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Sulfur-Rich Ageing Mechanism of Silicone Encapsulant Used in LED Packaging: An Experimental and Molecular Dynamic Simulation Study

Wei Chen^{1,2†}, Ye Chen^{2,3†}, Yixing Cao¹, Zhen Cui⁴, Xuejun Fan⁵, Guoqi Zhang⁴ and Jiajie Fan^{1,2,4,6*}

¹Institute of Future Lighting, Academy for Engineering and Technology, Fudan University, Shanghai, China, ²Changzhou Institute of Technology Research for Solid State Lighting, Changzhou, China, ³College of Mechanical and Electrical Engineering, Hohai University, Changzhou, China, ⁴Department of Microelectronics, Delft University of Technology, Delft, Netherlands, ⁵Department of Mechanical Engineering, Lamar University, Beaumont, TX, United States, ⁶Zhangjiang Technology Institute of Fudan University, Shanghai, China

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*Correspondence:

Jiajie Fan
jjajie_fan@fudan.edu.cn

[†]These authors have contributed
equally to this work and share first
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In a light-emitting diode (LED) package, silicone encapsulant serves as a chip protector and enables the light to transmit, since it exhibits the advantages of high light transmittance, high refractive index, and high thermal stability. However, its reliability is still challenged under harsh operation conditions. In this study, the optical and mechanical properties of silicone encapsulant, including appearance, light transmittance, Young's modulus, and tensile strength, were experimentally monitored during the sulfur-rich ageing process. Meanwhile, the Fourier transform infrared (FTIR) spectroscopy and molecular dynamics (MD) simulation were used to reveal its degradation mechanism. The results show that 1) in the sulfur (S₈)-rich ageing process, the severe vulcanization reaction occurred in silicone encapsulant assisted only by high temperature and high moisture, with the existence of H₂S as the reaction product of S₈ and H₂O vapor. 2) Vulcanization characterized by the formation of the sulfhydryl (-SH) group lowered both optical and mechanical properties of silicone encapsulant. 3) The hydrolysis reaction featured by the formation of the hydroxyl (-OH) group decreased the mechanical performances of silicone encapsulant but brought slight harm to its optical performances.

Keywords: LED packaging, silicone encapsulant, sulfur-rich, humidity, degradation mechanism, molecular dynamics

INTRODUCTION

As one of the most environmentally friendly light sources, the light-emitting diode (LED) exhibits promising performances, such as long lifetime and low power consumption (Taguchi, 2008; Watzke and Altieri-Weimar, 2015; Singh and Tan, 2018; Tan et al., 2021), and LED is popular in the lighting industry since it is highly reliable and efficient (Zhang et al., 2016; Alim et al., 2021; Bento and Cardoso, 2021; Bispo-Jr et al., 2021). Silicones are polymeric substances consisting of repeating units of siloxane (alternating silicon and oxygen chains) and organic side groups, showing a high refractive index and high optical transparency (Lin et al., 2010; Kim et al., 2013; Tong et al., 2018; Kim et al., 2019). Therefore, they are widely used as one of the encapsulant materials in LED packaging with the functions of light-extraction and chip-protection. However, their optical and mechanical properties

are often affected by harsh environmental conditions containing moisture, temperature, pollutions, and contaminants, such as sulfur (Lee et al., 2015; Luo et al., 2016; Khalilullah et al., 2017; Made et al., 2017).

Some previous researchers have revealed that the stability of silicone encapsulant materials determines the performance and lifetime of LEDs. For instance, Zhang (2015) used the finite element method to quantitatively evaluate the degradation of organosilicon and developed a lumen depreciation model, which could help LED manufacturers to avoid time-consuming reliability tests. Chang et al. (2016) studied the drying and wetting air ageing processes involving silicone materials, and the results revealed that high humidity and temperature will exacerbate the degradation of silicone, which was explained by chemical decomposition of cross-linker units that connect polysiloxane backbones and methyl groups attached to silicon atoms. Wu et al. (2017a) analyzed the thermal oxidation degradation mechanism of silicone by using the X-ray photoelectron spectroscopy (XPS) and nuclear magnetic resonance (NMR) techniques. The results revealed that the hardness and compression set of silicone increases with ageing time. The increases in the surface roughness and ageing time all potentially resulted in the deteriorated sealing performance. Luo et al., (2017), Fan et al., (2019) studied a long-term degradation mechanism of phosphor/silicone composites under the conditions of high temperature and humidity with comparing the optical and mechanical properties of the aged composites. Khalilullah et al. (2017), Hoque et al. (2019) investigated the influence of humidity on phosphor/silicone composites and reported the reversibility of the hygroscopic expansion process occurring in the absorption/desorption cycle. They also concluded that exposure to moisture will cause permanent damage to silicone materials. Huang et al. (2015a) presented the failure mechanism of mid-power white-light LEDs aged under saturated moisture conditions as the silicone was carbonized during the ageing process. They summarized that the phosphor's self-heating and the excessive absorption of blue light contribute to a significant rise in the internal temperature, resulting in silicone carbonization (Huang et al., 2015b). Cai et al. (2020) studied the effect of silicone encapsulation degradation on the LED lumen decay and color shift, and they found the yellowing failure of silicone is concluded as the oxidation and hydrolysis of silicone materials.

The LED was attacked by the sulfur and sulfide coming from the air atmosphere, when working in harsh environments such as mine, chemical fertilizer plant, livestock farm, and sewage treatment plant. Silicone is prone to absorb sulfur and sulfide causing the degradation of itself (Wang et al., 2019). For example, Zibold et al. (2017) studied the impacts of hydrogen sulfide on light output power of LEDs. Different decreases were measured in different LED packages, after 380 h of ageing with 10 ppm hydrogen sulfide. Wu et al. (2017b) conducted the room-temperature-vulcanization (RTV) process on silicone under varying temperatures and humidity. The results revealed that the humidity and temperature in the vulcanization environment highly influence the hydrophobicity transfer ability, functional groups, and thermal stability of silicone. Besides, if the sulfur

penetrates the packaging, silver-plated copper in the LED lead frame is susceptible to corrosion featured with forming Ag_2S , which will reduce the light extraction efficiency (ChenlanXu et al., 2018).

According to the aforementioned literature review, there are numerous studies on the degradation mechanism of silicone under the conditions of high temperature and humidity; however, reports on the sulfur-rich ageing mechanism of LED silicone encapsulant are rare. Thus, in this study, we conducted the high temperature, high humidity, and sulfur-rich ageing experiments on the LED silicone encapsulant samples. Their optical and mechanical properties were measured during ageing, and the inherent degradation mechanisms were investigated by using both experiments and molecular dynamic (MD) simulation. The remaining parts of this article are organized as follows: *Sample Preparation, Experiment, and Simulation Methods* section introduces the methods of sample preparation, experiment setup, and simulation process; *Results and Discussion* section analyzes the ageing mechanism based on both experimental and simulation results; *Conclusion* section presents the concluding remarks.

SAMPLE PREPARATION, EXPERIMENT, AND SIMULATION METHODS

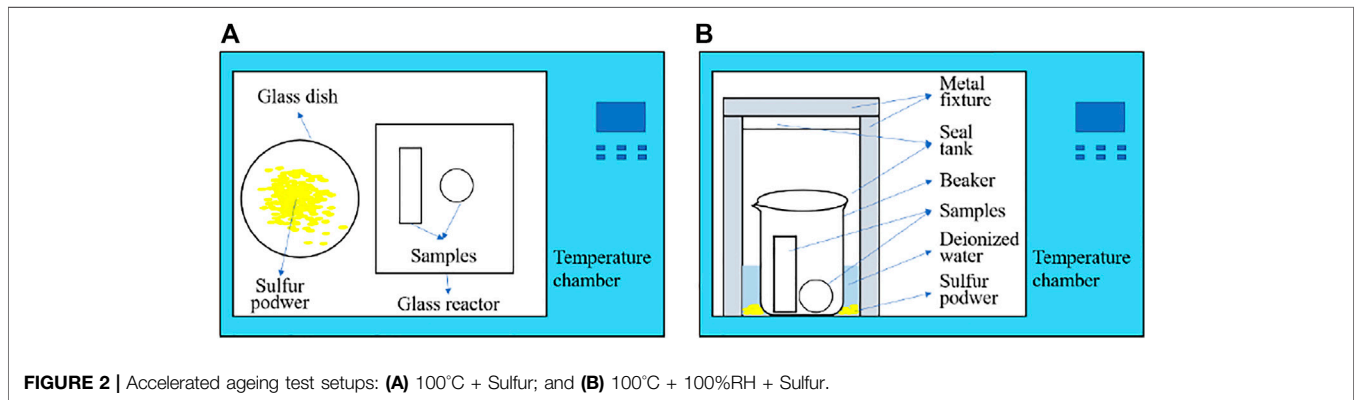
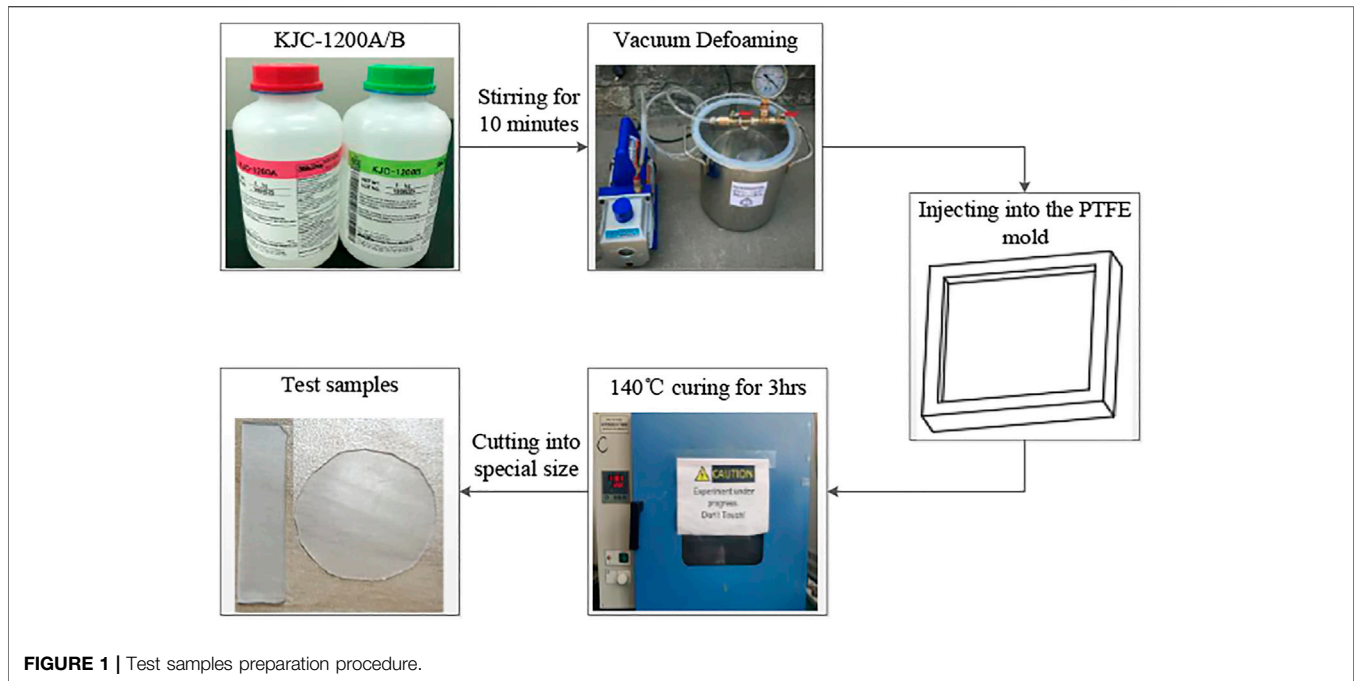
In this section, the preparation process of test samples is introduced first. Then, the four different ageing tests are designed. The simulation procedure based on molecular dynamics (MD) is given at last.

Sample Preparation

The preparation procedure of the test sample is shown in **Figure 1**: first, the precursors KJC-1200A and KJC-1200B purchased from Shin-Etsu Chemical Co. Ltd. were mixed in the mass ratio of 1:1 and manually stirred for 10 min. Next, the mixture was placed in a vacuum bucket to remove foam. Subsequently, the foamless mixture that was poured into a polytetrafluoroethylene (PTFE) tube was cured in a temperature chamber operated at 140°C for 3 h. After cooling, the cured silicone film with the size of 50*50*1 mm was prepared. Finally, the cured silicone film was cut into a rectangle-shaped sample with the size of 40*5*1 mm and disc-shaped sample with the size of $\Phi 23*1$ mm, used for mechanical properties measurement and optical properties measurement, respectively.

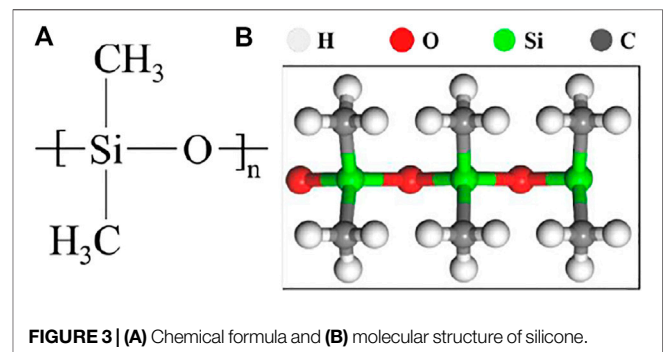
Ageing Experiments

To evaluate the influence of sulfur and humidity on the degradation of silicone, this article presented four different accelerated ageing conditions: 1) 100°C ageing; 2) 100°C + 100%RH ageing; 3) 100°C + Sulfur ageing; and 4) 100°C + 100%RH + Sulfur ageing. To accelerate the degradation, a high temperature of 100°C was applied in all four conditions. The conditions 100°C ageing and 100°C + Sulfur ageing were carried out in the setup shown in **Figure 2A**. The test samples placed on the glass reactor were heated in the temperature chamber with a temperature of 100°C. In 100°C + Sulfur



ageing, 10 g chemically pure sulfur (S_8) placed on the glass dish was put into the thermal chamber. As shown in **Figure 2B**, a 300-ml PTFE seal tank with 30 ml deionized water was used to guarantee the saturated wet condition. Compared to 100°C + 100%RH ageing, 10 g chemically pure sulfur (S_8) was added in the deionized water in 100°C + 100%RH + Sulfur ageing.












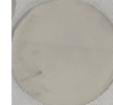







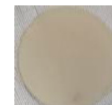





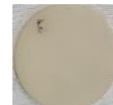


All test samples were subjected to a constant temperature chamber with a 1008 h ageing process. Each group consisted of 35 rectangle-shaped samples and five disc-shaped samples. A total of five rectangle-shaped and five disc-shaped samples were taken out for the property measurement every 168 h. The mechanical properties of the rectangle-shaped samples, including Young's modulus and tensile strength, were measured under the tensile test machine (ZQ-980A, Zhiqu). The light transmittances of the disc-shaped samples were measured using the spectrophotometer (CM-3700A, Konica), and their functional groups were identified using the FTIR spectrometer (iS50, Nicolet).

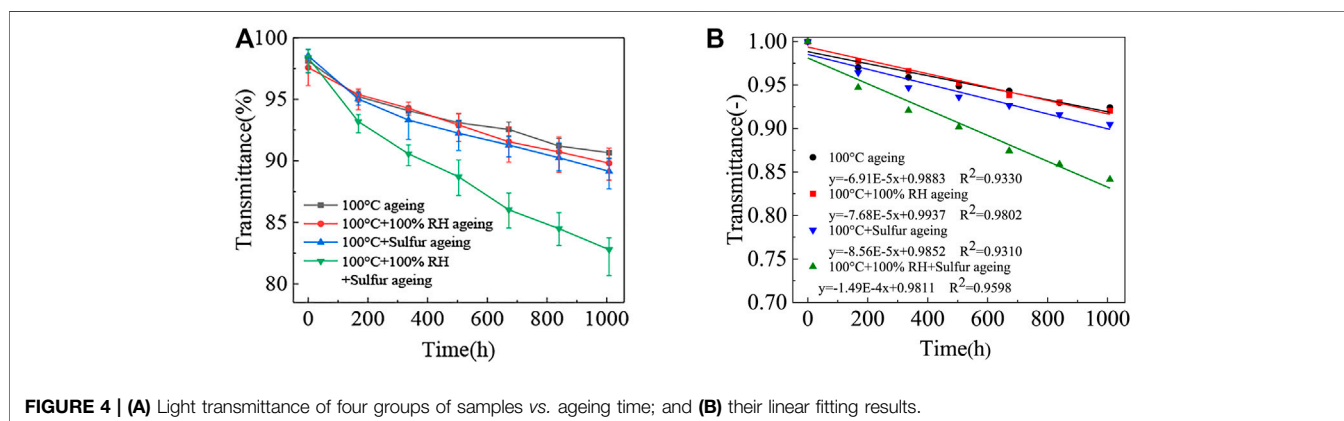


Simulation Setup

To understand the adsorbing mechanism of H_2O and H_2S on the silicone (polydimethylsiloxane, PDMS) molecules, as shown in **Figure 3**, the quantum mechanical calculation based on the

TABLE 1 | Appearance observed in test samples subjected to four different ageing conditions.

Group	Time (h)						
	0 h	168 h	336 h	504 h	672 h	840 h	1,008 h
100°C ageing							
100°C + 100%RH ageing							
100°C + Sulfur ageing							
100°C + 100%RH + Sulfur ageing							



density functional theory (DFT) was conducted in DMol³ and CASTEP. The energies originated from electronic interaction were dealt with in using the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) method (Fan et al., 2020). Double numerical basis sets with polarization functions (DNPs) with the basis file 3.5 were selected in this study. The Grimme custom method for DFT-D was used to dispose weak interactions between PDMS and H₂O or H₂S. The convergence tolerances of geometry optimization were set at: energy = 1.0e-5Ha, max, force = 0.002 Ha/Å, max, and displacement = 0.005 Å. The adsorption distances between PDMS and H₂O or H₂S were 3 Å.

RESULTS AND DISCUSSION

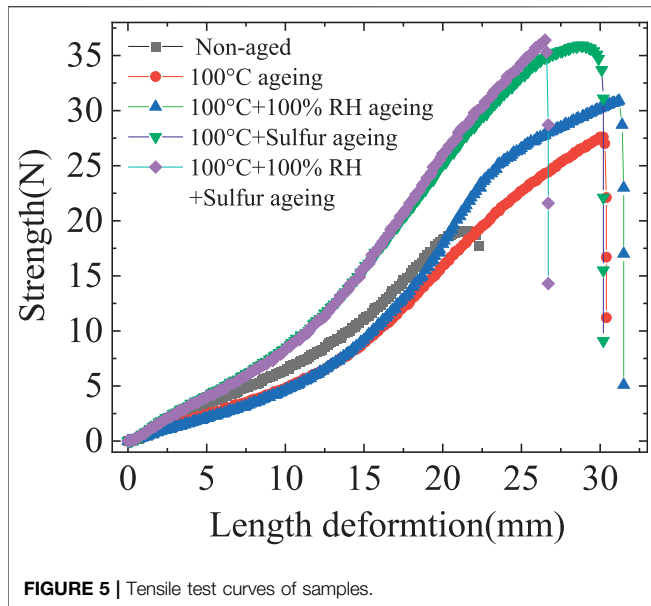
In this section, the optical and mechanical properties of prepared test samples undergoing different ageing processes are discussed,

and the degradation mechanisms are revealed by using the FTIR and MD simulation.

Optical Properties

The data presented in **Table 1** reveal that the appearance of the silicone samples changes when the samples were aged. It shows that the 1008 h-long-term ageing increased the degree of yellowing of test samples. The 100°C ageing and 100°C + 100%RH ageing groups showed the similar phenomenon that no evident appearance of color changes was observed at the end of the ageing. However, in the 100°C + Sulfur ageing and 100°C + 100%RH + Sulfur ageing, the appearance of the color of samples changed to deep yellow after ageing, more severe in 100°C + 100%RH + Sulfur ageing, which indicates that both sulfur and moisture exerted an acceleration impact on the yellowing of silicone samples.

The light transmittance is one of the key indicators for silicone encapsulant, since the light extraction efficiency of LED



packaging is highly affected by the light transmittance (Pan et al., 2021; Wang et al., 2014). Furthermore, the light transmittance degradation path of the four groups of samples and their linear fitting results are demonstrated in **Figure 4**. The transmittance data in **Figure 4** are an average value of transmittances measured in the visible spectrum range, and the measurement step is 10 nm. The degradation rate in light transmittance is indicated by the slope of linear fitting, and the order of slopes under four different ageing conditions was that: 100°C ageing: $-6.91e-5 > 100^\circ\text{C} + 100\%RH$ ageing: $-7.68e-5 > 100^\circ\text{C} + \text{Sulfur}$ ageing: $-8.56e-5 > 100^\circ\text{C} + 100\%RH + \text{Sulfur}$ ageing: $-1.49e-4$. The 100°C ageing and 100°C + 100%RH ageing groups showed the similar degradation rate in light transmittance, and a slight increment can be observed in 100°C + Sulfur ageing. The reason is that vaporized sulfur in 100°C + Sulfur ageing was deposited and permeated to the surface of silicone, but no chemical reaction occurred, resulting in obvious appearance of color change and slight light

transmittance change. However, the degradation rate of light transmittance in 100°C + 100%RH + Sulfur ageing was the largest compared to that of other conditions. According to Wang et al., (2019) and Manconi and Lens, (2009), the sulfur (S_8) can be transformed into hydrogen sulfide (H_2S) with existence of water vapor, and the strong sensitivity of silicone toward H_2S was confirmed. Therefore, the chemical reaction between silicone and H_2S might lead to the most serious optical property deterioration of test samples in 100°C + 100%RH + Sulfur ageing.

Mechanical Properties

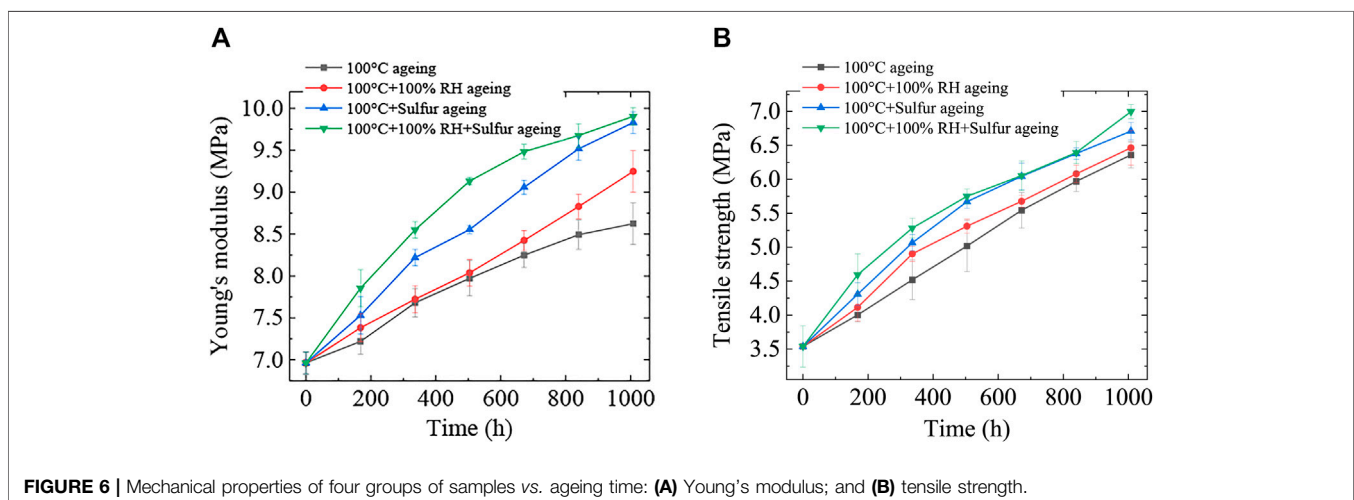
The typical tensile test curves of samples before and after ageing are plotted in **Figure 5**. Tensile strength (σ) and Young's modulus (E) can be calculated using tensile test data by following **Eqs 1, 2**:

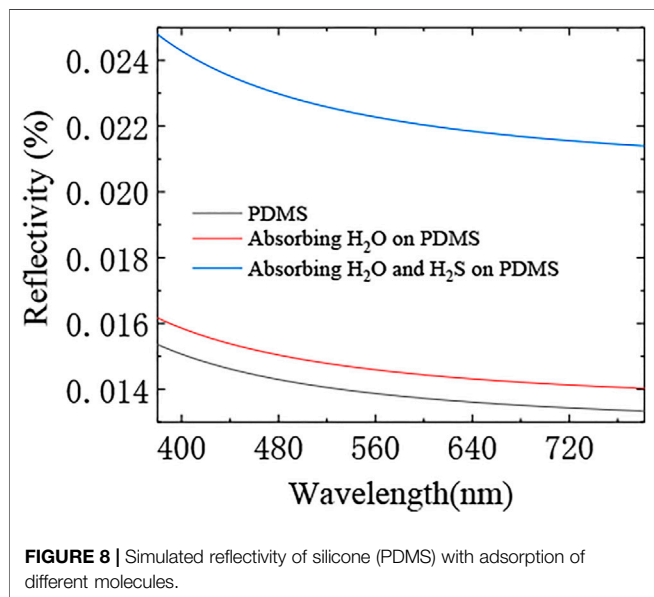
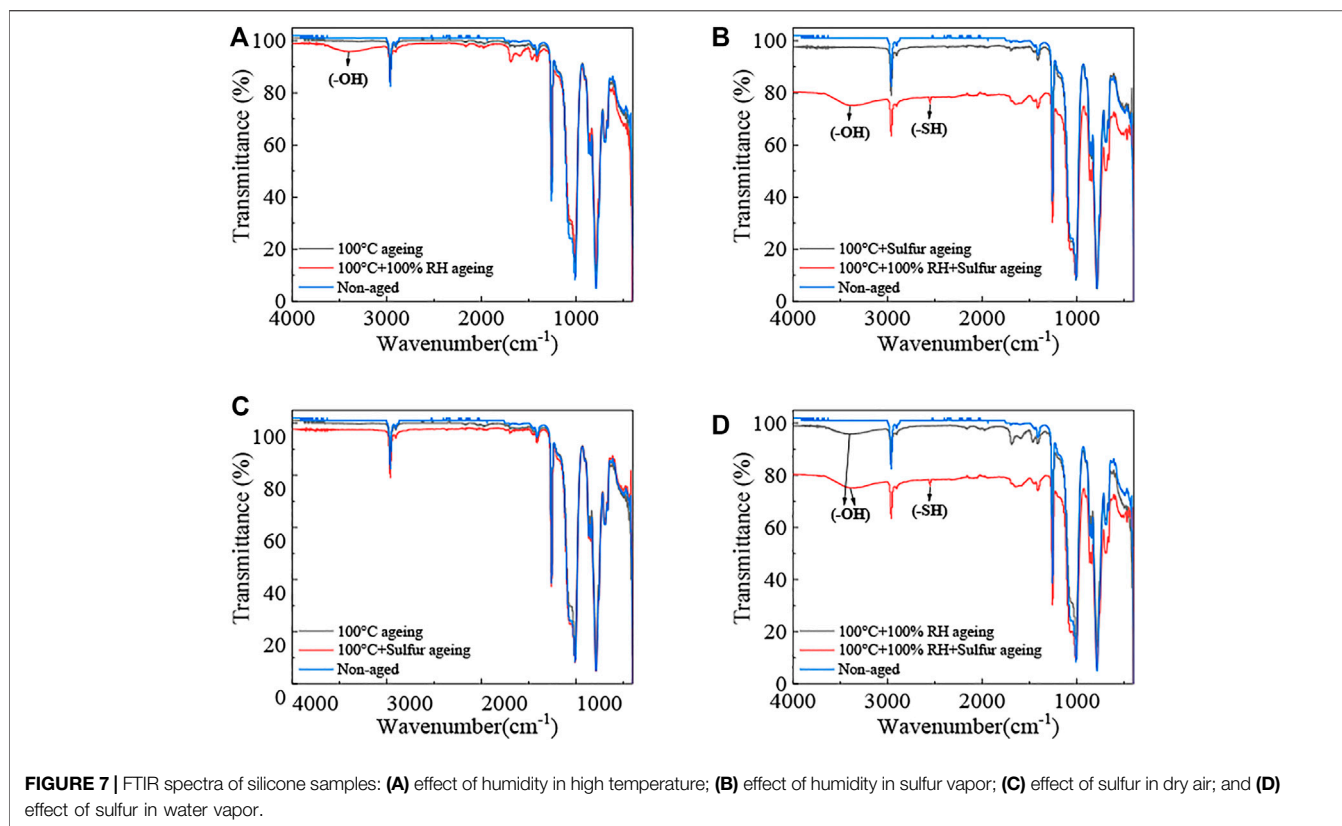
$$\sigma = \frac{F_{max}}{A} \quad (1)$$

$$E = \frac{\sigma}{dL/L} \quad (2)$$

in which F_{max} , A , L , and dL are maximum strength at sample breaking, cross-section area of the sample, length of the sample, and length deformation at sample breaking, respectively. In this study, the values of A and L are 5 mm^2 and 40 mm, respectively.

Figure 6 shows the mechanical properties of the silicone samples subjected to four different ageing conditions. The increases in Young's modulus and tensile strength had occurred in the four groups of silicone samples. The Young's modulus and tensile strength of silicone under humidity stress ageing conditions were higher than those of the samples aged under dry conditions because the hydrolysis reaction occurred under high humidity conditions (Fan et al., 2019; Hoque et al., 2019). In addition, the Young's modulus and tensile strength of the silicone samples treated under the sulfurized environment were largely higher than those of the samples aged without sulfur, which indicated that sulfur could accelerate the mechanical degradation of silicone. As the most severe mechanical degradation of the silicone samples was occurred in the 100°C





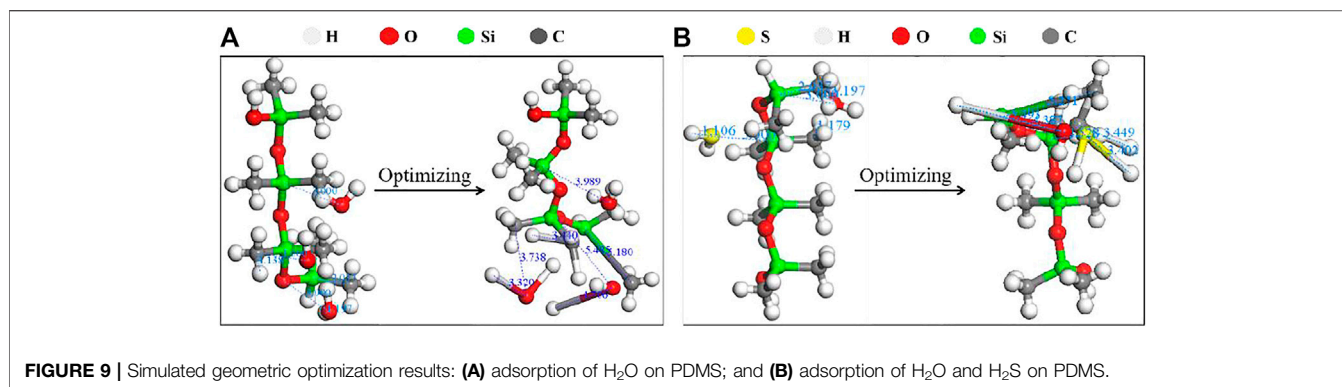
+ 100%RH + Sulfur ageing group, it was speculated that besides the hydrolysis reaction, the samples also reacted with H_2S .

Degradation Mechanism Analysis

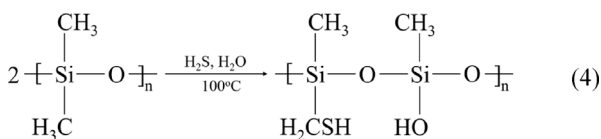
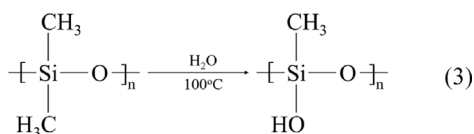
To explain the aforementioned optical and mechanical degradation of the silicone samples, FTIR and MD simulation

techniques were used to analyze their degradation mechanisms under different ageing conditions.

Figure 7 shows and compares the FTIR spectra recorded for silicone samples subjected to four different ageing environments. Compared to unaged test samples, the absorption peak intensities of the aged samples around 787 cm^{-1} (C–H rolling vibration), $1,260\text{ cm}^{-1}$ (C–H stretching vibration), $2,960\text{ cm}^{-1}$ (C–H stretching vibration), and $1,080\text{ cm}^{-1}$ (Si–O–Si stretching vibration) dropped by varying degrees, indicating various degrees of degradation in the main and side chains of silicone samples (Wu et al., 2017a). Hydrolysis and vulcanization reactions are represented by the hydroxyl group (-OH) with FTIR absorption peaks around $3,400\text{ cm}^{-1}$ (Salehpour and Dube, 2012) and sulfhydryl group (-SH) with FTIR absorption peaks around $2,570\text{ cm}^{-1}$ (Fei et al., 2017). As shown in **Figure 7**, the hydrolysis reaction happened in both $100^\circ\text{C} + 100\%\text{RH}$ ageing and $100^\circ\text{C} + 100\%\text{RH} + \text{Sulfur}$ ageing; however, vulcanization reactions only appeared in $100^\circ\text{C} + 100\%\text{RH} + \text{Sulfur}$ ageing. Meanwhile, the new absorption peaks between $1,550$ and $1,800\text{ cm}^{-1}$ were attributed to the reaction of sulfur and small amounts of impurities in silicone such as unsaturated vinyl group $-\text{CH}=\text{CH}_2$ (Nazi et al., 2012). No extra absorption peak was observed in 100°C ageing and $100^\circ\text{C} + \text{Sulfur}$ ageing, indicating that no new group formed after ageing. Generally speaking, high temperature damaged the skeletal structure of silicone; the hydrolysis reaction occurred with presence of moisture; sulfur did not directly react with silicone; the vulcanization reaction occurred with the existence of H_2S as the reaction product of sulfur and water vapor.



To reveal the reactions under ageing, molecular simulations between PDMS and H₂O or H₂S were conducted in DMol³ and CASTEP. The simulated reflectivity and geometric optimization results are shown in **Figures 8, 9**, respectively. The reflectivity of silicone slightly increased when H₂O was adsorbed on the PDMS molecules, while a marked increase in reflectivity was observed when both H₂O and H₂S were adsorbed on the PDMS molecules. Light transmittance of silicone is inversely proportional to the reflectivity, so the simulated reflectivity results are consistent with experimental light transmittances of any aged samples subjected to 100°C + 100% RH ageing and 100°C + 100%RH + Sulfur ageing as shown in **Figure 4**. The adsorption of H₂O on PDMS resulted in the elongation of the Si–C bond in Si–CH₃ and the H–OH bond in H₂O, generating the –Si–OH group. The adsorption of H₂O and H₂S on PDMS led to the elongation of the Si–C bond in Si–CH₃, the C–H bond in –CH₃, the H–OH bond in H₂O, and the H–SH bond in H₂S, generating the –Si–OH and –CH₂SH groups. Finally, hydrolysis and vulcanization reactions are assumed as shown in Eqs 3, 4.



CONCLUSION

In this study, the optical and mechanical degradations of LED silicone encapsulant aged under the sulfur-rich and high humidity conditions were studied with both experiments and molecular dynamics (MD) simulation. The results reveal that 1) a significant deterioration in the optical and mechanical performances of silicone encapsulant was

observed in the ageing condition of sulfur-rich and high humidity environments, attributing to the formation of H₂S as the reaction product of sulfur and water vapor; 2) both hydrolysis and vulcanization reactions took adverse effects on mechanical properties of silicone, but optical properties deterioration was more sensitive to vulcanization reactions; 3) hydrolysis and vulcanization were characterized by the formation of the hydroxyl (–OH) group and sulfhydryl (–SH) group, respectively, and their reaction equations were derived by FTIR results and verified by MD simulation. These results obtained in this study can help in the selection of silicone encapsulant materials used in high-power LED packaging and give solutions to improve the reliability of the LED packaging.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusion of this article will be made available by the authors, without undue reservation.

AUTHOR CONTRIBUTIONS

WC: writing—original draft preparation. YeC: experiments, data collection, and analysis. YiC: simulation and analysis. ZC: technical support on simulation. XF: supervision. GZ: supervision. JF: conceptualization, methodology, writing—review and editing, project administration, funding acquisition, and supervision.

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