Cure Monitoring of Hydrosilation-curable Silicones by Fluorescence Spectroscopy

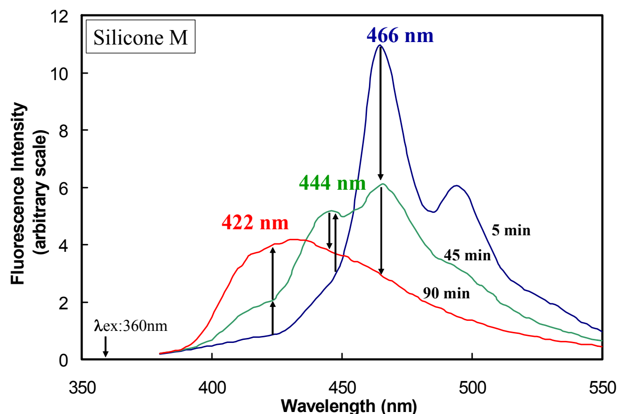
Yasuhiro Hotta[1,2], Koichi Komatsu[1,3], Francis W. Wang[1]
[1]National Institute of Standards and Technology, Gaithersburg, MD, USA
[2] Showa University, School of Dentistry, Tokyo, Japan
[3]Nihon University, School of Dentistry at Matsudo, Matsudo, Chiba, Japan

Statement of Purpose: Cure monitoring of hydrosilation is needed to control the fabrication of medical devices from hydrosilation-curable silicones. The fluorescence spectrum of a probe with one or more unsaturated bonds in its chromophore changes when the probe reacts with a hydrosilating agent. If the probe's hydrosilation rate is comparable to that for a hydrosilation-curable silicone, the cure of the silicone can be monitored by measuring the change in the fluorescence spectrum of the probe. However, there has been no report on cure monitoring of hydrosilation by fluorescence spectroscopy. The purpose of this study was to evaluate a fluorescent probe for cure monitoring of hydrosilation-curable silicones. A fluorescent probe [9,10-bis-(phenylethynyl)anthracene, BPEA] was dissolved in a hydrosilation-curable silicone, and the change in the fluorescence spectrum of the probe was measured during the cure of the silicone. The change in the elastic modulus of the silicone was also measured and compared with the change in the fluorescence spectrum.

Methods: The hydrosilation-curable silicone consisted of vinyl terminated polydimethylsiloxane as the base silicone (74.9 %, all compositions are given in mass fraction), methylhydrosiloxane-dimethylsiloxane co-polymer (25.0 %, 2000 g/mol in relative molecular mass), and 1,3-divinyltetramethyldisiloxane (0.1 %) as the inhibitor. (All silicon-containing chemicals were from Gelest, Inc., Tullytown, PA.) The catalyst consisted of the same base silicone (99.7 %), the same base silicone containing 3.5 % of a platinum catalyst (0.3 %), and a trace amount of the fluorescent probe BPEA. Three base silicones (9400, 28000, and 49500 in relative molecular mass; Silicones L, M, and H) were investigated. The hydrosilation-curable silicone and the catalyst were mixed at the mass ratio of one to one and the mixture was placed in a mold made of a silicone o-ring (10 mm in diameter,1 mm in height) sandwiched between two glass slides. Fluorescence emission spectra were taken on a spectrofluorometer (Fluorolog 2, SPEX Industries, Inc., Metuchen, NJ). During the cure of the mixture at 22 °C, the fluorescence spectrum of the probe was measured every five minutes at an excitation wavelength (λ_{ex}) of 360 nm until the spectrum ceased to change. For the elastic-modulus measurement, the mixture of the hydrosilation-curable silicone and the catalyst was placed on the stage of a rheometer (CSR-10, BOHLIN Instruments Inc., Cranbury, NJ) operated in the oscillatory mode, and in the cone-and-plate configuration with a separation of 150 µm. All experiments were carried out at 22 °C, 1 Hz and a sampling number of 250, with the use of a 40 mm-diameter, stainless steel cone having a cone angle of 4°.

Results / Discussion: Initially, the spectrum of the fluorescent probe BPEA showed two bands at 466 nm and 494 nm. As a result of the hydrosilation of the probe during the cure, the fluorescence intensities of these bands decreased. In addition, bands characteristic of the spectra of vinyl anthracene and methyl anthracene appeared at 444 nm and 422 nm. The intensity of the band at 444 nm initially increased as a result of the hydrosilation of the fluorescent probe to form vinyl anthracene moieties and then decreased as a result of the hydrosilation of the vinyl anthracene moieties. However, the intensity of the band at 422 nm increased gradually throughout the cure. Initially,

Fluorescence Spectra of BPEA at Various Cure Times



the elastic moduli changed slowly, but then increased rapidly as a result of the increase in molecular mass. The elastic moduli leveled off and reached the plateau values at the setting times of (92, 61, and 38) min for Silicones L, M, and H, respectively, with standard uncertainties (each estimated as standard deviation of the mean from five measurements) of (3, 4, and 2) min. The ratio of the fluorescence intensities at 422 nm and 466 nm increased steadily, then leveled off and reached the plateau values at the setting times of (90, 56, and 42) min for Silicones L, M, and H, respectively, with standard uncertainties of (2, 2, and 3) min, in agreement with the setting times determined from the changes in elastic moduli.

Conclusions: The change in the fluorescence spectrum of BPEA in a hydrosilation-curable silicone can be measured reproducibly and related to the change in the elastic modulus of the silicone. In particular, the setting time of the silicone can be determined from the change in the fluorescence spectrum.

#Certain commercial equipment, instruments, or materials are identified here to adequately specify experimental procedure. Such identification is not intended to imply recommendation or endorsement by NIST, nor does it imply that the materials or equipment identified are the best available for the purpose.

*Official contribution of the National Institute of Standards and Technology (NIST); not subject to copyright in the United States.