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Visible light-activated hydrosilation reaction

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ABSTRACT

The synthesis of silicon compounds is usually performed by vulcanization at high temperatures in the presence of a platinum catalyst. The activation can also be achieved by UV light irradiation. When a suitable sensitizer is added to the formulation, the reaction can be triggered by lower wavelengths (in the visible spectra). In this way, both energy saving and greater safety are carried out. In the present paper, the reactivity of the trimethyl(methylcyclopentadienyl)-platinum(IV) catalyst (Me-Cp)Pt(Me)$_3$ was investigated under visible light activation (380–515 nm) in the presence of different amount of 2-chlorothioxanthen-9-one (CTX) sensitizer. A proceeding of the curing after the irradiation was also observed leading to the formation of thick samples after short period of irradiation. The properties of the cured material were compared to those obtained by UV light activation.

1. Introduction

The vulcanization by using platinum catalyst progressively became the method of choice for synthesizing organofunctional silicon compounds. This method is known as hydrosilation reaction and is still used in silicone industry to form crosslinked silicone polymers. This reaction usually occurs by thermal activation which requires high energy consumption. Recent works demonstrated that some platinum catalysts can also be activated by UV light.

Several platinum compounds such as platinum acetyl acetonate are known to be efficient catalysts for the hydrosilation reaction and have been used extensively [1–4]. However, some cyclopentadienyl platinum complexes such as cyclopentadienyl trialkylplatinum (named in the following CpPt(CH$_3$)$_3$) have been used much less extensively as their effective properties as catalyst were discovered later on [5,6]. These complexes have been also employed as catalyst of the hydrosilation reaction in light-curable silicone elastomer compounds for applications such as dental imprints, adhesives as well as light emitting devices (LEDs) using silicon-based encapsulants [7].

Visible light radiation curing requires less energy than does either ultraviolet curing or thermal curing and provides greater safety than does the use of ultraviolet radiations. It results therefore an efficient and more advantageous way to induce the hydrosilation reaction [8].

Sensitizers can optionally be included in the formulation to both: increase the overall rate of the curing process at a given wavelength of initiating radiation (as in the UV region for example) and/or shift the optimum effective wavelength of the initiating radiation to longer values (in the visible region for example) [7]. Indeed, a sensitizer is capable of transferring energy to the platinum complex such that the hydrosilation reaction is initiated upon exposure to actinic radiations (light having a wavelength between 200 and 800 nm). This compound must have a triplet energy level of at least 31 kcal/mole and must not inhibit the hydrosilation reaction [8].

The most common sensitizers used are 2-chlorothioxanthen-9-one (CTX), 9,10-dimethylanthracene, 9,10-dichloroanthracene and camphorquinone. The main disadvantage of the last one is the air inhibition and is therefore not usually used for the hydrosilation reaction which does not require inert atmosphere. It results moreover from the literature [8] that the CTX is the most effective sensitizer with a gel enhancement 4 times faster. The amount should be otherwise at least 100 ppm and no greater than 5000 ppm [7,9].

In this paper, the visible light-activated hydrosilation reaction was investigated evaluating the influence of the sensitizer concentration on the photocuring process. The presence of a dark-curing, that is the proceeding of the curing after irradiation, as previously observed under UV light activation [3,4] was also

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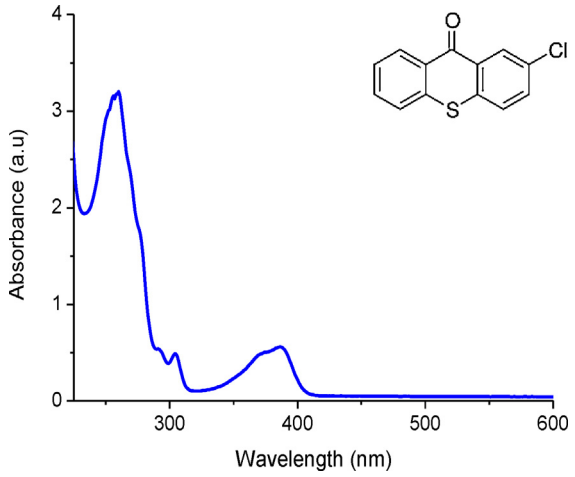

Fig. 1. UV–vis absorption spectrum of the CTX in 1,3-dioxolane as a solvent.

evaluated. The properties of the cured material were then compared to those obtained for the curing under UV-light activation with the same platinum catalyst.

2. Experimental

2.1. Materials

The following materials were purchased from ABCR (Karlsruhe, Germany) and employed as received: polydimethylsiloxane vinyldimethylsiloxane terminated (PDMS-V, Mw 800 g mol^{-1}, vinyl-eq/kg 2.4–2.9, purity 95%), polymethylhydrosiloxane trimethylsiloxy terminated (MH-PDMS, Mw 2250 g mol^{-1}, SiH equivalent 64, purity 100%), and the catalyst trimethyl(methylcyclopentadienyl)-platinum(IV) (Mw 319 g mol^{-1}, purity 99%) named in the following (Me-Cp)Pt(Me)$_3$. The sensitizer (CTX) 2-chlorothioxanthen-9-one (Mw 246 g mol^{-1}, purity 98%) and the 1,3-dioxolane (Mw 74 g mol^{-1}, purity 99%) were purchased from Sigma–Aldrich and employed as received.

2.2. Sample preparation

The mixture was prepared by adding an equimolar amount of vinyl and silane reactive groups within the formulation. The platinum catalyst and the sensitizer were first solved in 1,3-dioxolane to increase their solubility and then added in the formulations. The concentration of the platinum catalyst was kept fixed at 2.4%, while different amounts of the sensitizer were added in the solvent so that the final quantity within the silicone formulation was varied between 500 and 4000 ppm.

2.3. Characterization

The visible activated hydrosilation reaction was reached by means of a visible light emitting diode (an Astralis 5 gun lamp from Ivoclar Vivadent) with an intensity of approximatively 500 mW cm^{-2} and a wavelength range between 380 and 515 nm.

UV–vis spectra were performed using a UV–vis spectrophotometer ATI Unicam UV2.

The kinetics of polymerization were determined by FTIR spectroscopy employing a Thermo-Nicolet 5700 FTIR device. The decrease of the peak area centered at 2160 cm^{-1}, characteristic of the silane bond, was followed during the irradiation in real-time. The formulations were coated on silicon wafer with a thickness of 50 μm. The photopolymerization was induced using the visible light emitting diode described previously.

Thermogravimetric analyses (TGA) were performed with a TGA/SDTA 851 instrument (Mettler Toledo, Switzerland) between 20 °C and 800 °C in air at a heating rate of 10 °C min^{-1}.

Dynamic mechanical thermal analyses (DMTA) were performed with a Triton Technology (Mettler Toledo) instrument, at a frequency of 1 Hz in the tensile configuration. The samples prepared for these analyses had a thickness of 5 mm and dimensions of 100 × 50 mm^2.

3. Results and discussion

Visible light induced hydrosilation was investigated for formulations containing a fixed amount of (Me-Cp)Pt(Me)$_3$ catalyst and different amounts of sensitizer in order to evaluate the influence of the latter on the curing rate. The sensitizer, 2-chlorothioxanthen-9-one (CTX), was dissolved in 1,3-dioxolane so that the concentration of the solution was 2.4%. The UV–vis absorption spectrum was collected and reported in Fig. 1. This sensitizer shows a high absorption peak in the UV region but also a broad band in the range between 350 and 400 nm, suitable for the activation with longer wavelengths.

Different formulations containing an equimolar amount of PDMS-V and MH-PDMS and 1000 ppm of (Me-Cp)Pt(Me)$_3$ catalyst were prepared with an amount of photosensitizer ranging from

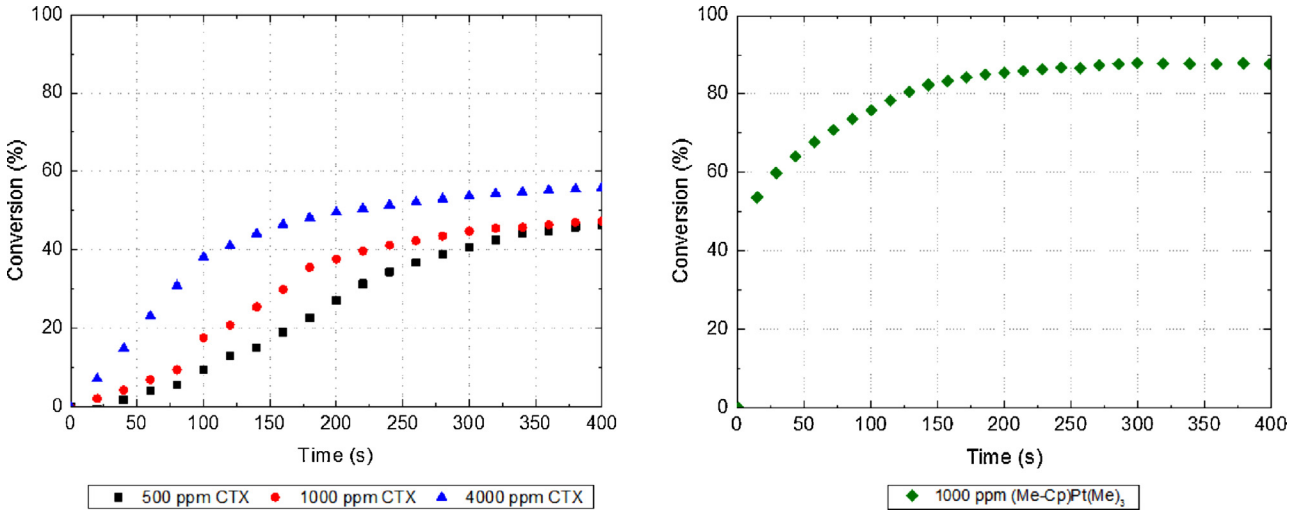

Fig. 2. Silane conversion for different amounts of CTX (1000 ppm of (Me-Cp)Pt(Me)$_3$) in visible light (left) and UV light (right) activation.