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PDMS with designer functionalities—Properties, modifications strategies, and applications

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ABSTRACT

Rapid progress in micro- and nanotechnologies such as lab-on-a-chip (microfluidic networks, sensors, actuators, and connectors), soft lithography (replica moulding, microcontact printing and affinity contact printing), and stretchable transparent electronics has strongly benefitted from high-performance polymers like poly(dimethyl)siloxane (PDMS) that are suited for high-fidelity microsystem construction and rapid prototyping. While basic PDMS has been a unique enabling material, recent progress in tailoring PDMS to specific requirements will render this material even more valuable in the future.

Basic PDMS is elastic, transparent, biocompatible, gas-permeable, and forms conformal contact with surfaces.

Surface modifications of PDMS, inducing properties such as hydrophilicity, electrical conductivity, antifouling, energy harvesting, and energy storage (supercapacitors) are of major interest.

Bulk modifications can alter PDMS properties such as elasticity, electrical and thermal conductivity. Such bulk modified PDMS composite materials can be created by embedding free molecules (e.g., dyes), nanoparticles (graphene, carbon nanotubes, and various other of organic and inorganic nature) or microparticles, or by altering the composition of the prepolymers before polymerization.

Both, surface and bulk modifications of PDMS open avenues to a multitude of tuneable characteristics optimized for a diverse set of applications ranging from integrated micro- (lab-on-a-chip) to macro-systems (biomedical devices and epidermal electronics).

In microfluidic systems design exploiting modified PDMS, a key aspect of this review, the unique features of these materials permit rapid, easy, and reproducible construction without the need for elaborate facilities and trained personnel as compared to other materials like silicon.

This review focuses on recent progress in modification strategies to alter deliberately PDMS surface and bulk properties, especially for microfluidic, biological, flexible electronics, e-skin, and self-healing applications.

Contents

Abbrevations: AgNW, silver nanowires; APTES, 3-aminopropyl)triethoxysilane; ATRP, atom transfer radical polymerisation; BSA, bovine serum albumin; CNT, carbon nanotubes; CuNW, copper nanowires; CVD, chemical vapour deposition; FITC, fluorescein isothiocyanate; GO, graphene oxide; LBL, layer-by-layer; MAM, mechanically assembled monolayer; MWCNT, multi-walled carbon nanotubes; NHS, *N*-hydroxysuccinimide; PDA, polydopamine; PEG, polyethylene glycol; SWCNT, single-walled carbon nanotubes; TRITC, tetramethylrhodamine isothiocyanate; WCA, water contact angle; XPS, x-ray photoelectron spectroscopy.

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1. Introduction

In general, polymers with a $-R_2Si-O-$ unit are termed silicones, while the $-Si-O-$ repeat unit is also called siloxane. The strength of the Si—O bond gives the polymer its thermal and chemical stability, which is important for its use in high-temperature applications [1,2]. In PDMS, the flexibility of the siloxane backbone permits the chains to easily arrange and rearrange themselves so as to place the methyl groups at their surfaces and interfaces [3]. Several silicone elastomers are available, with Sylgard 184® from DOWSIL being the most cited in the scientific literature in lab-on-a-chip devices [4,5] within the last two decades [6–12]. The composition of Sylgard 184® is not disclosed by the manufacturer. However it is reported to be as follows: Base: dimethylsiloxane oligomers with vinyl end groups (>60%), silica filler (dimethylvinylated and trimethylated silica, 30–60%), tetra(trimethylsiloxy) silane (1–5%) and ethylbenzene (<1%), and a platinum catalyst. Curing agent: a cross-linking agent (dimethyl methylhydrogen siloxane, 40–70%) and an inhibitor (tetramethyl tetravinyl cyclotetrasiloxane 1–5%). The composition of another PDMS used in microfluidics, RTV-615 from Momentive Materials, is Base: polyvinylsiloxane (60–90%), polyalkylalkenylsiloxane (10–30%), and a catalyst. Cross-linking agent: polyvinylsiloxane (30–60%), modified silica (SiH) (30–60%), octamethylcyclotetrasiloxane (<1%) and toluene (<1%) [13]. Elastomer fillers such as silica fillers are added to base polymers to increase elastic modulus. A reaction scheme of PDMS polymerized by platinum catalysts is presented in Fig. 1 (cross-linking by addition). In larger volume applications in industry and household, other, inexpensive polymerization chemistries for siloxanes, e.g. cross-linking by condensation, is widespread. These materials are also called one-part room temperature vulcanization (RTV) sealants, although requiring moisture as a second component. However, the release of acetic acid during polymerization limits the usefulness of such chemistry for sensitive and biomedical applications [14].

Table 1
Some relevant characteristics of PDMS (Sylgard 184, 1:10 catalyst to base polymer).

Characteristic	Value	References
Optical transparency	240–1100 nm	[16–18]
Surface tension	21–22 mN/m	[1]
Glass transition temperature	−125 °C	[1]
Electrical conductivity	2.9 E + 14 Ω*cm	[22]
Heat conductivity	0.27 W/m*K	[22]
Young's elastic modulus *E*	~1–3 MPa	[19,43]
Surface tension	21 mN/m	[1]
Water vapour diffusion coefficient	$\sim$1000–6000 $\mu m^2 s^{-1}$	[41]
Oxygen diffusion coefficient	$\sim$2000–4000 $\mu m^2 s^{-1}$	[49]
CO_2 diffusion coefficient	$\sim$1000 $\mu m^2 s^{-1}$	[50]

Some physical properties of PDMS are listed in Table 1. PDMS is optically transparent (240 – 1100 nm) [16–18], is biocompatible [13] forms conformal contact (van der Waals contact or molecular contact) and has a low surface free energy (is hydrophobic; contact angle with water ~110°). It has a unique flexibility with a Young's