Novel Fluorescence Method for Cure Monitoring of Hydrosilation-Curable Silicones

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ABSTRACT: This study aimed to evaluate a reactive fluorescent probe, 9,10-bis-(phenylethynyl) anthracene (BPEA), for cure monitoring of hydrosilation-curable silicones. The hydrosilation-curable silicones consisted of a vinyl-terminated polydimethylsiloxane prepolymer, a methylhydrosiloxane-dimethylsiloxane copolymer, and an inhibitor, 1,3-divinyltetramethyldisiloxane. The hydrosilation reaction was catalyzed with the solution of a platinum catalyst in the prepolymer. The catalyst solution also contained a trace amount of the reactive fluorescent probe. Three hydrosilation-curable silicones, with the prepolymer of varying molar mass, were investigated. Each of the hydrosilation-curable silicones was mixed with the catalyst solution at the mass ratio of 1 : 1 to initiate the cure. During the cure of each mixture at 22°C, the elastic modulus of the mixture and the fluorescence spectrum of the probe at the excitation wavelength of 360 nm were measured. Initially, the elastic modulus changed slowly, but then increased rapidly as a result of the increase in molar mass. The elastic modulus leveled off and reached a plateau value at the setting time. The ratio of the fluorescence intensities at 422 and 466 nm increased steadily, and then leveled off and reached a plateau value at the setting time, in agreement with the setting time determined from the change in elastic modulus. The reactive fluorescent probe, BPEA, can therefore be used for nondestructive fluorescence monitoring of hydrosilation-curable silicones. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2441–2444, 2009

Key words: curing of polymers; dental polymers; fluorescence; modulus; silicones

INTRODUCTION

In the manufacture of a variety of products, such as polymer matrix composites and vinyl polymers, as well as in the applications of dental or medical resins, the cure or polymerization reactions of polymerizing materials must be adequately monitored and controlled to produce the desirable products. Fluorescence techniques are particularly useful for cure monitoring because they are sensitive and adaptable to nondestructive, inline, real-time monitoring. Although Oster and Nishijima[1] described a viscosity-sensitive fluorophore as early as 1956, which is sensitive to the change in local viscosity or mobility, it was not until a quarter century later that Loutfy[2–4] reported the application of viscosity-sensitive fluorophores to cure monitoring of methyl methacrylate. Since then, various viscosity-sensitive fluorophores have been applied to cure monitoring. For example, Wang et al.[5] used an excimer-forming fluorophore to monitor the polymerization of methyl methacrylate. Wang et al.[6] monitored the cure of an epoxy resin by measuring the ratio of the fluorescence intensities of two fluorophores, a viscosity-sensitive probe and a viscosity-insensitive internal standard. Scarlata and Ors[7] disclosed a method to determine the extent of cure by measuring the change in the fluorescence anisotropy of a fluorophore in a polymerizing material. With the use of a viscosity-sensitive fluorophore, similar to that described by Grabowski et al.,[8] Lin and Wang,[9] Wang et al.,[10,11] and Komatsu and Wang[12] applied a wavelength-shift method to cure monitoring of epoxy resins, methyl methacrylate, and a photocured dental resin, by measuring the change in the peak fluorescence wavelength of the fluorophore. In a similar method, Song and Sung[13] measured the room-temperature phosphorescence of an aromatic diamine to monitor the cure of an epoxy resin. Itagaki et al.[14] reviewed earlier applications of viscosity-sensitive fluorophores to cure monitoring of epoxy resins and vinyl monomers. More recently,

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Strehmel et al.[15] gave a review of the applications of fluorescence cure monitoring and described fluorescence cure monitoring of photoinduced radical and cationic crosslinking.

In the examples cited earlier, a variety of viscosity-sensitive fluorescent probes were successfully used for cure monitoring of epoxy resins and methacrylic resins. However, viscosity-sensitive fluorescent probes become less sensitive to the polymerization of a prepolymer resin as the molar mass of the prepolymer becomes higher, because further increase in the molar mass of the resin has only a small effect on the resin's local viscosity, which affects the fluorescence properties of the viscosity-sensitive fluorescent probes. Therefore, a different approach is needed for cure monitoring of prepolymers of higher molar masses, such as prepolymers for polyurethanes and hydrosilation-curable silicones.

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 hydrosilation rate of the probe is comparable with the hydrosilation rate of 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 found 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.

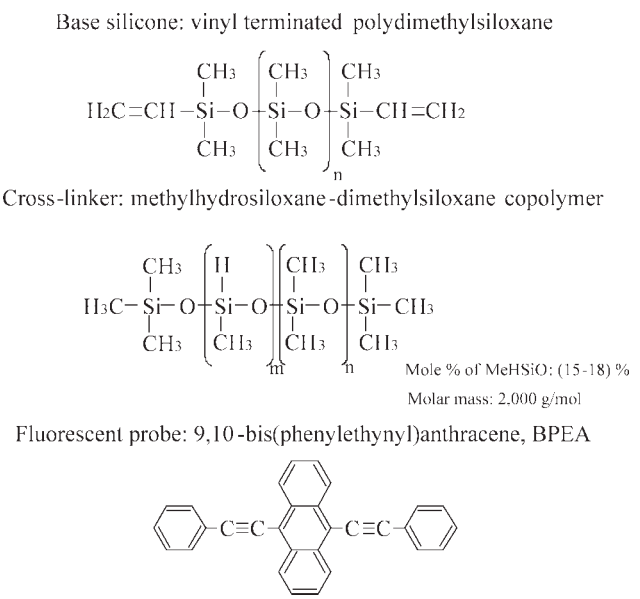

Figure 1 Chemical structures of base silicone, crosslinker, and fluorescent probe.

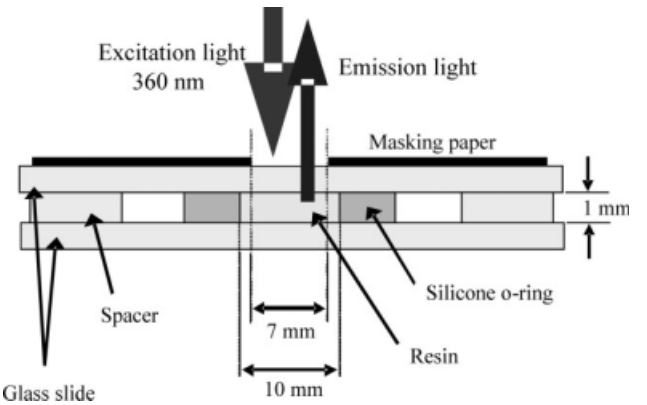

Figure 2 Specimen holder for measuring fluorescence spectrum.

EXPERIMENTAL

Figure 1 gives the chemical structures of the base silicone, the crosslinker, and the fluorescent probe that were used in this investigation. The hydrosilation-curable silicone consisted of vinyl-terminated polydimethylsiloxane as the base silicone (74.9%, all compositions are given in mass fraction), methylhydrosiloxane-dimethylsiloxane copolymer as the crosslinker (25.0%, 2000 g/mol in molar mass), and 1,3-divinyltetramethyldisiloxane (0.1%) as the inhibitor (all silicon-containing chemicals were obtained from Gelest, Tullytown, PA). The catalyst consisted of the same base silicone (99.7%), 3.5% of a platinum-divinyltetramethyldisiloxane complex in the same base silicone (0.3%), and a trace amount of the fluorescent probe BPEA. Three base silicones (9400,

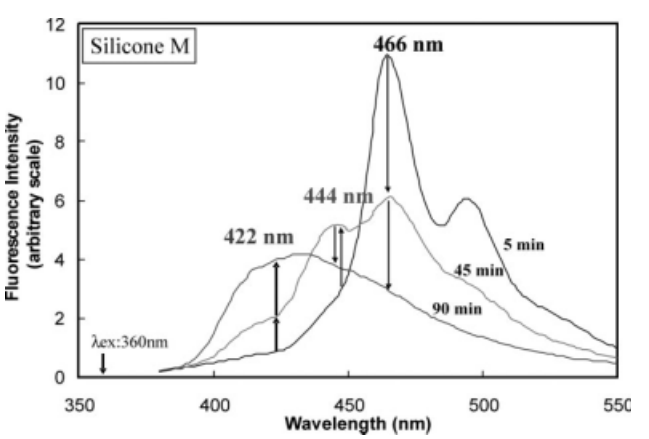

Figure 3 Fluorescence spectra of BPEA at various cure times.

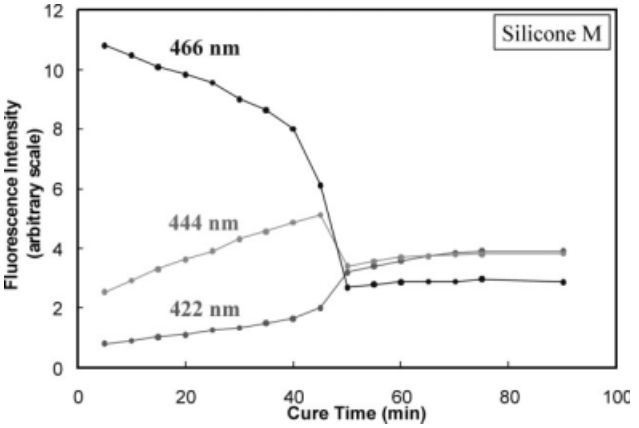

Figure 4 Changes in peak fluorescence intensities of BPEA during cure for mixture containing Silicone M.

28,000, and 49,500 g/mol in molar mass; hereafter referred to as Silicones L, M, and H, respectively) were investigated. The hydrosilation-curable silicone and the catalyst were mixed at the mass ratio of 1 : 1 and the mixture was placed in a mold (schematically shown in Fig. 2), which was made of a silicone o-ring (10 mm in diameter and 1 mm in height) sandwiched between two glass slides. Fluorescence emission spectra were taken on a spectrofluorometer (Fluorolog 2, SPEX Industries, Metuchen, NJ). During the cure of the mixture at 22°C, the fluorescence spectrum of the probe was measured every 5 min 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, 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°.

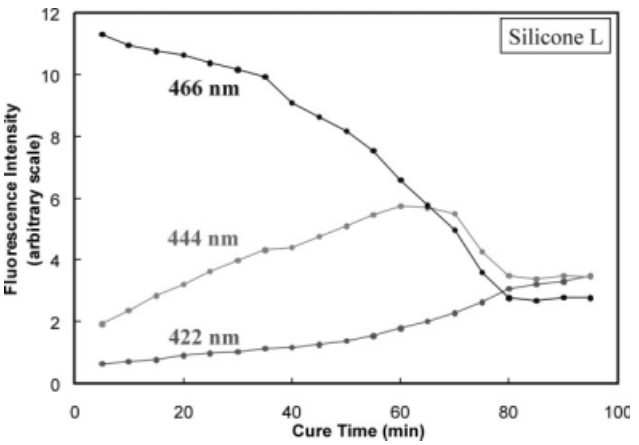

Figure 5 Changes in peak fluorescence intensities of BPEA during cure for mixture containing Silicone L.

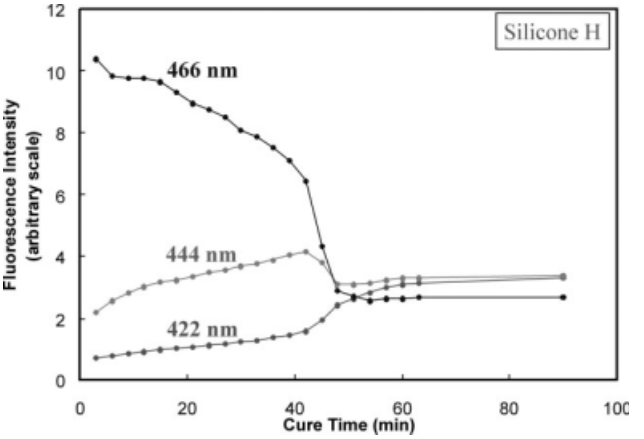

Figure 6 Changes in peak fluorescence intensities of BPEA during cure for mixture containing Silicone H.

RESULTS AND DISCUSSION

Figure 3 shows the fluorescence spectra of BPEA (5, 45, and 90 min), after the hydrosilation-curable silicone (containing Silicone M) and the catalyst were mixed. At 5 min, the spectrum of the fluorescent probe BPEA showed two bands at 466 and 494 nm. At 45 min, as a result of the hydrosilation of the probe during the cure, the fluorescence intensities of these two bands decreased. In addition, bands characteristic of the spectra of vinyl anthracene and methyl anthracene appeared at 444 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 shown in the spectrum at 90 min, 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.

Figures 4–6 show the changes in peak fluorescence intensities of BPEA at 422, 444, and 466 nm for the

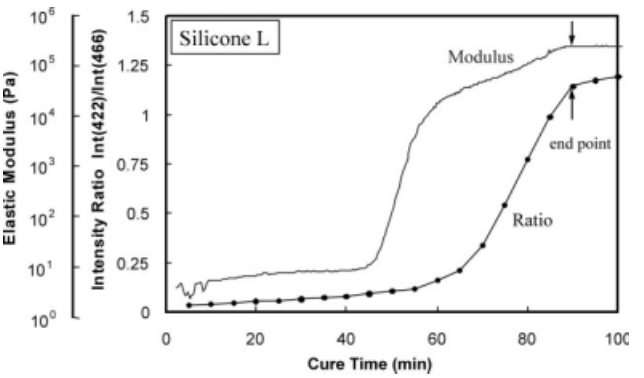

Figure 7 Changes in elastic modulus and fluorescence intensity ratio during cure for mixture containing Silicone L.

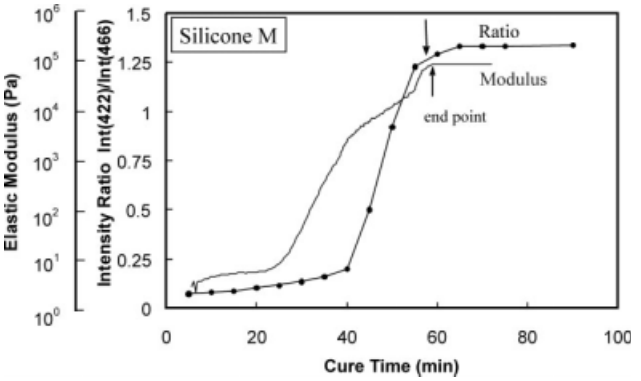

Figure 8 Changes in elastic modulus and fluorescence intensity ratio during cure for mixture containing Silicone M.

mixtures containing Silicones M, L, and H, respectively, during the cure of the mixtures. In Figure 4 for BPEA in the mixture containing Silicone M, the intensity of the band at 466 nm decreased monotonically and then reached a plateau value. Initially, the intensity of the band at 444 nm increased monotonically, then decreased at the cure time of $\sim$ 46 min, and then reached a plateau value. The intensity of the band at 422 nm increased monotonically and then reached a plateau value. Similar changes in peak fluorescence intensities at 422, 444, and 466 nm are shown in Figures 5 and 6 for BPEA in the mixtures containing Silicones L and H, respectively.

Figures 7–9 show the changes in elastic moduli and the ratios of the fluorescence intensities at 422 and 466 nm for the mixtures containing Silicones L, M, and H, respectively, during the cure of the mixtures. Initially, the elastic moduli changed slowly, but then increased rapidly as a result of the increase in molar mass. The elastic moduli leveled off and reached the plateau values at the setting times of 92, 61, and 38 min for the mixtures containing 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.

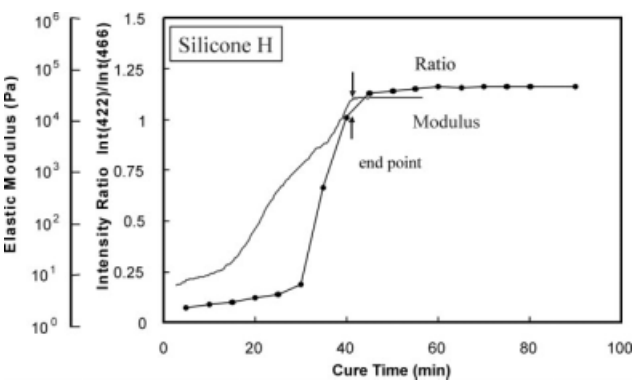

Figure 9 Changes in elastic modulus and fluorescence intensity ratio during cure for mixture containing Silicone H.

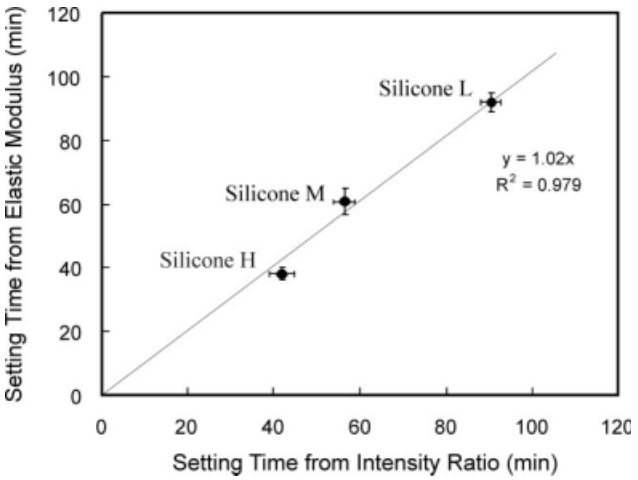

Figure 10 Setting times of mixtures containing Silicones L, M, and H.

The ratio of the fluorescence intensities at 422 and 466 nm increased steadily, and then leveled off and reached the plateau values at the setting times of 90, 56, and 42 min for the mixtures containing 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. Figure 10 shows that, for the mixtures containing Silicones L, M, and H, the setting times that were determined by measuring the ratios of fluorescence intensities at 422 and 466 nm agreed well with those determined by measuring elastic moduli, with a correlation coefficient of 0.98. In summary, the change in the fluorescence spectrum of BPEA in a hydrosilation-curable silicone can be measured nondestructively 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.

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