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# Ultraviolet Light Stable and Transparent Sol−Gel Methyl Siloxane Hybrid Material for UV Light-Emitting Diode (UV LED) Encapsulant

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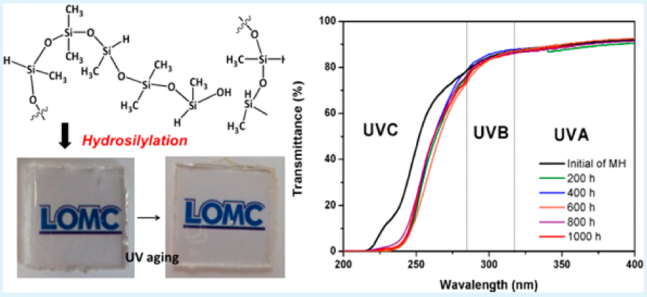
*Supporting Information*

**ABSTRACT:** An ultraviolet (UV) transparent and stable methyl-siloxane hybrid material was prepared by a facile sol−gel method. The transparency and stability of a UV-LED encapsulant is an important issue because it affects UV light extraction efficiency and long-term reliability. We introduced a novel concept for UV-LED encapsulation using a thermally curable oligosiloxane resin. The encapsulant was fabricated by a hydrosilylation of hydrogen-methyl oligosiloxane resin and vinyl-methyl siloxane resin, and showed a comparable transmittance to polydimethylsiloxane (PDMS) in the UVB (∼300 nm) region. Most remarkably, the methyl-siloxane hybrid materials exhibited long-term UV stability under light soaking in UVB (∼300 nm) for 1000 h.



**KEYWORDS:** *UV transparency, sol−gel, hybrid materials, UV LED encapsulant, methyl siloxane*

The LED (light-emitting diode) is a solid-state illumination device currently being used for lighting and display applications. Advantageous features of LED include long service lifetime, high energy efficiency, and environmentally friendly characteristics.[1−4] Although most LEDs are designed to serve as a general lighting (i.e., visible light emission), there is another class of LEDs designed to operate for nonlighting purposes. UV-LEDs, which emit ultraviolet light (wavelength of less than 400 nm) are currently being studied for extended uses such as in radiation curing, sterilization, water purification, counterfeit detection, and sensor applications in place of traditional UV lamps. For these nonconventional uses, UV-LEDs are tailored to emit different wavelength range of UV radiation, as shown in Figure 1a. UV light can be divided into UVA (320−400 nm), UVB (280−320 nm), and UVC (200−280 nm). UV-LEDs with near UV emission (i.e., UVA) are applicable to sensor, tanning, and UV curing, whereas deep UV-LEDs using UVB or UVC are studied for applications in disinfection, water purification, and sterilization.[5−7]

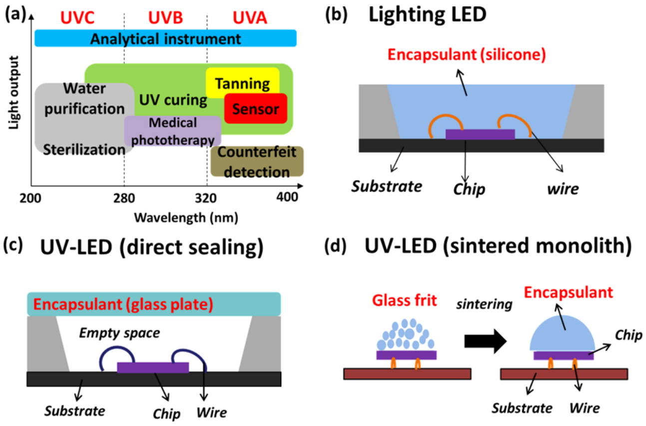


**Figure 1.** (a) Classification of UV-LED applications according to the wavelength of UV light. Schematic cross-sectional view of (b) general lighting LED using silicone encapsulant, (c) UV-LED using glass plate encapsulant, and (d) UV-LED using sintered glass monolith encapsulant.

Unexceptionally, most LEDs are packaged with an encapsulant that plays important roles in promoting the light extraction and protecting the bottom LED chip from stress sources such as mechanical damage, heat, and humidity. Solution-processable thermosetting epoxy and organo-siloxane resins are widely used as encapsulant materials for LED lighting devices.[8−12] These encapsulant resins are directly dispensed on the chip and cured to form solid encapsulant (Figure 1b). However, such conventional encapsulating materials are prone to considerable UV absorption because of the extensive organic phases and thus are not transparent to UV, making them inappropriate for UV-LED encapsulants; the UV absorbance by the organic phases becomes profoundly significant in the UVB and UVC region.[13,14]

For this reason, today's UV-LEDs are retrofitted with silica glass ($SiO_2$) as encapsulants. The silica encapsulation of UV-LEDs can be processed by either directly sealing the LED chip with a thin glass plate (Figure 1c) or forming a sintered

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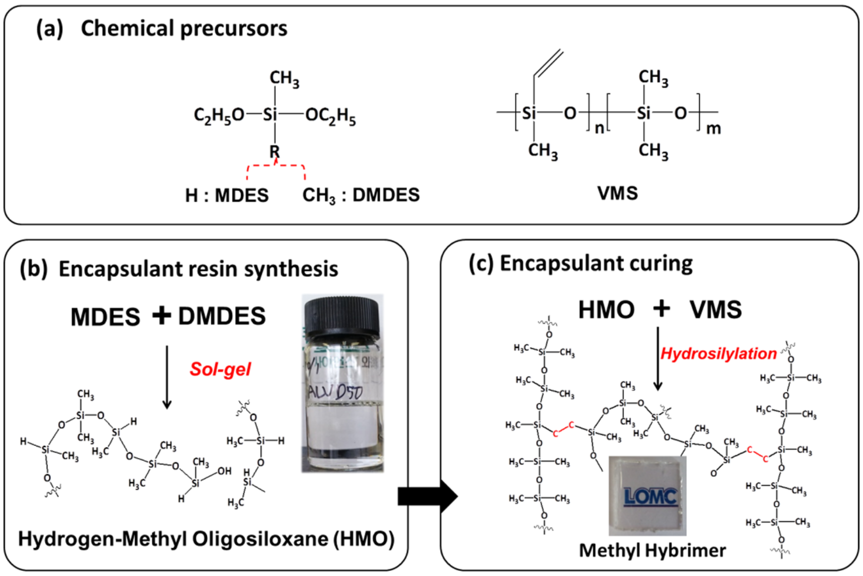

**Figure 2.** (a) Chemical structure of silane precursors and vinyl-methylsiloxane dimethylsiloxane copolymers (VMS) resin. (b) Schematic illustration of the synthesis process of hydrogen-methyl oligosiloxane (HMO) resin by sol−gel method. (c) Fabrication of a methyl siloxane hybrimer using HMO and VMS resin by thermal hydrosilylation reaction.

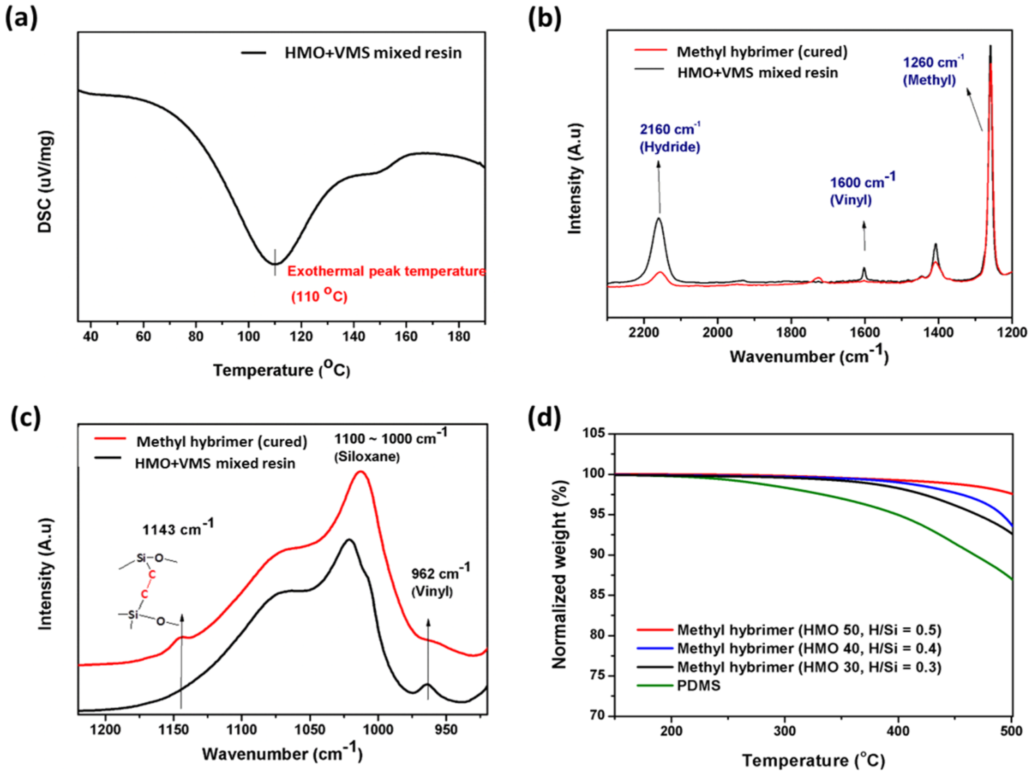

**Figure 3.** (a) DSC spectra of the HMO and VMS resin; FT-IR spectra of mixed resin of HMO and VMS (prepolymer) and the corresponding cured methyl hybrimer: (b) 2300−1200 $cm^{-1}$ and (c) 1230−870 $cm^{-1}$; (d) TGA spectra of the PDMS and methyl hybrimer bulk according to the HMO composition in nitrogen.

monolithic silica from glass frits (Figure 1d). Although silica glasses offer excellent UV transparency and gas barrier performance, the encapsulation using silica glass have several drawbacks such as limited light extraction, which is due to the existence of chip/void interface and chip damage from the high-temperature sintering process.[15,16] Therefore, it is highly desirable to develop UV-LED encapsulant materials that can meet the requirements of high UV transparency/stability and low-temperature solution processability.

Herein, we report on a novel sol−gel-derived organo-siloxane hybrid material exhibiting high UVB transparency and a long-term UVB stability, and demonstrate its potential as an encapsulant for UV-LEDs. From molecular structural perspective, our hybrid encanpsulant features only methyl groups in its backbone siloxane chains and short hydrosilylation-derived

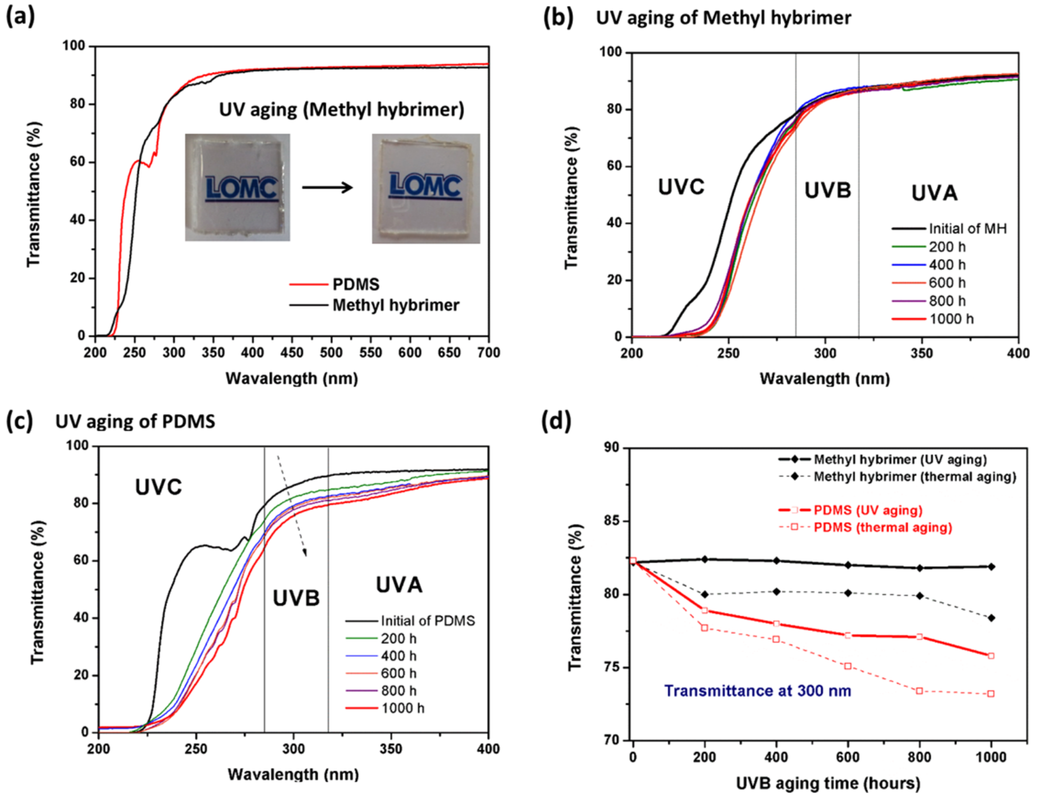

**Figure 4.** (a) Initial transmittance spectra and photographs (before/after UVB aging for 1000 h) of the methyl hybrimer and PDMS bulk. Transmittance spectra changes of the (b) methyl hybrimer and (C) PDMS bulk according to the UVB aging time. (d) Transmittance (at 300 nm) changes of methyl hybrimer and PDMS bulk during thermal aging at 200 °C and light soaking under UVB source.

cross-link chains, both of which contribute to the high UV transparency and stability; hereinafter, the material is denoted "methyl hybrimer". As shown in Figure 2, the methyl hybrimer is fabricated by hydrosilylation-curing of a resin blend consisting of sol−gel derived hydrogen-methyl oligosiloxane (HMO) and vinyl-methyl siloxane (VMS). The molecular structures of the precursor chemicals and the synthesized resin are displayed in Figure 2a and 2b, and detailed experimental procedure of synthesis, fabrication and characterization of the resin and hybrimer can be found in the Supporting Information. We discuss the molecular structure of the resin using $^{29}$Si NMR (nuclear magnetic resonance), FT-IR (Fourier transform-infrared) and MALDI-TOF (matrix assisted laser desorption/ionization-Time of Flight) spectrometry. Successful hydrosilylation curing was confirmed by DSC (differential scanning calorimeter) and TGA (thermal gravimetric analysis). Also, the high UV transparency and stability of the cured methyl hybrimer were confirmed by UV/vis spectrophotometer and UV-tester under UVB region.

The HMO resin was synthesized by an acid-catalyzed hydrolytic sol−gel reaction of methyl-diethoxysilane (MDES) and dimethyl-diethoxysilane (DMDES), resulting in clear viscous resin as shown in Figure 2b. Molecular structure analyses of HMO using $^{29}$Si NMR and FT-IR revealed that HMO is a linear oligosiloxane with hydrogen (-H) and methyl ($-CH_3$) pendants (Figure S1 in the Supporting Information). For UV transparency and stability of the silicone-based encapsulant, it is important to form a fully condensed siloxane structure with minimized unreacted alkoxy or silanol groups, which can be a source of UV absorbing radicals or chromatic sites. The HMO resin has highly condensed siloxane bonds with little unreacted alkoxy or hydroxyl groups because of the low steric hindrance of hydrogen and methyl groups, as evidenced by the high siloxane condensation degree (95%) determined from the $^{29}$Si NMR (Figure S1b in the Supporting Information).[17−19] Molecular weight of the HMO was characterized to be 500−900 g/mol from MALDI-TOF characterization, confirming the HMO's linear oligosiloxane structure (Figure S1c in the Supporting Information).

As shown in Figure 2c, the methyl hybrimer bulk for the solid encapsulant was fabricated via Pt (Platinum)-catalyzed hydrosilylation reaction of HMO and VMS. The hydrosilylation curing, a typical addition polymerization of vinyl and hydrogen groups, has advantages in achieving high optical transparency and stability due to the inhibited formation of byproducts or radicals.[20−23] However, Pt catalyst residues that may remain in the final cured product can act as free radical receptors, which are active sites for UV absorption. Thus, in such hydrosilylation curing, it is essential to minimize the residual Pt catalyst content to achieve high UV transparency.[24] In the hydrosilylation curing of methyl hybrimer, the optimal Pt catalyst content was determined to be 5 ppm (Figure S2 in the Supporting Information).

The hydrosilylation curing behavior of HMO and VMS was monitored by a DSC analysis (Figure 3a). There is an exothermic bands (peak temperature = 110 °C) showing a cross-linking reaction of the mixed blends. The end temperature of hydrosilylation reaction was around 160 °C, thus the blends are fully curable at 170 °C. As a result of low spatial hindrance of methyl groups and the multitude of hydrogen groups, effective curing is possible with 5 ppm of Pt catalyst.

We can confirm the curing of HMO and VMS and resultant cross-linked structure by analyzing FT-IR spectra (Figure 3) and $^{13}C$ NMR spectra (Figure S3 in the Supporting Information). After thermal hydrosilylation curing, the intensity of the vinyl (1600 and 962 $cm^{-1}$) and hydrogen (2160 $cm^{-1}$) groups is reduced as a result of cross-linking between them, while bands assigned to Si−C−C-Si (1143 $cm^{-1}$) linkage derived from hydrosilylation of vinyl and hydrogen groups were newly formed.[25] The degree of conversion of vinyl and hydrogen of the HMO resin was calculated from the FT-IR spectra, which were 97% and 78%, respectively. The introduction of a high amount of hydride (Si−H) groups not only increases the reactivity of the precursor resin but also increases cross-linked bonds in the solid bulk.

The thermal decomposition behavior of the methyl hybrimer were also confirmed by TGA as shown in Figure 3d. As a reference for comparison, we also examined hydrosilylation-derived PDMS using commercial silicone resin (Dow Corning Sylgard 184), which are known to be transparent and stable toward UV radiation.[26,27] The composition of HMO are varied to study relationship between cross-linking density and thermal decomposition of methyl hybrimer (Table S1 in the Supporting Information). The optimized molar ratio of hydrogen to methyl was 1:3 (HMO50, H/Si = 0.5), because an increased hydride functional groups impose densely cross-linked structure of the methyl hybrimer, and thereby resulting a highest thermal decomposition temperature among various HMO compositions and PDMS. The optimized methyl hybrimer using HMO 50 starts to decompose over 350 °C, and the onset temperature increases as hydrogen content increases. In comparison, the PDMS thermally degrades at a much lower temperature (250 °C), because it contains a low amount of hydrogen groups and has a low cross-linking point. For methyl hybrimers, as the amount of hydrogen groups and carbon cross-links ($CH_2$−$CH_2$) increases, the 5 wt % decomposition temperature increases up to 490 °C. The high cross-linking density of organic groups, as well as high condensation of inorganic siloxane bonds increases thermal stability of the materials.[28] Thus, we fabricated the methyl hybrimer using HMO 50 resin, in order to have highest cross-linking density expecting improved UV stability compared to conventional silicone-based encapsulant.

Figure 4a provides an initial UV/vis transmittance curve of the methyl hybrimer and PDMS bulk. The light extraction of the UV-LED is enhanced by an encapsulant having high transparency at the wavelengths of the emitted light. Thus, the encapsulants used for UV-LED must also be evaluated for their ability to maintain optical transparency through extended periods of UV light exposure. The UV/vis curve clearly shows the high transmittance of the methyl hybrimer in the UV region, which is comparable to that of general methyl-siloxane polymer (PDMS). For the two bulk samples fabricated by the same curing condition, the methyl hybrimer has a similar average transmittance at wavelengths over 270 nm, and a lower transmittance under 260 nm (UVC region) compared to the PDMS. The transmittance value at UVC (<280 nm) rapidly decreased because of the increased light energy and unavoidable UV absorption by organic groups. As shown in Figure 4b, c, optical degradation caused by long-term UV irradiation was analyzed by tracing the transmittance spectra during exposure of UVB light (280−320 nm) with an intensity of 10 mW/$cm^2$. As a result of light soaking, the transmittance curves of the PDMS are shifted down and to the right, moving the spectra further into the visible part. Thus, the UV transparency in the UVA, UVB, and UVC region decreases to about 80% from the initial value after 100 h of aging time, indicating the organic phases are easily degraded by UV absorption. However, the methyl hybrimer maintained its initial transmittance (83%) and lost its transparency only at the deep UV region under 280 nm. Also, there was no indication of cracks or shrinkage during UV light soaking, which can be generated by the UV energy induced chains scission of organic groups.

Figure 4d clearly present the UVB transmittance value changes according to the UV and thermal aging time. The transmittance curves during thermal aging (200 °C) were also traced to verify thermal resistance against optical degradation (Figure S5 in the Supporting Information). It is important to increase long-term thermal resistance of the encapsulant, because heat is consistently generated during operation of a high performance UV-LED. The organic groups are susceptible to thermal degradation, and thereby resulting in a rapid decrease of transmittance from 230 to 400 nm. The PDMS has advantages on initial deep UV transparency because of its large free volume, homogeneous and long siloxane backbone with high molecular weight, however the low cross-linking density has adverse effects on UV and thermal stability. However, the methyl hybrimer shows little decrease of transmittance in all UV regions, indicating the highly cross-linked organo-siloxane has benefits on thermal stability of organic groups. Environmental factors such as free volume restriction and strong cross-linked carbon linkages around the methyl groups lead to an inhibition of UV and thermal degradation of methyl groups. As noted earlier, the unreacted vinyl and hydrogen groups, methyl groups, and remained catalysts act as extrinsic chromophores, which absorb UV light to form radicals. Then, they react with oxygen to form UV induced products, such as peroxy radicals and hydroperoxides, which consistently absorb UV light and lead to a decrease in transparency.[24,29,30] However, the vinyl and hydrogen groups in methyl hybrimer are highly cross-linked and methyl groups are caged by a densely condensed and cross-linked siloxane network, which inhibits the degradation of organic groups. As a result, the methyl hybrimer is more thermally and UV stable compared with polydimethylsiloxane (PDMS) because of the combined effects of decreased radical sources (Pt catalyst, unreacted organic phases), robust siloxane network, hyper-branched cross-linking, and high cross-link density of vinyl and hydrogen groups.

In summary, we report on a novel UV transparent and stable LED encapsulant using methyl hybrimer based on hydrogen-methyl oligosiloxane resin. The methyl hybrimer was fabricated by the thermal hydrosilylation reaction of hydrogen-methyl oligosiloxane resin with Pt catalyst. Most significantly, high UV transparency, up to 82% (at 300 nm), and long-term (1000 h) UV stability was achieved in the UVB region (280−320 nm), which has not been reported to the best of our knowledge for any commercial silicon based UV-LED encapsulant. The achieved UVB transparency and stability of the novel methyl hybrimer is beneficial for use in encapsulant of deep UV-LED chips. Building on these studies, further optimization of the siloxane structure or incorporation of other functional groups is needed to achieve UV transparency in deeper UV region.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The experimental details and supporting datas of the fabrication and characterization of the methyl hybrimer.This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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