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APPLICATION OF POLYDIMETHYLSILOXANE (PDMS) POLYMERS AS STRUCTURAL ADHESIVES, SEALANTS, AND HIGH-PERFORMANCE FUNCTIONAL COATINGS

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Key words: polydimethylsiloxanes, adhesion, adhesives, functional coatings, super-hydrophobic, icephobic, durability.

Abstract: This work presents the outcome of our research on the application of polydimethylsiloxanes (PDMS) as base materials for the formulation of high-performance structural adhesives, sealants, and multifunctional coatings. The unique properties of these polymers, such as (i) the excellent adhesion to various materials used by automotive, aerospace, construction and maritime industries, (ii) inherent chemical inertness of cross-linked polymers, (iii) outstanding long-term durability, (iv) in-built hydrophobicity and icephobicity, and (v) flexibility and in some systems, self-healing ability, present PDMS resins as an attractive high-performance material offering versatility in a broad spectrum of engineering applications, e.g., from structural bonding and joint sealing to self-cleaning and icephobic coatings applicable to surfaces of structures exposed to sub-zero service temperatures, where potential ice accretion imposes severe danger to reliable and safe performance of engineering structures, through to antifouling and biomedical applications.

Zastosowanie polimerów na bazie polydimethylsiloxanu (PDMS) jako wysoko wydajnych powłok uszczelniających

Słowa kluczowe: polidimetylosiloksany, adhezja, kleje, powłoki funkcjonalne, superhydrofobowe, przeciwołdzeniowe, długowieczność.

Streszczenie: Przedstawiono wyniki badań nad zastosowaniem polidimetylosiloksanów (PDMS) jako materiałów wyjściowych do formułowania wysokiej jakości klejów strukturalnych, uszczelnaczy i powłok wielofunkcyjnych. Unikalne właściwości tych polimerów takie jak: (i) doskonała adhezja do różnych materiałów stosowanych w przemyśle motoryzacyjnym, lotniczym, budowlanym i okrętowym, (ii) naturalna obojętność chemiczna usieciowanego polimeru, (iii) wyjątkowa długowieczność, (iv) wbudowana hydrofobowość i lodofobowość (własności przeciwołdzeniowe), (v) elastyczność i w przypadku niektórych systemów samonaprawialność, prezentują żywice PDMS jako atrakcyjny materiał o wysokiej jakości, oferujący wszechstronność w szerokim spektrum zastosowań inżynierskich: od klejenia strukturalnego i uszczelniania połączeń po samoczyszczące się i lodofobowe powłoki nakładane na powierzchnie urządzeń i konstrukcji narażonych na użytkowanie w temperaturach ujemnych, w których potencjalne narastanie lodu stwarza poważne zagrożenie dla niezawodnego i bezpiecznego działania konstrukcji inżynierskich, a także dla zastosowań przeciwporostowych i biomedycznych.

Introduction

Due to their specific organic/inorganic hybrid structure, polydimethylsiloxane (PDMS) polymers are unique enabling materials allowing relatively easy

bulk and/or surface modification and formulation into a broad range of specialty functional materials, such as elastomeric adhesives, coatings, or specialty biomedical systems. Specifically formulated PDMS resins offer reliable (often primer-less) adhesion to a variety of

substrates. Their low glass transition temperature, transparency in the UV-vis range, and low surface energy afford them outstanding flexibility, chemical resistance (including excellent UV-, ozone- and high-temperature resistance), and long-term durability under adverse service and environmental conditions. They exhibit excellent water repellency, making them suitable not only for structural bonding, but also for high-performance superhydrophobic, icephobic, or antifouling coatings. These attributes have been demonstrated through over 50 years of application in demanding markets, such as the automotive, marine, aerospace and spacecraft systems, building & construction, electronic, biomedical, power transmission, and consumer products.

The key features of siloxane polymers that contribute to the unique combination of properties of PDMS-

-based products are listed in Table 1. Almost all of these inherent attributes are a consequence of the following fundamental aspects: (i) the *low intermolecular forces* between dialkylsiloxane molecules, (ii) the *dipolar nature*, (iii) the *strength of the siloxane bond*, and (iv) the *flexibility of the siloxane backbone*.

Typically, hydroxy-terminated PDMS (see Fig. 1a) is used as the polymer base in most elastomeric silicone coatings, adhesives, and sealants, which usually comprise the following ingredients [1]: (i) 60–85% hydroxy-terminated silanol polymer (PDMS): MW 15,000–150,000 (ii) 10–20% of a plasticizer (trimethoxy terminated PDMS), (iii) 5–10% fumed silica, (iv) 5–7% of a cross-linker, (v) 0.05–0.1% of tin catalyst (e.g., dibutyl tin dilaurate), and (vi) 0.25–2% of adhesion promoter (e.g., aminopropyltriethoxy silane, γ -APS).

Table 1. Key attributes and fundamental properties of PDMS (Polydimethylsiloxane) polymers

Attribute	Material Property
Excellent substrate wetting (facilitating adhesion enhancement)	Low surface tension of liquid (uncured) PDMS
High water repellence	Low surface energy of crosslinked polymer
Excellent flexibility	<ul style="list-style-type: none"> • Low glass transition temperature • Large free volume • Low apparent energy of activation for viscous flow • Low activation energy of Si-O-Si bond rotation
Small temperature variation of physical properties	<ul style="list-style-type: none"> • Configuration of siloxane polymer chain and low interaction between methyl groups • Low activation energy of Si-O-Si bond rotation
Low reactivity	Configuration of siloxane polymer chain and small interaction between methyl groups
High gas permeability	<ul style="list-style-type: none"> • Large free volume • Low activation energy of Si-O-Si bond rotation
High thermal and oxidative stability	High Si-methyl bond energy
Ultraviolet light resistance	High Si-O bond energy

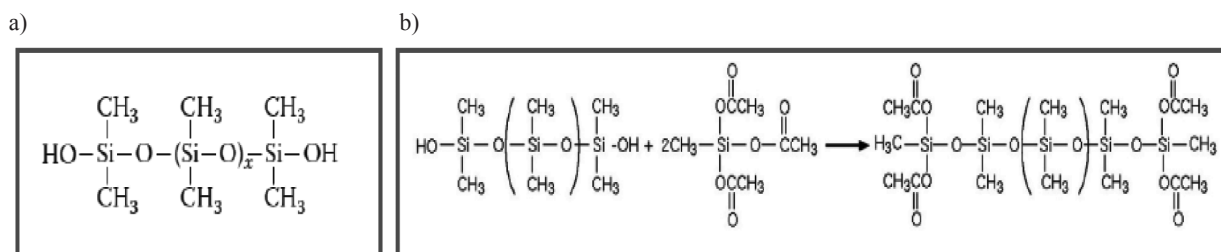


Fig. 1. (a) Hydroxy-terminated polydimethyl siloxane (PDMS) polymer, and (b) 1st stage reaction of hydroxy-terminated PDMS with the acetoxy cross-linker [1]

Condensation cure one-part, (RTV-1; Room Temperature Vulcanizing) and two-part (RTV-2) systems are typically formulated from hydroxy-terminated polymers with molecular weights ranging from 15,000 to 150,000. The most widely used in practical applications are RTV-1 systems, which are cross linked with moisture-sensitive multi-functional silanes in a 2-stage reaction. In the first stage, after

compounding with fillers, the silanol is reacted with an excess of multi-functional silane [1]. The silanol is, in essence, displaced by the silane, as depicted in Fig. 1 in an example of the acetoxy-cross-linked system.

The silicone resins in the form presented in the right-hand side of Fig. 1b, with two groups at each end of silicone susceptible to hydrolysis, is stored and hermetically protected from moisture until ready for use.

The second stage of the reaction takes place immediately after use as a coating, sealant, or adhesive, as the end groups become exposed to atmospheric moisture causing a rapid cross-linking reaction.

1. Formulating PDMS polymers for engineering applications

Formulating a new PDMS material for designated application, e.g., as an adhesive or coating, poses several challenges necessitating comprehensive understanding of the following issues:

- What are the service conditions and performance requirements of the product pertinent to the targeted market segment, and how these relate to the desired properties of the material?
- What properties are inherent to the base formulation ingredients (e.g., polymer, plasticizer)?
- What properties can be influenced by the formulation and/or by the compounding process?

Due to their hybrid organic/inorganic structure, the PDMS polymers can be easily formulated into high-performance composite materials due to their compatibility with various inorganic nano- and micro-sized materials and organic molecules, or by altering the structure and composition of prepolymers before polymerisation.

One of attractive characteristics of PDMS-based materials is the ease of their use due to relatively low viscosity and adjustable flow properties. Importantly, temperature changes influence their rheological properties to a much lesser extent than those of organic products. This characteristic is attributed to the low activation energy for viscous flow of silicone polymers, which is a result of the low inter- and intra-molecular interactions.

Pure PDMS networks have low inherent strength, as demonstrated by low tensile strength (<0.4 MPa) and very low tear strength (<0.1 N/mm), which do not satisfy the cohesive requirements of most engineering applications in which the adhesively bonded joints or exterior coatings are subjected to repetitive service-related static and dynamic mechanical stresses. The poor strength of 'unreinforced' elastomers is a result of weak interactions between PDMS polymer chains, which conversely are beneficial in providing a high movement capability to silicone materials.

The strength of these materials can be increased substantially by the addition of reinforcing fillers amongst which fumed silica, with a surface area in excess of 125 m²/g plays a dominant role. Silanol groups on the silica surface, possessing an average surface density of $\sim 4.9 \times 10^{14}$ cm⁻², or an average surface area of 20.4 Å² per silanol group, play the main role in influencing the interfacial adsorption and adhesion-enhancing behaviour. A typical

PDMS-based sealant or adhesive containing 10% by weight of a 200 m²/g silica has approximately 20 m² of filler surface per 1 ml (millilitre) of liquid polymer available for polymer-filler interactions. Because of the open and branched chain nature of the silica aggregates, a significant increase in the tensile strength of the filled elastomer with silica structure occurs [2].

The strong bonding of silica to PDMS matrix is attributed to a combination of chemical and physical bonds. The latter include van der Waals forces and the hydrogen bonding of silica surface silanols with polymer silanols and the oxygen atoms in the PDMS chain. Even after surface treatment of the silica, a substantial number of active silanol groups remain on the surface. Chemical bonding occurs as a result of condensation reactions, especially in the presence of a cross-linker and catalyst. The exact nature of the bonding forces is dependent on the filler surface energy and the accessibility and surface density of the silanol groups [3]. A recent study suggests that, although interfacial chemical bonding has a positive effect on reinforcement, the influence of physical interactions at the interface overrides that of chemical bonding [4]. Increasing the silica loading, surface area, silanol group density (and activity), as well as the structure, increases the number of polymer-filler interactions and hence, the network strength.

In the wet, uncured material, these polymer-filler interactions increase viscosity and, for untreated, high surface area silicas, especially when added to silanol-endblocked PDMS (condensation cure) polymers, may lead to 'crepe hardening' (strong thickening of the uncured material to the extent that it makes its handling, e.g., extrusion or spraying very difficult). Crepe hardening, which is caused by hydrogen bonding between the silica filler surface and the polymer chains, can be avoided by surface treating the silica, for instance, in-situ by the addition of a short-chain siloxane diol, e.g., HOSi(Me)₂O(Si(Me)₂O)_nH with $n \approx 6-20$. A similar effect is achieved by pre-treating the filler with methylsilanes, disilazanes, or low molecular weight cyclic siloxanes, such as octamethylcyclotetrasiloxane. Treated silicas interact more weakly with the siloxane polymer molecules, because their remaining surface silanol groups are shielded by the larger organosilicon surface groups; therefore, the primary polymer-filler interaction is based on the weaker van der Waals forces.

2. PDMS as specialty adhesives for construction applications

2.1. PDMS with enhanced adhesion to low surface energy (LSE) plastics

Achieving good adhesion to low surface energy materials [LSE] such as polyethylene or polypropylene

without the need for substrate pre-treatment remains one of the most challenging objectives for adhesion scientists and formulators. One of numerous prerequisites for this (the detailed discussion on adhesion fundamentals resides beyond the scope of this paper) is that the adhesive or coating thoroughly ‘wet out’ the surface of the material to be bonded or coated. It is demonstrated by spontaneous spreading of the coating’s or adhesive’s liquid resin over the substrate, intimately covering it, and thus maximizing the effectiveness of attractive forces between the molecules of the materials in immediate contact [5].

To achieve this, the surface tension of an uncured (liquid) adhesive must be lower than the surface energy of the solid substrate, (see schematic depiction of alternative scenarios regarding solid’s wettability states in Fig. 3 below). This, in turn, leads to the apparent

contact angle $[\theta_L]$ depicted in Fig. 2, and appearing in the fundamental Young-Dupré equation [Eqn (1)] achieving the value of $[\theta_L = 0^\circ]$,

$$W_A = \gamma_{LV} (1 + \cos \Theta_{SL}) + \pi_e \quad (1)$$

where γ_{LV} and γ_{SV} are the surface free energies of liquid (e.g., PDMS uncured resin) and the solid substrate, γ_{SL} is the solid-liquid interfacial tension, and Θ_{SL} is the equilibrium contact angle reflecting the balance of surface forces acting at the air-liquid-solid triple contact line, whilst W_A is the thermodynamic work of adhesion and π_e the equilibrium spreading pressure.

As seen in Figure 3(a), satisfying this requirement, i.e. $(\gamma_{\text{silicone}} < \gamma_{\text{substrate}}) \rightarrow [\theta_{\text{silicone}} \approx 0^\circ]$, results in the formation of a uniform film of the PDMS resin over the substrate surface.

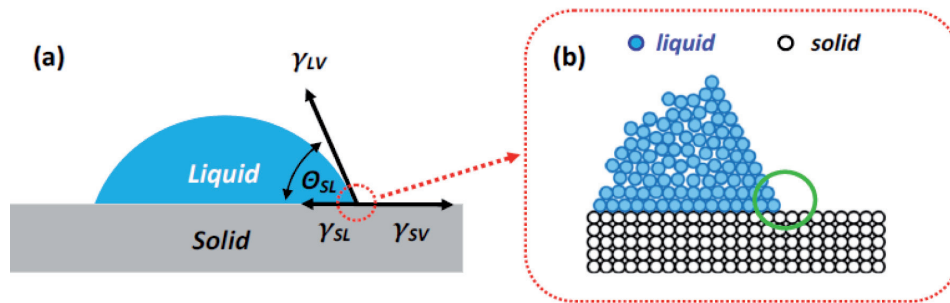


Fig. 2. (a) Sessile droplet of a liquid residing on ideally smooth substrate at the equilibrium controlled by the vectors of interfacial forces acting at the perimeter of the liquid-solid contact line; (b) schematic arrangement of liquid and solid molecules at the droplet perimeter (the contact line)

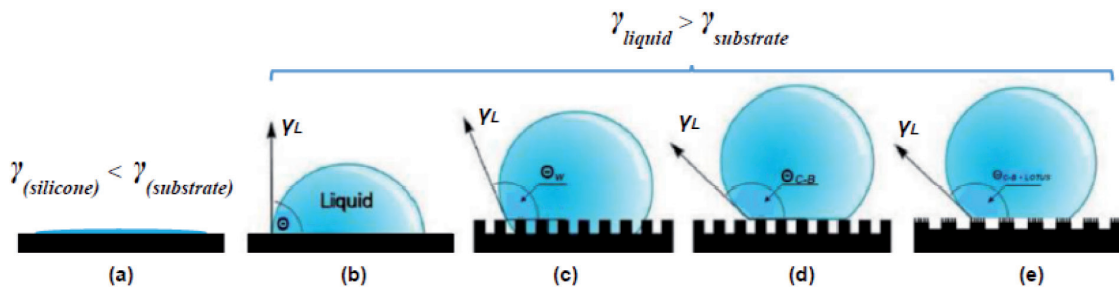


Fig. 3. Alternative substrate ‘surface wettability states’ in relation to the balance of surface tension of sessile liquid *versus* surface energy and surface roughness of the solid substrate, as demonstrated by the apparent surface wettability: (a) low-surface tension liquid PDMS resin on the surface of an ideally smooth solid substrate when $\gamma_{PDMS} < \gamma_{SUBSTRATE}$ (complete spreading, i.e. ‘surface wet-out’ of the solid by PDMS resin); (b) ideally flat solid substrate with the solid-liquid equilibrium described by the Young-Dupré equation [Eqn (1)]; (c) *Wenzel state*: homogeneous wetting regime where the liquid completely fills the grooves of rough surface; (d) *Cassie-Baxter superhydrophobic state*, which is a liquid-air ‘composite surface system’ with the liquid phase residing on the top of substrate asperities filled by air pockets; and, (e) The ‘*Lotus*’ state, which is an advanced form of the *Cassie-Baxter* state with surfaces of micro-asperities ‘decorated’ by nano-sized brush

While PDMS resins exhibit an inherently low surface tension ($\gamma_{\text{silicone}} = 21\text{--}21.6$ mN/m) and thus meet this specific requirement (see Table 2 [6]), it still is challenging to achieve durable adhesion of traditional PDMS materials to LSE substrates. Often, the only option available is to increase their surface energy *via*

a designated surface treatment, e.g., corona discharge or flame treatment, or alternatively to use solvent-based adhesion promoters. These options, however, increase the costs and (with the exception of priming) are difficult to implement at construction sites.

Table 2. Surface energy of common engineering materials, including commodity polymers 6

Solid Surface	Critical Surface Tension [mN/m]
Poly(tetrafluoroethylene) (PTFE)	18,5
Silicone	24
Poly(vinylidene fluoride)	25
Polyethylene (PE)	31
Polypropylene (PP)	31
Polystyrene	33
Poly(vinyl chloride) (PVC)	39
Nylon-6,6	43
Poly(ethylene terephthalate) (PET)	43
Aluminium	~500
Glass	~1000

One of the recently developed elastomeric PDMS adhesives, DC758 (Dow Corning) overcomes this

difficulty achieving, through the addition of a specific adhesion-promoting additive, an excellent adhesion [7, 8] to chemically inert LSE substrates such as spun-wound polyolefin (PO) mats or polyethylene (PE) film materials.

Figure 4 presents the results of adhesion tests of DC 758 and other types of elastomeric sealants to polyolefin-based barrier substrates commonly used by building and construction industries as weather-barrier materials.

Data in Table 3 demonstrates excellent durability achieved in bonding LSE weather membranes with the use of this novel PDMS adhesive (DC 758) after exposure to accelerated weathering in a fluorescent ultraviolet and condensation chamber (QUV-Tester operated in accordance with ASTM G154-12a [10]), which realistically reproduces the service-related damage caused by the combined influence of sunlight, rain, and dew. For tensile testing, ASTM D412 “C”, dumbbell specimens were used [11].

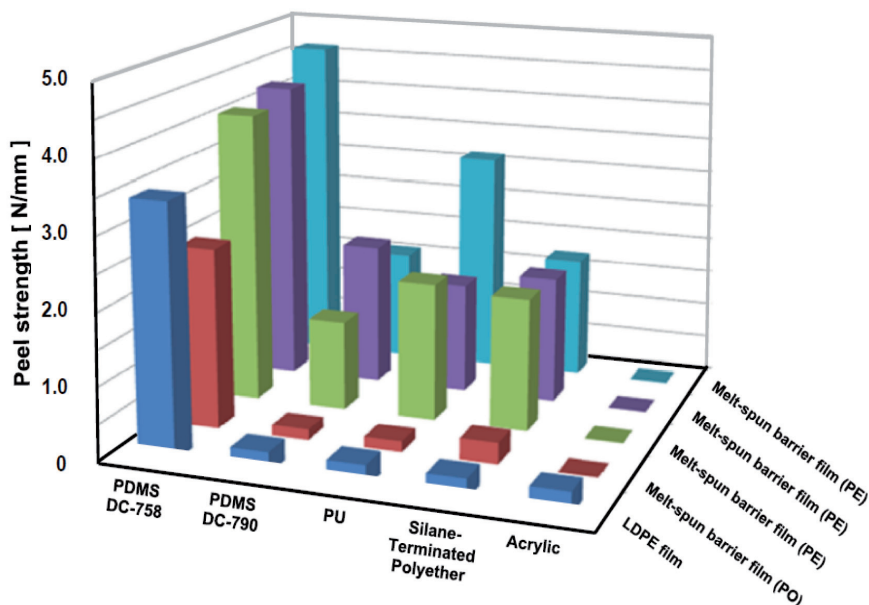


Fig. 4. Peel adhesion of various elastomeric adhesives on LSE weather barrier membranes [8] (ASTM C794-10; 180° peel test carried out at the rate 50 mm/min 9 after 7-day cure)

Table 3. Properties of PDMS (DC 758) sealant after exposure to accelerated QUV weathering [12]

Test Parameter	Laboratory conditions*				Accelerated Weathering (QUV-A)		
	7 Days	1000 h	5000 h	10,000	1000 h	5000 h	10,000 h
Peel Strength on glass (N/mm)	10.86	12.09	14.54	14.89	12.26	10.51	10.86
Durometer hardness (A Scale)	NA	55	57	63	53	53	60
Tensile Strength (MPa)	NA	2.75	3.16	2.92	2.30	2.29	2.08

(*) Laboratory Climate Conditions (approx.: 23 ±2 °C and 50±10% rel. humidity)

The above DC 758 sealant was additionally tested according to ASTM C719-13 for adhesion and cohesion under $\pm 25\%$ cyclic movement using a modified substrate specimen with an anodized aluminium surface on one side of the sealant bead, and a commonly available self-adhered flashing (SAF) with a HDPE surface on the opposite side [12] of the bead. The sealant passed all tests without the need for using primers on the HDPE surface.

2.2. The mechanisms of adhesion increase of PDMS by surface-grafted connector molecules

The bond strength and the long-term performance of bonded or coated products involving any type of adhesive or coating on polymeric substrates (which include coated/painted metallic substrates) can be significantly improved by controlling the physico-chemical structure and spatial architecture of interphase, which is an intermediate zone between the substrate and

adhesive or coating as schematically illustrated in Fig. 5. The interphase comprises an array of tethered connector chains which, at one end, are chemically attached (grafted) to the molecular backbone of a polymeric substrate, while the unbonded ‘free-floating end’ (see Fig. 5b) becomes either (i) on application of a chemically cross-linking adhesive – chemically bonded to it (see Fig. 5c), or alternatively, (ii) on contact with a non-reactive adhesive or coating – it interpenetrates into the bulk of this material (Fig. 5d) providing some level of adhesion enhancement through entanglement of molecular chains.

The mechanisms of such alternative interfacial interactions between the surface of polymeric solids ‘decorated’ by end-grafted flexible molecular chains and adhesives or coatings have been explored by numerous researchers who determined that the following mechanisms, as schematically illustrated in Fig. 8, may contribute to the fracture of such interface reinforced by ‘connector chains’: (i) chain scission, (ii) chain pull-out, and (iii) craze formation (in ductile polymers).

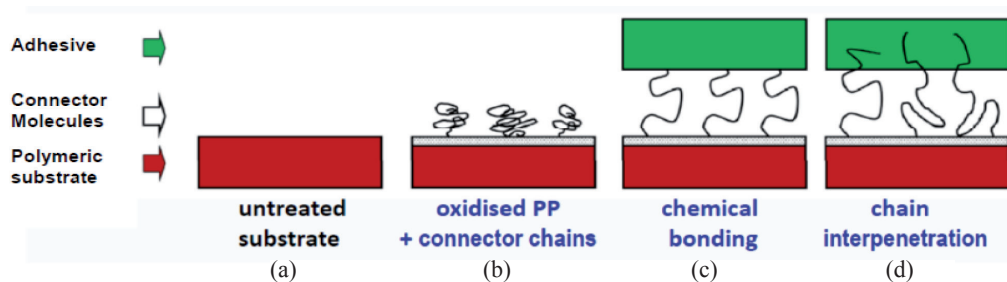


Fig. 5. Schematics of molecular brush interphase between polymeric substrate and coating or adhesive, and that of their alternative connectivity modes: (a) untreated substrate, (b) prior to bonding, the substrate surface is decorated with chemically grafted flexible molecular chains (connector molecules), (c) connector molecules unfolded and chemically bonded with adjacent coating or adhesive, and (d) connector molecules interpenetrated into the coating or adhesive layer (adapted from [13])

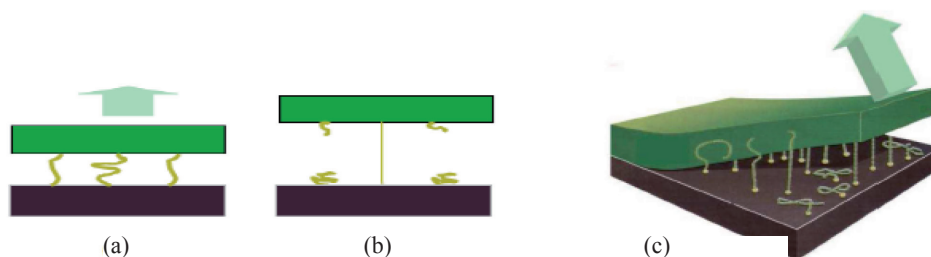


Fig. 6. Interfacial failure modes for two principal connectivity modes of surface grafted flexible molecular chains: (a) substrate-adhesive or substrate-coating assembly chemically bonded by an array of molecular bridges before strain application, (b) chain scission along the interface upon excessive deformation causing the rupture of single C-C bonds, and (c) surface grafted connector molecules interpenetrated into adhesive layer (no chemical bonding occurring) are gradually extracted from an elastomeric adhesive along the propagating crack front [14]

Therefore, increasing the load-bearing capability of the interface (Figs. 5 and 6) relies on inserting (to a desirable optimum of their surface density [σ_{OPT}]) the arrays of molecular bridges connecting a substrate with

adhesive or paint, and the mode of molecular bridge connectivity between these materials. If both ends of connector molecules are chemically bonded, i.e. one to the substrate and the other to a coating or adhesive

(Fig. 6a), while surface density, σ , of molecules bridging the interface is below the optimum [σ_{OPT}] required for exerting stress level capable of causing fracture of one of the adhering polymers (substrate and adhesive), then, on exceeding the failure stress of individual C-C bonds within connector molecules (*at approx. 1.6–2.4 nN*), they are broken along their backbone, as schematically illustrated in Fig. 6b. Under such conditions, interfacial fracture occurs along an interface subsequent to molecular chains scission at the failure stress, S_i , which is determined using the following equation:

$$S_i \sim f_b \sigma \quad (1)$$

where f_b is the force required to break individual chain ($\approx 1.6\text{--}2.4\text{ nN}$), and σ is the surface density [chains/mm²] of grafted chains.

2.3. Surface grafting connector molecules for PDMS adhesion increase

Many types of polymers are difficult to bond or coat due to their inherent low surface energy and the absence of reactive surface chemical groups facilitating adhesion. To overcome this deficiency, nylons, PET, and many other polymers exhibiting a moderate level of polarity frequently require the application of specifically formulated adhesion promoters, which is sufficient for most non-structural applications.

However, the non-polar polymers, e.g., polyethylene or polypropylene, must be surface-treated (pre-activated) by oxidising their surface by the means of corona discharge, flame, ozone, or UV treatment using equipment such as that illustrated in the photos in Fig. 7 in order to introduce active moieties in the form of -OH, -C=O, or -COOH groups to the surface of those originally inert polymers (see Fig. 8b).

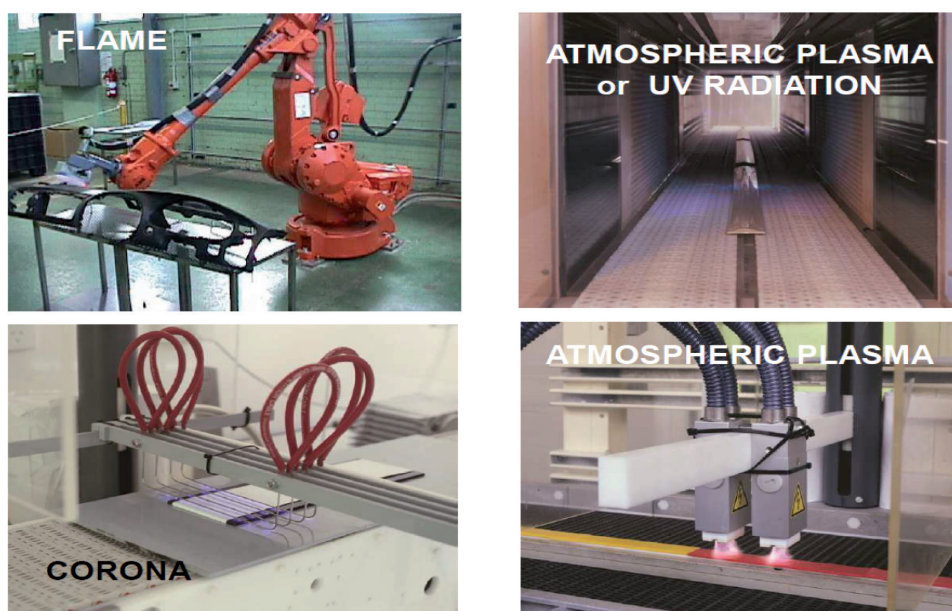


Fig. 7. Examples of typical equipment for surface activation (pre-oxidation) of polymers for enhanced adhesion: flame treatment, atmospheric plasma and UV treatment, corona discharge

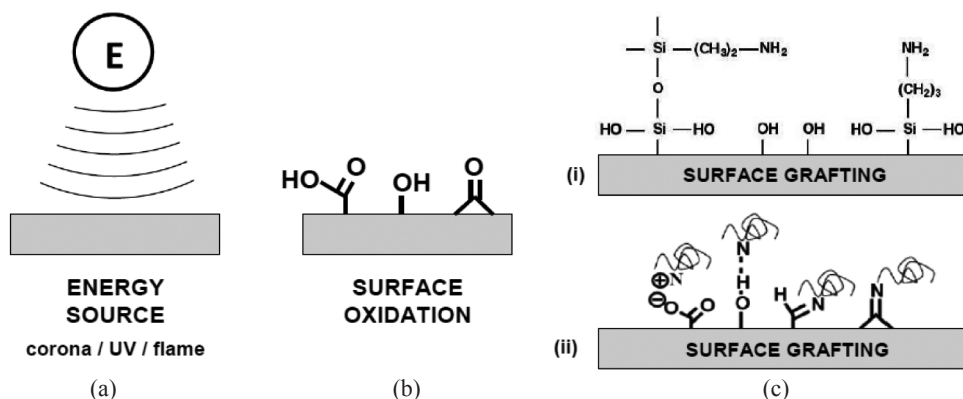


Fig. 8. Schematics of surface activation and/or surface grafting process analysed in this paper; (a) polymer surface pre-oxidation by corona discharge, UV radiation, flame, or oxygen plasma; (b) typical surface chemistry of oxidised polyolefins; (c) surface grafting: (i) amino-functional silane, and (ii) polyethyleneimine (PEI)

Appropriately dense surface arrays of such moieties can be subsequently utilised for grafting individual adhesion-promoting organo-functional molecules, e.g., linear or branched polyamines, e.g., polyethyleneimines (PEIs) and silanes, or other types of organo-metallic compounds, as schematically illustrated in Fig. 8c.

The functionality of pendent groups is chosen to provide reactivity with adhesives or coatings to be used in product assembly through bonding or in product surface finishing by a decorative or functional coating.

2.4. The effectiveness of surface grafted connector molecules in improving PDMS adhesion to difficult-to-bond engineering polymers

The effectiveness of improving the adhesion of difficult-to-bond engineering polymers by PDMS adhesives was demonstrated using an example of assembly of polyoxymethylene (acetal) mounting bracket in the lifter mechanism (see schematics in Fig. 9), which enables vertical movement (opening and closing) of automotive side windows in some models of Nissan vehicles.

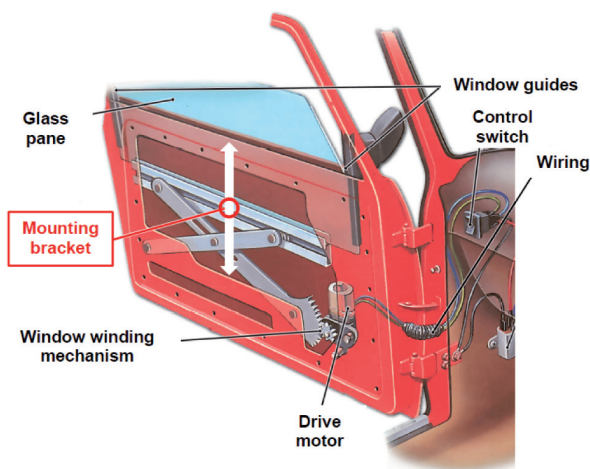


Fig. 9. Schematics of the automotive side window lifter mechanism

In this work, two types of elastomeric PDMS adhesives were evaluated for potential suitability in the assembly of polyoxymethylene/glass side window lifter mechanism: Dow Corning 983 and General Electrics GE 100.

The following surface preparation methods of polyacetal substrates for bonding were examined:

1. Solvent wipe only (acetone);
2. Corona discharge treatment using Tantec EST HV 2010 equipment; and,
3. CSIRO proprietary 'SICOR' process involving:
 - a) surface oxidation (corona discharge), followed by

b) spray-application of highly diluted solution of organo-functional adhesion promoter:

- see process schematics in Fig. 8:
 - amino-functional: N-(2 aminoethyl)-3-aminopropyltrimethoxy silane: Z-6020
 - epoxy-functional silane: 3-Glycidoxypropyltrimethoxy silane: Z-6040.

The strength of PDMS/Acetal bonded specimens was determined using 180° peel specimens (ASTM C-794-10 [9]) modified by CSIRO [17] by reducing the adhesive thickness from the ASTM-recommended 1.6 mm to 0.2 mm. This procedure results in a significant increase of the adhesive's modulus of elasticity which, in turn, creates a stress concentration at the substrate-elastomeric adhesive interface causing delamination of adhesive from the substrate surface rather than cohesive failure within the relatively weak PDMS adhesives.

The specimens were tested in an Instron mechanical tester at the strain rate of 10 mm/min. Two peel specimens were tested per experimental point.

The analysis of experimental data summarised in Table 4 reveals the following:

- “As received” polyoxymethylene cannot be bonded with DC 983 or GE100 without surface treatment due to negligible bond strength and complete delamination (100%) at the acetal/PDMS interface.
- Surface oxidation of acetal by corona discharge does not provide any notable improvement in the quality of PDMS adhesion.
- Excellent PDMS adhesion with interfacial bond strength increase to the level causing 100% cohesive failure within PDMS adhesive is achieved when the acetal is surface-engineered by a 2-step process comprising:
 - Surface oxidation (e.g., by corona discharge), followed by
 - Surface grafting by amino-functional silane.

Further analysis of data in Table 4 allows the following suggestions to be made regarding the mechanism of interfacial interactions between surface-grafted acetal substrate and both types of PDMS adhesives:

- **GE 100:** Although it provides very high bond strength (19–20 N/cm) on surfaces tethered with amino- and epoxy-terminated silane, it most likely interacts with these molecules through relatively shallow inter-digitation and not through chemical bonding. The latter is deduced based on the fact that all GE100 bonded specimens fail through 100% delamination of the PDMS adhesive along the substrate/adhesive interface.
- **DC 983:** It appears to be capable of cross-linking with functional ends of both the amino- and epoxy-functional graft molecules, due to the fact that very high bond strength observed (up to 24 N/cm) is associated with cohesive fracture (80–100%) within the bulk of this PDMS adhesive.

Table 4. The peel strength [N/cm] of PDMS/Acetal adhesive bond following various surface treatments on the acetal substrate

Surface treatment	PDMS adhesive			
	Dow Corning 983		GE 100	
	Strength	Failure mode	Strength	Failure mode
None	0.0	100% AF	3.65	100% AF
Corona discharge [C]	3.25	100% AF	7.5	100% AF
C + amino-silane grafting	17.5	80% CF	19.0	100% AF
C + epoxy-silane grafting	24.0	100% CF	20.0	100% AF

Note: AF: adhesion failure → delamination at the substrate/sealant interface; CF: cohesive failure within sealant.

3. PDMS in specialty functional coatings: superhydrophobic and icephobic applications

It is well established that multi-tiered hierarchical structures on surfaces of leaves of numerous plants, such as Lotus or rice grass, and those seen in some living organisms produce the superhydrophobicity (SH)

effect characterised by high water contact angles (CAs) exceeding 150–160°, and small CA hysteresis resulting in spontaneous shedding of water and self-cleaning effect, as illustrated in Fig. 10.

Intensive fundamental studies on SH in the past decade stimulated numerous scientific and technological advances producing a variety of multifunctional surfaces, such as water-repellent, self-cleaning, omniphobic, antifouling, and icephobic. Some of these effects utilise

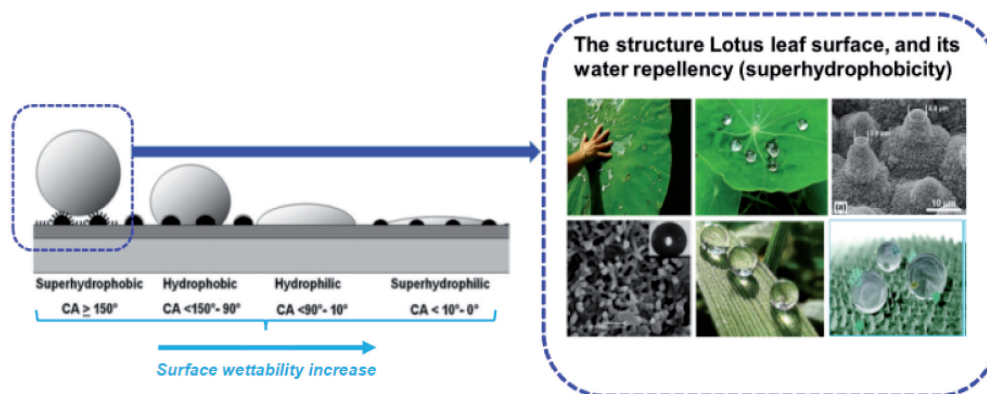


Fig. 10. Superhydrophobicity (SH) effect characterised by high water contact angles (CAs) exceeding 150–160° (schematics of the illustration partially adopted from [15])

the presence of composite fractal interfaces (solid-liquid-air) minimising the fraction of liquid-solid interface owing to the presence of air pockets between protruding micro-/nano-features of the substrate and the surface of liquid (see schematic illustration in Fig. 3e).

In this work, we summarise the outcome of our research (see Reference [16] for details) on such functional surfaces formed by mechanically stable hybrid coatings comprising surface arrays of closed or partially open hollow mesoporous spheres (see Figure 11 below) self-assembled from a master-solution comprising a 2-component PDMS (Sylgard 184) resin in THF reinforced with 5–10% of POSS.

The above coating applied as a micro-atomised spray (air-brush) leads to the following:

- 1) excellent coating adhesion to a broad range of engineering substrates,
- 2) spontaneous formation of a hierarchical surface comprising high surface density arrays of micro-/nano-structured mesoporous hollow microspheres (hybrid structure comprising closed and opened micro-spheres), and
- 3) The fabrication of low-friction surfaces by the incorporation of pendent PDMS chains attached to the cross-linked polymer network, which act as boundary lubricant chains.

The above coatings are applicable in a broad range of engineering, biomedical, and commodity applications, such as self-cleaning, icephobic, antifouling, low-friction, and bio-medical coatings.

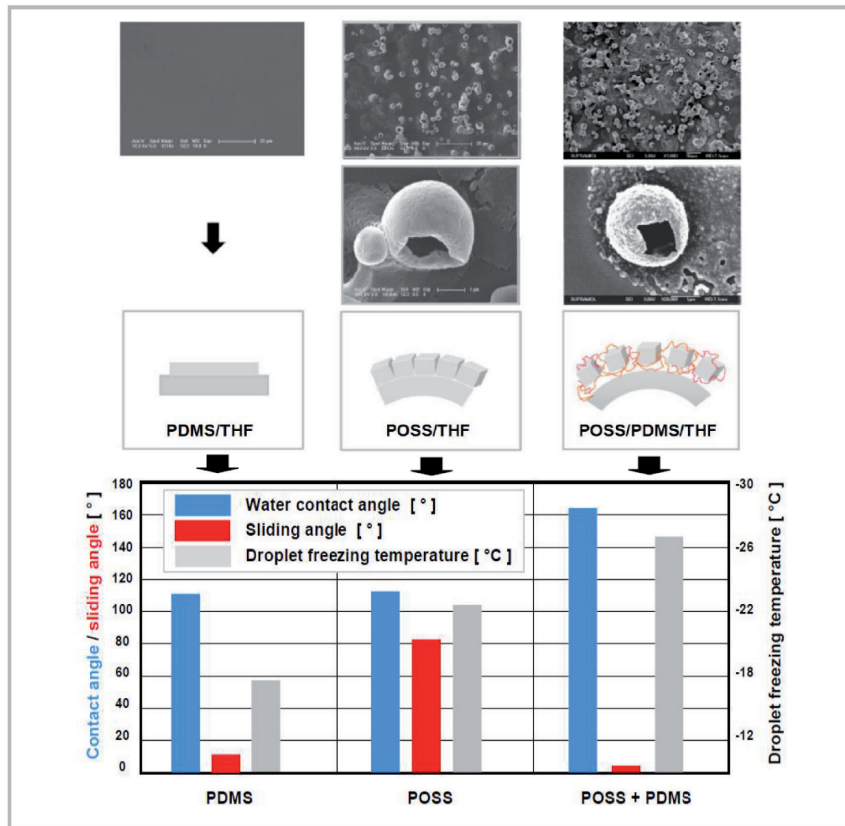


Fig. 11. The structure and selected properties (water CA, sliding angle, water droplet freezing temperature) of multi-functional coatings comprising closed and opened hollow mesoporous spheres formed through Ostwald ripening mechanism during aerosol-assisted self-assembly of POSS nanoparticles in the presence (or absence) of a carrier solvent, PDMS molecules (2RTV PDSM: Sylgard 184), and boundary lubricant chains (SEM photos: adopted from [16])

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