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Polymeric and ceramic silicon-based coatings – A review

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Silicon-based polymers are outstanding materials for coating applications. These compounds have excellent properties, such as strong adhesion to most substrates, and high chemical, thermal and UV resistance. Additionally, they can be converted into ceramic materials (polymer-derived ceramics) by a heat treatment and, in some cases, by chemical reactions or radiation. Hence, ceramic coatings can be obtained after deposition of the polymers by simple lacquer techniques. The properties and composition of polymeric and ceramic coatings can be changed by tailoring the chemical structure of the precursors or by the addition of fillers. This enables the preparation of coatings with a great variety of properties for different applications. In this review paper, the main aspects of the use of silicon polymers for coatings are elucidated. The advantages and disadvantages of these materials, and the processing methods developed are discussed. Finally, a summary of the applications and the prospects for future research are presented.

1.   Introduction

The constant development of our society pushes the limits of materials to achieve maximum efficiency, lower costs, durability, and to reduce damage to the environment. Often, the property requirements cannot be met by single material systems, leading to deployment of complex systems containing different types of materials. For many applications, however, a modification of surface properties by suitable coatings is sufficient to obtain significantly improved performance. Coatings may be used to enhance the resistance of the substrate to environmental factors, to give specific functions to the system by changing surface properties or even simply as a design factor.

Coatings may be prepared from polymers, metals, or ceramics and glasses. Polymers have the general advantages of lower material and processing costs, and simpler deposition techniques, but suffer from relatively low hardness and reduced chemical and thermal stability. Metallic coatings have high electrical and thermal conductivity, but processing is usually more expensive and complex than for polymeric coatings, and resistance to corrosion and oxidation is limited. In contrast, ceramic coatings combine a high hardness, wear and temperature resistance, with corrosion and oxidation stability. The main drawbacks of this type of coatings, though, are the higher processing costs compared to polymeric and metallic coatings, and the characteristic brittleness of ceramics. Ultimately, the choice of coating material will depend on the desired properties, environmental conditions during application and processing, on the compatibility with the substrate, and on material and processing costs.

Considering these aspects, silicon-based polymers standout as coating material. Coatings based on these compounds have a higher thermal stability and chemical resistance when compared to most organic coatings.[1]

Moreover, they generate ceramic materials when subjected to thermal, chemical and/or radiative processes – the so-called polymer-derived ceramics (PDCs) technology. This is the reason why these polymers are also known as precursors or preceramic polymers.[2] Since conversion from polymer into ceramic takes place only after coating deposition, polymer deposition techniques can be applied to obtain ceramic coatings as well. Thus, in addition to the advantages in the polymer state, silicon polymers enable a simpler preparation of ceramic coatings, reducing processing costs in comparison to other methods, such as physical vapor deposition (PVD), chemical vapor deposition (CVD), thermal spraying and sol-gel techniques.[3–5]

2.   Preceramic polymers

Preceramic polymers are mostly metalorganic compounds, usually based on silicon with additional elements, such as carbon, nitrogen, oxygen, or even metals, like boron or aluminium, in the backbone structure. Side groups, mainly organic, are connected to the backbone. Typical side groups are hydrogen, alkyl, vinyl, aryl, etc.[6,7] Properties, such as chemical and thermal stability, solubility, rheological behavior, and optical characteristics of preceramic polymers, and the composition of final PDCs are strongly influenced not only by the backbone structure, but also by the side groups. Moreover, simply the modification or addition of side groups enables the adjustment of precursor's physicochemical behavior, which is critical to cross-linking and polymer-to-ceramic conversion processes.[2,7,8]

Although silicon-based precursors have been known since the beginning of the 20th century,[9–11] industrial production began only in the 1940s, after development of the Müller-Rochow process to produce organochlorosilanes. These halogenosilanes can be converted into silicon polymers or oligomers by reactions, such as hydrolysis, alcoholysis, ammonolysis, aminolysis, etc. The study of Fritz and Raabe[12], published in 1956, is considered to be the initial step on the use of silicon polymers as precursors for ceramic materials. Following their work, other studies in the 1960s, like those of Ainger and Herbert[13], and Chantrell and Popper[14], continued developing the PDC technology. However, it was only in the 1970s that shaping processes were combined with the PDC route to obtain ceramics with defined shapes,[15–17] culminating in the breakthrough work of Yajima and colleagues[18,19], who prepared SiC fibers from silicon polymers.

Several precursors have been developed and investigated during the last century. Some representative examples are presented in Fig. 1. The best known group of the preceramic polymers are the polysiloxanes (also called silicones), which contain alternating silicon and oxygen atoms in the backbone. Common polymers in this family are poly(organo)siloxanes – i.e. polysiloxanes with organic substituents. Although called silanes, monomeric silicon-based molecules, such as those used as adhesion promoters in many multilayered systems, are a special category of siloxanes, since they usually contain oxygen attached to the silicon atom.[20] Polysiloxanes were first synthesized and studied by Kipping and coworkers as early as 1901.[9–11] Since then, silicones have been extensively used in the polymer state as coatings for several applications.[21] When thermally treated, siloxanes are converted into SiO_2, or

SiCO in the case of organosiloxanes. Another important family of precursor is polycarbosilanes, which transform into SiC when thermally treated under inert conditions.[22] Finally, silicon polymers containing nitrogen, such as polysilazanes, polycarbosilazanes and polysilylcarbodiimides, have also drawn much attention for coating applications. By a thermal treatment in inert atmosphere, these materials can be converted into Si_3N_4, in the case of polysilazanes, or SiCN ceramics, in the case of poly(organo)silazanes, polycarbosilazanes and polysilylcarbodiimides.[23–29] Modified versions of these three main types of precursors containing boron[30,31], aluminium[32–35], as well as transition metals (e.g. Fe, Co, Ni, Pd, Pt, Cu, Ag and Au)[36–40] and fluorine[41–44] have been investigated. Geopolymers are another class of silicon-based compounds which can be used to obtain coatings. However, for the sake of brevity, geopolymers are not considered in this review. Comprehensive information on this topic can be found elsewhere.[45]

To enable preparation of coatings from silicon polymers, some important requirements must be met, especially if conversion into ceramic is intended. First, precursors must be liquids or have an appropriate solubility in common solvents to enable coating deposition in liquid state. Another requirement, important both for polymeric and ceramic coatings, is a latent reactivity, provided by the presence of specific chemical groups, which induce cross-linking upon exposure to thermal, radiative or chemical stimuli. Due to the cross-linking, the liquid or soluble polymers and oligomers become unmeltable and insoluble thermoset materials. This latent reactivity is normally related to unsaturated organic groups (e.g. vinyl) or to reactive bonds, such as Si-H or N-H.[46] Finally, a sufficiently high molecular weight is required, to prevent volatilization of compounds with low molecular weight during cross-linking and conversion into ceramic.[2]
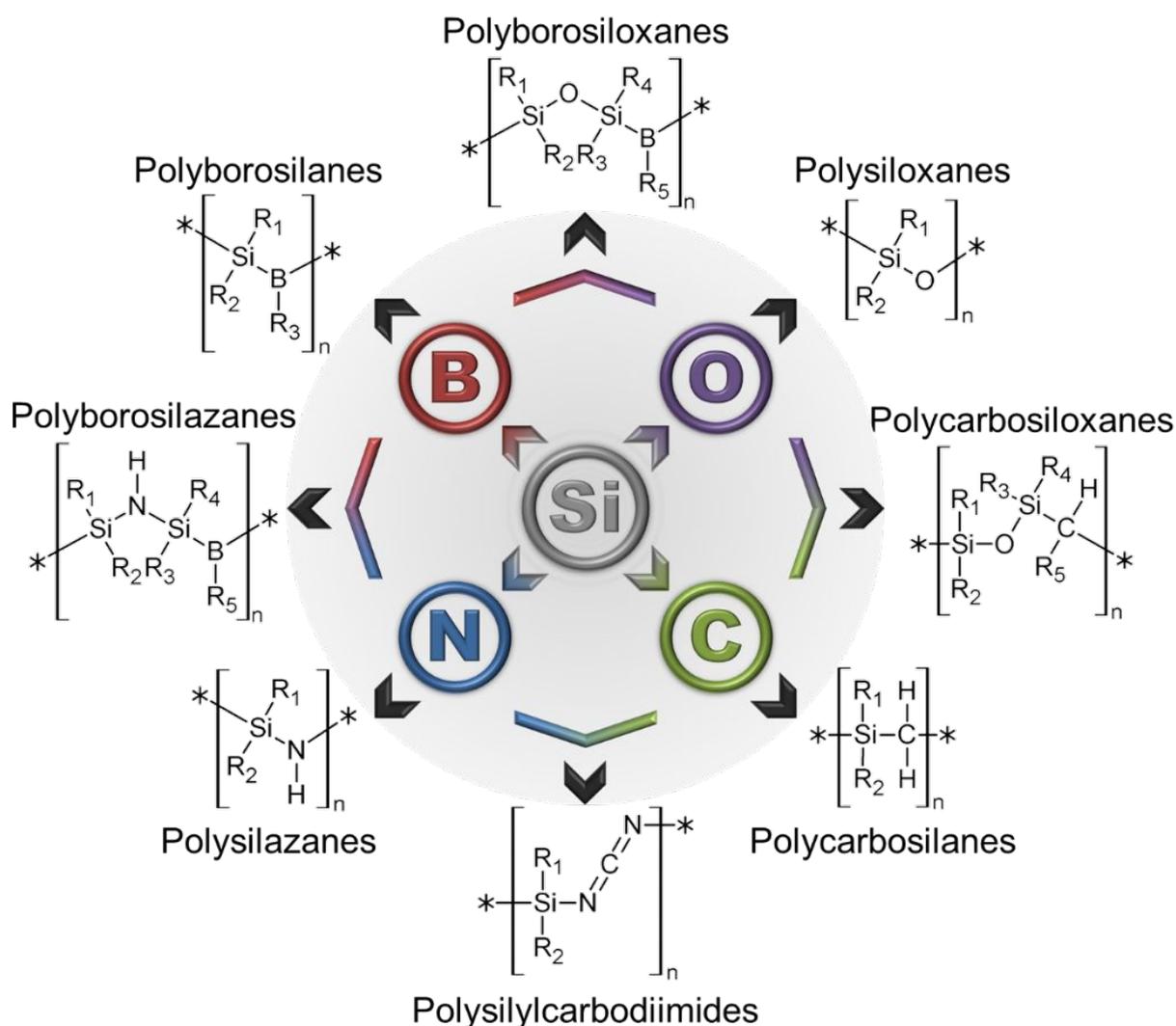
Fig. 1 Examples of common families of silicon-based polymers and their fundamental chemical units.[47]

3.   Polymer-to-ceramic conversion

The transformation of precursors into preceramic and ceramic materials is related to a series of reactions, resulting in changes of composition and properties. As already mentioned, a certain latent reactivity is required to obtain highly cross-linked preceramic and ceramic materials from organometallic precursors. This is because precursors are usually mixtures of oligomers and low molecular weight polymers, which may easily volatilize and depolymerize, resulting in low mass yields during conversion processes. To reduce this volatilization, cross-linking is necessary, resulting in an increase of the mass yield during the polymer-to-ceramic transformation.[23,48] Cross-linking may be carried out by different techniques, which will be discussed in details in Section 7. These techniques induce condensation and/or addition reactions of certain functional groups – such as Si-H, Si-OH and Si-vinyl[2,49,50] – causing the formation of 3D polymeric networks, whereby precursors become unmeltable and insoluble preceramic thermosets.[8,51]

After cross-linking, if further heat treatments are carried out, usually at temperatures above 300 °C, thermolysis – generally called pyrolysis in PDC technology – leads to an organic-to-inorganic transformation, from a thermoset polymer into an amorphous ceramic.[52] This transformation is caused mainly by rearrangements, condensation and radical reactions, which result in cleavage of chemical bonds, formation of new bonds and elimination of organic groups, such as CH_4, C_6H_6, CH_3NH_2, NH_3 and H_2.[6,50] CO and CO_2 can be eliminated as well, especially in an oxidizing environment. For most precursors, conversion into ceramic is complete below 1100 °C.[2] A measure of the efficiency of a preceramic polymer regarding the conversion into a ceramic material is the ceramic yield $\alpha_c = m_c/m_p$, where m_p is the initial mass of polymer and m_c is the residual mass after complete transformation of the polymer into ceramic. The conversion of suitable preceramic polymers to a ceramic is usually associated with a mass loss in the range of 10-30%.[6]

Amorphous PDCs may be further heat-treated to convert them to crystalline ceramics. For a great number of applications, crystallization is not necessary or even undesired, and processing is terminated once the amorphous ceramic has been obtained. While most PDCs – especially ceramics containing oxygen – may crystallize at temperatures as low as 1000-1200 °C,[6] some materials have the capability of avoiding crystallization at temperatures up to 1700 °C.[30] Fig. 2 is a representative example of the changes in the mass during the different phases of the conversion of a preceramic polymer to a crystalline ceramic. This figure also highlights the temperature range in which different phases of PDC processing take place.
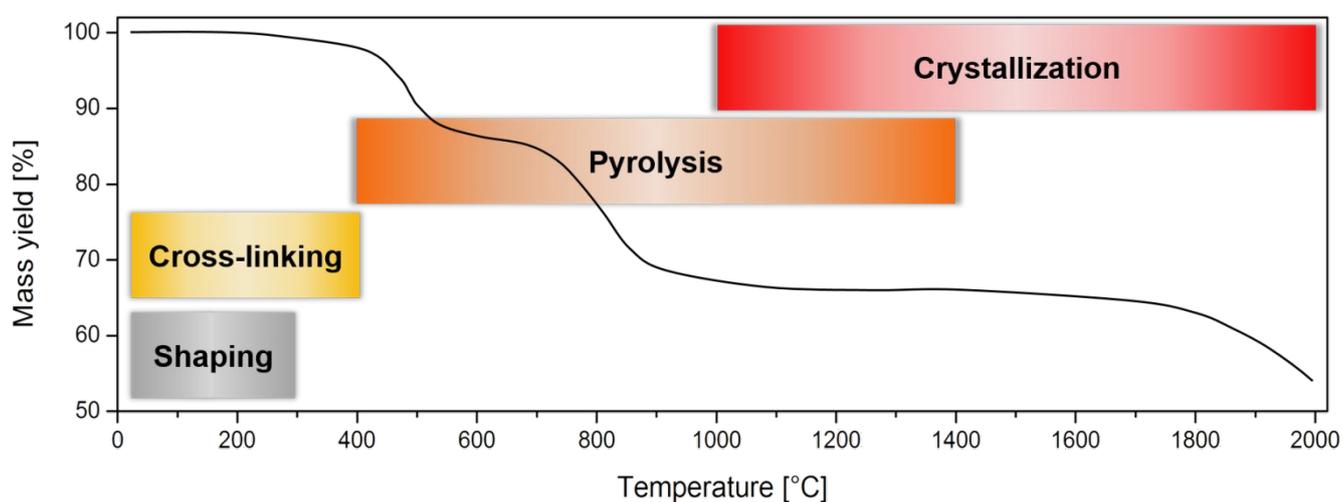
Fig. 2 Correlation of the temperature with the processing phases and mass changes occurring during PDC processing of a polycarbosilane under inert atmosphere. Based on Colombo *et al.*[2] and Greil[53].

Ideal conditions for cross-linking and polymer-to-ceramic conversion (ceramization) depend strongly on the chemical structure of the precursor. In fact, by changing conditions for cross-linking and/or ceramization (temperature, heating rate, atmosphere, etc.), materials with different properties may be obtained, even from the same precursor.[54,55]

In addition to mass loss (see Fig. 2), precursors undergo a densification during the polymer-to-ceramic transformation from a density of about 1 g cm⁻³ as precursor to > 2 g cm⁻³ as ceramic (Fig. 3). This density increase

together with the mass loss implies that the volume of material decreases significantly during the conversion process. These changes in mass and volume have two main effects. The most evident is a shrinkage of the shaped part, which can easily reach values around 40% (linear shrinkage).[56] The second effect is the formation of porosity. In early stages of ceramization, the release of gaseous pyrolysis products leads to the formation of open pores, some of which may disappear during thermal treatment, due to the shrinkage of the parts. This type of porosity is referred to as transient porosity. However, some residual porosity may be retained in the final product.[6]
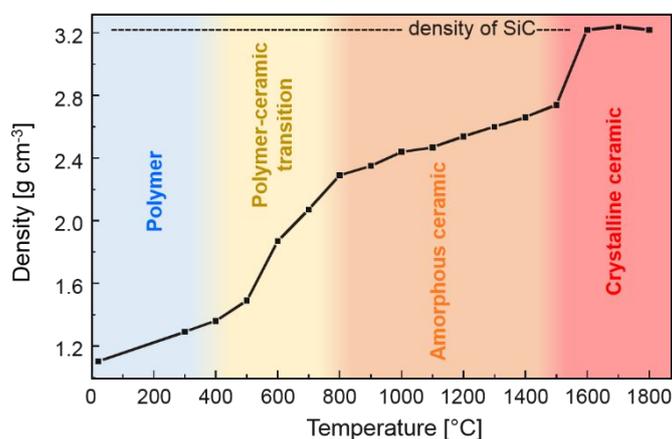
Fig. 3 Density increase during conversion of a poly(organo)silazane into a SiCN ceramic (pyrolysis under protective atmosphere).

The shrinkage of materials during the conversion from polymer to ceramic can lead to significant stresses during processing, if the strains in a differential pyrolysis system are incompatible. Thus, stresses will occur when different parts of the system shrink at different rates. Indeed, overcoming the differential shrinkage issue is the most significant challenge of the PDC technology, especially in the case of coatings. Due to the high creep resistance of the PDCs, stress relaxation, during processing, by viscous flow is insufficient. Moreover, since pyrolysis processes occur rapidly, stress relaxation by diffusional material transport is also unlikely. Hence, stresses due to differential shrinkage may result in formation of cracks, reducing the mechanical stability of the system and sometimes leading to the collapse of the part during pyrolysis.[7,53] Because of this behavior, PDC processing of precursors without the addition of fillers is mostly suitable for preparation of ceramics with small dimensions, like fibers, thin coatings, and cellular ceramics (thin cell wall), which have the potential of uniform shrinkage during pyrolysis.[2]

In contrast to free-standing parts, the geometry of coatings is constrained in two dimensions by the adhesion to the substrate, whereas shrinkage can only occur freely across the thickness. This phenomenon is analogous to the phenomenon of constrained sintering observed in non-PDC glass and ceramic coatings.[57–62] For this reason, the thickness of silicon-based coatings has a maximum value known as critical coating thickness, above which extensive cracking and even spallation occurs. This critical coating thickness is usually below 10 μm,[63] but depends on properties of both coating and substrate, and on the maximum temperature during conversion and application. To enable preparation of PDCs with larger dimensions, such as dense bulk parts and thicker coatings, shrinkage must be minimized or compensated, which can be achieved by the use of suitable fillers.

4. Particle-filled coatings

In order to extend the range of application of coatings based on silicon polymers, fillers are frequently introduced into coatings. In polymeric systems, fillers can be used to modify appearance, to generate surface structures or to give certain functionalities to the system. In PDC processing, fillers have a more crucial role, since they are an innovative approach to manage the shrinkage of precursors during the polymer-to-ceramic transition, enabling the preparation of thicker ceramic layers. In addition, the microstructure and properties of ceramic coatings can be tailored with fillers.

Coating fillers may be polymers, ceramics, glasses or metals, and are usually added in the form of particles with size ranging from a few nanometers to a few micrometers. These fillers may be subdivided into four basic types, according to their behavior during heat treatment of the system: passive, active, glass (meltable) or sacrificial fillers.

As the name suggests, passive fillers are inert in the system. They maintain their initial composition, mass and particle size (except for thermal expansion) during processing and application. Such fillers are the most common type used in polymeric coatings. Basu and colleagues[64], for example, used silica nanoparticles in polysiloxane coatings to tailor the surface microstructure and wettability, while Tavares *et al.*[65] used TiO_2 in polysiloxane coatings to obtain surfaces with photocatalytic activity. In PDC processing, passive fillers reduce coating shrinkage simply by reducing the volume fraction of the shrinking phase, i.e. the preceramic polymer. Günthner[66] and Kraus[67] *et al.* used this approach to increase the maximum coating thickness of polysilazane-derived ceramic coatings from about 1 μm to more than 10 μm without crack formation (Fig. 4). However, some filler materials are only inert under certain conditions, such as non-oxidative atmosphere or lower temperatures. These conditions are frequently not met during processing and application of PDC coatings. Pyrolysis conditions generally lead to degradation of organic polymers, melting of glasses and oxidation of metals. As a result, passive fillers are, in most cases, ceramic materials.[68] Ceramics, such as SiC, Si_3N_4, ZrO_2, TiO_2, BN, Al_2O_3, SiO_2 have high temperature stability and melting point, and are either stable oxides or have high oxidation resistance, maintaining a passive behavior over a broad temperature range without requiring a protective atmosphere. Due to their passive behavior, high volume fractions of filler can be added to the coating systems, in order to tailor functionality of the final ceramic. In some cases, precursors might be used simply as temperature-resistant binders for passive filler particles.[69,70] Based on this approach, Barroso *et al.*[47,71] used high loads of yttria-stabilized zirconia and a polysilazane-derived PDC as ceramic binder to obtain coatings with low thermal conductivity and high coefficient of thermal expansion, characteristic properties of the selected filler. Although this strategy may avoid completely the macroscopic shrinkage of the coatings caused by precursor densification during ceramization, residual porosity will always remain in the coatings when medium to high volume fractions of passive filler are used. Furthermore, the amount of porosity increases with increasing volume fraction of filler, especially if the fillers have a narrow particle size distribution.[56] Despite the reduction of the macroscopic shrinkage, crack formation may still occur due to localized stresses (e.g. around filler particles), especially in thicker coatings.[47,71]
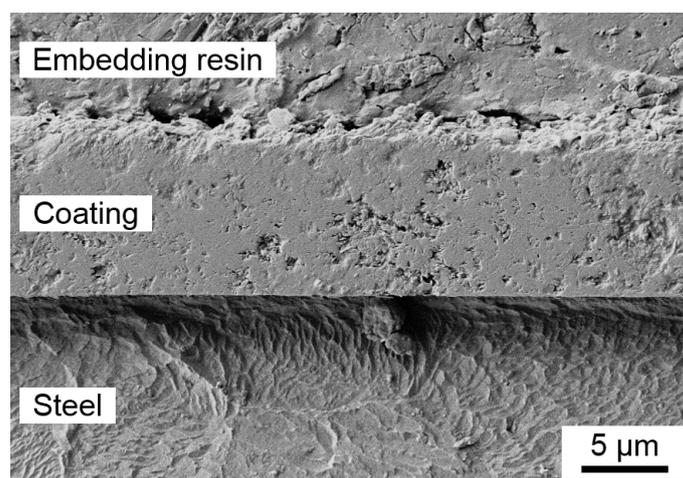
Fig. 4 Microstructure of the cross-section of a polysilazane-based coating with hexagonal BN passive filler on steel AISI 304 after pyrolysis in air at 500 °C for 1 h. Adapted with permission.[66] Copyright © 2009, John Wiley and Sons.

Fillers, which undergo chemical reactions during coating processing, are called active fillers. These reactions may occur with the precursor, with gaseous products generated during pyrolysis or with the pyrolysis atmosphere, resulting in new phases. Since these reactions generally require high temperature, active fillers are uncommon in polymeric coating systems. In contrast, they are a common approach to overcome the issues related to precursor shrinkage in PDC coatings. Since many reactions involving active fillers lead to a volume expansion of the filler particles, this strategy can be applied to compensate for precursor shrinkage (Fig. 5). This approach of using volume-expanding fillers in PDCs is called active-filler-controlled pyrolysis (AFCOP).[56,72,73] Taking into account changes in mass and volume of precursor and filler, it is possible to estimate the filler loading, which leads to dense PDCs with zero shrinkage during ceramization process. Moreover, active fillers can also be used to introduce new phases into a PDC system, in order to modify functionality and performance. In this case, however, the volume fraction of filler might be limited to smaller values. Indeed, if the reactions of the active filler are associated to a volume increase, a large amount of filler may lead to an excessive expansion of the system, resulting in coating failure. Additionally, active fillers may be used to obtain completely new materials by reactions with precursors.[74,75] Since a reactivity is desired, metallic and semimetallic materials, especially Si, B, Al, transition metals from groups 4 to 6 of the periodic table, and the respective silicides and borides, are the most common active fillers.[53,68,76] Torrey[77] and Wang[78] *et al.* used the oxidation of silicide fillers during pyrolysis in air at 800 °C to obtain crack-free polysiloxane-derived coatings with more than 20 μm of thickness. However, as previously mentioned, even carbides, nitrides and oxides may become reactive and behave as active fillers under appropriate conditions. Liu[79] and Lenz Leite[75] *et al.* used, for example, rare earth oxides as fillers, which upon reaction with the precursors at temperatures above 1000 °C, yield silicate-based coatings (Fig. 6).
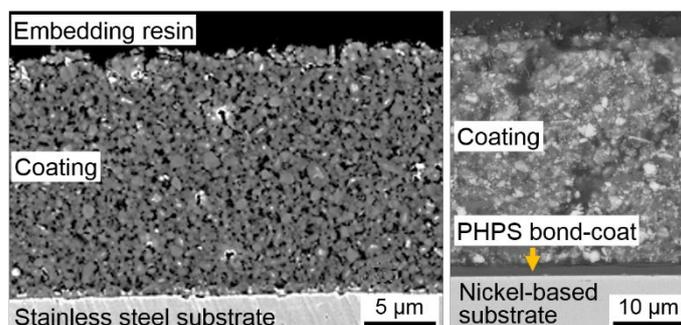
Fig. 5 Coatings based on polysiloxane PHMS with active fillers after pyrolysis in air at 800 °C for 2 h: (left) TiSi$_2$ as active filler (Reproduced with permission.[80] Copyright © 2007, Materials Research Society.); (right) ZrSi$_2$ as active filler (Reproduced with permission.[78] Copyright © 2011, Elsevier Ltd.)
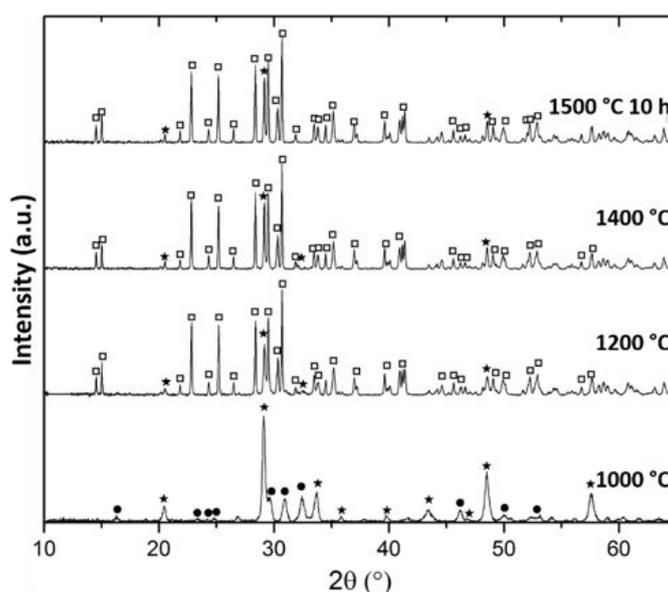
Fig. 6 Formation of silicate phases by reaction of a silazane and yttrium oxide active filler during pyrolysis in air in the temperature range of 1000-1400 °C for 1 h and at 1500 °C for 10 h (★ Y$_2$O$_3$; ● x$_1$-Y$_2$SiO$_5$; □ x$_2$-Y$_2$SiO$_5$; Δ α-Y$_2$Si$_2$O$_7$; ♦ β-Y$_2$Si$_2$O$_7$; ∇ Y$_{4.67}$(SiO$_3$)$_4$O). Reproduced with permission.[75] Copyright © 2017, Elsevier Ltd.

The third type of fillers used in PDC coating systems are the meltable ones, which are generally glasses. During pyrolysis and use at high temperatures, glasses may melt or simply soften, sealing porosity and densifying the layer, resulting in an improved protective performance against oxidation and corrosion.[63,81] After cooling below the softening point, these fillers enhance the hardness and abrasion resistance of coatings.[82] By softening, at high temperatures, they also reduce the Young's modulus of the coating and enable a relaxation of thermomechanical stresses caused by thermal expansion mismatches between substrate and coating, and between fillers and precursor matrix. Using these advantages, Günthner and colleagues[63] developed crack-free polysilazane-derived ceramic coatings with thickness of more than 100 μm in a single deposition and pyrolysis process (Fig. 7). In addition to the change in physical state, these fillers may also react with other components in the system, acting also as active fillers.[83] The use of meltable fillers requires the selection of suitable materials for each application and a fine-tuning of the thermal treatment. If an unsuitable glass is used, pyrolysis at high temperatures may cause an excessive reduction of the glass melt's viscosity or even crystallization/decomposition of the glass. Low

temperatures, in contrast, may not lead to softening/melting, and the glass particles will behave simply as passive fillers.
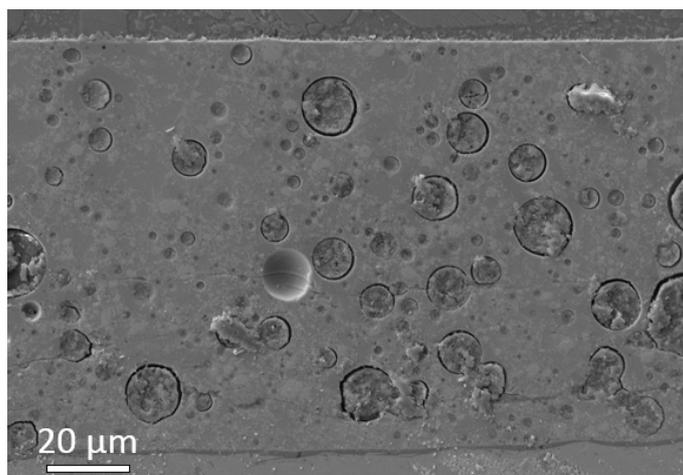
Fig. 7 Microstructure of the cross-section of a polysilazane-based coating with ZrO_2 passive filler and two types of glass on mild steel after pyrolysis at 700 °C for 1 h in air. Reproduced with permission of The American Ceramic Society.[63]

Sacrificial fillers are mostly organic compounds. Such materials can be mixed with the precursors and, after coating deposition and cross-linking, eliminated by thermal decomposition or by dissolution in a solvent. Such fillers are used to generate porosity, e.g. in gas separation membranes.[84–86] Form, amount, size and distribution of pores in PDC coatings can be tailored by selecting suitable fillers with specific particle size and shape. The elimination of sacrificial fillers, forming porosity, is also an approach to control stresses in coatings, since porosity reduces the effective elastic modulus of the coating, increasing the strain compliance.[87]

In addition to their role in processing and microstructure control, fillers may be necessary to obtain the required properties for application. One good example is the thermal expansion behavior of coatings. During processing and use at high temperature, problems may occur if a thermal expansion mismatch exists between substrate and coating. This is the case for almost all PDC coatings on metallic substrates, since most silicon-based materials have a low coefficient of thermal expansion (CTE).[88] This issue becomes even more relevant when thicker coatings are required, since the larger thickness increases the likelihood of cracking for the same thermal expansion mismatch.[89] The following equation[90] (Eq. 1) gives an estimate of thermal stresses arising in coating systems upon change of temperature:

$$\sigma_t = E_c(\alpha_s^l - \alpha_c^l)\Delta T \qquad (1)$$

where E_c is the effective Young's modulus of the coating, α_s^l and α_c^l are the linear CTEs of substrate and coating, respectively, ΔT is the change of temperature, and σ_t is the resulting thermal stress. According to this equation, there are two ways to reduce thermal stresses in coatings. The first and more obvious approach is to reduce the CTE mismatch between coating and substrate. This can be realized by adding fillers with a high CTE – such as ZrO_2, MgO and CeO_2, or even metallic particles – to the preceramic polymers. The second way is to reduce the effective Young's modulus of the coatings. The Young's modulus is an intrinsic property of materials, and therefore is

independent of microstructure. However, there is an effective Young's modulus, which takes into account the Young's modulus of the material and its porosity. Several models describe this correlation,[87,91] but all have in common that the effective Young's modulus decreases as porosity increases, fact which is also demonstrated experimentally. Thus, a reduction of the overall Young's modulus of PDC coatings can be realized by introducing sacrificial fillers into coating systems, which generate a controlled amount of porosity during pyrolysis.
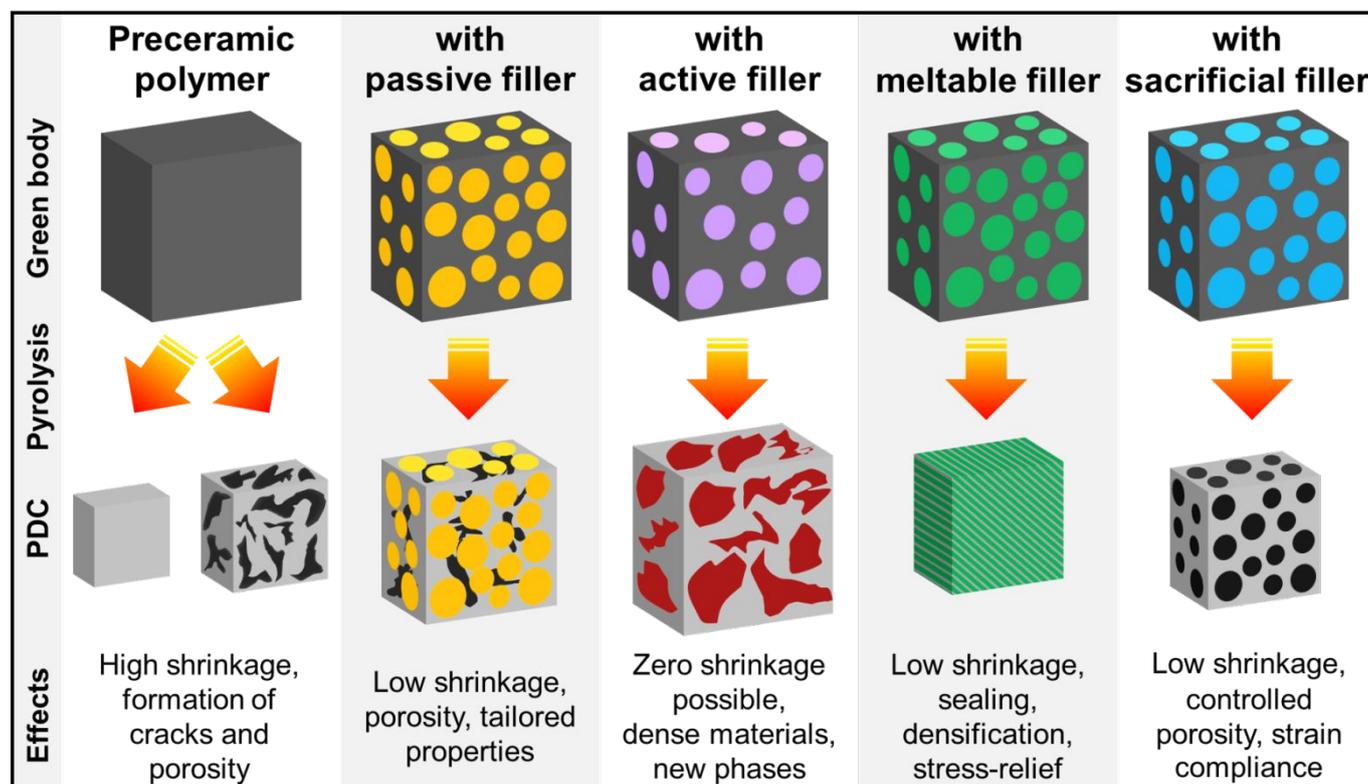
Fig. 8 Types of fillers and their effects in the precursor-based coating systems.[47]

Fig. 8 summarizes the types of fillers and their respective effects in the PDC systems. Using one of these types of fillers or combinations thereof, novel coating systems with outstanding properties can be prepared using the PDC processes.

Independent on the type of filler, it is important to achieve a good dispersion of the filler particles in the coating suspension. This will insure a uniform distribution of the fillers in the deposited coatings, improving coating strength and surface quality. Agglomerates in the suspensions may also hinder an adequate coating deposition, especially in the case of spraying due to clogging of the spray nozzle. A good dispersion is usually achieved by using suitable dispersing agents and/or adequate methods for dispersion, such as ultra-sonication, ball-milling and mechanical stirring. However, the reactivity of the precursors must be considered when dispersing fillers. Highly energetic methods, such as ultra-sonication and ball-milling, may cause a premature cross-linking of the polymers. Hence, in some cases it is recommended to first prepare the coating suspensions without the precursor, which is only added after a proper dispersion of the particles. In these cases, homogenization of the suspension with the precursor should be carried out by milder methods, such as low-speed stirring. In addition, the particle size of the fillers has a considerable effect on dispersion. However, the most suitable particle size depends not only on the dispersibiltiy

of the particles, but also on the intended properties of the coatings. Typical particle sizes of filler powders remain in the range of a few nanometers to a few micrometers which makes dispersion more challenging due to the tendency of fine particles to agglomerate.

5.   Mechanisms of adhesion

In the processing of coatings based on silicon polymers, good wetting and adhesion between the liquid precursor (or precursor solution) and the substrate is required to facilitate film formation. This good adhesion must also be maintained after conversion into a solid coating. Wetting is determined by the surface free energy of the substrate, the surface tension of the liquid coating material, and by the interfacial tension between them. This relationship is given by the Young's equation[92] (Eq. 2) as

$$\cos \theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}} \tag{2}$$

where, θ is the contact angle between the liquid and the solid surface, γ_{SG} is the solid's surface free energy at the interface with the surrounding atmosphere, γ_{LG} is the surface tension of the liquid in contact with the atmosphere, and γ_{SL} is the tension at the interface between solid and liquid. The contact angle is the angle measured between the surface of the solid and the tangent to the contour of a drop placed at the surface, at the triple point (interface between solid, liquid and gas phases), as shown schematically in Fig. 9. One of the important interpretations of Eq. 2 is that the contact angle is small when the surface free energy of the solid is high and the surface tension of the liquid is low.
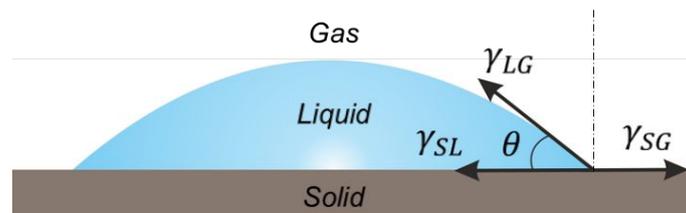
Fig. 9 Schematic representation of the contact angle of a liquid with a solid surface.

Another property described by the relations between the surface energy/tension of substrate, coating and interface is the so called work of adhesion W_A (Eq. 3). This is a measure of the work, which has to be performed in order to separate a coating from its substrate, if no kind of chemical or mechanical interactions would occur between them. The combination of Eq. 2 and 3 yield the so called Young-Dupré equation (Eq. 4), which describes the relationship between work of adhesion and contact angle, thus indirectly between adhesion strength and wetting. As the Young-Dupré equation describes, smaller contact angles lead to higher works of adhesion. As a consequence, coating precursors have generally better adhesion to ceramics, glasses and metals (all with high surface free energies) and poorer adhesion to polymers.[93]

$$W_A = \gamma_{SG} + \gamma_{LG} - \gamma_{SL} \tag{3}$$

$$W_A = \gamma_{LG}(1 + \cos\theta) \tag{4}$$

Although a good wetting in the liquid state is essential to obtain coatings with strong adhesion to the substrates, it does not guarantee it. For solid coatings, adhesion strength is usually determined by mechanical factors and more importantly by chemical interactions.

The mechanical interactions are associated with the surface roughness of the substrate, which may lead to a mechanical interlocking between coating and substrate, depending on its morphology. Since deposition of silicon polymers is carried out mostly in liquid phase, cavities at the surface of the substrate can be filled by the coating material (if surface wetting is sufficient). After solidification, the coating material becomes clamped within the cavity, increasing the adhesion strength.

In general, surface roughness contributes to an increase of adhesion strength, if there is good wetting between the liquid precursor and the substrate, since both the interfacial area and mechanical interlocking increase. In the case of the PDC coatings, however, an inadequate roughness may be detrimental to the overall adhesion of the system, because the accumulation of precursor in a cavity may lead to a coating thickness above the critical value in that area, increasing the probability of cracking and spallation due to coating shrinkage (Fig. 10). Therefore, for PDC coatings, the surface roughness should be well controlled to ensure high interfacial strength. As a guideline, small amplitude (at least an order of magnitude less than the coating thickness) and high wave length surface roughness should provide the optimal adhesion enhancement.
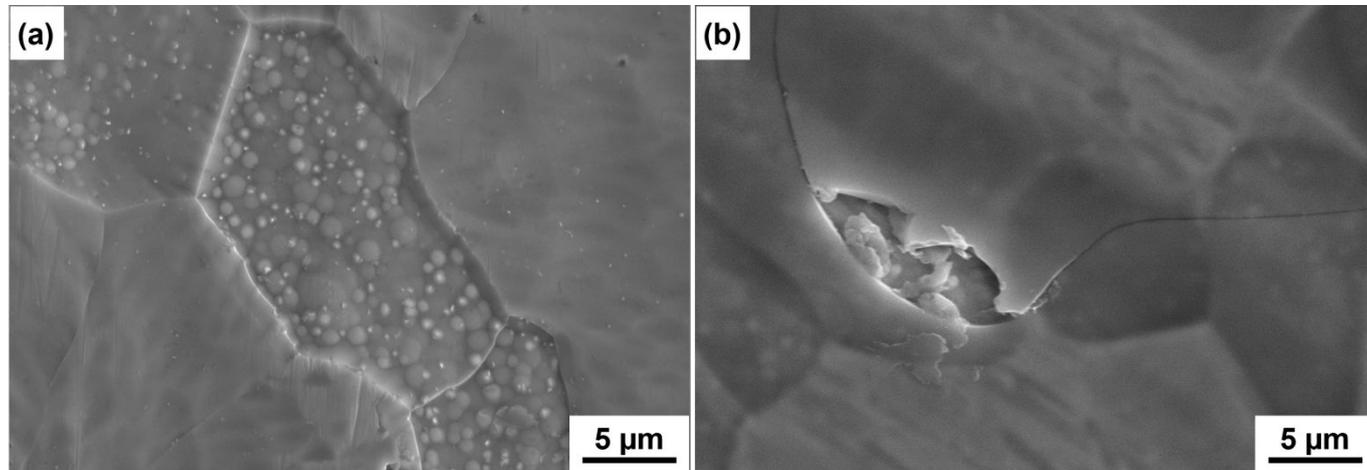
Fig. 10 SEM images of (a) the surface of a cold-rolled steel grade 441 as received; and (b) of the same steel with a polysilazane coating after pyrolysis at 500 °C in air for 1 h. Coating cracking and spallation on a depression at the substrate's surface is evident.[47]

In addition to the mechanical contributions, chemical interactions are primarily responsible for the adhesion of silicon polymers and of the ceramic coatings derived from them to the substrates. During processing of coatings from most organic polymers, electrostatic, intermolecular or acid/base interactions with the substrates are the dominant adhesion mechanisms. For polymer substrates, interactions with polymeric coatings can also lead to interdiffusion between polymers. In contrast, many silicon polymers can adhere to most substrates by chemical bonding, which yields much stronger adhesion.[94,95] The chemical bonding between Si-polymer and substrates takes

place mostly by hydrolysis/alcoholysis and condensation reactions.[96] In the presence of humidity, silanol groups are generated in the polymer, which interact with –OH groups at the surface of substrates and condense to form oxygen bridges between the substrate and the polymer chain upon elimination of water.[95,97] Hydrolysis/alcoholysis can be carried out prior to coating deposition, in the case of polymers soluble in water or alcohol, or *in situ* after evaporation of the organic solvents by reaction with water adsorbed at the surface of the substrate or with moisture from the atmosphere. In general, *in situ* hydrolysis processes may require much longer times.[95] The presence of groups, such as Si-H, is particularly interesting, since they are easily hydrolyzed.[50] However, they also increase the sensitivity of the precursor to the environmental conditions, since the silanol groups formed can condense also with each other, causing a premature cross-linking of the polymer upon handling in air. Silazanes have an advantage in comparison to other silicon polymers, because amine groups not only can be hydrolyzed by moisture to form silanols, but also can interact directly with –OH groups at the surface of the substrate, leading to the formation of oxygen bridges, even in the absence of moisture.[98] However, some silicon polymers, especially silicone elastomers, may require an adhesion promoter to achieve a suitable adhesion. A base coating with a silane is frequently used to improve adhesion of this class of polymers.[95]

A prerequisite to obtain a chemical bonding between the silicon polymers and the substrates is the presence of reactive groups at the surface of the substrate. The first step of surface pre-treatment is the removal of any kind of material, which could block the direct interactions between coating and substrate, such as dust, grease, weakly adhered oxide scales (e.g. rust) in the case of metals, and plasticizers in the case of plastics.[94] This cleaning process may be carried out by mechanical methods, such as grinding or sandblasting; by chemical methods using solvents, acids or bases; or by other methods, like plasma and corona discharge, ozone, laser, flame, and electrochemistry.[94,95]

Aside from surface cleaning, metals, glasses and ceramics may not require any additional pre-treatments. In the case of metals, however, the removal of the inhomogeneous natural oxide scale followed by controlled growth of a thin homogeneous oxide scale (e.g. by short oxidation treatment), can improve the reproducibility of the adhesion properties.[95,99] In contrast, adhesion to organic polymers is significantly more challenging, due to poor wetting and chemical compatibility problems. Treatments such as oxygen plasma can simultaneously clean the substrate's surface and generate oxygen-containing functional groups, which can lead to a chemical adhesion of silicon compounds.[100] In addition, precursors can be functionalized with certain reactive groups capable of reacting with groups in the organic polymer chain, yielding strong adhesion even in the absence of –OH groups at the surface of the substrate.[96]

6.   Deposition methods

All techniques used for deposition of coatings in liquid state, such as dipping, spinning, spraying, screen printing, doctor blade/bar coater, roll coating, curtain coating, and brushing, can be used to apply silicon-based polymer

coatings. However, since each technique has its particular characteristics, suitability of the methods to specific systems and applications must be evaluated for each case individually. Moreover, a crucial factor affecting the liquid-state deposition of silicon-based coatings is the rheology of the coating solutions and suspensions. Thus, the rheology of the coating liquids must be carefully controlled to achieve high quality coatings. The required rheology depends on many factors including the deposition technique and the equipment used.[101] It is important to mention that, since deposition is carried out in liquid phase, edge effects occur, independently of the selected method. Usually, rounding or chamfering the edges of substrates minimizes such defects.

Deposition of Si-polymer coatings from gaseous or solid states is possible but uncommon, since processing becomes significantly more complicated and costly. Plasma polymerization, plasma-assisted CVD (PA-CVD, also known as plasma-enhanced or PE-CVD), and other types of CVD processes have been used to form coatings from silicon-based precursors.[100,102–117] In these cases, plasma is used as energy source to induce polymerization of liquid or gaseous monomers and oligomers directly at the surface of the substrate during deposition, yielding highly cross-linked polymer coatings and, in the case of CVD, even ceramic coatings. Powder coatings have also been developed using Si-polymers,[118,119] although in several cases the Si-polymer is used simply as an additive in organic coatings.

Among the great variety of possible deposition techniques from the liquid state, dip, spin and spray coating methods are the most frequently used to prepare coatings of silicon-based polymers. The principle and the main characteristics of these three techniques are summarized in Fig. 11 and discussed below.

	Dip coating	Spin coating	Spray coating
Principle of the technique	Film formation during hoisting of the substrate after immersion in the liquid coating solution (multi-face coating)	Spreading of the liquid coating solution by the centrifugal force acting on a spinning substrate (single-face coating)	Atomization and transport of the liquid coating solution toward the substrate (single-face coating)
Characteristics	▲ Simple equipment ▲ Low waste ▲ Reproducibility and uniformity with simple automation ▼ Mostly for simple shapes ▼ High volume of liquid required ▼ Mostly for liquids with low viscosity	▲ Simple equipment ▲ Low volume of liquid required ▲ Reproducibility and uniformity with simple automation ▼ Considerable waste ▼ Mostly for flat substrates ▼ Mostly for liquids with low viscosity	▲ Flexibility (properties of the liquid) ▲ Also for more complex shapes ▼ High amount of parameters ▼ More complex equipment ▼ High waste ▼ Reproducibility and uniformity with more complex automation
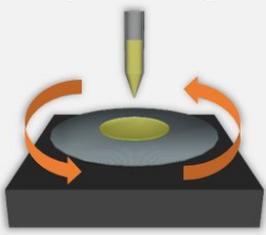
Fig. 11 Principle and main characteristics of dip, spin and spray coating deposition methods.[47]

6.1   Dip coating

Dip coating was one of the first coating methods commercially applied[120] and, together with spin coating, is the most commonly used method for the development of coatings based on silicon polymers. This deposition technique consists of the formation of a film onto the surface of a substrate while the substrate is withdrawn from a liquid

bath.[120] Therefore, the film is formed onto all exposed faces of the substrate simultaneously, which is, for some applications, a great advantage. Masking of specific areas enables a selective coating deposition, although the influence of the mask on film formation may affect the quality of the coatings.

The required equipment for dip coating is simple and processing has a small number of parameters. The liquid characteristics, specifically viscosity, density and surface tension, must be optimized. In addition, if fillers are used, then their dispersion in the liquid must be ensured. With suitable slurry characteristics, dip-coating is a simple process, in which only the control of immersion time and withdrawal speed yields excellent reproducibility. The technique has the advantage of little waste, whereas the most relevant cause of waste are evaporative losses, which can be reduced by using solution containers with small apertures.[121]

One of the most significant drawbacks of the technique is the limitation to simple geometries – sheets, plates, cylinders, tubes and slightly irregular shapes – when homogeneity of the coating thickness is needed.[122] Although deposition of coatings onto substrates with more complex shapes is possible, changes in the flow of the coating solution during withdrawal leads to inhomogeneous coatings.[123] Moreover, edge effects are quite extensive in dip coating, affecting thickness homogeneity. The area affected by these edge effects is usually in the range of 15 to 20 mm inwards from top and bottom edges and of 8 to 15 mm from the side edges.[124] These effects become more pronounced with increasing withdrawal speed, but are not affected by the size of the substrate, thus hindering deposition of homogeneous coatings onto small substrates.[125] This technique requires large volumes of coating solution relative to the volume that actually forms the film. Considering that several precursors are air and moisture-sensitive, the process may require additional equipment to ensure a constant quality of the coating solution over long periods of time, increasing processing costs. Difficulties also arise when liquids with higher viscosity or those containing fillers must be used, due to inhomogeneous flow of the liquid.

The thickness of the formed film depends on the withdrawal velocity and on properties of the liquid, such as surface tension, viscosity, density and volatility of solvent. A model for the prediction of thickness of coatings deposited by dip coating in a Newtonian fluid without evaporative losses was developed by Landau and Levich.[126] According to this model, which was also experimentally validated,[127] the coating thickness is proportional to the withdrawal speed. The exact correlation between speed and thickness is then given by the properties of the liquid.[122] Layers deposited by a single dip coating procedure usually have a thickness up to about twenty microns. Repeating the process can increase coating thickness, but a re-dissolution of previously applied layers must be avoided. In the case of silicon polymers, at least a cross-linking step between each repetition must be carried out. For the processing of ceramic coatings, even a complete ceramization of each layer might be necessary to avoid excessive overall shrinkage and coating failure.[124]

6.2   Spin Coating

Spin coating is another coating method commonly used for deposition of silicon-based polymers. Industrially, it has been used extensively in the electronic industry for the coating of silicon wafers.[128,129] The technique consists of the

spreading of the coating solution – usually deposited at the center of the substrate – towards the edges by the centrifugal force generated upon rotating the substrate.[130]

The spin coating equipment is relatively simple and the process reproducible. When compared to dip coating, the amount of coating solution required to coat a given substrate is significantly smaller. However, considerably more coating solution is wasted during spin coating process.[128] Moreover, the technique is mostly suitable for flat or slightly curved surfaces and deposition can be carried only in a single face each time. Additionally, deposition of solutions with higher viscosity is difficult and usually leads to coatings with surface defects.[128,131,132] This is a challenge especially for coatings with fillers.

Similarly to dip coating, coating thickness depends on the velocity of rotation and on the properties of the liquid, although in spin coating an increase in the velocity leads to thinner coatings.[129] Typical coating thicknesses are in the range of a few nanometers to a few micrometers.[131] Like in dip coating, deposition of several consecutive layers may lead to thicker coatings, if a re-dissolution of the previously applied layer is avoided.

6.3   Spray coating

Spray coating is one of the most common ways to apply coatings both at the industrial scale and in research and development. The principle of the technique consists of the atomization and transport of a coating solution towards the substrate, where a film is formed by the impact of the droplets on the surface. Atomization may be realized by pressure (airless), by a pressurized carrier gas (usually air), by a supercritical process, by an electrostatic process or by rotation.[133] The most common method used in combination with silicon polymers is the atomization using a pressurized carrier gas, generally air, in which the coating solution is fed into the gas stream exiting the spray nozzle.[134] Although inert gases can be used as carrier gas, deposition is carried out in air, preventing the use of highly reactive polymers and the preparation of oxygen-free coatings.

In contrast to dip and spin coating, spray deposition has a large number of parameters, including pressure of the carrier gas, aperture of the spray nozzle, distance between nozzle and substrate, angle of impact, form of the spray jet, and the velocity of the relative movement between nozzle and substrate. On the one hand, this high number of parameters complicates the development of the coating process. On the other hand, it increases the versatility of the method, since parameters can be adjusted to enable deposition of coating solutions with a wide range of properties – viscosity, size of filler particles, and volatility of solvent – and also to control characteristics of the coatings, like thickness and surface structure.[128,135]

A typical spraying equipment consists of a pressurized gas source, a solution container, the spray nozzle, and an exhaust system, since most coating formulations are solvent-borne and contain filler particles.[121] Spray coating can be carried out by free-hand movements using a spray gun. However, in this case, reproducibility and homogeneity will strongly depend on the abilities of the operator. More complex systems with mechanic or electronic control during operation are able to improve the reproducibility of the process (Fig. 12).[133] Despite the large amount of

waste due to overspray, spray coating requires a relatively low amount of coating solution per area of substrate to deposit coatings.[123]
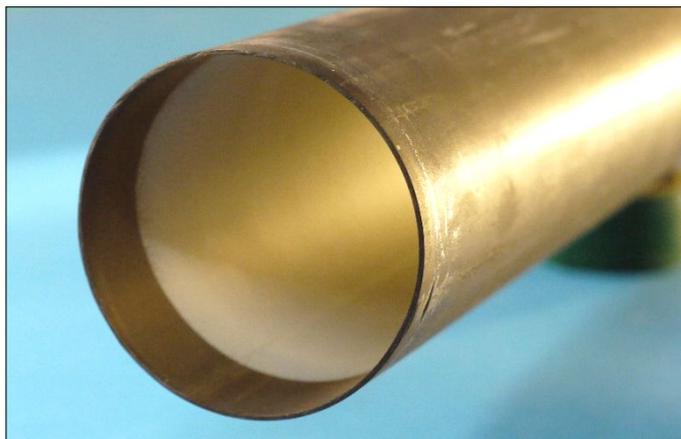
Fig. 12 Stainless steel pipe with PDC-based thermal barrier coating deposited onto the inside face by spray coating using a semi-automatic equipment and pyrolysis at 1000 °C in air for 1 h.[47]

7.   Curing and ceramization techniques

Section 3 was focused on the chemical and physical changes in the precursor during its conversion from polymer to a ceramic. This section is focused on the techniques used to realize this conversion. In contrast to free-standing ceramics – such as fibers, foams and monoliths – processing of coatings involves also a substrate, which must be subjected to the same conditions as the coatings. Hence, the choice of a conversion method must take not only properties of the coating but also of the substrate into account. Moreover, even when using the same coating material and substrate, different processing methods may yield different types of coatings. Thus, the choice of the processing will also depend on the desired coating properties and intended application.

A number of publications in the field of coatings based on preceramic polymers deal with the development and investigation of new techniques for conversion of coatings, in order to overcome limitations of the commonly used methods. Hence, the following sections are dedicated to a summary of the available techniques, which are divided into common and alternative techniques, where the former are the more general techniques and later the emerging ones, which have been developed and applied for a small number of systems.

7.1   Common techniques

By far, the most common technique used for the conversion of silicon-based polymer coatings into thermosets and ceramics is by thermal treatment. The greatest advantage of this method is its simplicity and the fact that the thermal processing can be carried out batchwise or continuously. However, the presence of a substrate is an important limiting factor. As discussed in Section 3, temperatures up to 400 °C may be required to achieve a complete cross-linking of the coatings, and above that to obtain ceramic coatings. As a consequence, ceramic

coatings cannot be prepared on materials with low melting temperature – such as most organic polymers, aluminium and magnesium – by thermal treatment without risk of degradation or deformation of the substrate. Hence, thermal treatment in a furnace is mostly suitable for systems intended for application at higher temperatures, and the thermal treatment is carried out at or above the maximum application temperature. Yet, a thermal treatment at higher temperatures may be interesting also for systems intended for low temperature applications, since higher temperatures lead to a densification of the coating material and to an increase of hardness and Young's modulus (Fig. 13).[136] As shown in Fig. 13, although both hardness and the Young's modulus increase as the heat treatment temperature increases, there is a subtle interaction between the coating material and the heat treatment atmosphere. For coatings pyrolyzed to the ceramic state (pyrolysis temperature higher than 600 °C), the coatings pyrolyzed in nitrogen have higher hardness and Young's modulus because oxygen-free silicon-based ceramics have, in general, higher hardness and modulus than the oxygen-containing counterparts. For coatings pyrolyzed to cross-linked thermoset state (pyrolysis temperature less than 400 °C), the coatings pyrolyzed in air have higher hardness and Young's modulus because of the reactivity of these precursors with humidity, leading to a faster cross-linking in air than under nitrogen atmosphere.[136]
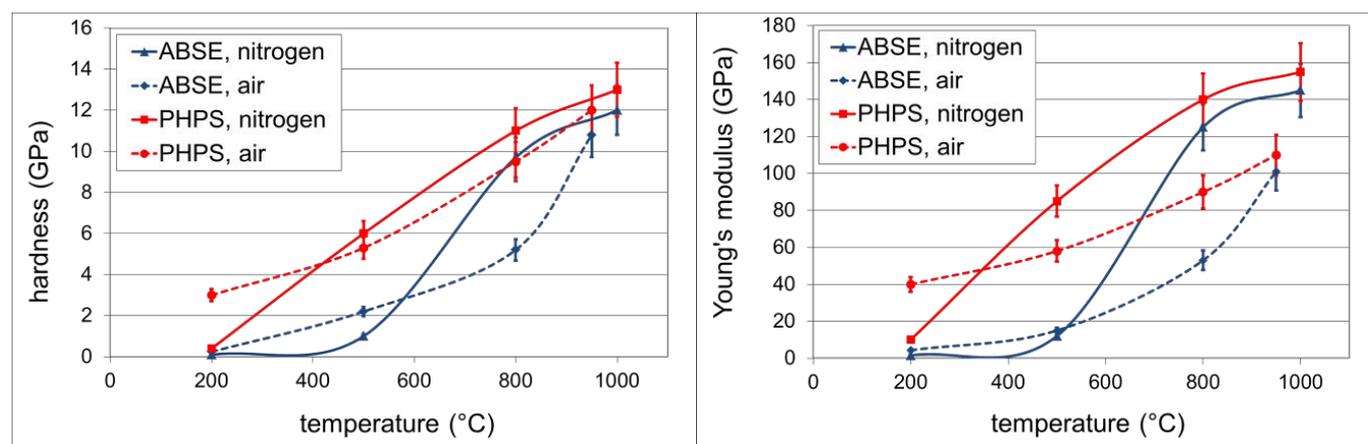
Fig. 13 Dependency of hardness and Young's modulus with temperature and atmosphere during heat treatment of two polysilazane-based coatings on stainless steel. Reproduced with permission.[136] Copyright © 2012, Elsevier Ltd.

In addition to processing temperature, an important factor to be considered during thermal treatment is the atmosphere. For most industrial applications, air is the most desired atmosphere, owing to the lower processing costs. Moreover, the presence of oxygen facilitates the use of active fillers, since conversion of metals and non-oxide ceramics into their respective oxides is usually associated with a volume expansion. However, if the substrate does not have sufficient oxidation stability, a thermal treatment under inert gas (e.g. argon) or vacuum is required. Independent of substrate's oxidation stability, inert atmospheres can also be used to prepare oxygen-free coatings, like SiC and Si_3N_4.[137–139] In this case, however, the use of active fillers is limited to those materials, which react with the precursor or with gaseous products of pyrolysis reactions. Also nitrogen gas can be used as atmosphere to generate oxygen-free coatings and to protect the substrate against oxidation. Since nitriding reactions may occur during pyrolysis, additional active fillers can be used, although these reactions occur slower and require higher temperatures than oxidation.[140] Moreover, a reactive ammonia-containing atmosphere during pyrolysis can be

used to obtain silicon nitride coatings from nitrogen-free precursors.[141] A general limitation of thermal conversion process is the requirement of a chamber large enough to accommodate the coated parts, which may be difficult for very large substrates.

Cross-linking processes are commonly assisted by the use of catalysts and initiators.[142–150] In these cases, suitable chemical compounds are mixed with the precursors, reducing the onset temperature of cross-linking reactions, and consequently reducing the evaporation of lighter molecules at higher temperatures. If enough time is provided, cross-linking may occur even at room temperature. In some cases, more reactive silicon polymers may be added to less reactive ones to accelerate cross-linking of the later.[151,152] Depending on the onset temperature of the catalyzed cross-linking reactions, the catalysts must be mixed with the precursor just before coating deposition, to avoid premature cross-linking.

To enable the preparation of coatings onto substrates with more limited temperature resistance, several methods for the conversion of precursor-based coatings into ceramic-like materials at low temperatures have been developed. Precursors with a high sensitivity to moisture can be cross-linked at low temperatures under humid atmosphere.[29,144,147,148,153–155] An innovative approach of using humid air containing ammonia as catalyst has been established for the conversion of silazane coatings deposited in air into SiO_X coatings at temperatures below 200 °C.[154,156–164] The presence of humidity leads to hydrolysis of Si-H and Si-N bonds, forming silanol groups. The condensation of these silanol groups is then catalyzed by ammonia, forming the SiO_X networks. Humidity can be also used during pyrolysis at higher temperatures to enhance oxygen incorporation.[165]

Another method extensively investigated to induce cross-linking of silicon-based polymer coatings, especially polysilazanes, is the use of vacuum ultraviolet (VUV) radiation in the presence of oxygen.[153,166–176] In this technique, ozone and oxygen radicals formed by the VUV radiation are responsible for oxidation and, thus, conversion of coatings into highly cross-linked materials.[167,169] This technique has been developed especially for the preparation of diffusion barriers into polymer foils, for the encapsulation of electronic devices. A pilot plant for the continuous roll-to-roll deposition and VUV curing of Si-based polymer coatings onto organic polymer foils has already been developed.[166]

As previously mentioned, although more complex than the other methods, plasma polymerization and CVD techniques, which are methods for simultaneous deposition and conversion of coatings, have also been common approaches to obtain polymeric and ceramic coatings based on silicon.

7.2   Alternative methods

Although the low temperature methods, discussed in Section 7.1, yield highly cross-linked coatings, their performance is still below that of coatings obtained by thermal treatment of the same precursors at higher temperatures, and of SiO_2 coatings obtained by sol-gel or conventional CVD.[153,156,157,160] Therefore, there is still a

need for alternative methods to prepare coatings, especially ceramic ones, without exposing substrates to high temperatures.

One way to introduce energy into coatings without affecting the substrate is by means of radiation. In addition to the VUV technique, several approaches using other types of radiation have been investigated, such as UV/Vis/IR[148,177–184], synchrotron[183], laser[185,186], electron-beam[178,187–189], ions[190–194], and x-rays[178]. It is important to mention that some of these techniques can only induce cross-linking, requiring a complementary method, such as a heat-treatment, if a ceramic coating is desired. However, approaches using laser[185,186] and ion irradiation[190–194], for example, have been successful at the direct conversion of coatings from silicon-based oligomers and polymers into ceramics (Fig. 14). Moreover, a method called rapid thermal processing of PDC coatings using different types of radiations has been patented.[177]
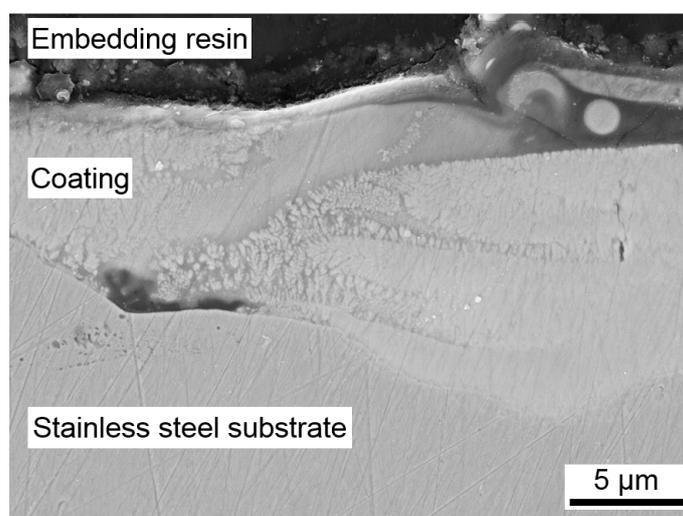
Fig. 14 Cross-section microstructure of a polysilazane-based coating with glass and ZrO_2 as passive filler after laser pyrolysis (power = 7.7 W, speed = 14 mm s^{-1}, hatching distance = 30 μm, cw-mode). Adapted with permission.[186] Copyright © 2016, Elsevier Ltd.

Aside from plasma polymerization and plasma-assisted CVD, less common approaches using plasma have been developed. Jeong and colleagues used oxygen plasma to improve conversion into SiO_2 of silazane coatings pre-treated at low temperatures.[195,196] Similarly, Park *et al.* studied the effect of a N_2O plasma post-treatment onto precursor-derived coatings.[197] Moreover, a pyrolysis process assisted by nitrogen plasma has been developed to improve conversion of active fillers in the absence of oxygen with promising results (Fig. 15).[140]
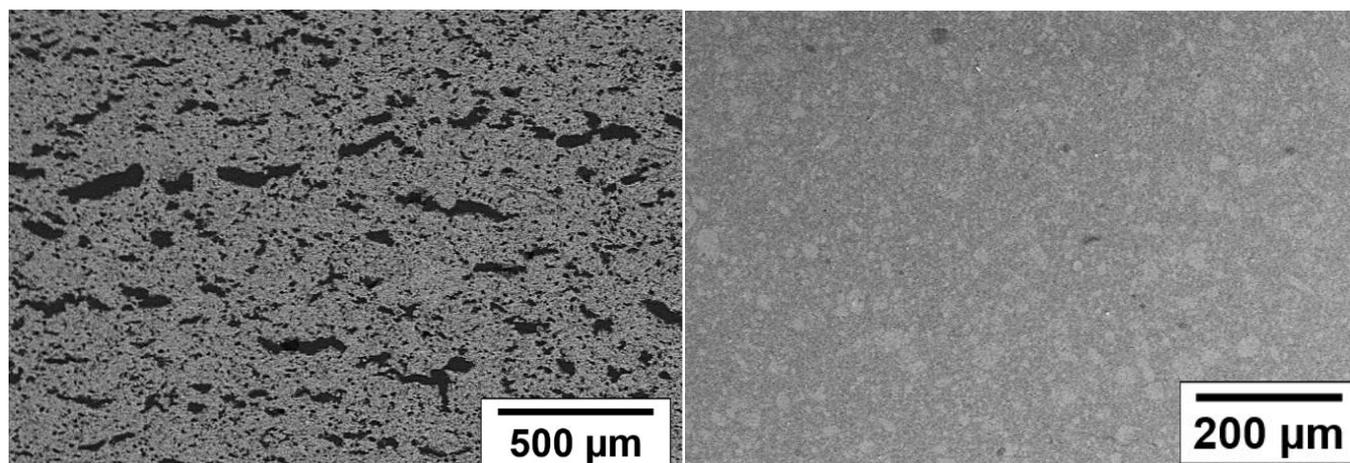
Fig. 15 Comparison of the cross-section microstructure of monolithic samples from polysilazane with $TiSi_2$ active filler after treatment at 1150 °C for 2 h by (left) conventional pyrolysis in a furnace under nitrogen atmosphere; and (right) plasma-assisted pyrolysis in cathode configuration under nitrogen plasma. Reproduced with permission.[140] Copyright © 2016, Elsevier Ltd.

Finally, preceramic monomers, oligomers and polymers have also been used as feedstock in more traditional techniques for deposition of ceramic coatings, such as CVD,[198–204] plasma spraying,[205] and cold spraying of powders.[206] These approaches are, however, less common, since one of the significant advantages of the PDC method, the simple processing, disappears with these processes.

8.   Properties and applications

Owing to the great variety of precursors and processing techniques available, as well as to the tailorability of systems through the addition of fillers, coatings with a wide range of properties can be achieved. Hence, coatings based on silicon polymers have been developed for many different applications. Especially polyorganosiloxanes, i.e. silicones, have been extensively applied in many low temperature coating systems. Although some of these studies are mentioned herein, we encourage readers to refer to further sources, such as the review paper of Eduok and colleagues[21], for more comprehensive information on this topic. Another topic, which, for the sake of brevity, is not extensively considered in this review, is the use of silicon-based compounds, such as silanes, as adhesion promoters.[1,20,97,207–209] These are silicon-based molecules with structure $X_3Si(CH_2)_nY$, where X are hydrolysable groups to provide adhesion with the substrate and Y is a functional group with affinity to the coating material to be applied.[94] Since most of these adhesion promoters act only as bridges between substrate and a coating, without necessarily forming a polymeric coating itself, this application was considered beyond the scope of this review paper. For further information, we recommend the review of van Ooij and colleagues.[210]

One of the most prominent and industrially established applications of coatings from silicon-based precursors are dielectrics for electronic devices. Dielectrics are usually SiO_2 layers deposited by CVD, which isolate the different structures of an electronic system. However, miniaturization of circuits with ever increasing power has led to systems with gaps of a few nanometers in width and high aspect ratio between the individual structures (Fig. 16).

Due to shadowing effects, such narrow gaps cannot be completely filled by CVD. Since precursors can be deposited in liquid phase, e.g. by spin coating, they are able to fill these tight gaps. A post-deposition treatment then yields the dielectrics. For this reason, such systems are known commercially as spin-on dielectrics. The most common precursor for this application is the perhydropolysilazane (PHPS), which after a treatment under oxidative conditions, yields suitable silica dielectric coatings.[147,195–197,211–214]
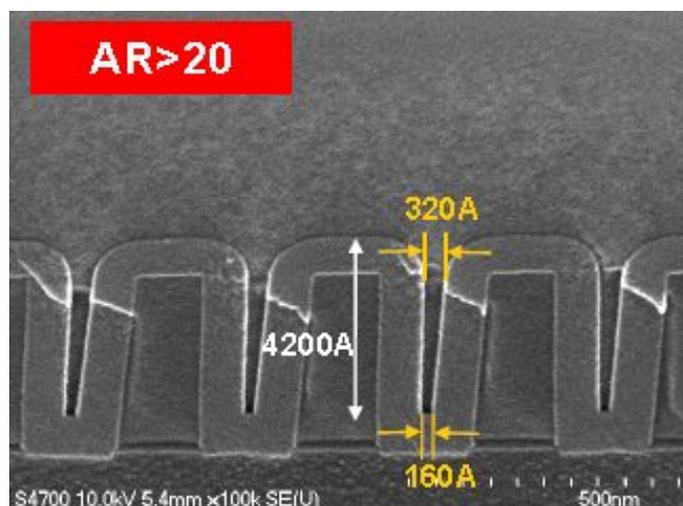
Fig. 16 Electronic circuit with a polysilazane spin-on dielectric coating (aspect ratio larger than 20). Reproduced with permission of The American Ceramic Society.[213] Courtesy of Merck KGaA.

A second type of application in electronics is related to the encapsulation of devices. Permeation of water vapor and oxygen through the plastic foils commonly used for encapsulation leads to degradation of devices. However, the performance of these foils can be enhanced by gas barrier coatings prepared from silicon-based polymers.[104,153,156,166–168,172–175,215] During application in low earth orbit, degradation by atomic oxygen also becomes an issue, which can be hindered by precursor-based coatings.[216–218] In addition, coatings have been designed to have functional properties, especially in the case of solar cells. Some examples are the thermal management of solar cells used in space by coating systems with high emissivity[219], passivation on silicon-based solar cells to avoid recombination and increase efficiency[220,221], as well as absorbing coatings to increase the efficiency of solar collectors[222].

During the early years of the development of PDC coatings, the preparation of gas separation membranes was one of the most intensively researched topics.[84,85,181,187,189,223–233] For such application, PDC coatings with a selective permeability, obtained by a precise control of porosity, are deposited onto porous substrates. This results in composite membranes capable of separating gases, like hydrogen or oxygen, present in a gas mixture.

Currently, the most investigated application of coatings based on silicon polymers are environmental barrier coatings (EBCs). Due to their intrinsic high stability in harsh environments, ceramics are especially well suited for such systems (Fig. 17). Indeed, the PDC route has been applied in many studies to obtain ceramic coatings aiming at prevention of corrosion and oxidation of metallic and ceramic substrates at high temperatures.[63,66,67,75,77–82,136,182,234–248] However, protection of substrates at low temperatures has also been targeted by many studies. In

these cases, both polymeric and ceramic coating systems based on silicon polymers have been developed focused on corrosion protection against acids, bases and salts.[97,144,152,242,249–256] In addition, protection of substrates at low temperatures has also been targeted by many studies. In these cases, both polymeric and ceramic coating systems based on silicon polymers have been developed focused on corrosion protection against acids, bases and salts.[105,142,152,257–260]
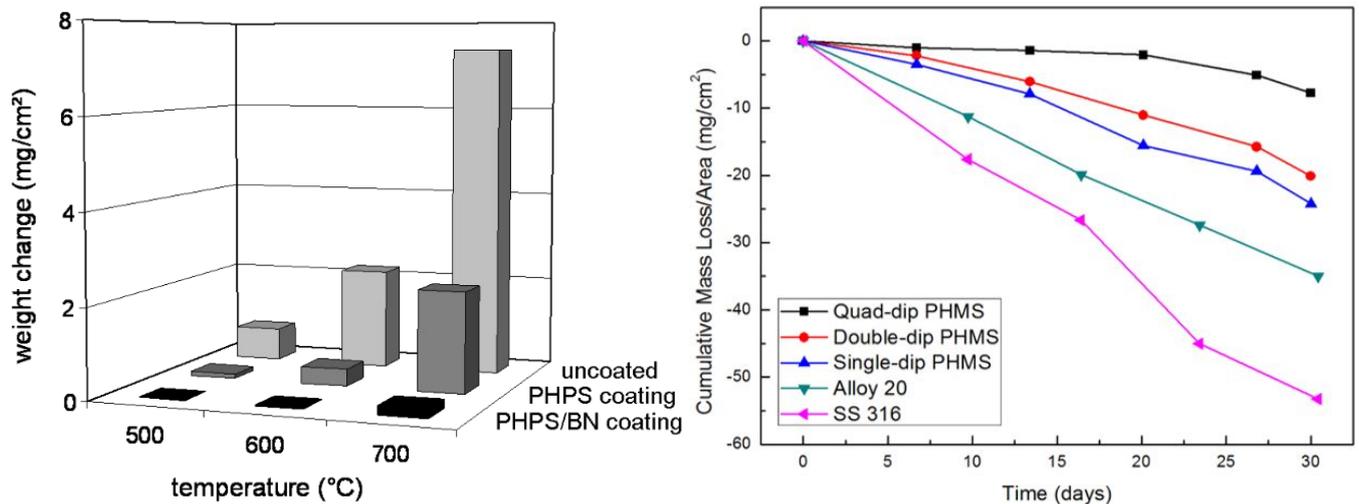
Fig. 17 Protective effect of silicon-based ceramic coatings on metallic substrates: (left) oxidation protection of coatings based on the polysilazane PHPS with and without BN passive filler on mild steel (Reproduced with permission.[66] Copyright © 2009, John Wiley and Sons.); (right) protection against hot concentrated sulfuric acid provided by coatings from polysiloxane PHMS and TiSi$_2$ active filler of various thicknesses on stainless steel (Reproduced with permission.[242] Copyright © 2014, Elsevier Ltd.)

Another advantage of ceramic coatings is the high hardness, modulus and strength. For this reason, the PDC route using silicon-based polymers has been proposed as an alternative to CVD, PVD and thermal spraying to generate surfaces with improved wear resistance, with promising results.[136,204,261–265]

It is well known that the free energy of a surface is determined by its chemical characteristics and its structural features. As mentioned in Section 3, the chemical structure and composition of precursors changes during the polymer-to-ceramic transformation. This can be used to obtain coatings with tailored surface free energy, as has been demonstrated for PHPS coatings after treatment in air at different temperatures (Fig. 18).[266] The possibility of tailoring the chemical properties of silicon polymers by manipulating the structure and composition of molecules, together with different methods for surface structuring – such as by fillers, templating, ablation, and others – has led to many coatings with low surface energy, resulting in hydrophobic, anti-icing, self-cleaning, anti-graffiti and anti-sticking surfaces.[42,64,106,107,146,213,259,266–274] In addition, coatings with high surface energy can be obtained, which improves the wettability of the surface, e.g. to promote adhesion.[184,266,275–277]
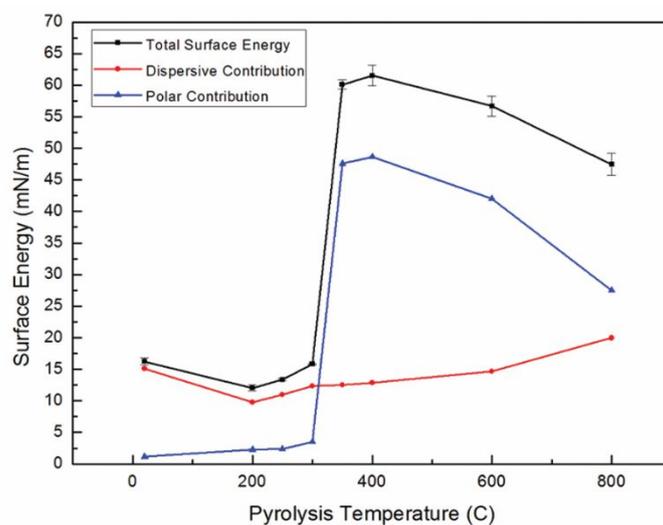
Fig. 18 Evolution of the surface free energy of smooth polysilazane PHPS coatings in dependence with the temperature during thermal treatment in air. Reproduced with permission.[266] Copyright © 2013, American Chemical Society.

Furthermore, silicon polymers can be used to obtain coatings for many biological and biomedical applications.[150,259,278–283] Such coatings can be used to avoid proliferation and adhesion of bacteria and other microorganisms, to increase the biocompatibility of prosthetic materials with the human body, and to protect these materials against premature degradation, e.g. in dentistry.

The liquid phase deposition makes coatings obtained from silicon-based polymers interesting also for the modification of the surface of fibers used as reinforcement in CMCs.[284–289] On the one hand, the coatings can protect the fibers against oxidation and degradation during the following steps of the processing of the composites. On the other hand, they can be used to tailor the fiber-matrix interactions, in order to optimize the mechanical behavior and the damage tolerance of the CMCs.

Other applications of silicon-based polymeric and ceramic coatings include photocatalysis,[65] radiation shielding[290], thermal barrier coatings[47,71], diffusion barriers[291], surfaces with tailored IR-emissivity for defense and thermal management applications[292–294], strengthening and protection of glass[163,295], strengthening of ceramics[296], photochromism[164,297], light conversion[298], sensors[103,299], fire protection[300], buffer layers for diamond coating[301], cathode material for fuel cells[302], thin-film electrolytes[303], and water adsorption[304].

9.   Organic-inorganic hybrid polymer coatings

Owing to the ever increasing performance requirements, coatings based on organic polymers have become insufficient for many applications.[305] However, despite the many superior properties, silicon-based (inorganic) polymers are in general more expensive than most organic polymers, which is one of the factors limiting their application on a large scale. A way to obtain coatings with enhanced properties when compared to organic coatings and, at the same, lower costs than the purely inorganic systems is to combine both classes in one material, forming organic-inorganic hybrids or interpenetrating polymer networks. Since this is a large field of research, for the sake

of brevity this paper offers only an introduction to the technology and applications of organic-inorganic hybrid coating systems.

By far, the most frequently used inorganic component in hybrid materials for coating applications are silicones. As organic component, three main types of polymers stand out: epoxy[305–320], polyurethanes[321–331], and polyacrylates[332–343]. In these systems, aside from reducing the overall costs of the materials, the organic component is essentially responsible for an increase of the coating hardness, whereas the inorganic part reduces the surface energy and increases the thermal, chemical and UV resistance of the systems (Fig. 19). Other examples of organic polymers, which have been combined with polysiloxanes for coating applications are polyethyleneglycol[344–346], polyimides[347–350], and polyesters[351]. Although much less frequently, organic-inorganic polymers have been synthesized using polysilazane and polysilsesquiazane inorganic polymers as well.[352–356]

The vast majority of these hybrid polymeric coating systems were developed aiming at more efficient and resistant anti-corrosion[308–312,315,316,319,320,337,338,341,351,353] and anti-fouling[307,322,323,330,343–345,355] coatings. However, some systems for other applications, such as photoluminescence[324], IR emissivity[313], protection against atomic oxygen[347], and dielectrics[342,352] have also been developed.
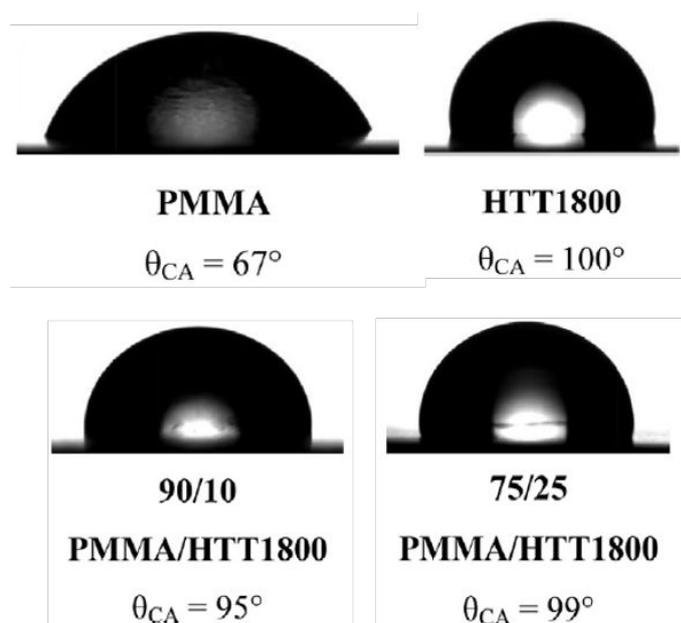
Fig. 19 Contact angle with water of coatings composed of pure PMMA, pure poly(organo)silazane HTT 1800, and of hybrids composed of 90 wt% PMMA and 10 wt% HTT1800, and 75 wt% PMMA and 25 wt% HTT1800 after treatment at 60 °C for 24 h. Reproduced with permission.[353] Copyright © 2015, Elsevier Ltd.

10. Topics for further research and prospects

Coatings based on silicon polymers is an expanding field and many systems for different applications have been realized. However, there are still challenges to overcome. A large contribution to the field of coatings based on silicon polymers in the future will likely come from chemistry. The chemical modification of precursors to obtain tailored properties is a promising approach, which has already yielded interesting results. The modification of

precursors with metals, for example, can lead to a new class of coatings with catalytic activity, as well as tailored thermal, electric and magnetic properties.

As the properties of silicon polymers become better known and understood, novel organic-inorganic hybrid coatings are expected to be developed. The combination of properties from organic and inorganic polymers is an intelligent strategy to obtain coatings with enhanced properties. This could lead to thick coatings with low surface energy, high chemical, thermal and UV resistance which will extend the range of application and the lifetime of the coatings, when compared to purely organic counterparts.

New coating systems based on silicon polymers are also likely to be further developed aiming at improved corrosion protection. The potential of these coatings as barriers against different corrosive media has been demonstrated. However, performance is still not sufficient for industry requirements. Thus, intensive research on this topic, especially towards smart coatings, is likely be conducted during the next few years. Such systems are able to respond to different stimuli – like changes in pH, moisture, or mechanical stress – activating corrosion inhibitors or self-healing agents, increasing efficiency and lifetime of coatings and substrates.

Despite the simpler processing, properties of ceramic coatings prepared by PDC technique are, in some cases, still inferior to those of CVD, PVD and thermal-sprayed coatings. One example is the low coating thickness of PDC coatings. Plasma spraying and PVD can yield robust ceramic coatings with more than 300 μm of thickness on metallic substrates for application at temperatures above 1000 °C. PDC coatings, in contrast, are still limited to a few tens of microns. The challenge in this case is to increase the coating thickness and, at the same time, keep the process simple and cost-effective.

Also tribological properties of PDC coatings are still not comparable to those of conventional coating systems, processed e.g. by CVD, PVD or thermal spraying. Intrinsic stresses caused by precursor shrinkage, together with low coefficients of thermal expansion, make PDC coatings on metallic substrates more prone to failure upon mechanical stresses. Strategies to control stress evolution and improve the compatibility between coatings and substrates may lead to coatings with improved tribological properties.

The processing of PDC coatings is also expected to be further addressed in the future. Novel techniques for the conversion of silicon polymers into ceramic coatings without affecting the substrates can lead to a great advance of the PDC technique for coating applications. Ceramic coatings for less heat-resistant metals, such as aluminium and magnesium, as well as for plastics and polymeric composites could find application in many lightweight systems.

11. Conclusions

Silicon-based polymers are materials with outstanding properties, which can be used to prepared polymeric and ceramic coatings. Since most of these compounds are liquids or soluble in common solvents, deposition of coatings can be carried out in liquid state, e.g. by dip, spin or spray coating techniques. A treatment by heat, chemical

reaction, radiation or combinations thereof leads to cross-linking of polymer chains, forming unmeltable and insoluble polymeric coatings. These coatings have, in many cases, superior properties than organic coatings. A further treatment, mostly at elevated temperatures (pyrolysis), results in conversion of the polymers into ceramics (polymer-derived ceramics technique). Because of this, such silicon polymers are also known as preceramic polymers or precursors.

A great variety of precursors is commercially available. For coating applications, the most important families of precursors are polysiloxanes, polysilazanes, polycarbosilazanes, polysilylcarbodiimides, polycarbosilanes and polysilanes. Since the composition and chemical structure of the precursors determine the behavior of the polymers during processing, as well as the properties and composition of polymeric and ceramic coatings, many different coating systems are possible. Moreover, by tailoring the chemical structure of precursors, systems with improved properties for specific applications can be realized.

The polymer-to-ceramic conversion is typically associated with a mass loss in the range of 10-30%. Moreover, a significant densification of the material occurs, from about 1 g cm^{-3} as polymers to more than 2 g cm^{-3} as ceramic. Combination of both effects results in significant shrinkage during pyrolysis. If this shrinkage is inhomogeneous or constrained, stresses can be generated, which may cause cracking and failure of the parts. In the case of coatings, the shrinkage is constrained by the adhesion of the coating to the substrate, leading to large tensile stresses. Because of this, the PDC technology, using unfilled silicon polymers, is limited to ceramics with small dimensions, such as fibers, thin coatings, and cellular ceramics (thin cell wall), which are able to uniformly shrink. A way to control the shrinkage of parts is by the use of fillers. Usually added in the form of particles, fillers (ceramics, metals, polymers or glasses) can, directly or indirectly, reduce the coating shrinkage during pyrolysis. This enables the preparation of thicker coatings. In addition to shrinkage control, fillers are frequently used to add new functionalities to polymeric and ceramic coating systems.

One of the advantages of silicon-based polymers in comparison to the organic counterparts is the strong adhesion to most substrates and fillers. This results from chemical bonding, due to reactions between the precursor molecules and –OH groups at the surface of substrates and filler particles. After deposition, the inorganic polymer layers can be converted into strong adherent ceramic coatings as well.

The variety of precursors available and the tailorability of properties by chemical modification or addition of fillers has led to the development of coatings for several applications, both at low and high temperatures. Especially coatings for corrosion/oxidation protection of many different substrates have been developed, owing to the excellent environmental barrier properties of these coatings. Other applications include encapsulation of electronic devices, gas separation membranes, dielectric coatings, easy-to-clean or self-cleaning coatings, thermal barriers, diffusion barriers, antibacterial surfaces, and biocompatible coatings.

Despite many studies involving coatings using silicon-based polymers, there is still plenty of room for new developments. Modification of polymers, hybrid materials, novel processing techniques and strategies to control

stresses arising during conversion into ceramic coatings should lead to advanced coating systems with outstanding properties in the future.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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