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## ***“Utilization of Antioxidant Hydrogen Gas: Hydrogen-Releasing Film for Recovery of UV-Induced Skin Damage and Immediate Wrinkle Reduction”***

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### **1. Introduction**

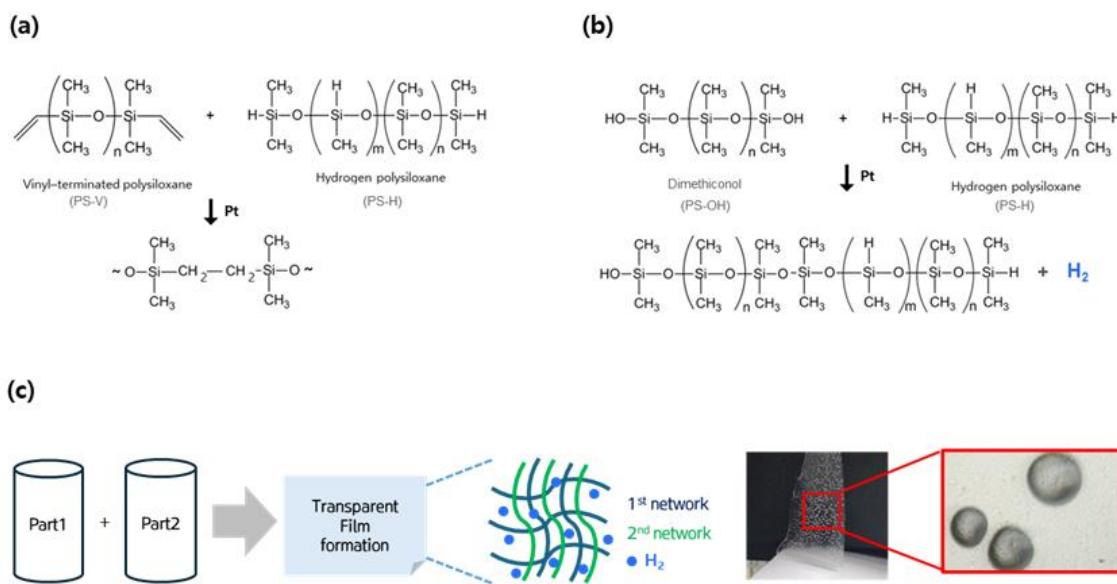
Ultraviolet B (UVB) radiation (280–320 nm) is a well-established environmental factor that induces acute and chronic skin damage [1]. Upon exposure, UVB penetrates the epidermal layer and initiates a cascade of biological responses, including the generation of reactive oxygen species (ROS), lipid peroxidation, DNA damage, and pro-inflammatory cytokine expression [2]. These oxidative and inflammatory pathways disrupt skin barrier homeostasis and accelerate photoaging, resulting in erythema, pigmentation, and dermal extracellular matrix degradation [3]. Notably, UVB-induced ROS degrade collagen and elastin fibers by upregulating matrix metalloproteinases (MMPs), leading to visible wrinkle formation and loss of skin elasticity [4]. Conventional approaches to mitigating UVB-induced skin damage have primarily relied on antioxidant-rich formulations such as vitamins C and E, polyphenols, and enzymatic antioxidants [5]. However, these molecules are often limited by instability, insufficient penetration, and transient efficacy [6]. Consequently, the development of alternative strategies capable of sustained antioxidant activity within the skin microenvironment remains a pressing demand in dermatological science [7].

Molecular hydrogen ( $H_2$ ) has emerged as a potent biological antioxidant with the ability to selectively neutralize cytotoxic ROS, such as hydroxyl radicals [8]. Its small molecular size facilitates rapid diffusion across membranes, allowing efficient penetration into subcellular compartments [9]. Multiple *in vitro* and *in vivo* studies have validated hydrogen gas as an effective therapeutic agent in reducing oxidative stress, suppressing inflammatory responses, and enhancing tissue regeneration [10]. Despite these advantages, the practical application of hydrogen in cosmetics remains underdeveloped due to challenges in storage, delivery, and sustained exposure at the target site [11].

Crosslinked polysiloxane networks that form films directly on the skin surface are commonly produced via hydrosilylation reactions using a platinum catalyst at room temperature, without the need for an external energy source [12]. This *in situ* crosslinking process offers the advantage of rapidly generating three-dimensional elastomeric films that replicate the mechanical properties and appearance of youthful skin. The hydrosilylation mechanism, which proceeds without byproduct formation, ensures high biocompatibility and mechanical durability under skin deformation.

In this study, we developed a stable, skin-adherent film capable of releasing hydrogen, utilizing hydrosilylation-based film formation technology. We present a solid-state hydrogen

delivery platform utilizing dual-crosslinked silicone films, synthesized via a hydroxylation-mediated crosslinking reaction. The system employs a double crosslinking strategy integrating hydrogen polysiloxane (PS-H), vinyl terminated dimethicone (PS-V), and dimethiconol (PS-OH) (Figure 1). The resulting formulation enables the formation of stable film with hydrogen gas ( $H_2$ ) and superior skin adhesion, leveraging hydrogen gas as an active antioxidant. This polysiloxane film concurrently facilitates antioxidant delivery, restoration of skin barrier function, and biomechanical reinforcement of cutaneous tissue. Collectively, this technology offers significant potential for clinical and consumer applications in skin regeneration, improvement in skin wrinkles, and photoprotective activity.



**Figure 1.** Schemes depict Pt-catalyzed crosslinking mechanisms of polysiloxane systems. (a) Hydrosilylation reaction (1<sup>st</sup> crosslink reaction) (b) Dehydrogenative coupling reaction (2<sup>nd</sup> crosslink reaction) (c) Double crosslinked polysiloxane film formation and hydrogen gas release. Part1; hydrogen polysiloxane (PS-H), Part2; vinyl terminated polysiloxane (PS-V) and dimethiconol (PS-OH)

## 2. Materials and Methods

### Materials

Vinyl terminated polysiloxane (PS-V), hydrogen polysiloxane, and dimethiconol (PS-OH) were purchased from certified cosmetic-grade suppliers. Platinum catalyst was used to initiate hydrosilylation reactions. Fumed silica with hydroxyl surface groups was employed as a mechanical reinforcement and rheology modifier.

### Fabrication of Hydrogen-Releasing Films

Dual cross-linking was implemented to prepare the hydrogen-releasing film matrix. In the primary cross-linking reaction, PS-V and PS-H were mixed at varying molar ratios (1:1 - 3:1) to control base network formation. PS-OH was subsequently introduced to initiate secondary silanol–hydrosilane dehydrogenative coupling. Hydrogen generation during film curing was monitored qualitatively using hydrogen detection tape placed in proximity to the films. The appearance of a color change on the tape indicated the release of molecular hydrogen gas. The

homogeneous mixture was cast onto polyethylene substrate plate and cured at 25 °C (room temperature).

### Structural and Mechanical Characterization

Mechanical properties, including tensile strength, elongation distance, hardness, and film thickness, were measured using a texture analyzer. The crosshead speed was set at 1 mm/s, and all measurements were conducted at 25 °C. Tensile strength and elongation were determined using films prepared with a sample weight of 5 g. Hardness measurements were performed on the same films. Adhesive strength was evaluated separately using thinner films prepared with 1.5 g of material. Adhesive strength was determined by measuring the maximum force required to detach the film from a flat substrate using the same texture analyzer setup.

### Antioxidant Effects

The antioxidant capacity of the hydrogen-releasing films was assessed using a DPPH (2,2-diphenyl-1-picrylhydrazyl) radical scavenging assay. DPPH solution was prepared freshly before each test. Films fabricated were immersed in the DPPH solution in sealed glass vials. The vials were maintained at 25 °C without agitation, and the color change of the DPPH solution was visually monitored over a 12-hour period. The decrease in absorbance at 517 nm, corresponding to DPPH radical consumption, was measured using a UV-Vis spectrophotometer. The radical scavenging activity (RSA) was calculated according to the following formula:

$$\text{RSA (\%)} = [(A_0 - A_t)/A_0] \times 100$$

where  $A_0$  is the initial absorbance of the DPPH solution without film, and  $A_t$  is the absorbance after exposure to the hydrogen-releasing film at each time point.

### Investigation of Skin Aging Improvement

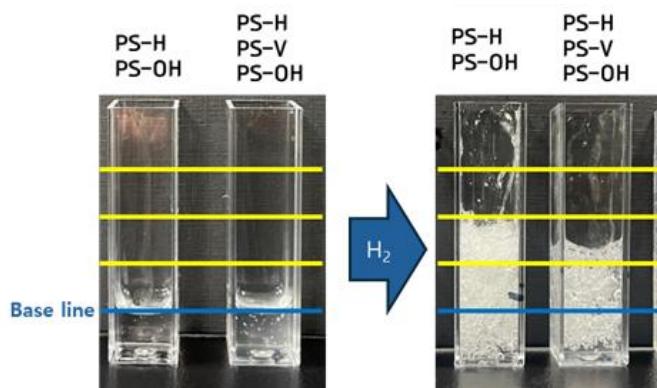
TEWL measurements were conducted using a Tewameter under controlled environmental conditions (22–25 °C, 40–60% relative humidity). TEWL values were recorded before and immediately after film application on the forearm. Neck wrinkles were analyzed by capturing 3D images using an Antera 3D system before and after application on the neck area. The Indentation Index was calculated to quantify wrinkle depth changes.

## 3. Results

### Fabrication of Hydrogen-Releasing Films

The primary network of the hydrogen-releasing silicone film was formed by a platinum-catalyzed hydrosilylation reaction between vinyl dimethicone and hydrogen dimethicone. This reaction successfully produced a transparent film without any noticeable color change on the hydrogen detection tape, indicating that the primary cross-linking reaction was completely carried out without hydrogen gas evolution. This primary hydrosilylation reaction provides the film-forming ability and baseline adhesion.

In Figure 2, the hydrogen generation texture by the primary bonding of PS-H and PS-OH increased in volume by about 3 times as hydrogen was generated. When PS-V was added here to add a double crosslinking bond, the volume decreased by about 60%. This significantly affected the thickness of the film after forming the film. We selected a film formulation containing all three components to optimize for a thin and compact structure without altering the hydrogen release amount.



**Figure 2.** Textures of the polysiloxane network deformed by hydrogen gas

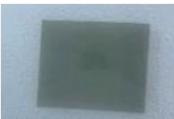
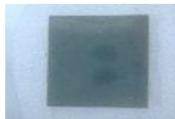
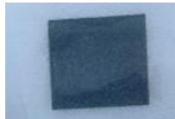
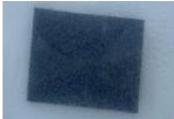
To stabilize the network and induce hydrogen release, double crosslinking reaction was prepared by reacting complex A, a mixture of PS-V and PS-OH, with PS-H to generate hydrogen gas. The hydrogen release amount according to the PS-OH content of 10% to 40% of complex A was determined over time (2 to 10 min). 10% started to release hydrogen gas as the film was formed in 5 min. 20%-40% formed the film and released hydrogen in 2 min (Figure 3). The higher the PS-OH ratio, the faster the hydrogen release rate, and the degree of film swelling varied as the release amount increased. In both cases, film formation was completed within about 2 min, and a distinct color change was observed on the hydrogen detection tape. When the PS-OH concentration was 20%, a uniform gas distribution and minimal pore formation were observed, but as the concentration increased (30-40%), gas pockets were formed, deteriorating the film uniformity. This confirmed that hydrogen gas was generated by the reaction of PS-OH and residual functional groups in the matrix during the secondary curing process.

PS-OH in Complex A(%)	initial	10	20	30	40
2 min					
5 min					
10 min					

**Figure 3.** Colorimetric change triggered by hydrogen gas (light brown → blue)

Fumed silica is known to enhance flexibility and adhesion in silicone films [12]. We performed further optimization by fixing PS-OH at 20% and adding fumed silica. The silica content was varied from 5% to 15% by weight. When the silica content was 5%, the hydrogen detection tape showed a color change after about 2 min, but the resulting film was sticky, suggesting incomplete network stabilization. When the silica content was increased to 10%, the hydrogen

detection rate was faster (about 1.5 min) and a uniform, sticky film was formed, which improved the mechanical properties. However, when the silica content was 15%, hydrogen generation was achieved within 1 min, but the film swelled and the structural integrity was compromised, which was likely due to excessive cross-linking and gas entrapment in the matrix. Fumed silica played a dual role: improving the mechanical flexibility and changing the internal microenvironment, which contributed to the controlled diffusion hydrogen release. These results demonstrate that solid silicone films can be used as passive on-demand hydrogen generators.

Silica (%)	5	10	15
2 min			
5 min			
10 min			

**Figure 4.** Influence of silica incorporation on the kinetics of silicone film formation and hydrogen gas release

These results suggest that the dual cross-linking mechanism of fumed silica, consisting of primary platinum-catalyzed network formation and secondary PS-OH induced cross-linking, plays an important role in achieving mechanical stability and controlled hydrogen release. In particular, the addition of 10% fumed silica was found to be optimal for balancing film strength and hydrogen evolution rate without compromising the surface quality or elasticity of the film. The rapid film formation and uniform hydrogen gas evolution highlight its potential as hydrogen gas transport cosmetic material for skin care and therapeutic applications.

### Structural and Mechanical Characterization

The structural and mechanical properties of the dual cross-linked hydrogen-releasing films were evaluated by analyzing tensile strength, elongation distance, film thickness, hardness, and adhesive strength. All measurements were conducted using a texture analyzer at a constant crosshead speed of 1 mm/s under controlled conditions (25 °C). For mechanical property testing, films were cast with a sample weight of 5 g, while adhesive strength testing was performed using films prepared with 1.5 g of material, yielding an approximate thickness of 0.25 mm.

The tensile strength of the films increased with silica content up to 10%, reaching a maximum of 27 N, followed by a slight decrease to 25 N at 15% silica content. This trend suggests that moderate silica incorporation enhances mechanical reinforcement by contributing to network densification, while excessive silica loading may induce brittleness and defect formation, thus reducing tensile strength.

Silica (%)	5	10	15	20
Tensile strength (N)	9.5	11.4	27.0	25.0
elongation distance(mm)	20.9	31.4	42.7	44.4
Thickness (mm)	2.5	2.7	2.6	2.7
Hardness (ShoreA)	10	15	20	20

**Figure 5.** Effect of silica ratio on the physicochemical properties of the polysiloxane film

The film thickness was consistently maintained at an average of 2.6 mm across all formulations, indicating that silica concentration did not significantly affect film casting uniformity. In terms of hardness, a gradual increase was observed with increasing silica content, consistent with the expected role of silica as a rigid filler enhancing the stiffness of the polymer matrix. Films with higher silica content exhibited progressively stronger adhesion to the substrate. This improvement is attributed to the increased cohesive strength and surface roughness of the films induced by silica particles, which enhanced interfacial interactions.

Overall, the mechanical analysis demonstrates that the incorporation of 10% silica optimally balances tensile strength, hardness, and adhesive properties without compromising film thickness uniformity. These findings suggest that controlled silica loading is critical for achieving robust yet flexible hydrogen-releasing films suitable for skin application.

### Antioxidant Effects

The antioxidant effects of dual cross-linked films are evaluated through a DPPH radical scavenging assay, which indirectly measured the antioxidant capacity of the released hydrogen gas. Films containing 10% silica and varying concentrations of PS-OH were tested. During this time, a gradual color transition from purple to yellow was observed in the DPPH solution, indicating the continuous release of hydrogen gas and subsequent RSA.

Quantitative analysis showed that the film containing 20% PS-OH achieved a maximum RSA value of approximately 70%, 10% PS-OH (57.4%) and 30% PS-OH (62.6%).

Hydrogen gas released from the film was sustained under physiological temperature, with maximum cumulative concentrations aligning with reported therapeutic thresholds for ROS neutralization. This result confirms that the hydrogen gas maintained potent antioxidant activity over an extended period.

The consistent color change and high RSA % suggest that the dual cross-linked silicone network supports sustained hydrogen generation, which could be crucial for long-term therapeutic applications in oxidative stress-related skin conditions.



	DPPH 0.5mM	PS-OH 20%	PS-OH 30%	PS-OH 40%	PS-OH 10% + Silica 10%	PS-OH 20% + Silica 10%	PS-OH 30% + Silica 10%
RSA (%)	0.0	63.3	50.7	66.2	57.4	70.4	62.6

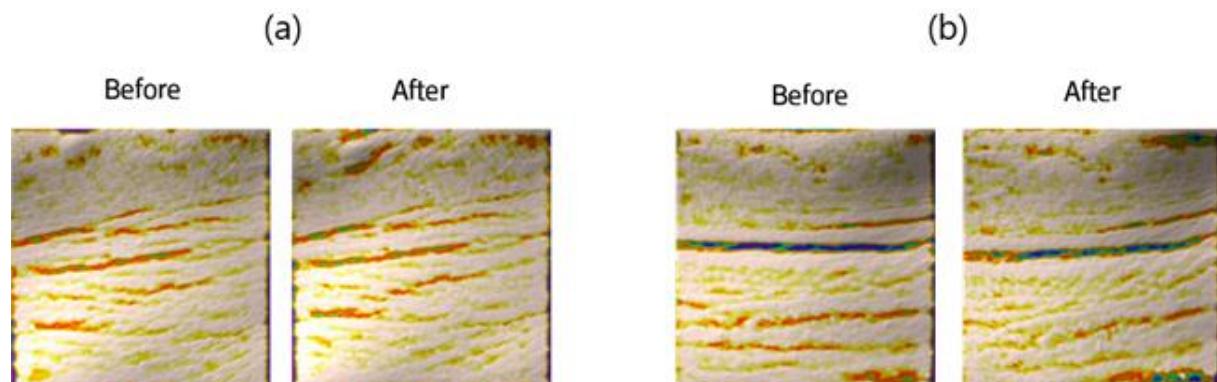
**Figure 6.** Effect of films with varying silica content and PS-OH concentrations on DPPH radical scavenging activity

## Investigation of Skin wrinkle Improvement

The clinical efficacy of the hydrogen-releasing film was evaluated in comparison with a non-hydrogen-releasing normal film. Two main indicators were assessed: immediate changes in transepidermal water loss (TEWL) and immediate improvement in neck wrinkles.

The TEWL values were measured using a Tewameter® before and immediately after film application. In the normal film group (A+B composition without silica and PS-OH), TEWL slightly increased from 14.23 g/m<sup>2</sup>/h to 14.46 g/m<sup>2</sup>/h, indicating a 1.62% deterioration of the skin barrier. In contrast, the hydrogen-releasing film group (containing 10% silica and 30% PS-OH) exhibited a reduction in TEWL from 13.52 g/m<sup>2</sup>/h to 13.22 g/m<sup>2</sup>/h, corresponding to a 2.22% improvement in skin barrier function. These findings suggest that the hydrogen-releasing film not only forms a physical barrier but also exerts a biochemical effect, possibly through its antioxidant properties, contributing to enhanced skin moisture retention immediately after application.

Neck wrinkle improvements were assessed using Antera 3D imaging by measuring changes in the Indentation Index. In the normal film group, the Indentation Index decreased from 22.00 to 21.74, yielding a minor 1.18% improvement. However, the hydrogen gas-releasing film group showed a substantial decrease from 25.70 to 23.77, achieving a 7.51% improvement rate. This superior performance implies that the continuous release of molecular hydrogen enhances the dermal microenvironment by neutralizing oxidative stress, leading to a more pronounced immediate reduction in wrinkle depth compared to normal film.



**Figure 7.** Neck wrinkle improvement before and after application. (a) normal film, (b) hydrogen gas-releasing film

Overall, the results demonstrate that the hydrogen-releasing film significantly outperforms the non-hydrogen-releasing normal film in terms of both skin barrier reinforcement and wrinkle reduction. These effects are likely attributed to the sustained antioxidant activity provided by the hydrogen gas released from the dual cross-linked silicone network. The findings support the potential utility of hydrogen-releasing silicone films as innovative skincare materials for immediate skin recovery and anti-aging applications.

## Conclusion

In this study, a dual cross-linked hydrogen-releasing silicone film was successfully developed through platinum-catalyzed hydrosilylation and secondary cross-linking with a multifunctional siloxane compound. The optimized film formulation, containing 20% PS-OH and 10% silica, achieved rapid film formation, controlled hydrogen generation over 12 hours, and demonstrated potent antioxidant activity. Mechanical characterization revealed that silica

reinforcement enhanced tensile strength and adhesive properties without compromising film uniformity. UV radiation is known to induce oxidative stress that accelerates skin aging by promoting ROS generation and subsequent cellular damage. In this context, the application of hydrogen gas as an antioxidant agent represents a novel and groundbreaking strategy for protecting the skin against UV-induced oxidative damage. These results suggest that the developed hydrogen-releasing film holds strong potential as a novel antioxidant cosmetic for skin protection and regeneration against oxidative stress.

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