RTV ANALYSIS WITH RAMAN SPECTROSCOPY

APPLICATION NOTE RAMAN-017 (US)

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Abstract

This application note documents the acquisition and analysis of spectra of room-temperature vulcanized silicones (RTV) with a TSI ChemLogix ProRaman-L.

Background and Motivation

Silicone sealants have been in use since the 1940s, the early recipes containing only a filler and polydimethylsiloxane PDMS) fluid. They did not, as modern materials do, cure to an elastomeric solid. They offered one chief benefit over other sealants in use at the time: they did not need to be painted to prevent weathering.

Elastomeric silicone sealants were developed in the 1950s. The first of them was a two-art system consisting of an acid-ended polysiloxane and a polysilicate. This system cured at room temperature, giving rise to the now-common description of these materials – Room-Temperature Vulcanizing, or RTV. These early RTVs were mixed like epoxies before they were applied.

The modern one-component version of this material, available at hardware stores today, is composed of hydroxyl-ended polydimethylsiloxane and acetoxy-silanes. They cure when exposed to moisture in the air. They require no mixing before use and can be stored for months to years so long as no moisture is present. These materials are currently in use as adhesives and sealants, but also in encapsulating and impregnating applications.

These sealants derive their unusual and unique properties from their constituents. All the products used in this study were dominated in terms of weight percent by hydro-terminated poly(dimethylsiloxane). Siloxanes are long-chain molecules with alternating Si-O-Si bonds. This is a strong bond, with a low barrier to rotation. It is this low barrier to rotation that results in flexibility at both high and low temperatures. Adhesion characteristics are tailored to surfaces to be bonded by modifications to the chemistry of the mixture, as well as the addition of fillers.

Fillers contribute to strength of the cured material (addition of 15% fumed silica is known to increase tensile strength by 30x) and also imparts flow control (thixotropy) to keep the sealant from pouring out of the seal joint before the material is cured. Other fillers enhance electrical insulating, weather resistance and heat stability properties.[1]

Measurements and Results

Three samples of RTV were procured from a local hardware store; two more were borrowed from TSI Incorporated's manufacturing department. These samples were Permatex blue (low odor formula), clear and red (high temperature formula) gasket maker materials and Momentive RTV157 and RTV167. Both the Momentive products were gray in color. These samples were applied to an aluminum surface and allowed to cure to a tack-free state before analysis was begun.

Figure 1. Photo of 5 RTV samples, applied to an aluminum surface

Analysis was performed with a ChemLogix ProRaman-L instrument with a 785 nm excitation laser. Approximately 200 mW of laser power was used on all samples. The samples were positioned with an XYZ translator, and Raman spectra collected with a high numerical aperture lens tube.

The silicone features can be assigned as Si-O-Si symmetrical stretch (488 cm^{-1}), Si-CH_3 symmetric rocking (687 cm^{-1}), Si-C symmetric stretching (708 cm^{-1}), CH_3 asymmetric rocking 862 cm^{-1}), CH_3 asymmetric bending (1412 cm^{-1}), CH_3 symmetric stretching (2907 cm^{-1}) and CH_3 asymmetric stretching (2965 cm^{-1}). [2]

The features near 200 cm^{-1} also originate in Si-O bonds from SiO_2, tetra-n-propylsilicate, H_4SiO_4, $C_8H_{20}SiO_4$ (TEOS) and trimethylsilanol ($(CH_3)_3SiOH$).[3]

Non -i-O features in the red RTV are Fe_2O_3, and in the blue RTV, limestone, $CaCO_3$ and stearic acid. These ingredients are documented in the safety data sheets available on the Permatex website.[4-5]

Spectra of all except the blue sample are shown in Figure 2. There is a large amount of similarity in these spectra, dominated as they are by the features of the silica-oxygen bonds in the bulk material. The main features differentiating the red RTV from the others is iron oxide. These features match database entries for hematite well.

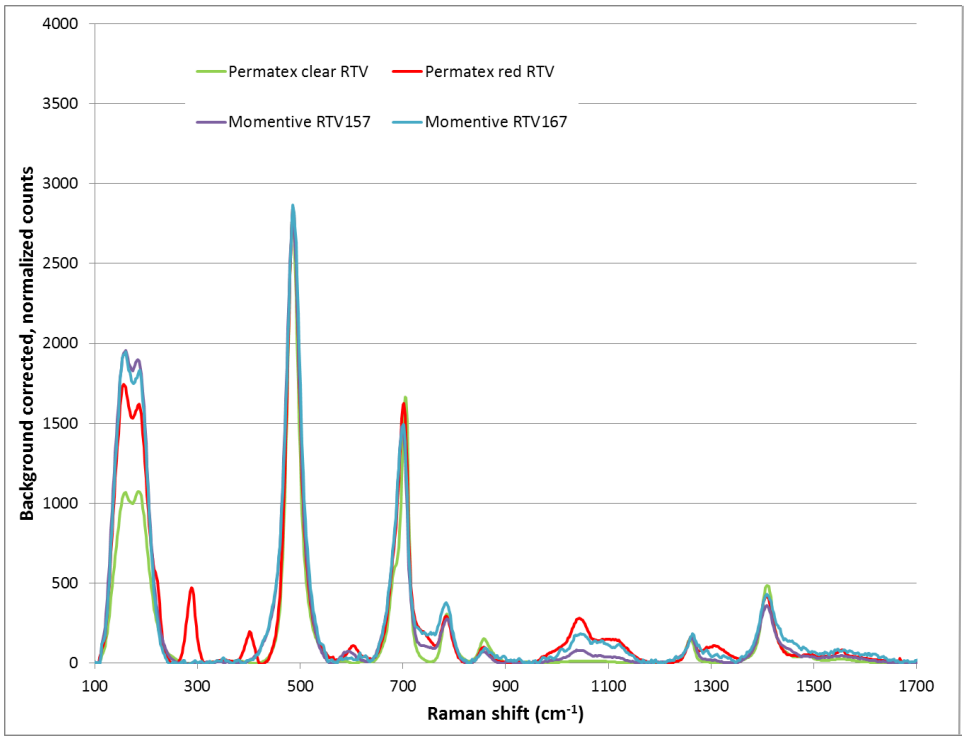

Figure 2. Spectra of all clear, gray and red RTV samples.

The spectrum of the blue RTV is sufficiently different that it is presented in another graph. Figure 3 shows a spectrum of the Permatex blue RTV, which contains materials not present in the other samples, including stearic acid, limestone and calcium carbonate. It is clear that the Si-O features are still present, but that this spectrum is more complicated than the others. The safety data sheet on this material indicates that there is a considerable amount of non-PDMS material present in this product (10-30 %wt $CaCO_3$ and 10-30 %wt limestone).[4]

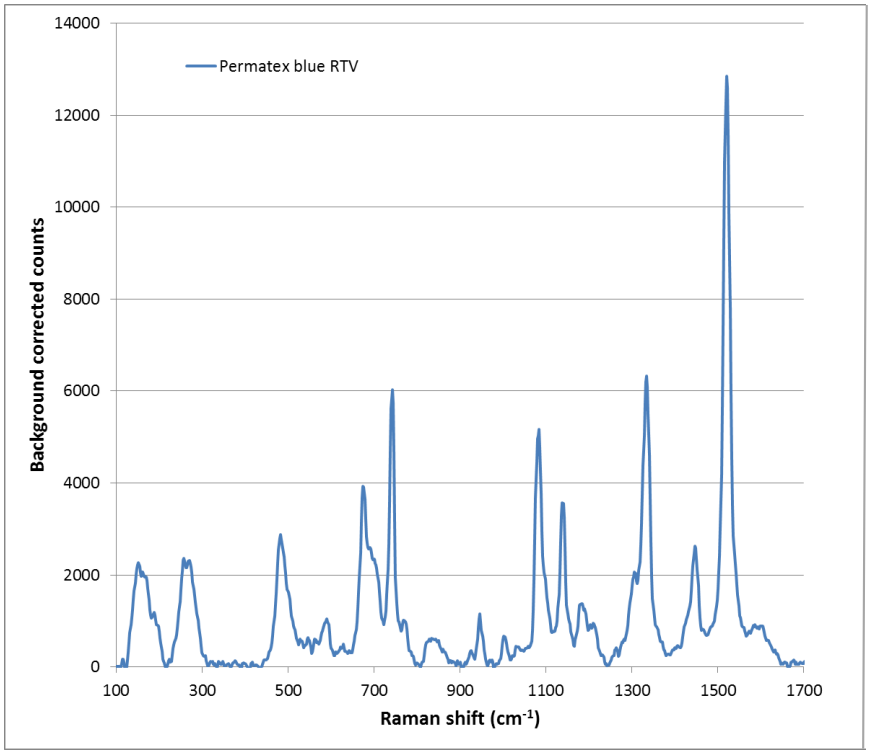

Figure 3. Raman spectrum of Permatex blue RTV.

Summary

This application note documents the use of a ChemLogix ProRaman-L to acquire spectra of silicone sealants and gasket forming systems. The spectra show an interesting variety of extra ingredients that modulate the performance of these products.

References

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3. Hanrahan, F.Z. and N.J. Ianno, "Relationship between photofixed condensate, effluent and bulk composition of several common RTV materials," *J. Spacecraft and Rockets*, **51** (3) 978, 2014.
4. Permatex SDS – 85915.
5. Permatex SDS – 81860.

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