Optical Second Harmonic Generation in Bitumen Films

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Abstract. The ability of asphalt binders, or bitumen, to self-heal is critical to maintaining a durable highway system. Yet, the process of self-healing is not well understood at the molecular level. Visible-IR Sum Frequency Generation (SFG) is a potential probe of bitumen self healing mechanisms because it can monitor molecular vibrational resonances at internal cracks non-invasively and in real time. However, bitumen's material properties present challenges to nonlinear spectroscopy. First, bitumen's low thermal conductivity and softness make it susceptible to thermal damage at intensities required to generate interface nonlinear optical signals. Thus energy, duration and repetition rate of incident pulses must be chosen carefully. Second, because of bitumen's strong broadband optical absorption, samples must be prepared as thin films spin-coated onto transparent substrates. Thus relative contributions of substrate-film interface ad the free film surface to second-order nonlinear optical signals must be determined. Thirdly, strong white-light continuum from film and/or substrate can overwhelm SHG, and must be carefully evaluated. Here we present a systematic study of single-beam, single-wavelength second harmonic generation (SHG) from single bitumen films spin-coated onto glass slides that addresses these preliminary questions about second-order nonlinear optical spectroscopy.

Overview. An understanding of the molecular mechanisms by which asphalt binders self-heal is essential for guiding the development of improved binders that are resistant to formation of cracks and potholes. Bitumen, a crude oil derivative, is one example of a wider class of so-called "self-healing materials", that also includes bone and concrete.

Engineered Self Healing Materials mimic the behavior of biological systems that are self-maintaining. They provide an alternative to the engineering philosophy of damage prevention.

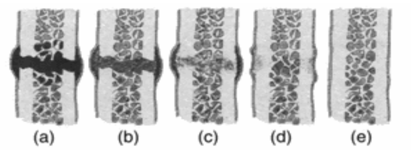


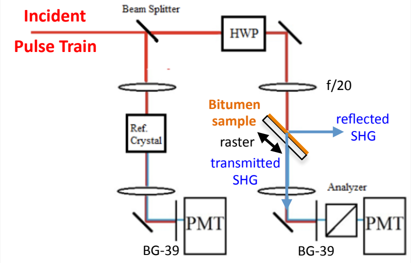
Fig. 1—Healing stages of bone: (a) internal bleeding, forming a fibrin clot; (b) unorganized fiber mesh develops; (c) calcification of the fibrocartilage; (d) calcification converted into fibrous bone; (e) transformation into lamellar bone

Defining characteristics: Formation of a crack in a self-healing material initiates a mobile phase in which matter moves to and fills the crack, often restoring the original strength. Self-healing can be an intrinsic material property, but sometimes requires an external trigger or catalyst.

Examples of self-healing mechanisms:
- Fluid flow (*e.g.* in liquid capsules)
- Diffusion of polymer chains
- Phase changes within the material
- Oxidation reactions to fill cracks

Conventional analysis of self-healing materials: Self-healing is often studied with a dynamic shear rheometer (DSR). The DSR generates cracks by impulse-stressing the material, then measures the material's time-varying strength (shear modulus) as it heals by applying a controlled shear stress and measuring the material's strain. This method, however, provides no microscopic information about the healing mechanism.

Experimental SHG set-up. SHG was used to test the feasibility of performing VIS-IR SFG studies of molecular bonds at bitumen free surfaces and internal cracks. SHG can also monitor chemical surface dynamics (w/o molecular specificity) in real time.



***Incident laser*.** 3 laser excitation formats were studied:

(a) fs Ti:S oscillator
$f = 100$ MHz, $\tau = 30$ fs, $E \leq 1$ nJ

(b) fs Ti:S amplifier*
$f \leq 1$ KHz, $\tau = 180$ fs, $E \leq 1$ mJ

(c) Q-switched Nd:YAG
$f = 10$ Hz, $\tau = 5$ ns, $E \leq 1$ J

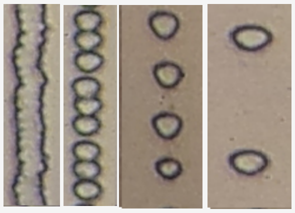
***Sample*.** 1 µm semi-transparent bitumen film spin-coated onto 1 mm thick glass slide; mounted on x-y stage that rastered sample over ~1 mm² in the focal plane during data acquisition to avoid cumulative damage.

***SHG Detection*.** Photomultiplier tube (PMT) + photon counter placed after UV transmission filters (BG-39) and/or spectrometer. Here we show *transmitted* SHG results; however reflected SHG is also being studied.

Findings. SHG was generated from bitumen films without damaging them, detected and distinguished from white-light continuum and other background sources, and determined to originate from the free surface of the bitumen film.

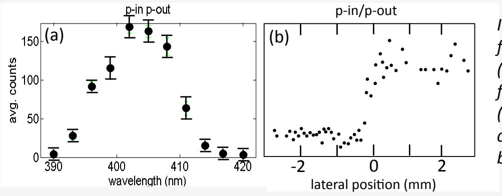
***(1) Optimum excitation pulse format*.** Avoiding optical damage of the soft, absorptive bitumen film while exciting intensely enough to generate detectable SH signals was the main experimental challenge. Results with our 3 excitation formats were:

(a) *fs oscillator*: 100 MHz rep. rate too fast for mechanical sample raster; rapid cumulative heating melted sample well below threshold for detectable SHG
(b) *fs amplifier*: KHz rep. rate enabled single-pulse excitation by rastering sample; single-pulse damage threshold F_d ~ 0.02 J/cm² was measured; SHG signals were detectable using excitation fluence as low as ~0.1 F_d. Signal level ~200 cts/s near F_d, scaling as I^2.
(c) Q-switched YAG: 10 Hz rep. rate favorable for single-pulse excitation, but duration too long and intensity too low to generate detectable SH signals below damage threshold.



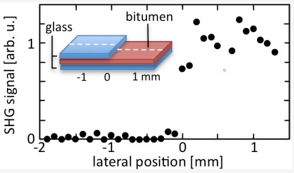
Damage tracks in bitumen film following excitation at $F > F_d$ with amplified 180 fs pulses as sample rasters in focal plane of incident laser pulses. Rep. rate decreases from left to right. These measurements were used to determine single-pulse damage threshold F_d. SHG was detectable down to F ~ 0.1 F_d.

***(2) Identification of SHG from bitumen*.** Detected signals were determined to be SHG from bitumen films in 3 ways: (*i*) detected signals scaled with incident intensity I as I^2, consistent with SHG; (*ii*) spectral analysis of detected signals with a spectrometer (panel "a" below) showed they were peaked narrowly around 400 nm (half the fundamental wavelength), also consistent with SHG; (*iii*) step-function increases in signal were observed as the incident laser focal spot scanned across the boundary between uncoated glass and a bitumen-coated region (panel "b" below), showing that the most of the signal originated from the bitumen film.

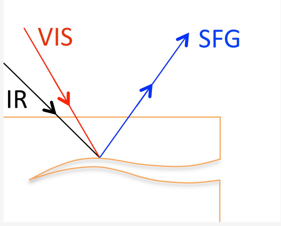


Identifying features of SHG from bitumen films:
(a) spectrum peaked at ½ fundamental wavelength;
(b) step-function signal increase across glass-bitumen boundary (at zero).

***(3) Identification of free surface as SHG signal source*.** We further narrowed the source of the signal by partly covering a spin-coated bitumen film with a glass cover slip, as shown in the inset of the figure below. A lateral scan of the focused laser spot across the sample showed that SH signal was generated only from the part of the sample with exposed surface, demonstrating that the free surface was responsible for the observed SHG signals.



SHG signal vs. lateral position from a bitumen film spin-coated on glass. The left half of the film is covered with a glass covers slip, and yields no SHG signal. The right half, with its exposed bitumen surface, generates a strong SH signal, demonstrating that the free surface is the main source of SHG.



Conclusion and Future Work. We acquired SHG data that demonstrate the feasibility of SHG/SFG as a probe of the self healing mechanism in bitumen. We isolated the bitumen-air interface as the source of SHG. Next we will use SHG to characterize self-healing at a simulated crack between two bitumen films, and relate the results empirically to molecular diffusion models of self-healing. This will lead to VIS-IR SFG experiments that probe the molecular mechanism of self-healing

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