Applications of Self-Reparable Antimicrobial Polysiloxanes

Subjects: Polymer Science

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Organosilicon polymers (silicones) are an important part of material chemistry and a well-established commercial product segment with a wide range of applications. Silicones are of enduring interest due to their unique properties and utility. New application areas for silicone-based materials have emerged, such as stretchable electronics, wearable stress sensors, smart coatings, and soft robotics.

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1. Introduction

Polymers made of siloxane bonds (silicones: polysiloxanes and polysilsesquioxanes) are recognized high-value materials of excellent low-temperature flexibility, high and low-temperature stability, low surface energy, high permeability, electrical resistance, high oxidation stability, and resistance to environmental conditions, as well as biocompatibility, sterilization tolerance, biological durability, and hemocompatibility [1][2][3][4]. Owing to their intrinsic properties, silicones can be used not only in the electronics or aerospace industry but also in the biomedical field and the food industry, where durability, sterility, and chemical purity of polymeric materials are required. Poly(dimethylsiloxane) (PDMS) is the most well-known example of silicone-based materials, a precursor of covalently cross-linked elastomers that are soft, stretchable, and almost creep-free. The mechanical performance of siloxane polymers can be tuned by adjusting their molecular weight or degree of cross-linking. However, conventional chemical cross-linking does not guarantee durability, and thus the main disadvantage of traditional silicone elastomers is their susceptibility to physical damage.

While silicone materials of this type are still in high demand, modern technologies, much more oriented towards sustainability, recyclability, and reusability, tend to focus on the dynamic crosslinking of siloxanes with tailored mechanical properties by means of self-healing (S-H). The introduction of a S-H mechanism into silicone materials may be a promising alternative to covalent network formation, and self-regenerating polysiloxane elastomers that are capable of healing minor physical damage are the focus of recent research [5][6][7][8][9]. The self-repair capability can not only extend the life of silicone coatings but also help meet the specific requirements of emerging new applications such as stretchable electronics, wearable stress sensors, smart coatings, and soft robotics.

An important concern for materials intended for such applications, aside from their self-healing effectiveness and excellent mechanical properties, is their resistance to biological factors. Frequent and prolonged contact with skin, moisture, and the external environment makes each type of silicone material susceptible to unwanted microbial deposition and biofilm growth. Any major damage but also any small changes in the continuity of polymer coatings (e.g., minor scratches) can create favorable conditions for biofilm formation and have a huge impact on the rate of surface colonization by microorganisms. Scratches can become specific habitats—protective environmental niches for bacterial growth. In this context, the capability for effective re-mending and, at the same time, discouraging microorganisms from colonizing the surface is a very desirable and advantageous feature. High-value materials of this type are gaining increasing attention.

2. Applications of Self-Reparable Antimicrobial Polysiloxanes

Research interest in developing self-reparable, fouling-release, and corrosion-resistant polymer coatings has been growing during the last decade (**Table 1**) [6][10]. Enhancement of adhesion strength may adversely affect antifouling properties. Low wear resistance also reduces the anticorrosion effect. That is why the focus on the antifouling action of silicone coatings is accompanied by efforts to make them resistant to mechanical damage. Self-healing is a very attractive option, yet a special design of the chemical structure is required to support the action of environmental factors, e.g., seawater.

Table 1. Self-healing silicones of antimicrobial properties designed for particular applications.

Use	S-H system [1]	Microorganisms [2]	Ref.
Antifouling coating	PTS/PSO	Marine microorganisms	[11]
	PDMS/PDMAEMA/PU	Marine microorganisms	[12]
	PDMS/PU/CUR/Eugenol	Marine microorganisms	[13]
	PMTMS/Ag NPs	*S. aureus*	[14]
	PDMS/UIa/OHBA	Benthic diatoms	[15]
	PDMS-PUa/DCOIT	Marine microorganisms	[16]
	PDMS/P(Ua-TUa)/TA	*P.* sp.; *E. coli*; *S. aureus*; *diatoms*	[17]
Biomedical devices	PDMS/SPU	*E. coli*; *S. aureus*	[18]
	PDMS/CMCS-PA@Fe	*E. coli*; *S. aureus*	[19]
	HPSi/LP	*E. coli*; *S. aureus*	[20]
	PDMS/PEG/DA/CUR	*E. coli*; *S. aureus*	[21]

Use	S-H system [1]	Microorganisms [2]	Ref.
Wearable electronics	SS-PDMS-DH/Zn^{2+}/Ag NPs	*E. coli*; *S. aureus;*	[22]

[1] antimicrobial/antifoulant unit introduced in the silicone formulation; [2] microorganisms killed by a given elastomer.

Polydimethylsiloxane-based polymers have been extensively studied for the development of fouling release coatings. Hydrophobicity and low elastic modulus make it difficult for marine organisms to attach to the surface of silicone films. Yet, the application of such coatings to polar substrates, including metals, is not facile, and thus their longevity is poor. Several research papers were devoted to silicone materials of this type, mainly designed for action against undesired colonization of bacteria, microalgae, and molluscs that can adversely affect ships and marine equipment. Toxic antifouling paints containing tributyl tin (TBT) based compounds have been banned, and there is a need for antifouling coatings that are innovative and efficient but safe for the environment.

Self-healing antifouling silicones have been prepared by the insertion of thiourea and ether groups into a silicone resin [11]. A polyether-thiourea-siloxane (PTS) copolymer of narrow molecular weight distribution was synthesized via free radical polymerization. Thiourea residues in PTS formed an H-bonded network, and it was used as an additive to antifouling coatings based on crosslinked PDMS in a mixture with phenylmethylsilicone oil (PSO). Incorporation of a small amount of PTS/PSO was enough to increase surface micro-roughness and hydrophobicity as well as improve the mechanical properties of the coating, including elongation at break. With an increasing amount of PTS, phase separation was promoted, and PSO encapsulated in the copolymer exhibited enhanced leaching onto the coating surface. The H-bonding between thiourea groups improved the adhesion strength between the coating and the substrate only up to a certain limit. The most effective antifouling performance was achieved with a composition of 12 g of PTS in 100 g of the PDMS network. Excessive amounts of PTS reduced the crosslinking density and deteriorated the mechanical performance of the coating.

A self-healing antifouling coating of excellent mechanical strength was prepared with the amphiphilic block copolymer polydimethylsiloxane-poly(2-(dimethylamino)ethyl methacrylate) (PDMS-PDMAEMA) that was introduced into the polydimethylsiloxane-based polyurethane (PDMS-PU) matrix and subsequently zwitterionized during solidification [12]. Polysiloxane segments of both polymers entangled to form a semi-interpenetrating network while the zwitterionic units migrated toward the external parts on immersion in water. This effect provided the hybrid coating with antifouling properties, especially the resistance towards adhesion of proteins (156 $\mu g/cm^2$ vs. 14 $\mu g/cm^2$) and marine microorganisms (425×10^3 n/cm^2 vs. 12×10^3 n/cm^2). Swelling of the zwitterionic segments increased the contact fusion rate of the mechanically damaged parts and promoted self-healing of the micro-phase-separated system.

A silicone-based coating with antifouling and anti-corrosion properties self-healed through supramolecular interactions involving hydrogen bonds and dynamic disulfide bond exchange between the functionalized monomers lipoic acid-benzothiazole (LA-BTZ) and lipoic acid-modified PDMS-based polyurea-urethane (PDMS-PUU-LA) [23]. Small scratches on the film disappeared completely within 40 minutes at room temperature in the air. The original toughness (2.58 MPa of ultimate strength) and stretchability (1014.7%) were recovered under ambient conditions or artificial seawater with healing efficiencies of 98.5% (4 h) and 94.6% (8 h), respectively. The adhesion of silicon-based coating epoxy resin and steel was very strong (~2.50 MPa and ~3.33 MPa), and long-term static fouling-resistant properties and good corrosion resistance in salt spray tests were observed.

A sea slug-inspired PDMS-based smart marine antifouling polyurethane coating with UV-responsive and controllable coumarin release was reported [13]. PU was modified by the insertion of coumarin and eugenol. Coumarin groups can undergo reversible dimerization on irradiation with 365 nm UV (release after treatment with 254 nm UV). Free or chain-grafted coumarin molecules can take part in this process, which leads to an efficient S-H of the resin on UV irradiation. The coating was transparent, highly adhesive (>1 Mpa), mechanically robust (Young’s modulus <4.5 MPa), and exhibited low surface energy (20–30 $mJ \cdot m^{-2}$) as well as good antifouling, anti-algae resistance, and antibacterial properties.

Self-healing, antibacterial, and antifouling coatings were also obtained by surface modification with a silicon oxide layer, followed by grafting of PDMS chains as a “lubricant liquid” [24]. As another example, a vinyl-terminated polydimethylsiloxane (Vi-PDMS) was grafted onto various substrates coated with sulfhydryl-modified hollow mesoporous silica (SHHMS) [25]. A lubricant-grafted slippery surface formed in this way was very stable, exhibited good antifouling properties, and effectively decreased the absorption of organic liquids, polysaccharides, and proteins. Functional antifouling and antibacterial materials of good mechanical and self-healing properties were obtained by UV/moisture dual curing of PDMS containing methacryloyloxy and methoxy silane groups (MAPDMS)-microcapsule-SiO_2 (MPMS) of hierarchical structure [26].

Self-healing and antifouling hybrid materials can also be prepared with the use of nanomaterials as well as artificial biocides or bioactive natural compounds. For example, silver nanoparticles (AgNPs) and polymethyltrimethoxysilane (PMTMS) were introduced into AZ31 Mg alloys via layer-by-layer (LbL) assembly and siloxane self-condensation reaction to obtain an antibacterial coating against *S. aureus* [14]. PDMS was also used as a hydrophobic binder for coating octadecylamine (ODA)-modified flower-like $Ni(OH)_2$ particles ($Ni(OH)_2$@ODA) that were applied for the modification of cotton fabric [27]. Excellent antifouling and self-cleaning performances, as well as durable superhydrophobicity, were achieved in this system.

4,5-dichloro-2-n-octyl-4-isothiazolin-3-one concentration-dependent antibiofouling activity of PDMS-PUa/DCOIT, based on the release of the antifoulant (1.5–4.5 $\mu g\ cm^{-2}\ d^{-1}$ for 1.0–10 wt% of DCOIT, respectively) was studied [16]. The self-stratifying properties of PDMS-PUa (the urea groups interact more strongly with the surface, while PDMS chains tend to migrate to the upper layer) were altered upon the addition of DCOIT. DCOIT affected the adhesion of PDMS-PUa to the substrate because of its competitive interactions with Ua units. Polydimethylsiloxane polymer containing imine and urea groups (PDMS-UIa) was used as an eco-friendly antifoulant after the addition of a small amount of N-octyl-2-hydroxybenzamide [15].

The bio-adhesive and good bacteriostatic effects of tannic acid improved both the adhesion strength and the antifouling properties of a PDMS-based coating. The macromolecular polyphenol is active against Gram-positive and Gram-negative bacteria, whereas the catechol/pyrogallol groups of TA can interact strongly with substrates through hydrogen bonds, ionic bonds, or hydrophobic interactions. The latter plays a major role in underwater adhesion. Correspondingly, PDMS-P(Ua-TUa)-TA displayed strong adhesion to the substrate (~2.2 MPa) as well as good antibacterial and anti-diatom properties (~96%, ~95%, ~93%, ~84% reduction, respectively, for *Pseudomonas* sp., *E. coli*, *S. aureus*, and diatoms) [17].

2.2. Wearable Electronics and Biomedical Devices

Flexible electronics applications require mechanically durable materials with the ability to accurately monitor electrical signals. A mussel-inspired self-healing antibacterial, conductive organosiloxane elastomer with good mechanical properties was thus designed for wearable strain sensors [22]. The PDMS-based copolymer with side 3-aminopropyl groups was transformed into a supramolecular network (SS-PDMS-DH) by dehydration coupling with carboxyl groups of DHBA, which resulted in the formation of amide bonds. It was further crosslinked by the presence of Zn^{2+} ions and silver nanoparticles (Ag NPs).

Tensile properties in this system were controlled by phase separation and multiple reversible interactions. Excellent mechanical properties were achieved by the synergistic effect of Zn^{2+} coordination on DHBA residues and dynamic disulfide crosslinks. The former were responsible for hard segment formation that stiffened the network, while the latter acted as soft domains that contributed to energy dissipation. The addition of Ag NPs to form S–Ag interactions with disulfide bonds reinforced the network and made the elastomer conductive. High tensile strength (2.4 MPa stress) and stretchability (1762% strain) were achieved at 10 wt% nanofiller content. The combination of the bactericidal effect of Ag NPs and zinc ions with the bacteriostatic effect of the hydrophobic surface of PDMS brought in an efficient antibacterial performance of the conductive elastomer against *E. coli* and *S. aureus* (antibacterial efficiency of 98.79% and 98.52%, respectively). The effect was related to the denaturation of bacterial respiratory enzymes by Ag NPs that penetrated cells and the adsorption of Zn^{2+} on cell membranes under the action of Coulomb forces.

The synergistic effect of multiple dynamic interactions and reversible covalent bonds made the SS-PDMS-DH-Ag elastomer self-repairable. It restored 91.2% of the original mechanical properties after 24 h of spontaneous self-healing at room temperature. In addition, elastomers of the $SS_{0.4}$-PDMS-$DH_{0.6}$-Ag_{10} composition were applied to self-repairing wearable strain sensors for monitoring the bending motions of human joints.

Silanol-terminated PDMS side grafted with fluorocarbon and poly(ethylene glycol) chains was used as a reactive amphiphilic polymer (RAP) in a blend with bis(dimethoxy)methylsilane-terminated polyurea (SPU) and oligosiloxane nanoclusters to form a surface-enriched antifouling coating that displayed superior antimicrobial action and strong substrate adhesion [18].

The oligosiloxane nanoclusters with free silanol groups can cross-link the alkoxysilane-terminated flexible SPU by sol-gel chemistry. A tough polymer network was formed and interlinked with the substrate via silanol groups. The low-surface-energy RAP siloxane self-enriches on the surface of the coating. The thin film of this composition is transparent (>85% transmittance), tough (tensile strength of ~12 MPa), and exhibits fouling resistance against proteins and bacteria. It strongly adheres to various substrates, including glass, ceramic, steel, Ti, and epoxy (3−15 MPa), and can possibly be used as an antifouling coating in flexible electronics and medical devices.

Moreover, PDMS-based optical fibers were integrated into carboxymethyl chitosan (CMCS)-protocatechualdehyde (PA)@Fe hydrogels (CMCS-PA@Fe) to obtain hybrid, pH-sensitive devices for real-time monitoring of the wound healing process [19]. The hydrogel operated by chelating PA@Fe with CMCS. A high antibacterial effect (>99.9%) was noted with the help of the NIR-assisted photothermal effect. The pH-sensitive optical fiber/CMCS-PA@Fe hydrogels can adapt to the movement, and wound bacterial infection can be quickly diagnosed by changes in the environment's acidity.

A hyperbranched polysiloxane terminated by multi-amine (HPSi) was reacted with a linear polyacrylate resin (LP) containing pendent sulfobetaine and acetoacetyloxy residues to form dynamic vinylogous urethane groups. The resulting hybrid material (LP-HP) can be used as a multi-functional coating with high mechanical strength, reversible self-healing, and high antibacterial ability against *E. coli* and *S. aureus* (>95%) provided by nontoxic sulfobetaine groups [20]. The structure of HPSi (large number of amine groups and easy segmental motion owing to fewer chain entanglements) and its concentration in LP resin proved to play a key role in adjusting these properties. As the amount of HPSi increased, the LP-HP coating exhibited higher tensile strength and Young’s modulus but lower elongation at the break because of the increased crosslinking density. The optimal parameters (tensile strength of ~17.89 MPa, the toughness of ~5.72 MPa, self-healing efficiency > 92% at 60 °C for 24 h) were obtained for a polyacrylate coating containing 6.3 wt% of HPSi (LP-HP6). The healed sample exhibited high self-healing efficiency (94.07% of the initial tensile strength, 95.81% of elongation at break, and 92.65% of toughness). The mechanical properties of LP-HP coatings were tuned by changing the amount of HPSi to meet different application requirements. Interestingly, a strain-softening behavior, where strain grows but stress reduces, appeared in the stress-strain curve of LP-HP9 after the yield point.

A smart self-healable PDMS-based hydrogel that inhibited protein adhesion and displayed antimicrobial action against Gram-positive (*S. aureus*) and Gram-negative (*E. coli*) bacteria was prepared with curcumin-loaded zwitterionic polymersomes consisting of PDMS and a tri-block copolymer poly([dimethyl-[3-(2-methyl-acryloylamino)-propyl]-(3-sulfopropyl)ammonium)](poly(sulfobetaine)). The polymersomes were mixed with amine-modified PDMS-based polymersomes, then the dual system was crosslinked with an aldehyde-modified PEG via a Schiff-base reaction [21]. The hydrogel displayed self-healing behavior in saline solution due to ionic interlocking between the poly(zwitterionic) segments. This system significantly enhances the bioavailability of curcumin. Sustained delivery of the hydrophobic drug was observed over 72 h. Moreover, the wettable, self-healing, fouling-resistant, transparent, and soft hybrid material efficiently reduced the deposition of a protein (BSA), and thus it can be potentially used in therapeutic contact lens applications.

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