Supplementary Materials for

Microscale mechanochemical characterization of drying oil films by in situ correlative Brillouin and Raman spectroscopy

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Sci. Adv. 8, eabo4221 (2022)
DOI: 10.1126/sciadv.abo4221

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Brillouin Data

A typical BLS spectrum, arising from the scattering of photons by acoustic phonons, consists of Stokes and anti-Stokes peaks, which are Doppler shifted in frequency from the elastic peak. The doublets were analyzed according to a well-established procedure \((14, 52)\), where each contribution \(I_B\) to the intensity of the total scattered light has been modelled using a damped harmonic oscillator (DHO) lineshape, Eq. S1:

\[
I_B(\omega) = R(\omega) \otimes I_0 \frac{r_B \omega B}{\pi (\omega - \omega_B)^2 + \omega_B^2}.
\]

\(R(\omega)\) is the instrumental resolution function, the symbol \(\otimes\) represents the convolution operator, \(I_0\) is an amplitude factor depending on the scattering cross-section, and \(\nu_B = \omega_B / 2\) and \(\Gamma_B / 2\) are the frequency shift and the full width at half-maximum (FWHM) of the Brillouin peaks, respectively. In particular, \(\omega_B\) and \(\Gamma_B\) are directly related to the longitudinal sound velocity, \(c_L = \omega_B / \nu\), and to the acoustic absorption, \(\alpha = \Gamma_B / 2c_L\), of the elastic wave propagating inside the medium; \(q\) is the exchanged wave number related to the wavenumber of the incident light \(k_i\), the scattering angle \(\theta\), and the refractive index \(n\) of the medium, through the relation \(q = 2nk_i\sin(\theta/2)\).

Possible multiple scattering contributions were considered using the method described in Ref. \((52)\). Furthermore, the finite back-scattering collection angle induces a distribution of exchanged wave number \((q)\), which also contributes to the broadening of the Brillouin peak. The \(\Gamma_B\) calculation was therefore corrected by considering that the numerical aperture of the lens used (NA=0.42), corresponding to a minimum scattering angle \(\theta_{min} = 155.2^\circ\), causes a widening in \(\Gamma_B\), which can be approximated to about 2.3% of the frequency position of the peak itself.

The adiabatic (zero-frequency) longitudinal modulus, \(M_0\), is related to the sound velocity through the relation: \(M_0 = \rho c_L^2\), where \(\rho\) is the density of the sample. For a system subject to relaxing phenomena, a complex frequency-dependent modulus has to be used: \(M'(\omega) = M(\omega) + i M''(\omega)\), with the real and imaginary part given by Eqs. S2, S3:

\[
\text{Eq. S2} \quad M'(\omega) = \rho c_L^2(\omega)\]

\[
\text{Eq. S3} \quad M''(\omega) = \frac{2\rho}{\omega} \alpha(\omega)c_L^2(\omega).
\]

Within the GHz frequency range, these two quantities can be derived in a unique way from Brillouin measurements. The imaginary part \(M''(\omega)\), is a measure of the energy dissipation of the sound waves within the medium, while the real part represents its dispersive behaviour. A decrease of \(M'(\omega)\), for example as a function of temperature, is simply indicating that the material is becoming softer; \(M_0\) can be considered as the zero-frequency limit of the real part. All these physical quantities are called “apparent” because of their frequency-dependency \((13, 52)\).

Refractive Index (n) and Density (\(\rho\))

In order to derive \(q\), \(M'(\omega_B)\) and \(M''(\omega_B)\), we need to know the refractive index and the mass density of the sample. The calculations were made considering the values of \(n(t^0)=1.48\) \((53-55)\) and \(n(t^*)_1=1.51\) at the initial time of the reaction and at the time when the Brillouin shift no longer showed noticeable changes, respectively, corresponding to an \(n\)-variation during desiccation of about 2%, in agreement with other polymerization experiments \((56)\). We based on a linear behaviour of \(n(t)\) between \(t^0\) and \(t^*\) then followed by a constant trend for the remaining time \((57)\). To have more safety margin on our data, considering that we also made calculations using \(n(t^*)_2=1.54\), and \(n(t^*)_3=1.57\), as suggested in Refs \((55, 58-59)\), which can be referred to as the maximum variation of \(n\) in our experiment. The \(p\) values were obtained through the Clausius-Mossotti law Eq. S4:

\[
\text{Eq. S4} \quad \frac{4}{3} \pi p \rho \rho = \frac{4}{3} \pi p \rho \rho
\]

where \(\rho\) is the effective optical polarizability, calculated from the values of \(n\) and \(\rho\) at \(t^0\) and considered almost constant during the reaction (Fig. S2).

To give an idea of how much different refractive index estimates affect the calculation of the longitudinal elastic modulus, Figure S3 shows the results for \(M'(\omega_B)\) as a function of the annealing time: we found that the different \(n\) values at \(t^*\) provide similar values for the physical quantities, reaching a maximum difference of 2%.

Raman Data

This technique has been widely used to classify oils of different origins and applications (food, environmental, biomaterials, and cultural heritage among others \((23, 24)\), a typical Raman spectrum of the pure linseed oil is reported in Figure S4 together with its main peak assignments \((60-61)\).

In our analysis, each Raman spectrum was baseline corrected and normalized to \(\text{CH}_2\) signal at 1440 cm\(^{-1}\) before other analysis. Three different peaks of the Raman spectrum were chosen as markers of linseed oil polymerization...
progression, namely the i) stretching and the ii) bending modes of (=C-H)\textsubscript{cis} vibration at 3014 and 1265 cm\textsuperscript{-1}, respectively, and iii) the stretching band of (C=C)\textsubscript{cis} at 1660 cm\textsuperscript{-1}. i) The (=C-H)\textsubscript{cis} vibration is part of a system of bands between 2800-3150 cm\textsuperscript{-1} (Figure S4), composed of several peaks originating from stretching of CH\textsubscript{2} and CH\textsubscript{3} bonds, which make it difficult to isolate the contribution of the solely (=C-H)\textsubscript{cis} vibration. Therefore, the peak intensity estimation was performed using a three-component multiple Lorentzian fit (the behaviour of this band with polymerization time is shown in the main paper where it is also directly compared with the variation of the BLS peak shift (Fig. 2A). ii) In a similar way, to follow the diminishing of the bending mode of (=C-H)\textsubscript{cis} vibration at 1265 cm\textsuperscript{-1} we recurred to a two-component multiple Lorentzian fit including the in-phase methylene twist at 1305 cm\textsuperscript{-1} which instead increases with the polymerization time (61). The spectral closeness as well as the opposite behaviour of the two bands is probably the reason for the larger dispersion observed in the diminishing of the 1265 cm\textsuperscript{-1} band (Fig. S5).
Fig. S1. Micro-Raman and FT-IR spectra of the ZnO-oil model during polymerization

Micro-Raman (upper) and FT-IR (lower) spectra recorded on the same ZnO-oil paint applied on a glass slide (Raman) and KBr pellet (FT-IR). Arrows indicate the bands assigned to the (≡C-H)\textsubscript{cis} stretching.
Fig. S2. Refractive index and mass density for linseed oil
Refractive index (left) and mass density (right) for the linseed oil as a function of the annealing time, determined as described in the text.
Fig. S3. Variation of the real part of the longitudinal modulus \([M'(\omega_B)]\) versus annealing time

\(M'(\omega_B)\) calculated from Eq. 2 by using the different \(n(t^*)\) values reached at the end of the polymerization process.
Fig. S4. Micro-Raman spectrum and band assignments of fresh linseed oil
Micro-Raman spectrum recorded on a fresh oil sample with the main spectral bands whose assignment is reported in the table.
Fig. S5. Multimodal Micro BLS-Raman of linseed oil polymerization

Correlative Brillouin and Raman investigation of oil polymerization: BLS frequency shift (red filled circle) and intensity of the $\delta(=\text{C–H})_{\text{cis}}$ @ 1265 cm$^{-1}$ (black filled circle);
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