Supporting Information

Time-Dependent ATR-FTIR Spectroscopic Studies on Fatty Acid Diffusion and the Formation of Metal Soaps in Oil Paint Model Systems

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1 Experimental procedures

Sample preparation

Metal sorbate complexes were synthesised by dissolving 550 mg sorbic acid (Aldrich, 99+%) with 1 mL triethylamine (Sigma-Aldrich, >99%) in 20 mL demineralised water at 50 °C. The addition of 1.0 g Zn(NO$_3$)$_2$·6H$_2$O (Sigma-Aldrich p.a.) or 1.1 g Pb(NO$_3$)$_2$ (Sigma-Aldrich, >99 %) dissolved in 5 mL water resulted in immediate precipitation of the white product. After stirring for 20 minutes, the product was separated by vacuum filtration, washed with water followed by ethanol and acetone, and dried overnight under reduced pressure. The metal sorbate salts were stored under N$_2$ atmosphere to avoid oxidation.

Binding medium model systems Znpol and Pbpol were made by grinding 250 mg zinc sorbate or an equivalent molar amount of lead sorbate with 1750 mg cold-pressed untreated linseed oil (LO, Kremer Pigmente) to a smooth paste with mortar and pestle. The concentration of metal ions was equivalent to a molar metal carboxylate bond to triacylglyceride (TAG) ester ratio (COOM/COOR) in the uncured sample mixture of 0.29. This concentration corresponds to roughly 420 mM zinc in the polymer. The mixture was applied to 50 × 75 mm glass slides and spread with a draw-down bar to achieve a wet thickness of 190 µm. The layers were cured overnight in an air-circulated oven at 150 °C, resulting in transparent homogeneous dark orange films with a thickness around 150 µm. Films of pure polymerized linseed oil pLO were prepared in a similar fashion. Model paint samples for zinc (ZnO-LO) or lead (Pb$_3$O$_4$-LO) were made by grinding ZnO and Pb$_3$O$_4$ with cold-pressed untreated LO in a 1:1 (w/w) ratio (zinc) and 2.75:1 (w/w) ratio (lead) to a smooth paste with mortar and pestle. The wet sample thickness was 190µm and the samples were dried at 60 °C in air for 7 days. For all measurements, 5 × 5 mm squares of the films were cut and lifted off the glass support. The thickness of each sample was measured with a digital micrometer accurate to 1 µm.

Analytical methods

ATR-FTIR spectra were measured on a Perkin-Elmer Frontier FT-IR spectrometer fitted with a Pike GladiATR module that included a heated top plate and a diamond ATR-crystal (φ = 3 mm). Spectra were recorded every 10, 30 or 60 s at 4 cm$^{-1}$ resolution and averaged over 4 scans. During time-dependent measurements, the ATR module was flushed with nitrogen to ensure a constant background signal. In order to measure spectra of polymer samples while they were exposed to solvents or solutions, a custom built stainless steel cylinder was used as illustrated in Figure S1. The cell volume was sealed with two solvent resistant O-rings between the top plate and the pressure clamp.
Figure S1 Illustration of the measurement cell used for time-dependent ATR-FTIR measurements of polymer films in contact with solvents or solutions. The spring provided a small pressure to keep a constant contact between the sample and the ATR-crystal as solvents swell the sample, while the porosity of the metal disk ensured unhindered diffusion of the solvent through the sample film.

In all experiments, analytical grade solvents were used (analytical grade acetone contained up to 0.3 wt% water). In reactive measurements on pre-swollen films, the polymer sample was first swollen with 0.4 mL of pure acetone, and 1 mL of palmitic acid in acetone (20 mg/mL HPa) was added when the recorded IR spectra showed that the samples were fully saturated with acetone.

For measurements with molten palmitic acid, an adapted setup was used in which the stainless steel cylinder was replaced by a rubber septum ring. The porous metal disk was submerged in molten palmitic acid for several minutes before a measurement, and then quickly placed on top of the sample that was pre-heated at 70 °C. Spectrum collection was started immediately after contact between the sample and palmitic acid, after which the spring and rubber ring were put in place. The top plate of the ATR module was kept at 70 °C throughout these measurements.

X-ray diffraction (XRD) measurements were recorded with Cu Ka radiation at 1°/min on ca. 5 × 5 mm squares of polymer sample film taped to a silicon low-background sample holder.
2 XRD trace of ionomer films after HPa exposure

Figure S2 XRD traces of Pbpol and Znpol ionomer films before and after exposure to a solution of palmitic acid (HPa) in acetone. In both cases, the samples show characteristic long spacing peaks corresponding to crystalline zinc and lead palmitate.[1] Pbpol also shows peaks of HPa that crystallised after remaining traces of the acetone solution evaporated.
3 Illustration of two band isolation methods

Figure S3 Illustration of two band isolation methods. (a) For isolation of crystalline metal palmitate bands (shown for Zn here), the spectrum at $t = 0$ (red curve in 1) was scaled to each spectrum in a series (dashed line in 2). The scaled $t = 0$ spectrum was then subtracted from each spectrum at $t > 0$ (green curve in 2), resulting a time-series of isolated crystalline metal carboxylate bands suitable for integration (3). (b) For isolation of the COOH band (1), a combination of two constrained Pearson IV band shapes was fitted to each spectrum in a series (2), resulting in a series of fitted band shapes that could be integrated (3).

To integrate overlapping absorption bands accurately in the large datasets recorded during time-dependent measurements, data correction and integration algorithms were written in the Wolfram Mathematica software, which are available from the authors on request.

To obtain accurate time-dependent areas of the sharp metal carboxylate bands corresponding to crystalline lead palmitate (1510 cm$^{-1}$, shoulder at 1540 cm$^{-1}$) and zinc palmitate (1538 cm$^{-1}$), it was necessary to subtract the contribution of the partially overlapping broad amorphous metal carboxylate band from each spectrum (see Figure S3a). First, the spectrum of an unreacted film at $t = 0$ (shown in red) was scaled to each spectrum at later times by matching the intensities at a fixed position on the broad amorphous metal carboxylate band (around 1600 cm$^{-1}$, where the contributions of surrounding bands are minimal). Subsequently, the scaled reference spectrum (dashed red curve) was subtracted from each spectrum in the series. The resulting isolated crystalline metal soap band (shown in green) could then be integrated by summing the intensity values in a fixed range that spanned most of the band.

During measurements of palmitic acid diffusion into linseed oil polymer films, the
COOH band of palmitic acid at 1710 cm$^{-1}$ overlaps with the ester carbonyl band of linseed oil with a maximum at 1740 cm$^{-1}$. A stepwise profile fitting algorithm was applied to integrate the carboxylic band accurately (see Figure S3b). First, a Pearson type IV band shape[2] was fitted to the ester carbonyl band at $t = 0$ and all band parameters except band height were fixed. Second, the sum of two Pearson IV band shapes—one constrained ester carbonyl band and one unconstrained function—were fitted to the overlapping carbonyl bands in the last spectrum in the measurement series, after which all parameters except band height were also fixed for the COOH band. Finally, a combination of the two constrained band shapes was fitted to the entire spectrum series, and the time-dependent area of the COOH band could be calculated.
4 Diffusion of HPa in LO polymer

![Graph showing diffusion of HPa in LO polymer](image)

**Figure S4** Integrated COOH band area of palmitic acid (HPa) during diffusion of molten HPa into a polymerised linseed oil film at 70°C. The data was fitted to a Fickian diffusion model appropriate for the ATR-FTIR measurement geometry as described by Fieldson and Barbari.[3]
5 Concentration of ZnPa$_2$ in ZnPol

Figure S5 FTIR spectra of (blue) Znpol ionomer after reaction with a HPa solution for 24 hours and (green) of a homogeneous suspension of ZnPa$_2$ and linseed oil. The latter sample contained the same ratio of metal-carboxylate bonds vs. ester bonds (COOM/COOR) as the initial unreacted Znpol ionomer film. The spectra were normalised on the maximum of the ester carbonyl vibration at 1740 cm$^{-1}$ to allow a comparison of the concentration of other molecular species relative to the concentration of ester groups. The fact that the asymmetric carboxylate stretch vibration at 1538 cm$^{-1}$ is so much more intense in the Znpol sample than in the mixture of ZnPa$_2$ suggests that there is a gradient in the concentration of ZnPa$_2$ in Znpol towards the bottom of the film after reaction with HPa solution. In other words, ZnPa$_2$ seems to exhibit preferred crystallisation at the bottom of the film. Bands associated with acetone are marked by •.
6 ATR-FTIR spectra of pigmented films before and after HPa exposure

Figure S6 ATR-FTIR spectra of Pb$_3$O$_4$-LO and ZnO-LO model paint films before (bottom) and after (top) reaction with a solution of palmitic acid in acetone. Note the broad ionomer metal carboxylate band in the spectra at t = 0, and the high intensity of the crystalline metal carboxylate band of the metal palmitates (1510 cm$^{-1}$ and 1538 cm$^{-1}$ for lead and zinc, respectively) compared to the ester carbonyl band at 1738 cm$^{-1}$. Spectra were normalised to the maximum of the ester carbonyl band at 1738 cm$^{-1}$ and vertically shifted for clarity. Bands associated with acetone are marked with •.
References

