

Surface Analysis

DSM Biomedical develops new surface technologies with the use of Sum-Frequency Generation (SFG) analysis. SFG is a sophisticated, non-destructive laser technique to study polymer surfaces. This highly-sensitive method possesses several unique advantages to conventional surface analysis techniques, including:

- Ability to identify the structure and orientation of functional groups at the surface with monolayer specificity
- Suitable for interfaces between centrosymmetric crystalline solids, amorphous solids, and isotropic gasses or liquids under the electric dipole approximation
- Effective at the polymer-gas interface and the polymer-liquid interface
- Good spatial, temporal, and spectral resolution
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Biocompatible surfaces are essential to the success of a continuously-increasing number of polymer applications in the biomedical field. Surface chemistry controls numerous chemical and physiological properties of a polymer, including thromboresistance, biostability, lubricity, permeability, and abrasion resistance. Surface-modified polymers need to be well characterized in order to correlate the surface chemistry to the biofunctionality of the application.

Historically, it has been a challenge to obtain such detailed information about surface structure due to the lack of probe techniques that are sensitive to molecular features, such as conformational sequences and hydrogen bonding. Various spectroscopic techniques-reflection infrared spectroscopy, attenuated total reflection infrared spectroscopy, and Raman spectroscopy-have been used to characterize polymer surfaces; however, these methods lack surface specificity, and the resulting spectra are often obscured by the bulk concentration. Surface-sensitive techniques, such as contact angle measurement, neutron reflection, and X-ray photoelectron spectroscopy (XPS) often do not provide structural information, and/or do not allow in situ measurement. (Table 1)

| Method | Surface/Interface Monolayer Specificity | Good Spatial and Spectral Resolution | Structural Information | Functional Group Orientation | Suitable for Liquid/Solid, Gas/Solid, Liquid/Gas, Liquid/Liquid Interfaces | <i>in situ</i> Measurement | Effective at Polymer-Liquid Interface | Non-destructive |
|---|---|--------------------------------------|------------------------|------------------------------|--|----------------------------|---------------------------------------|-----------------|
| SFG | ● | ● | ● | ● | ● | ● | ● | ● |
| Reflection Infrared Spectroscopy | | ● | ● | ● | ● | ●* | | ● |
| Attenuated Total Reflection Infrared Spectroscopy | | ● | ● | ● | ● | ●* | ●* | ● |
| Raman Spectroscopy | | ● | ● | ● | | ●* | | |
| Contact Angle Measurement | ● | ● | ● | | | | ● | ● |
| Neutron Reflection | ● | ● | ● | | | | | |
| X-Ray Photoelectron Spectroscopy (XPS) | ● | ● | ● | | | | | |
| Surface Light Scattering | ● | ● | | | | ● | ● | ● |
| Secondary Ion Mass Spectroscopy (SIMS) | ● | ● | ● | | | | | |

* Limited conditions apply

Technique

In the SFG technique, a pulsed visible green laser beam (532 nm) is overlapped on a surface with a tunable, pulsed infrared (IR) laser beam (2 to 10 μm). The two laser pulses combine to produce light at the sum of their frequencies (440 to 500 nm) by a nonlinear process. The light emitted at the sum frequency is detected by a photomultiplier and the spectrum is obtained by tuning the IR beam over the frequency range of interest. (Figure 1)

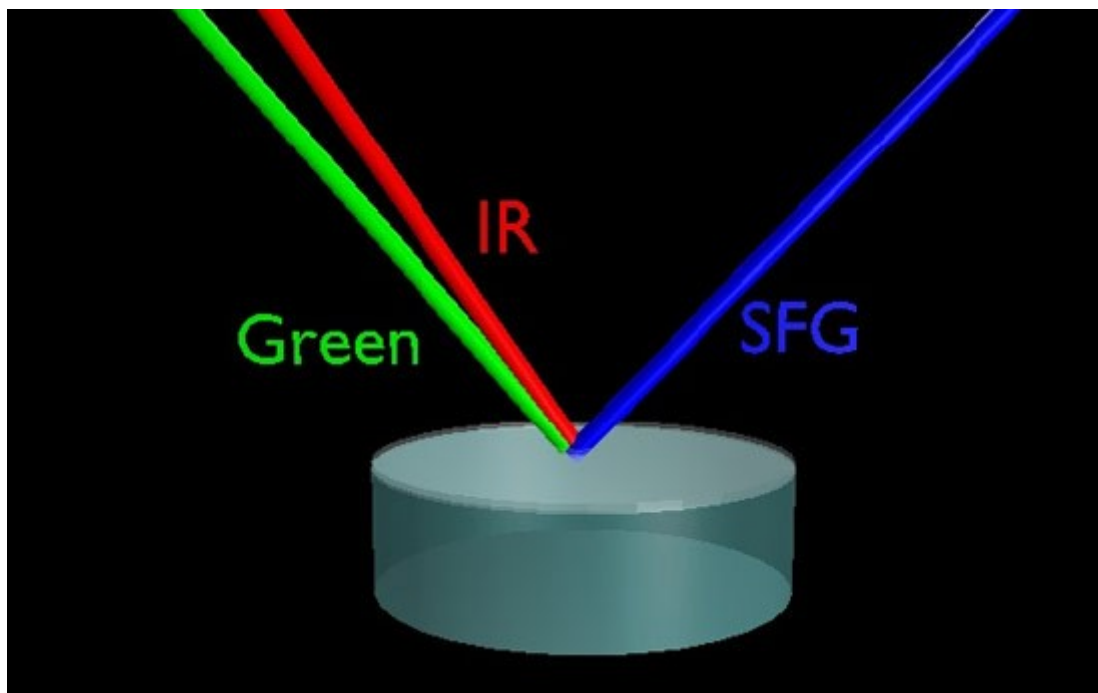


Figure 1. Overlap of the infrared (IR) and visible laser beams on a polymer surface to produce the sum-frequency beam.

An amorphous media, such as a polymer, does not generate a sum frequency signal because the bulk is randomly oriented, and second-order mixing is thus forbidden. However, polar ordering can occur at the surface of a polymer to reduce interfacial energy, resulting in a net orientation of molecules, and allowing a sum frequency response. Therefore, SFG is intrinsically surface specific.

Enhancement of the SFG signal occurs when either the IR or visible beam is in resonance with a vibrational mode or electronic state, respectively. Molecular-level information about the interfacial species can be derived from the vibrational spectrum obtained by tuning the IR beam. This allows both the identity and orientation of surface groups or molecules to be determined.

Equipment

The SFG apparatus is a complex laser system based on a high-power picosecond Nd:YAG laser and an optical parametric generator/amplifier (OPG/OPA). The fundamental output (1064 nm) of a Nd:YAG laser is frequency doubled to produce the 532 nm visible beam and is used to drive an OPO/OPA. The tunable (1300 to 4000 cm^{-1}) IR beam is generated from a series of non-linear crystals through OPG/OPA and difference frequency mixing. The sum-frequency (SF) spectra are obtained by overlapping the visible and IR beams on the polymer surface at incident angles of 60° and 55° , respectively. The SF signal from the polymer surface is collected by a photomultiplier tube (PMT) and processed using gated integrator. Surface vibrational spectra are obtained by measuring the SF signal as a function of the input IR frequency.

Surface studies

Whereas the bulk composition of a polymer generally governs its mechanical properties, its surface chemistry determines how it will interact with biological systems. Since the surfaces of biomedical polymers will be in contact with blood after implantation, control of surface properties is critical in order to prevent complications related to thrombosis and embolization.

DSM Biomedical developed a novel technology called Surface-Modifying End Groups (SME®) to optimize the surface properties of polyurethanes to the specific physiological environment of the application. This method covalently bonds monofunctional surface-active end groups to polymer molecules during synthesis. For example, when a hydrophobic end group such as poly(dimethylsiloxane) (PDMS) is attached to a polyurethane, the final polymer self-assembles to yield a surface similar to silicone rubber. Hydrophobic surfaces are known to extend blood clotting time and reduce blood platelet adsorption and thrombosis *in vivo*. SFG validates that there is in fact a difference between the surface chemistry of polymers chemically modified with SME® and those that are not. In a recent study that appeared in the Journal of the American Chemical Society, DSM Biomedical's BioSpan® *segmented polyurethane* modified with PDMS end groups (BioSpan® S) was analyzed using SFG. The results confirmed that the lower surface tension component effectively segregates to the surface in order to minimize the surface free energy of the system. Even at extremely low concentrations, the more hydrophobic silicone tail dominates the surface of BioSpan® S.

For a biopolymer intended to be in contact with living tissues or blood, it is very important to know the structure of the surface in the hydrated state. Because of its ability to study polymers under hydrated conditions, SFG was employed for this purpose. It was demonstrated that aqueous environments stabilize different functional groups of the polymer, so it is important to study the surfaces under the same conditions that the polymer is expected to be employed.

SFG can be attempted on almost any system in which the surface or interface can be accessed by the light. Some key points to consider are: the surface must be ordered, the medium through which the light passes must not interfere appreciably with the light, and the surface or interface must be optically flat.

The first application of SFG was to study catalytic systems in which molecules were adsorbed onto single crystal surfaces. SFG is currently used to study electrochemical surfaces, such as the sub-stoichiometric oxide (sub-oxide) that forms at the interface between silicon and silicon dioxide (a critical performance element of microelectronic devices). Liquid-liquid (oil-water) interfaces are being observed at the University of Oregon using SFG, and the technique has also been employed to examine how polymer surfaces react to bulk mechanical testing. Even the polymer-polymer interface can be probed using SFG, provided one of the polymers is very thin (100 nm) in order to prevent complete absorption of the IR light, and that the materials have different indices of refraction so the light will reflect off the buried interface.