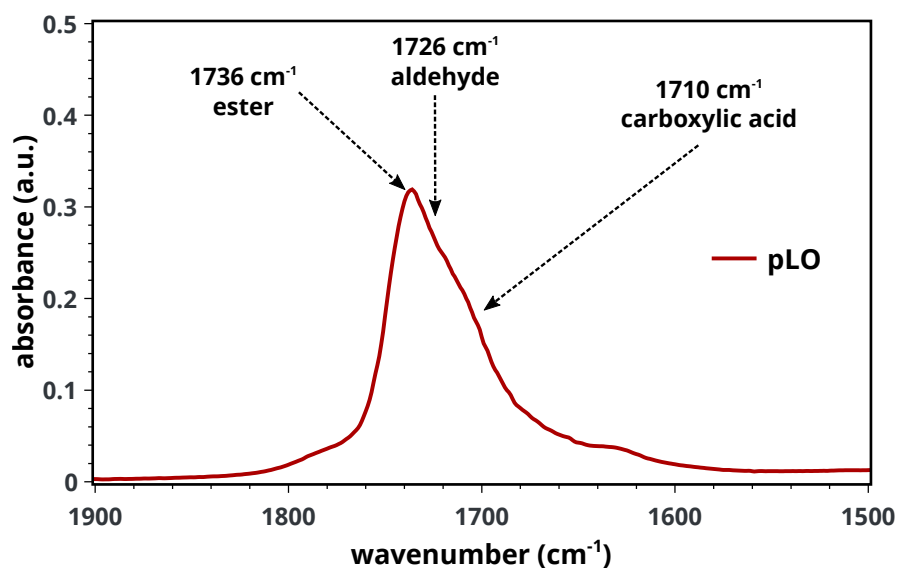


Figure S1 Overlapping IR absorption bands of the asymmetric stretching vibration (ν_a COO) of the ester (COOR, 1738 cm⁻¹), aldehyde (COH, 1726 cm⁻¹) and carboxylic acid (COOH, 1710 cm⁻¹) carbonyl function in polymerised LO.

COOZn IR band integration method

To integrate overlapping absorption bands accurately, data correction and integration algorithms were written in the Wolfram *Mathematica* software, which are available from the authors on request. Since the zinc carboxylate (COOZn) band present in ZnO-LO samples at 1685 cm^{-1} overlaps with the ester carbonyl band (maximum at 1738 cm^{-1}), a band fitting algorithm was applied to subtract the ester band and integrate the COO-Zn band accurately (see Figure S2a). After subtraction of the Pearson type IV band shape¹ fitted to the ester carbonyl band, the area of the COOZn band was calculated (Figure S2b, integration limits are indicated with a dashed line).

Ester band subtraction procedure

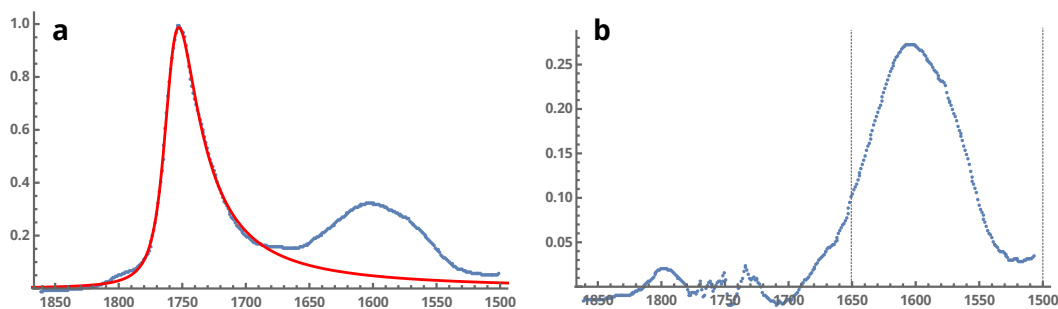


Figure S2 Subtraction procedure for the asymmetric stretching vibration ($\nu_a\text{ CO}$) of the ester (COOR, 1738 cm^{-1}) in polymerised LO. A Pearson type IV band shape¹ was fitted to the experimental data (a) and subtracted (b) before integration.

TiO₂ background estimation and subtraction procedure

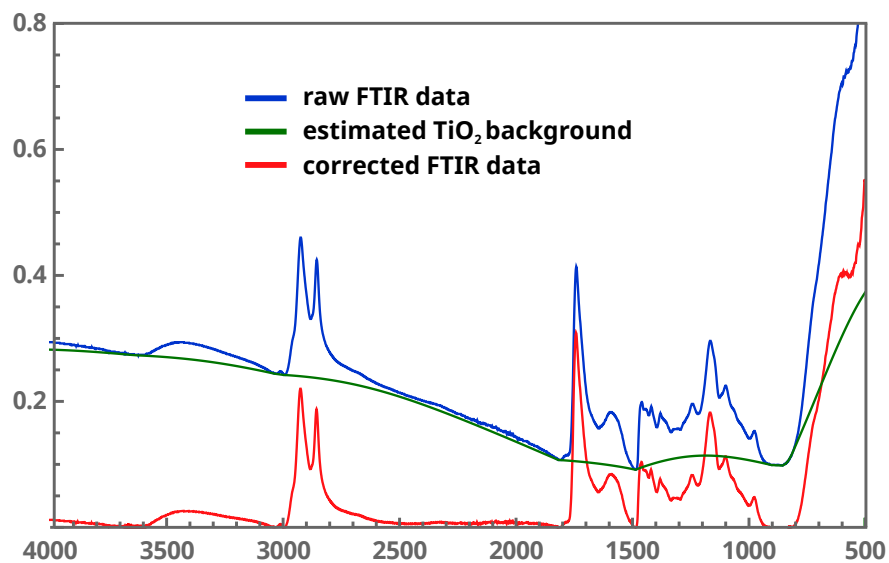


Figure S3 Automated background subtraction procedure using *Mathematica* software. The changing concentration of TiO₂ along the LO-ZnO-TiO₂ samples requires a different background subtraction for every sample. After TiO₂ background estimation, the COO-Zn band area was calculated according to Figure S2.

Composition of LO-ZnO-BaSO₄ series 0.5–20%

Sample	Mass LO (mg)	Mass ZnO (mg)	Mass BaSO ₄ (mg)	[ZnO] mol/L
LO-ZnO-BaSO ₄ -0.5	1000.2	4.80	995.0	0.045
LO-ZnO-BaSO ₄ -1	1000.1	10.2	989.7	0.097
LO-ZnO-BaSO ₄ -1.5	1000.6	15.2	985.2	0.14
LO-ZnO-BaSO ₄ -2.5	1000.3	25.0	975.2	0.24
LO-ZnO-BaSO ₄ -3	1000.3	30.1	970.0	0.28
LO-ZnO-BaSO ₄ -3.5	999.70	34.9	965.1	0.33
LO-ZnO-BaSO ₄ -4	1000.4	40.2	960.1	0.38
LO-ZnO-BaSO ₄ -4.5	999.50	44.9	955.0	0.43
LO-ZnO-BaSO ₄ -5	999.30	49.8	950.0	0.47
LO-ZnO-BaSO ₄ -7.5	999.80	75.1	924.9	0.71
LO-ZnO-BaSO ₄ -10	1000.5	100.3	900.4	0.95
LO-ZnO-BaSO ₄ -12.5	999.70	124.8	874.8	1.2
LO-ZnO-BaSO ₄ -15	1000.2	149.9	850.4	1.4
LO-ZnO-BaSO ₄ -17.5	999.80	175.2	824.9	1.7
LO-ZnO-BaSO ₄ -20	1000.2	200.0	799.7	1.9

Table 1 Composition of LO-ZnO-BaSO₄ series 0.5–20% with a constant (1:1) pigment to oil ratio by weight and a PVC of 17–18%.

Composition of LO-ZnO-TiO₂ series 0.5–20%

Name	Mass LO (g)	Mass ZnO (g)	Mass TiO ₂ (g)	[ZnO] mol/L
LO-ZnO-TiO ₂ -0.5	999.8	5.2	994.7	0.049
LO-ZnO-TiO ₂ -1	1000.3	9.9	990.1	0.092
LO-ZnO-TiO ₂ -1.5	1000.3	15.1	985.0	0.14
LO-ZnO-TiO ₂ -2.5	1033.2	25.0	975.1	0.23
LO-ZnO-TiO ₂ -3.5	1033.2	35.3	965.0	0.33
LO-ZnO-TiO ₂ -4.5	1033.2	44.2	955.0	0.41
LO-ZnO-TiO ₂ -5	999.6	49.8	950.3	0.47
LO-ZnO-TiO ₂ -7.5	999.4	75.0	925.2	0.70
LO-ZnO-TiO ₂ -10	1000.3	100.3	900.0	0.94
LO-ZnO-TiO ₂ -12.5	1000.2	124.8	874.9	1.2
LO-ZnO-TiO ₂ -15	999.9	149.9	850.0	1.4
LO-ZnO-TiO ₂ -17.5	1000.6	174.9	825.1	1.6
LO-ZnO-TiO ₂ -20	1000.1	200.3	800.1	1.9

Table 2 Composition of LO-ZnO-TiO₂ series 0.5–20% with a with a constant (1:1) pigment to oil ratio by weight and a PVC of of 17–18%.

Composition of rLO-ZnO-TiO₂ series 0.5–20%

Name	Mass LO (mg)	Mass ZnO (mg)	Mass TiO ₂ (mg)	[ZnO] mol/L
rLO-ZnO-TiO ₂ -0.5	199.5	1.3	198.4	0.059
rLO-ZnO-TiO ₂ -1	200.4	2.1	197.8	0.10
rLO-ZnO-TiO ₂ -1.5	666.4	10.0	646.3	0.14
rLO-ZnO-TiO ₂ -2.5	500.2	12.4	483.8	0.23
rLO-ZnO-TiO ₂ -3.5	500.1	17.5	481.7	0.33
rLO-ZnO-TiO ₂ -4.5	333.4	14.8	321.7	0.41
rLO-ZnO-TiO ₂ -5	332.8	16.6	321.5	0.47
rLO-ZnO-TiO ₂ -7.5	333.3	24.8	319.6	0.69
rLO-ZnO-TiO ₂ -10	251.4	25.4	239.8	0.94
rLO-ZnO-TiO ₂ -12.5	250.2	31.3	238.4	1.2
rLO-ZnO-TiO ₂ -15	200.7	30.1	191.0	1.4
rLO-ZnO-TiO ₂ -17.5	200.1	35.0	190.2	1.6
rLO-ZnO-TiO ₂ -20	200.7	40.1	189.4	1.8

Table 3 Composition of LO-ZnO-TiO₂ series 0.5–20% with a PVC of of 17–19%

Composition of LO-ZnO-SoA series 0–60%

Name	Mass LO (mg)	Mass ZnO (mg)	Mass SoA (mg)	[SoA] mol/L
LO-ZnO-SA-0	1033.2	1006.1	0	0
LO-ZnO-SA-10	1004.1	998.3	38.3	0.26
LO-ZnO-SA-20	1000.7	999.4	77.1	0.52
LO-ZnO-SA-30	999.4	1000.0	115.2	0.76
LO-ZnO-SA-40	1000.5	1000.2	153.8	0.99
LO-ZnO-SA-50	1000.6	1000.7	192.1	1.2
LO-ZnO-SA-60	999.7	1000.5	230.9	1.4

Table 4 Composition of sorbic acid (LO-ZnO-SA) series 0–60% with a constant (1:1) pigment to oil ratio by weight.

Composition of ZnO-TiO₂-LO series 30–90%

Name	Mass LO (mg)	Mass ZnO (mg)	Mass TiO ₂ (mg)	[ZnO] mol/L
LO-ZnO-TiO ₂ -30	1000.4	302.1	753.7	2.83
LO-ZnO-TiO ₂ -40	1000.2	401.3	682.0	3.76
LO-ZnO-TiO ₂ -50	1002.2	501.1	605.0	4.69
LO-ZnO-TiO ₂ -60	998.90	601.1	530.9	5.64
LO-ZnO-TiO ₂ -70	1000.6	703.1	457.9	6.59
LO-ZnO-TiO ₂ -80	1005.1	800.1	381.0	7.47
LO-ZnO-TiO ₂ -90	1001.1	902.2	308.0	8.45

Table 5 Composition of ZnO-TiO₂-LO series 30–90% with a constant PVC of 18%.

Composition of rLO-ZnO-TiO₂ series 30–90%

Name	Mass LO (mg)	Mass ZnO (mg)	Mass TiO ₂ (mg)	[ZnO] mol/L
rLO-ZnO-TiO ₂ -30	201.3	59.9	139.9	0.140829
rLO-ZnO-TiO ₂ -40	201.2	78.7	120.2	0.231425
rLO-ZnO-TiO ₂ -50	201.4	100.3	101.5	0.330388
rLO-ZnO-TiO ₂ -60	201.0	120.1	81.0	0.413875
rLO-ZnO-TiO ₂ -70	201.5	139.7	59.5	0.466398
rLO-ZnO-TiO ₂ -80	199.7	159.0	40.3	0.703532
rLO-ZnO-TiO ₂ -90	201.5	180.5	21.1	0.941005

Table 6 Composition of rLO-ZnO-TiO₂ series 30–90%. Pigment volume concentration 14–18%.

SEM images of pigment particles

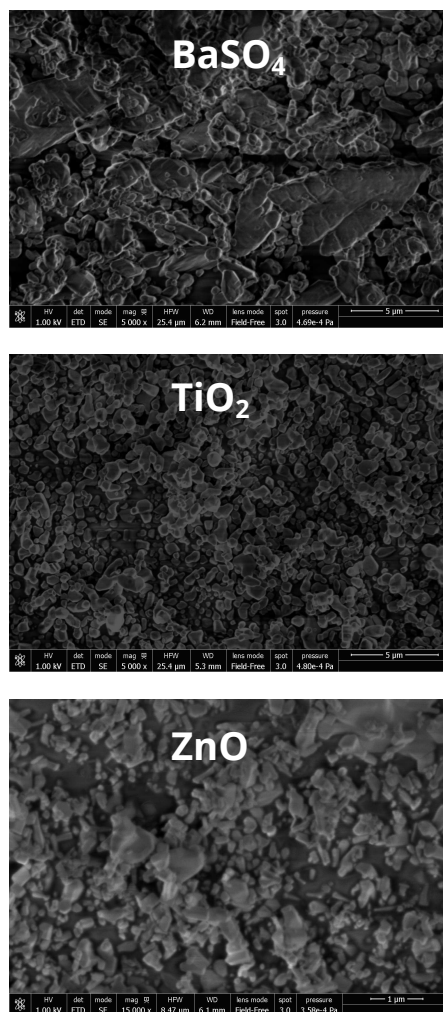


Figure S4 SEM images of BaSO₄, TiO₂ and ZnO pigments. BaSO₄ shows a more heterogeneous size distribution compared to TiO₂ but in the same 1 – 5 μm range, ZnO is smaller (≈ 0.5 μm).

BaSO₄ normalised XRD spectra for ZnO/BaSO₄ paints

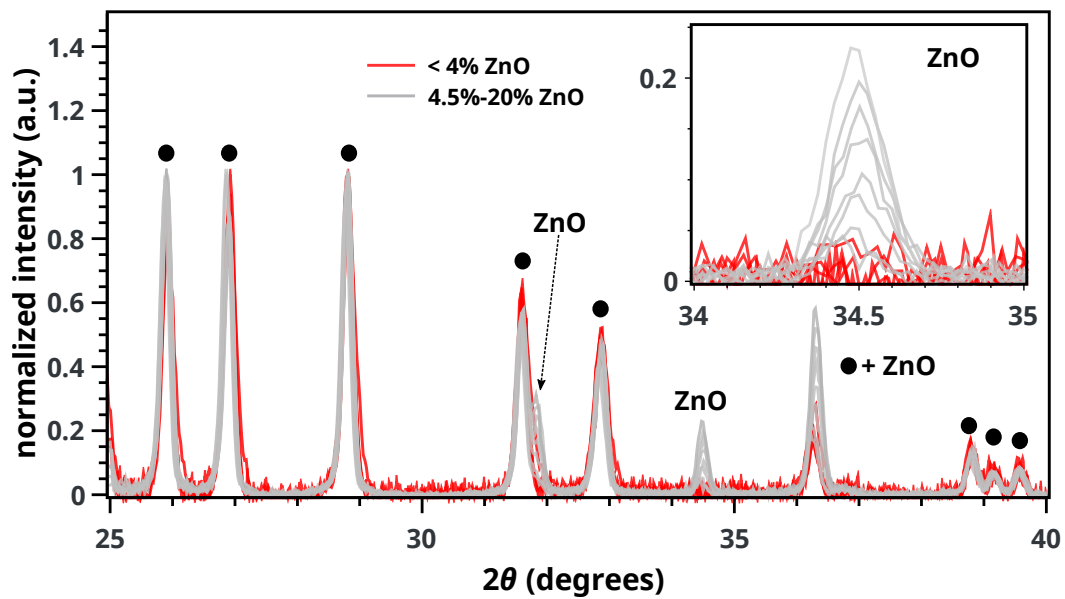


Figure S5 BaSO₄ normalised XRD spectra for mixed ZnO/BaSO₄ paints containing 0.5–20 wt % of ZnO. Inset shows that ZnO is completely consumed below \approx 4.5 wt%. BaSO₄ peaks are marked with ●.

TiO₂ normalised XRD spectra for ZnO/TiO₂ paints

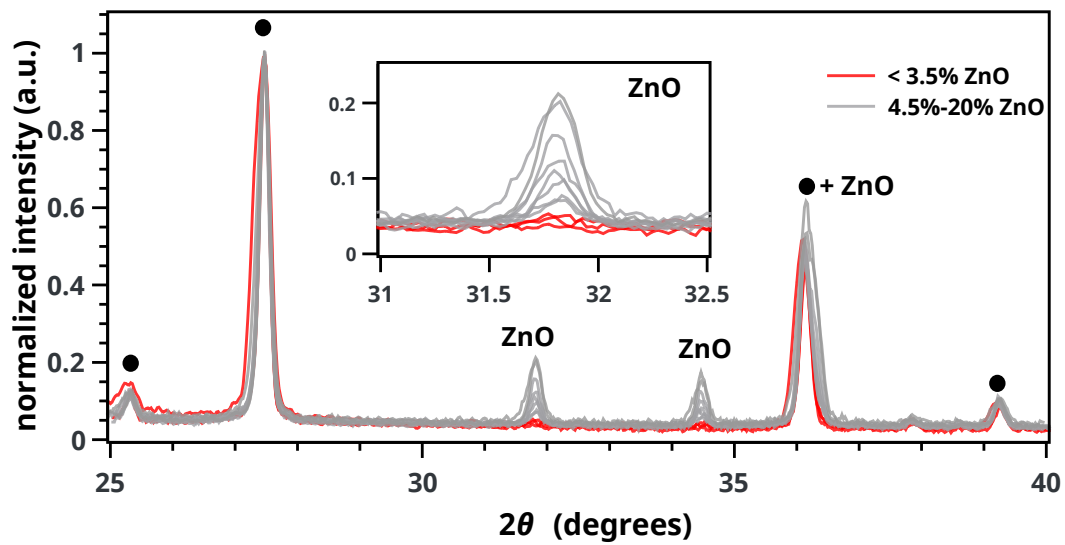


Figure S6 TiO₂ normalised XRD spectra for mixed ZnO/TiO₂ paints containing 0.5–20 wt % of ZnO. Inset shows that ZnO is completely consumed below ≈ 4.5 wt%. TiO₂ peaks are marked with •.

Reduction of linseed oil with LiAlH_4

The reduction of linseed oil with lithium aluminium hydride LiAlH_4 was done according to slightly modified literature procedures.^{2,3} LiAlH_4 (5.2 g, 138 mmol) was dispersed in 225 ml cold ($0\text{ }^\circ\text{C}$) tetrahydrofuran (THF) under nitrogen atmosphere. Cold-pressed untreated linseed oil (LO, Kremer Pigmente, 15 g, 17 mmol) was added while stirring the reaction in a ice bath. The reaction mixture was then stirred continuously at allowed to reach room temperature. After 17 h, the mixture was cooled again to $0\text{ }^\circ\text{C}$ and 40 ml of 2-propanol, ethanol and 20 ml of water was *slowly* added. The mixture was stirred for 15 min and filtered using a Büchner funnel. The solvent was removed under reduced pressure, dissolved in dichloromethane and filtered over MgSO_4 . The solvent was removed under reduced pressure to give the mixture of alcohols (14 g, 93% yield). ^1H NMR (300 MHz, CDCl_3) δ 5.50 – 5.21 (m, $-\text{CH}=\text{CH}-$), 3.64 (t, $J = 6.6$ Hz, $-\text{CH}_2\text{OH}$), 2.81 (t, $J = 5.8$ Hz, $-\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}-$), 2.17 – 1.96 (m, $\text{CH}=\text{CHCH}_2\text{C}^-$), 1.56 (s, $-\text{CH}_2\text{CH}_2\text{OH}$), 1.37 – 1.28 (br, $-\text{CCH}_2\text{C}-$), 0.97 (t, $J = 7.5$ Hz, CH_3).

FTIR spectrum of LO and reduced LO

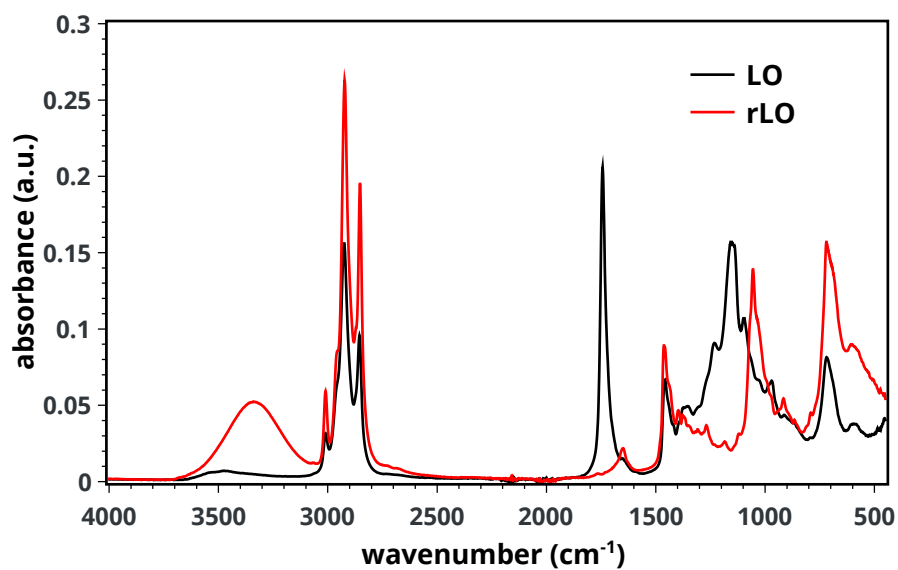


Figure S7 FTIR spectrum of LO and reduced LO (rLO), clearly showing the reduction of all esters (1736 cm^{-1}) for rLO and the presence of the OH stretch (3400 cm^{-1} , broad) in the mixture of alcohols.

FTIR spectrum of polymerised LO and polymerised reduced LO

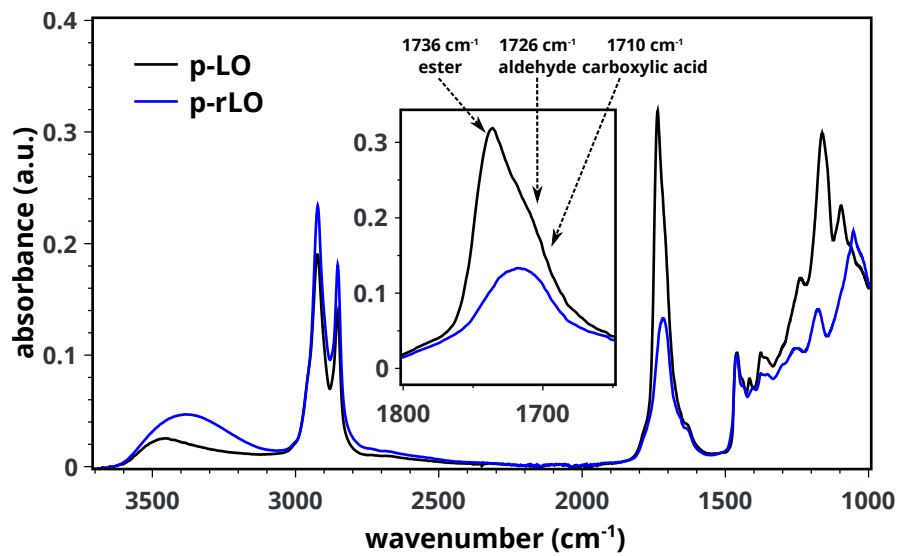


Figure S8 FTIR spectrum of polymerised LO (p-LO) and polymerised reduced LO (p-rLO).

FTIR spectrum of tristearin and tristearin-ZnO

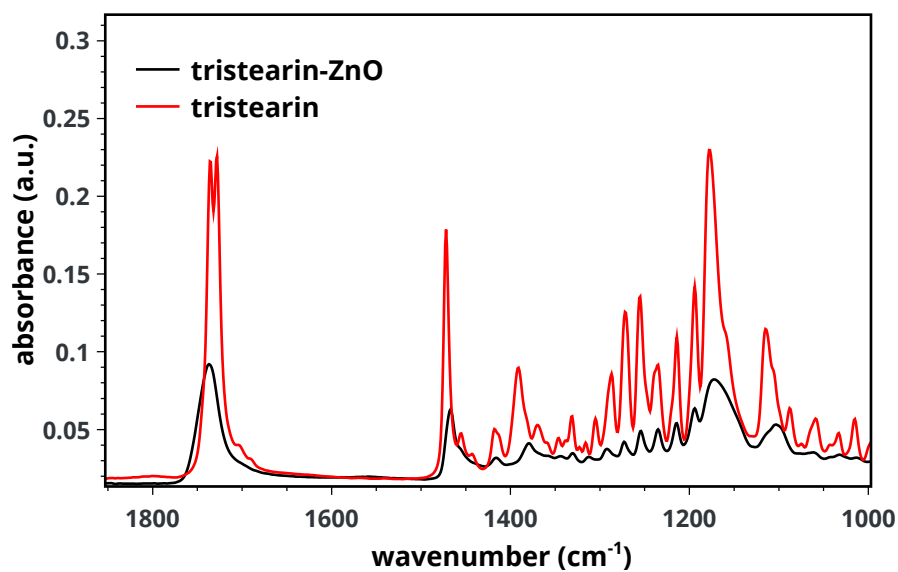


Figure S9 FTIR spectrum of tristearin and tristearin-ZnO, clearly showing that 1 week at 60°C and 12% RH did not lead to the formation of significant amounts of COOZn. A split ester carbonyl band is observed for tristearin due to the presence of different polymorphs.^{4,5}

References

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