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Optically Recoverable, Deep Ultraviolet (UV) Stable and Transparent Sol-Gel Fluoro Siloxane Hybrid Material for UV LED Encapsulant

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An ultraviolet (UV) transparent recoverable fluoro-siloxane hybrid material was prepared via a facile sol-gel process. The transparency and stability of a deep UV-LED encapsulant is a key factor in the light extraction efficiency and long-term reliability of a UV LED. In this study, we report a novel UV-LED encapsulation process through the thermal hydrosilylation curing of a vinyl-fluoro and hydrogen-methyl oligosiloxane resins. The fluoro-siloxane hybrimer showed high UV transparency in the deep UV (< 300 nm) region, with increased transmittance after UVB (300 nm) and UVC (250 nm) aging for 2000 hours from radical stabilization and a high cross-linking density. Specifically, vinyl radical formation and recombination during UV irradiation and their effects on deep UV transmittance were investigated. With its easy low-temperature solution processability and robust performance stability, the fluoro-siloxane hybrimer was used as a deep UV-LED packaging material to demonstrate its potential as a stable encapsulant that is also UV transparent.

Introduction

Ultraviolet light-emitting diodes (LEDs) have recently been studied for various applications such as counterfeit detection, sterilization, sensors, and water purification. Given the increasing demand for deep ultraviolet light-generating LEDs (with wavelengths of less than 300 nm), high optical transparency and stability in a certain wavelength range of UV radiation are essential for the efficiency and long lifetimes of the devices. For non-lighting purposes, UV-LEDs are designed to emit different wavelengths of light which are divided into the UVA (320-400 nm), UVB (280-320 nm), and UVC (200-280 nm) regions. In particular, deep UV-LEDs using UVC have been extensively studied for disinfection and water purification applications, requiring a high light radiation energy.[1-4]

Device performance and reliability levels are closely related to the characteristics of the encapsulant which significantly improves the light extraction capability and protects chips from stress sources such as heat, light, humidity, and mechanical damage.[5-7] Thus, the materials used for UV-LED encapsulation must be transparent under deep UV light and must maintain their initial transparency for extended periods of UV exposure. Long-term stability during operation requires UV resistance against transmittance decreases, induced by absorbed UV light energy and radical formation from organic phases.[8-10]

For this reason, silica-based glass encapsulants are widely used in current UV-LEDs providing superior deep UV transparency and resistance from their stable inorganic phases.[11,12] However, an extremely high processing temperature is needed for the encapsulation stage which involves the sintering of monolithic silica from glass frits, and consequently, the LED chip can be damaged from the heat. Compared to glass encapsulants, organo-siloxane based encapsulants offer a simple fabrication process using *in-situ* polymerization after direct application of the resin into the LED chip.[13-15] A recent issue regarding the use of siloxane encapsulants is the requirement of stability against deep-UV light, because the organic groups in siloxanes are susceptible to high UV energy induced oxidation in air. Thus far, no siloxane based encapsulants, having UVC transparency and resistance to UVC light induced degradation, have been reported. Therefore, it is highly desirable to develop stable materials that are UVC transparent which can also maintain optical transmittance during UVC irradiation.

Inorganic-organic hybrid materials (hybrimers) using sol-gel processed oligosiloxane resins provide the combined benefits of both inorganic and organic characteristics, such as optical transparency, flexibility, and thermal stability.[16-20] We investigated different hybrimers and then fabricated various optical devices with the hybrimers using a simple production process to achieve superior optical, thermal, and mechanical reliability. In our previous work, hybrimers with a high refractive index or a low refractive index were fabricated through the hydrosilylation of the vinyl and hydrogen groups in oligosiloxane resins, taking advantage of the *in-situ* curing inside the LED chip, low shrinkage and good adhesion.[6,7,13]

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†*Electronic supplementary information (ESI) available : experimental details and additional information about material characterization.*

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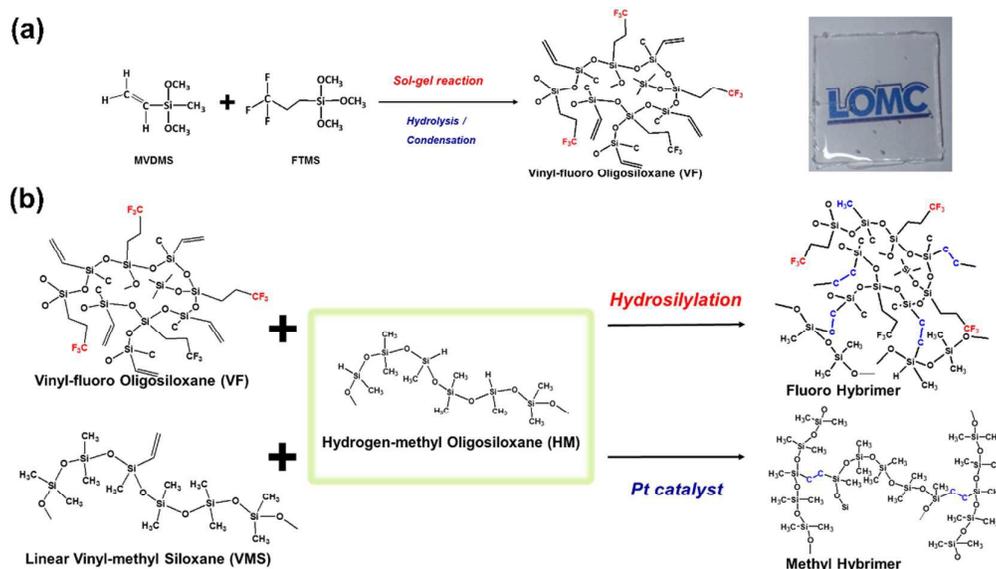
Scheme 1. (a) Illustration of the synthesis process of vinyl-fluoro oligosiloxane (VF) resin by a sol-gel reaction. (b) Fabrication of a fluoro hybrimer using vinyl-fluoro oilgosiloxane, and hydrogen-methyl oligosiloxane resins, and a methyl hybrimer using linear vinyl-methyl siloxane and hydrogen-methyl oligosiloxane resins by a thermal hydrosilylation reaction with a Pt catalyst.

Based on the above considerations, in earlier work, we reported that a sol-gel processed methyl hybrimer using a newly synthesized hydrogen-methyl oligosiloxane resin with a vinyl-methyl siloxane could be used as a UV transparent, stable LED encapsulant with UVB light resistance at 300 nm.[21] Owing to complete cross-linking, the methyl groups are caged by highly condensed siloxane bonds, inhibiting the cleavage of the methyl groups by UV light energy. However, there are still problems associated with limited deep UV stability, despite the fact, that methyl hybrimers show high UVC transmittance and UVB stability comparable to that of PDMS (polydimethylsiloxane).

Hybrimers, do nevertheless have inherent potential for use as a deep UV-LED encapsulant because the UV absorbing organic groups can be stabilized by adjusting the composition of the functional groups composition and the resulting UV irradiation induced radical formation, and oxidation phenomena. In this study, we introduce an optically recoverable fluoro-siloxane hybrid material (a fluoro hybrimer) which exhibits superior deep UV stability in the UVC region, and demonstrate its potential as an encapsulant for UV-LEDs using UVC light. The term 'optically recoverable' is used expressly to indicate that our hybrimer encapsulant exhibits increased UV transparency under practical UV radiation.

As shown in Scheme 1, we replaced the conventional linear vinyl-methyl siloxane resin with a sol-gel derived vinyl-fluoro

oligosiloxane resin to increase the vinyl functionality and to form a densely cross-linked and branched siloxane network. Due to the structural modifications, the fluoro hybrimer had a higher cross-linking density and fewer methyl groups and methyl radicals. The stabilization of UV absorbing vinyl groups led to an increase in the UVC transmittance during the long-term UV exposure of the fluoro hybrimer. Most notably, enhanced deep UV stability in the UVC (200 ~ 280 nm) region was achieved, which has never been reported to the best of our knowledge for any organo siloxane-based UV-LED encapsulant. The encapsulant based on the fluoro hybrimer can provide long-term stable UV transparency for the performance and reliability of deep UV generating LEDs.

Experimental Section

Synthesis of vinyl-fluoro oligosiloxane resin

The vinyl-fluoro oligosiloxane (VF) resin is prepared by initially reacting methylvinyldimethoxysilane (MVDMS, > 95%, TCI), 3,3,3-trifluoropropyl trimethoxysilane (FTMS, >98%, gelest) with acid-catalyzed water (0.1 N hydrochloric acid). The hydrolysis and condensation reaction was performed using a magnetic stirrer, reflux pipes, and a silicon oil bath. We mixed the MVDMS, FTMS and acid catalysed water (3 : 2 : 6 molar ratio) without any solvents at room temperature for 1 h, and then at 80°C for

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24 hours while stirring inside a 250 ml flask. The evaporation process was then performed at 100 °C for 12 hours in a N_2 gas purging condition in order to remove by-products, the solvent, and water. As a result of the hydrolysis and condensation reaction of the liquid silane monomers, a clear and viscous hybrid resin was obtained. In addition, the hydrogen-methyl (HM) oligosiloxane resin, reported in our previous research, was synthesized for a hydrosilylation reaction with the vinyl-containing resin.[21] The resins were filtered through a 0.45 μm teflon filter and vacuum-heated in order to remove impurities, residual catalysts and volatile components.

Fabrication of the fluoro hybrimer

Two synthesized resins were mixed and cast into a mold for the curing of the oligosiloxanes via catalytic hydrosilylation. The mixed resin blends were thermally cured to fabricate the fluoro hybrimer. The VF resin was mixed with a HM resin at a 1 : 1.1 equivalent molar ratio of vinyl to hydrogen groups. Then, 0.03 wt% (6 ppm) of Pt [Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution, Aldrich] was added as a catalyst to promote the thermal hydrosilylation reaction. The mixed resins were cast into a glass mold (thickness = 2 mm), then heated at 170 °C for 4 hours in air. A methyl hybrimer was also fabricated via a previously reported procedure, for a comparison with the fluoro hybrimer.[21]

Characterization of the fluoro hybrimer bulk

In order to study the degree of condensation of the VF resin, the ^{29}Si nuclear magnetic resonance (NMR) spectra of the oligosiloxane resins with Chromium acetylacetonate (concentration of 30 mg/L) in 30 vol% of chloroform-d were measured using a FT 600 MHz (Bruker Biospin, DMX600). The solid state ^{13}C and ^{29}Si NMR or the hybrimer bulk before/after UV irradiation was measured via cross polarization magic angle spinning (CP-MAS) NMR (Bruker DSX400) in order to obtain a high resolution. The Fourier transform-infrared (FT-IR) spectra (JASCO, FTIR 680 plus) of the VF resin was also measured to study the formation of siloxane bonds. Matrix assisted laser desorption ionization-time of flight (MALDI-TOF, Voyager-DE STR) measurements were taken to study the distribution of the molecular weight of the oligosiloxane resins with 2,5-dihydroxybenzoic acid as a matrix. Differential scanning calorimeter (DSC, Netzsch DSC 200 F3 Maia) was measured in air to study the thermal hydrosilylation curing behavior of the mixed oligosiloxane resins with Pt as a catalyst. A Thermal Gravimetric Analysis (TGA, TA TGA 2050) was conducted under a N_2 flow condition at a heating rate of 5 °C, to study the thermal decomposition of the hybrimers. The refractive index of the fluoro hybrimer bulk was obtained using a prism coupler (Metricon, 2010) at a wavelength of 632.8 nm. The optical transmittance of the hybrimer bulks were measured by an ultraviolet-visible-near infrared (UV/Vis/NIR) spectrophotometer (Shimadzu, UV-3101PC) with a grating to grating type double monochromater. The ultraviolet light irradiation test was performed using a UV tester (CT-UVT, Coretech) with a UV lamp power of 15 W (UVA, UVB, UVC type, Sankyo Denki), giving a power density of 10 mW/cm^{-2}. All bulks tested were placed 5 cm from the light bulb, where the temperature measured during the exposure step were in the range of 60 to 70 °C.

Results and Discussion

Synthesis and Characterization of Oligosiloxane Resin

Herein, we report on a fluoro-siloxane hybrid material (fluoro hybrimer) created via a hydrosilylation reaction of a sol-gel derived vinyl-fluoro oligosiloxane (VF) resin and a hydrogen-methyl (HM) oligosiloxane resin as shown in Scheme 1. The resins were synthesized through the hydrolytic sol-gel reaction of organo-silane precursors, which contain three alkoxy groups to form branched siloxane bonds, with the addition of acid catalyzed water for hydrolysis and condensation.

First, the alkoxy groups are hydrolyzed to form hydroxyl (-OH) groups, after which, condensation between the hydroxyl group and alkoxy group follows through a nucleophilic attack by deprotonation. As a result, covalently-linked siloxane (Si-O-Si) bonds are formed with a high degree of condensation (DOC), up to 94.2 %, shown in Fig. 1a.[22-24] The notations (D^n and T^n) in the ^{29}Si NMR spectra represent Si atoms from the MVDMS with di-alkoxy groups and FTMS with tri-alkoxy groups, for which n denotes the number of siloxane bonds attached to a Si atom. A high D^2 (-32 to -36 ppm) and T^3 (-66 to -71 ppm) species content fully condensed to have bridged siloxane bonds without any unreacted alkoxy or hydroxyl groups was clearly detected. Additionally, there were no remaining monomers (D^0 and T^0) and only a small number of partially condensed alkoxy or hydroxyl (D^1, T^1, and T^2) groups. The high degree of condensation is from the inductive effect of the electron-withdrawing fluorine groups; furthermore, there is a ladder-like siloxane structure induced by the T species. For UV transparency and stability of silicone-based materials, it is very important to form fully condensed siloxane bonds with a minimum number of unreacted groups, as they can be a source of UV absorbing radicals.

Additionally, the FT-IR spectra (Fig. 1b) show the formation of siloxane bonds with vinyl and fluoro groups after the sol-gel reaction with the silane precursors. We analyzed the molecular size and branched siloxane network of the VF using the MALDI-TOF spectra shown in Fig. 1c. It is well known that increases in the siloxane size

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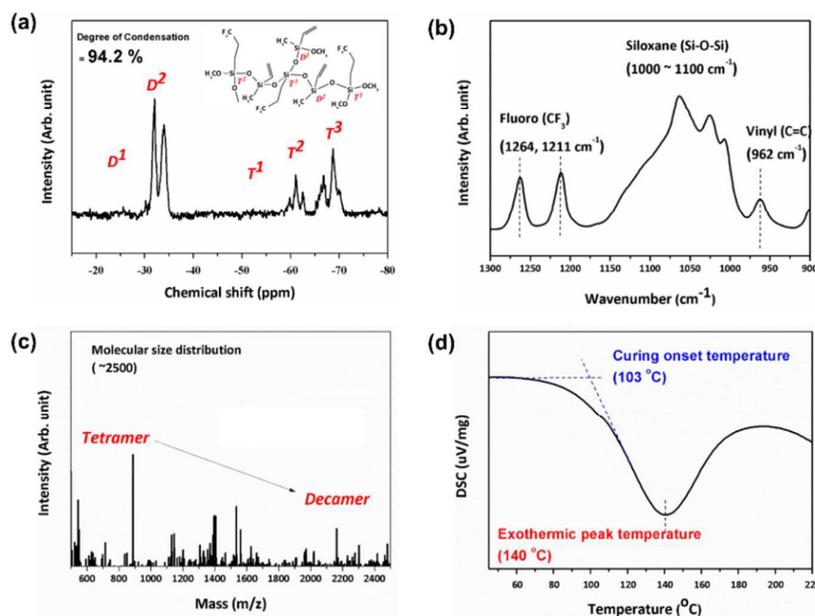
Fig. 1 (a) ^{29}Si NMR spectra (b) FT-IR spectra (c) MALDI-TOF spectra of the synthesized vinyl-fluoro oligosiloxane resin. (d) DSC spectra of the VF and HM mixed resin (prepolymer).

and number of vinyl groups are closely related to a high degree of cross-linking. The vinyl-fluoro oligosiloxane consisted of oligomers with a molecular size from tetramers to decamers (500-2500 g/mol). The empirical molecular weight of the oligomers matched the calculated molecular size assuming that the oligomers have a branched-linear structure, rather than assuming that the branched-linear siloxane chain is reduced by the presence of bulky trifluoromethyl pendants. The branched structure of the VF indicates a higher siloxane density compared to the linear structure of the methyl hybrimer in our previous study. The high molecular size and vinyl functionality of the VF helps to promote effective cross-linking and the formation of a densely linked structure of cured siloxane.

### Thermal Hydrosilylation Curing of Oligosiloxane Resin

As shown in Scheme 1b, cross-linked (polymerized) oligosiloxanes are formed through a hydrosilylation reaction with the vinyl (C=C) and silicone-hydrogen (Si-H) groups in the VF and HM, respectively. Thermal hydrosilylation reactions are promoted by highly active platinum catalysts, such as Karstedt's catalysts (Fig. S1, ESI†). Silicone-hydrogen (Si-H) bonds are added across unsaturated carbon-carbon (C=C) double bonds in the vinyl-siloxane, after which, silicone-carbon (Si-C) bonds are formed to cross-link hydrogen-siloxanes and vinyl siloxanes. C-silylation connects π-bonds in the vinyl groups and σ-bonds in the hydride

groups through π-σ rearrangement according to the Chalk-Harrod mechanism.[25-28]

As shown in Fig. 1d, the DSC spectra (onset curing temperature = 103 $^\circ$C) denote the curing behavior of the resin blends, showing an exothermic cross-linking reaction of the vinyl and silicone-hydrogen groups. According to the Pt catalyst content, we optimized the curing temperature and time for complete cross-linking. An excess amount of Pt catalyst in the cured hybrimer affects the UV transparency and stability because the catalyst strongly absorbs UV light.[29] Thus, we minimized the amount of catalyst to 6 ppm in the mixed VF and HM resins to increase the initial UV transmittance and UV resistance during long-term aging. Based on these analyses, thermal curing was effectively achieved with 6 ppm of the Pt catalyst at 170 °C in air for 4 h owing to the large number of vinyl groups.

UV Transparency of Fluoro-Siloxane Hybrid Material: Effects of the Vinyl Groups Content

To study the effects of unreacted vinyl groups and radicals on the UV transparency characteristics, the initial UV/vis transmittance curve of the fluoro hybrimer according to the –C=C (vinyl) / -H (hydrogen) content was measured, as shown in Fig. 2a. We varied the weight ratio of the VF and HM resin in the mixed blends to
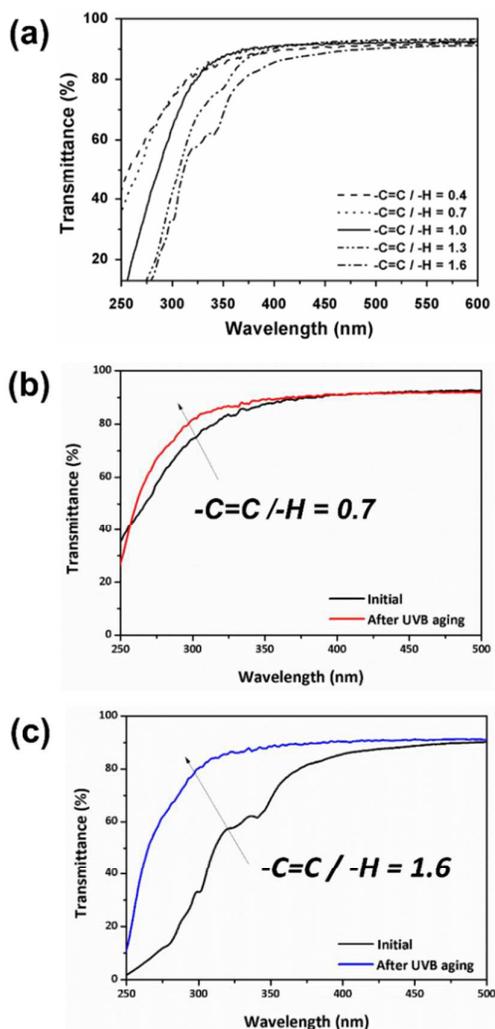
Fig. 2 (a) Initial transmittance of the fluoro hybrimer bulk according to the mixing ratio of the VF and HM resin. Transmittance spectra changes of the fluoro hybrimer, with a molar ratio of (b) –C=C(vinyl)/-H(hydrogen)=0.7 and (c) –C=C(vinyl)/-H(hydrogen)=1.6, before/after UVB aging.

change the molar ratio of the vinyl and hydride groups in the cured hybrimer. Complete cross-linking can be achieved with an equivalent molar ratio of the two reactive groups (-C=C/-H = 1); thus, excess vinyl groups remain after hydrosilylation curing when –C=C/-H exceeds 1.

As the unreacted vinyl groups increase, the transmittance decreases due to the presence of unsaturated double bonds and radicals formed by the thermal or UV degradation which can be sources for UV light absorption.[30] We showed that the number of vinyl groups is closely related to the initial UV transmittance of the fluoro hybrimer. An excess number of silicone-hydrogen groups did not have an adverse effect on the initial transparency; however, the remaining hydrogen groups also can be a source of UV degradation.[31] Based on these considerations, the molar ratio between the vinyl and hydrogen groups was optimized at 1:1.3 which has the highest initial UV transparency and cross-linking density. Additionally, we determined the refractive index of the

hybrimer (1.41) and achieved tunable shore hardness to fabricate soft or hard encapsulants.

To evaluate and compare the UV stability of the fluoro and methyl hybrimers, as-prepared bulks were aged under UVB lamps at an intensity of 10 mW/cm^2 for 2000 hours in air. The transmittance spectra in Fig. 2b show a slight increase in the UV transparency due to the minimum amount of unreacted vinyl groups, while there is a high transmittance increase as a result of the stabilization of excess vinyl groups in the fluoro hybrimer with a vinyl to hydrogen molar ratio of 1.6 : 1.0. (Fig. 2c). Thus, we can conclude that the remaining content of the vinyl groups in the fluoro hybrimer affects the degree of optical transparency recovery when the hybrimers are exposed to UV light.

UV stability of Fluoro-Siloxane Hybrimer: Recovery of UV Transparency.

Fig. 3a shows the transmittance spectra of the fluoro hybrimer according to the UVB aging time, the transparency of each sample was measured simultaneously during UV aging with a UV/Vis spectrophotometer every 72 hours. Fig. 3b shows the changes in the transmittance at 330 nm (UVA), 300 nm (UVB), and 270 nm (UVC) as a function of the aging time. The performance of the UV-LED is enhanced by an encapsulant with a high UV transmittance for the wavelengths of the emitted UV light. The methyl hybrimer is
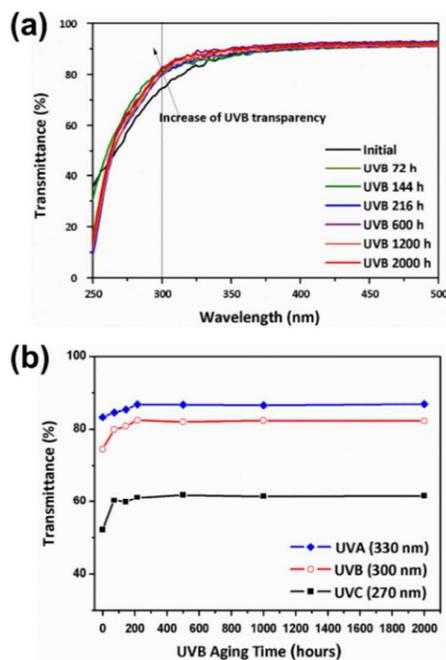
Fig. 3 (a) Transmittance spectra changes of the fluoro hybrimer according to the UVB aging time. (b) Changes of the transmittance at 330 nm (UVA), 300 nm (UVB), and 270 nm (UVC) according to the UVB aging time for 2000 hours in air.

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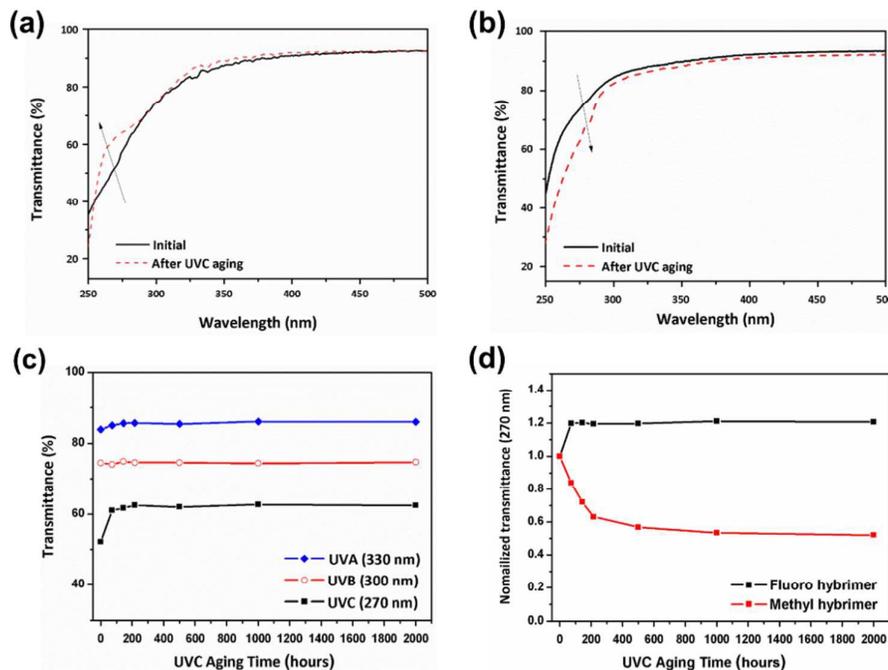
Fig. 4 Transmittance spectra changes of the (a) fluoro hybrimer and (b) methyl hybrimer bulk before/after 2000 hours of UVC aging. (c) Changes in the transmittance of the fluoro hybrimer at 330 nm (UVA), 300 nm (UVB), and 270 nm (UVC) according to the UVC aging time (d) Changes in the transmittance at 270 nm (UVC) of the methyl hybrimer and fluoro hybrimer according to the UVC aging time.

advantageous during the initial deep UV transmittance owing to its large free volume and long and homogeneous siloxane backbone. However, the UV radiation principally acts to degrade the organic phases resulting in delamination, embrittlement, and discoloration of the encapsulant. Thus, a UV stable material, which is not degraded by any emitted UV light, is more important as a UV-LED encapsulant regardless of the initial UV transparency.

Although the total amount of UV absorption in the fluoro hybrimer increases with the aging time, the transmittance is nearly identical showing only a slight change. The hybrimer features a substantial number of vinyl and fluoro groups, relatively few methyl groups, and hydrosilylation-derived short cross-links which contribute to the high UV stability. Even after 2000 h of aging, the transmittance of the fluoro hybrimer increases because the vinyl groups are stabilized by the extended UV light exposure, whereas the methyl hybrimer eventually shows a drastic decrease in its UVC transmittance to 59 % after 400 hours of aging.

The decrease in the optical transparency of the methyl hybrimer is due to the formation of methyl radicals and the radical-activated oxidative degradation of the organic pendants in the siloxane backbone which originate from the UV absorption of the methyl

phases as well as from the loosely cross-linked siloxane network.[32-34] However, the densely cross-linked fluoro hybrimer formed fewer methyl radicals compared to the methyl hybrimer with long linear siloxane chains and few cross-links. Additionally, the increased degree of condensation and branching of the siloxane bonds inhibited the cleavage of the methyl groups.

In addition to its excellent UVB stability, the fluoro hybrimer is highly transparent to radiation in the deep UV region (UVC), where UV absorption by the organic groups may become profoundly significant. As shown in Fig. 4, optical degradation caused by long-term UV irradiation was analyzed by tracing the transmittance curve during exposure to UVC light (200-280 nm). The UV/vis spectra clearly show the higher transmittance of the methyl hybrimer (Fig. 4b) before UV exposure compared with that of the fluoro hybrimer, as the presence of unreacted vinyl groups and the formation of vinyl radicals during thermal curing or UV irradiation have adverse effects on the initial UV transparency.

As shown in Fig. 4c, however, the UVA and UVB transmittance levels of the fluoro hybrimer were maintained for 2000 h of UVC expected, the methyl hybrimer ended up with severe discoloration in the lower UV region

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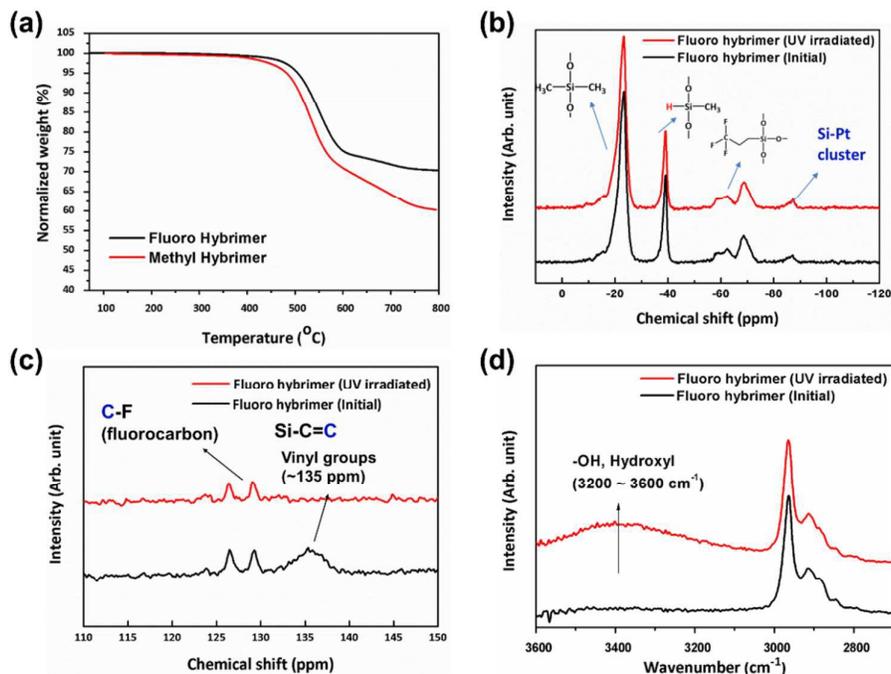
Fig. 5 (a) TGA spectra of the fluoro hybrimer and methyl hybrimer bulk in N_2. Solid-state CP/MAS (b) ^{29}Si NMR and (c) ^{13}C NMR spectra, and (d) FT-IR spectra of the fluoro hybrimer before/after UV irradiation for 2000 hours.

which was consistent with the results of the UVB test. The spectra of the methyl hybrimer are shifted down and to the right moving the transmittance curve further into the visible region. The UV transparency in the UVA, UVB, and UVC regions decreases; especially, the UVC transparency, which decreases by more than 10%. In contrast, the optical transmittance values of the fluoro hybrimer (52% at 270 nm), which were traced every 72 hours under environmental conditions identical to those used in the UVB test, increased to 62 %. The UVA and UVB transmittance levels were fairly stable until 2000 hours, and the curve showed little variation over the entire period without any discolorations or cracks in the bulk, confirming the superior UV stability of the fluoro hybrimer.

In general, methyl groups are susceptible to UV induced degradation because methyl radicals are cleaved from siloxane backbone chains by deep UV light energy. The fluoro hybrimer has fluorine groups with higher bonding energy and with a minimum number of methyl groups. The presence of strong carbon-fluorine and siloxane bonds and a densely cross-linked and branched structure formed by the complete condensation and hydrosilylation reaction of the precursors effectively inhibits the generation of methyl radicals. Thus, the low degree of degradation of the methyl groups can be attributed to their minimal exposure to extended UV light.

Organic phases in the linearly structured polysiloxanes are cleaved to form radicals, and siloxane bonds are cut during UV irradiation forming a cyclic ring structure. Additionally, the substantial number of remaining vinyl groups in the fluoro-siloxane network absorbs the
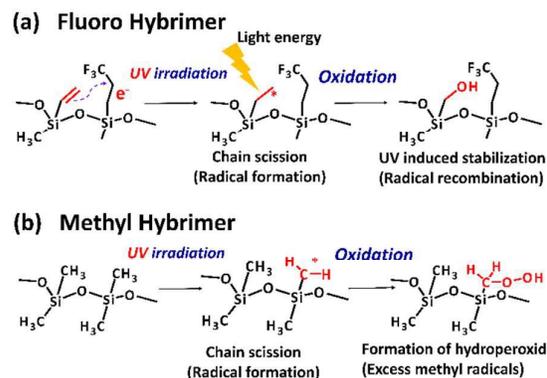
Scheme 2. UV induced radical formation, stabilization, and degradation mechanism during long-term irradiation of the (a) fluoro hybrimer and (b) methyl hybrimer.

deep UV light instead of methyl groups, thereby forming stable saturated bonds such as hydroxyl and carbon-carbon groups (Fig. 5).[30] During UV irradiation, the vinyl groups easily absorb the UV light energy, and are converted to stable species with oxygen such as hydroxyl and carbon saturated bonds (Scheme 2a). The methyl groups in the methyl hybrimer are more easily cleaved to form radicals, then forming UV absorbing hydroperoxide after UV irradiation (Scheme 2b). Thus, the low initial UV transparency of the fluoro hybrimer is increased by this UV induced radical stabilization effect, whereas the high initial UV transparency of the methyl hybrimer decreases due to the formation of methyl radicals. We confirmed that the fluoro hybrimer shows improved UV stability compared to methyl-siloxane which has a high number of methyl groups and a linear structure. Moreover, there was no indication of cracks or shrinkage during UV irradiation, these issues can arise due to the chain scission of the organic groups.

UV Stabilization of the Fluoro-Siloxane Hybrimer

As shown in Fig. 5a, the thermal decomposition of the fluoro and methyl hybrimer (fabricated by a procedure introduced in an earlier study) bulks was measured with TGA (thermogravimetric analysis) in N_2. The fluoro hybrimer, which replaces methyl groups with siloxane bonds and vinyl and fluorine groups, shows an increased number of cross-linking points and larger functional groups compared to the methyl hybrimer which has a large free volume and a substantial number of methyl groups. The fluoro hybrimer shows improved thermal stability exhibiting a higher decomposition temperature due to the densely cross-linked organo siloxane network.[35] The high cross-linking density of the organic groups as well as the high condensation of inorganic siloxane bonds inhibit the thermal decomposition of the organic pendants. The fluoro hybrimer loses 5% of its weight at 509 °C, whereas the methyl hybrimer loses 5% of its weight at 491 °C. During the thermal pyrolysis of the fluoro hybrimer, the high density from its branched structure contributes to the delay in the thermal decomposition of the organic functional groups from the siloxane backbone at an elevated temperature (Fig. S2, ESI†).

We performed detailed investigations of the formation and stabilization of radicals against thermal curing and UV-induced oxidation. During UV exposure, the presence of vinyl groups/radicals and structural density changes was investigated through electron spin resonance (Fig. S3, ESI†), carbon and silicone NMR analysis. The silicone (^{29}Si) NMR shown in Fig. 5b indicates that highly condensed and cross-linked siloxane networks are formed, these are not damaged by the extensive UVC irradiation which is consistent with the results from the thermal decomposition test (Fig. S4). The spectra before and after UV exposure show similar curves, and the bands from the fluorine, hydrogen, and methyl siloxane species are stable under prolonged UV radiation. There is no chain scission of the siloxane backbone or breakage of the attached organic species during UV irradiation. The densely cross-linked fluoro hybrimer from the highly condensed VF resin shows a reduced formation of organic radicals caused by remaining silane monomers and unreacted silanol or methyl groups.

The carbon (^{13}C) NMR spectra of the fluoro hybrimer clearly show the presence of vinyl groups and vinyl radicals in the cross-linked siloxane network. During UV radiation, the vinyl groups and radicals completely disappeared to form saturated chemical bonds, as described in Fig. 5c. For the UV-irradiated fluoro hybrimer, only characteristic bands from the carbon-fluorine (C-F) groups are seen, no bands from the vinyl groups and vinyl radicals (131~138 ppm) are observed.

The radical stabilization phenomenon was further confirmed in an additional analysis of the FT-IR curve showing the formation of hydroxyl groups (band at 3200 ~ 3600 cm^{-1}) in the fluoro hybrimer during UV irradiation (Fig. 5d). We can conclude that the vinyl radicals are converted to this hydroxyl species with oxygen, which provides supporting information regarding the presence of radical species in the material. Corresponding to the above mentioned structural analysis and the UV-induced radical stabilization proposed in Scheme 2, the cured fluoro hybrimer bulk contained a substantial number of hydroxyl groups after UV irradiation. After UV irradiation, there were relatively few resonance signals from the radicals owing to the recombination to form non-radical species (Fig. S3, ESI†).

Organic functional groups could have dissociated easily to form radicals at the high curing temperature during hydrosilylation. The methyl hybrimer has advantages with regard to initial UV transparency due to its low number of vinyl groups, large free volume and linear siloxane backbone; however, the low cross-linking density and high number of methyl groups have adverse effects on the UV resistance capabilities. The fluoro hybrimer replaces the methyl groups with vinyl and fluorine groups to inhibit decreases in the UV transmittance under deep UV irradiation. The combined effects of an initially high number of vinyl groups and the electron-withdrawing ability of the fluorine groups promote the formation of vinyl radicals during thermal curing and UV aging. However, relatively few amount of methyl groups are cleaved by UV light due to the highly cross-linked structure and the presence of fluoro groups.

The UV-induced radical stabilization, robust siloxane network, hyper-branched cross-linking, and high cross-link density of the fluoro hybrimer result in optical transmittance recovery during deep UV irradiation. Such UV stability is not commonly achieved with conventional organo-siloxane based LED encapsulants. We anticipate that the fluoro hybrimer will have many applications which take advantage of its inherent benefits including its ease of processing, high UV transparency and good stability.

Conclusion

A functionalized oligosiloxane resin with fluorine and vinyl groups was synthesized through the sol-gel reaction with MVDMS and FTMS. The resin was thermally cured by a hydrosilylation reaction with hydrogen-oligosiloxane under a Pt catalyst. The fabricated fluoro hybrimer showed excellent UV transparency with good stability during UV irradiation for long periods of time. We confirmed that the hybrimer has improved UV stability, compared to a previously reported hybrimer encapsulant based on methyl-siloxane, through the structural modification of the siloxane and the presence of fluorine functional groups. Due to the UV irradiation-

induced vinyl radical stabilization, the deep UV transmittance of the fluoro hybrimer did not decrease even after UVB and UVC aging for 2000 h. Our results provide evidence of the remarkable deep UV resistance of the fluoro hybrimer in the UVC region (200 ~ 280 nm), which is a promising feature that enables the stable operation of devices. The development of a deep UV transparent/stable and low-temperature solution processable siloxane hybrid material is very significant for the advancement of novel UV LED encapsulants.

Acknowledgements

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Graphical and textual abstract
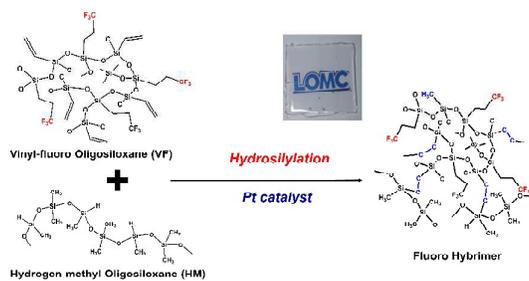
A UV transparent and stable fluoro-siloxane hybrid material was prepared for deep UV-LED encapsulant. The hybrimer was fabricated by hydrosilylation reaction of vinyl-fluoro oilgosiloxane and hydrogen-methyl oligosiloxane resins under Pt catalyst.