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May 13, 2005

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This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

# Assessment of Raman Spectroscopy as a Silicone Pad Production Diagnostic

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## Abstract

Silicone pressure pads are currently deployed in the W80. The mechanical properties of these pads are largely based on the degree of crosslinking between the polymer components that comprise the raw gumstock from which they are formed. Therefore, it is desirable for purposes of both production and systematic study of these materials to have a rapid, reliable means of assaying the extent of crosslinking. The present report describes the evaluation of Raman spectroscopy in this capacity.

## Introduction

The W80 presently uses Dow Corning DC-745U silicone material for several components. This material is known to be problematic when studied, owing to the fact that the gumstock (the uncured polymer blend from which the pad is prepared) is a proprietary substance, the composition of which is held as a trade secret by the manufacturer. It has been determined recently that the material is most likely a blend of polydimethylsiloxane with a small percentage of phenyl-methyl siloxane monomers<sup>1</sup>. Silica filler and a CaCO<sub>3</sub>-supported peroxide catalyst are also included in the gumstock. The material cures when the gumstock is subjected to heating, which activates the crosslinking reaction *via* the peroxide.

At present, production of DC-745 pads takes place at the Kansas City Plant, Honeywell FM&T. Using the proprietary gumstock, KCP forms and cures pads to system specifications. The process in general involves curing under carefully controlled conditions of heat and pressure for specific times. It is the combination of heat and time that is specifically tailored to provide crosslinking of a given degree. The extent of crosslinking is typically gauged at the production end by durometry of the cured pad's Shore hardness value. However, this can be an imprecise method, insensitive to local variations in crosslink density. In scientific studies the crosslinking degree can be determined by nuclear magnetic resonance. While NMR is a powerful tool for the measurement of crosslinking<sup>1</sup>, it is also highly specialized, expensive, and can typically sample only samples much smaller than a typical pressure pad, making it inconvenient for production work.

In principle, Raman spectroscopy could be a powerful tool for performing such an assay. The vinyl group, which is consumed during crosslinking, has a symmetric stretching mode known to give a moderate to strong Raman signal. This mode is better observed by Raman scattering than infrared absorption since it usually appears weakly in the IR<sup>2,3</sup>, depending upon the symmetry of the group alpha to the vinyl double bond itself. Other considerations make Raman a potentially useful technique. A modern Fourier-transform

Raman system is relatively inexpensive, and measurements can be made rapidly. The technique is inherently suited to sampling solids, and can be adapted to the use of fiber optic probes for remote measurement of large samples within a forming apparatus. It has experimental advantages over infrared absorption spectroscopy such as comparative freedom from matrix absorptions (depending on the excitation wavelength).

In this report, Raman spectroscopy is evaluated as a means of rapid determination of crosslink density in DC-745. Four different samples of varying degrees of crosslinking are examined. Although this method has proven successful in gauging extent of cure in other vinylic polymer blends, for the present system the vinyl content is evidently too low to be detected by conventional Raman spectroscopy.

#### Experimental and Results:

Samples of DC-745 were obtained from KCP. They were in the form of flat pieces typically about 4 mm thick. Four types were used, representing the uncured gumstock, and other samples of different degrees of cure: Shore 44, Shore 54, and Shore 56.5. The increasing index value indicates greater hardness and therefore more extensive crosslinking.

Spectra were collected using a Perkin-Elmer FT-Raman spectrometer in a  $180^\circ$  backscatter geometry, with excitation at 1064 nm, and incident powers ranging from 50 mW to 200 mW. 64 samples were typically accumulated for one spectrum. Representative spectra are presented in **figure 1**.

The presence of a background probably due to a combination of fluorescence and second-order scattering complicated direct normalization and comparison of the spectra. To compensate, the spectra were smoothed, then second derivatives were taken. In addition to minimizing the background, this also has the advantage of defining overlapping peaks that might otherwise be too difficult to distinguish by direct comparison. The unnormalized second derivative spectra are given in **figure 2**.

#### Discussion:

The relevant stretch is known to appear between  $1670$  and  $1620\text{ cm}^{-1}$ . For the composition of the material proposed, this should be a quiet region, allowing for straightforward detection of the vinyl mode. In order to normalize the spectra, the phenyl in-plane  $A_{1g}$  stretch at  $1000\text{ cm}^{-1}$  was selected as an internal standard, since the phenyl composition should be totally constant throughout the curing process. Examination of this peak in the second derivative spectrum in **figure 3a** indicated that a minor normalizing factor was required to bring samples Shore 44 and Shore 56.5 into overlap with the other spectra. The normalized spectrum is shown in **figure 3b**.

Inspection of the region from  $1620\text{ cm}^{-1}$  to  $1670\text{ cm}^{-1}$  does not reveal the anticipated stretch. A modest line near  $1590\text{ cm}^{-1}$ , **figure 4**, could be interpreted as arising from the vinyl group, but this is unlikely for several reasons. First, this would be an unusually low

frequency for this mode. Second, a Raman active  $E_{2g}$  phenyl mode is known to occur within ten wavenumbers of this frequency<sup>2</sup>. Finally, the normalized derivative spectra do not show any changes in the band intensity consistent with loss of vinyl content as a function of crosslinking. Instead, the lack of change as a function of crosslink reaction indicates that the  $1590\text{ cm}^{-1}$  band arises from the  $E_{2g}$ -derived phenyl mode.

To insure that the lack of a vinyl feature was not due to an inhomogeneous vinyl distribution that favored the interior of the material over its surfaces, the Raman spectra of the center portions of the samples were collected after splitting them down their midlines. The results obtained from the interiors were identical to those obtained from the outer surfaces.

#### Conclusion:

The vinyl stretch was not observed in these experiments, probably owing to very low native concentration of vinyl groups. This does not entirely rule against Raman spectroscopy as a diagnostic. It is possible that the use of a multisampling technique, such as waveguided Raman, would allow for the detection of low concentrations of vinyl groups. Another possibility, given that the vinyl group is optically absorbing, is the application of resonance Raman spectroscopy. However, this suffers from two major drawbacks: first, the technique is nontrivial; second, further complications arise from the sample heating that will be encountered when the excitation beam undergoes optical absorption by the polymer matrix.

#### References:

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  2. Bower, D.I.; Maddams, W.F. *The Vibrational Spectroscopy of Polymers*; Cambridge University Press, Cambridge, 1989.
  3. Silverstein, R.M.; Bassler, G.C.; Morrill, T.C. *Spectrometric Identification of Organic Compounds, Fifth Edition*; John Wiley & Sons, Inc., New York, 1991.

Figures

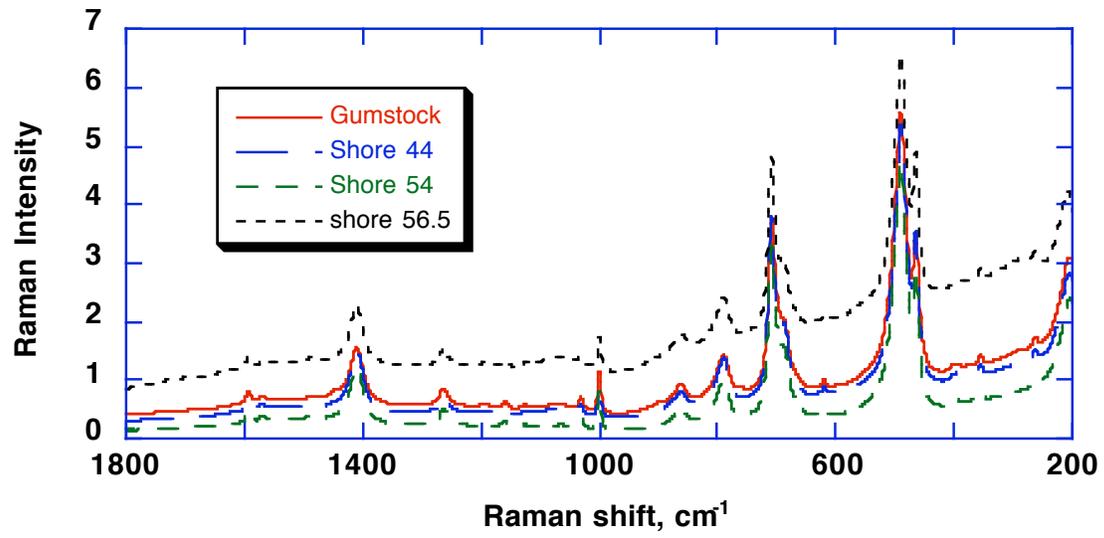


Figure 1

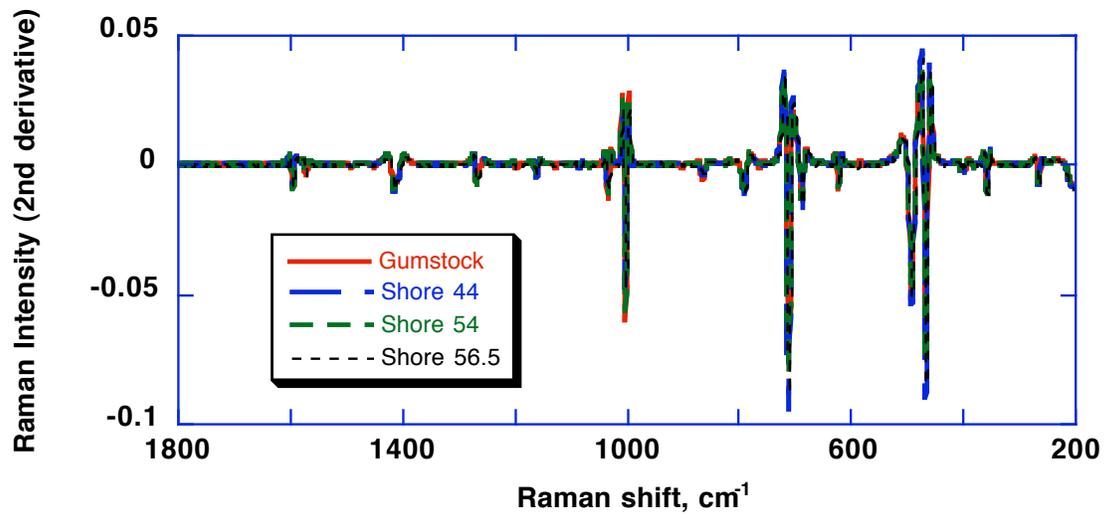


Figure 2

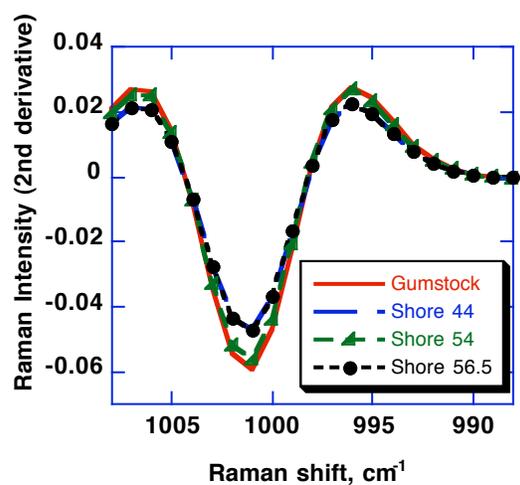


Figure 3a

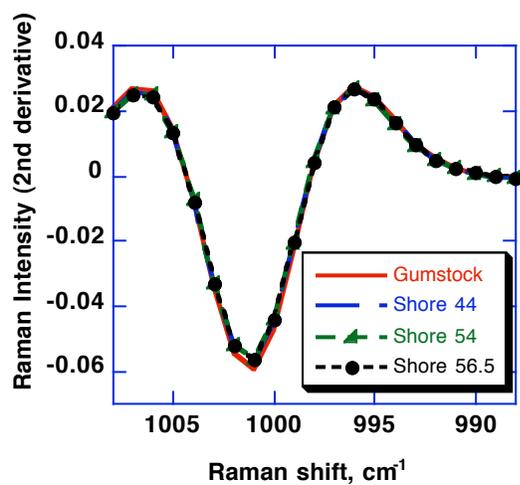


Figure 3b

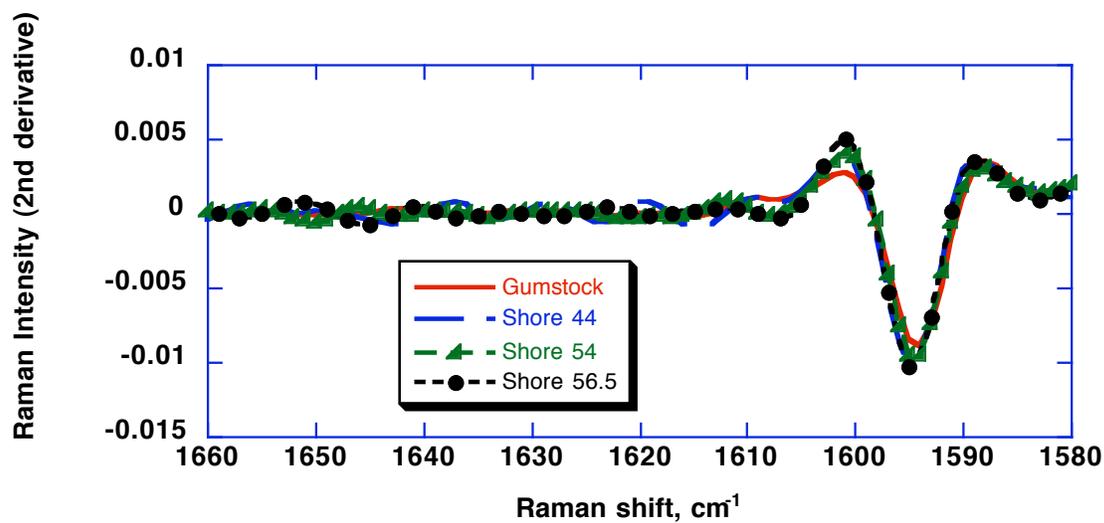


Figure 4