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Polydopamine as a Materials Platform to Promote Strong and Durable Interfaces in Thermoplastic Polymer-Titanium Joints

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Joining thermoplastic polymers (TPMs) and metals to form lightweight hybrid structures is of growing industrial and commercial importance. The performance of such materials relies on the bonding strength and endurance of the formed TPM–metal interfaces. The available joining technologies and the mechanisms that govern interfacial adhesion are reviewed in this contribution, highlighting thermal bonding as a commercially attractive joining method. By focusing on molecular interactions to optimize interfacial adhesion, the use of dopamine as a building block to form polydopamine (PDA) based adhesive interlayers in such interfaces is discussed. This work also highlights the potential of PDA to be applied as a load-bearing adhesive—a notion considered to date unfeasible.

1. Introduction

Hybridization of thermoplastic polymers (TPMs) and metals allows the formation of lightweight materials and structures that often possess superior properties compared to the individual constituents.[1–3] This, combined with the sustainable production and application of TPM–metal hybrids, has established them as competitive candidates for advanced applications in various industrial fields.[4–6] TPM–metal hybrid structures can be produced via a combination of joining techniques, such as mechanical joining, adhesive bonding, or thermal bonding.[7–9] Of these techniques, thermal bonding is of growing interest to the industry
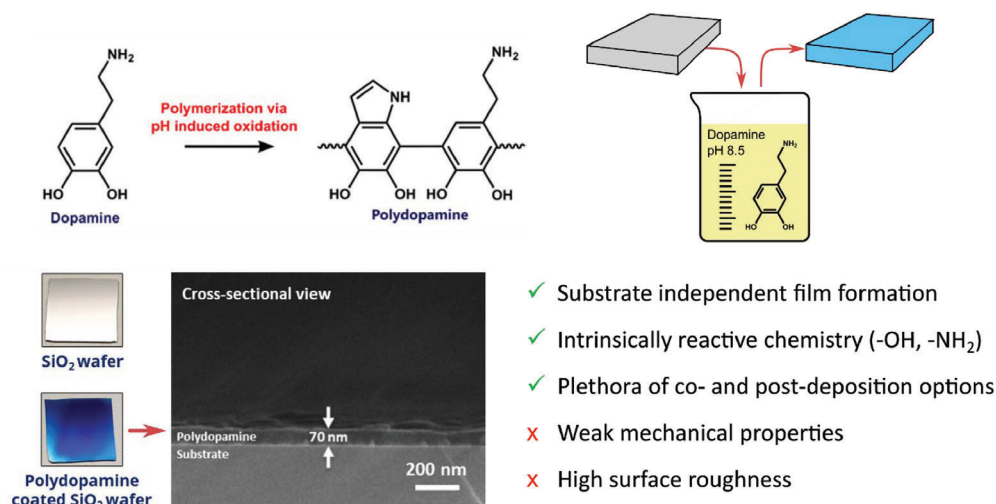
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mainly due to the short processing times it requires.[10] In thermal bonding, the TPM and the metal part are brought in contact under pressure, at a temperature above the melting point of the TPM, followed by a cooling step to consolidate the structure. The performance of thermally bonded joints relies heavily on the ability of the formed TPM–metal interfaces to transfer load without failing as well as to resist bond degradation from environmental conditioning. The strength and stability of such interfaces is affected by a number of parameters across length scales, such as the geometry of the joint, the interface morphology, and the molecular interactions at the interface.[11–13] It is intuitive that over a broad range of possible geometries, materials and applications, no single universal approach exists. Rather the objective is to develop new tools that will be available in the "industrial toolbox" to achieve the interfacial goals for respective applications.

Despite the decades long practices in joining polymers and metals, still a number of promising options remain unexplored, especially when molecular interactions are considered. A notable example is a bioinspired interlayer, i.e., polydopamine (PDA) which here is proposed as a suitable candidate to engineer adhesion in thermally bonded interfaces by optimizing the molecular interactions between adherent and adhesive. PDA was first introduced by Messersmith and co-workers in 2007[14] via the oxidative polymerization of dopamine under alkaline conditions. Virtually any object immersed in the polymerization solution of DA is coated with a PDA layer with thicknesses of a few tenths of nanometers (see **Figure 1**).[14] The as-formed coatings adhere strongly to substrates via a wealth of interactions, exhibit intrinsic reactivity with other chemical species, and offer a plethora of options to tune their chemistry via codeposition and postmodification approaches.[15–17] This unique set of features combined with the simplicity of application has established PDA as a powerful tool to engineer the surface/interfacial chemistry in a broad range research fields.[18] However, PDA commercialization has been challenged by two main factors, i.e., 1) the relatively high surface roughness of the formed coatings and 2) the poor cohesive material properties it exhibits.[18,19] The latter has also hindered the successful application of PDA-based coatings as structural adhesives, even at lab-scale experiments.[18,20]

Recent successful applications of PDA as a load-bearing adhesive in TPM-titanium thermally bonded joints[21–23] motivated

Figure 1. Polydopamine (PDA) polymerization, film deposition on substrates, and properties evaluation.

the scope of this contribution. We highlight under which circumstances PDA could pose a promising platform for promoting strong and durable interfaces in titanium-TPM thermally bonded joints. This work covers the methods available to join TPMs and titanium, identifies bonding mechanisms across length scales for thermally bonded TPM-titanium joints, and argues why PDA is an excellent candidate to connect such interfaces.

2. Joining Thermoplastic Polymers and Metals

Combining TPMs and metals allows the formation of cost-effective lightweight materials and structures that amalgamate the strength and stiffness of metals with the durability and formability of polymers.[1,2,24,25] In addition, such systems often exhibit other beneficial attributes such as enhanced damage tolerance, fatigue performance, impact, and chemical resistance.[3,26] The exceptional performance of TPM–metal hybrid materials combined with their cost-effective production and application has rendered them excellent candidates for advanced applications in industrial fields such as biomedical,[4,27] automotive,[5,28]

and aerospace.[6,29] The formation of TPM–metal hybrid materials and structures is achieved via joining methods that can be divided into three main categories, i.e., mechanical joining, adhesive bonding, and thermal bonding.[7–9,30] The respective methods are schematically summarized in **Figure 2**.

The application of the aforementioned joining methods to form TPM–metal hybrid materials is accompanied by their respective advantages and disadvantages (summarized in **Table 1**). For instance, mechanical joining is a method that connects parts by mechanical means, e.g., rivets and bolts. This method allows the assembly and disassembly of hybrid structures, facilitating the inspection, replacement, and by extent, repair of joined parts.[31,32] In addition, mechanically joined hybrid structures exhibit high tolerance to environmental effects and require no surface preparation before their assembly.[33,34] Most importantly, mechanical joining is reliable, and this facilitates material certification for demanding applications, e.g., airworthiness for aerospace materials.[35–37] However, rivets and bolts introduce additional weight to the structure and act as stress concentration points, which negatively impact its
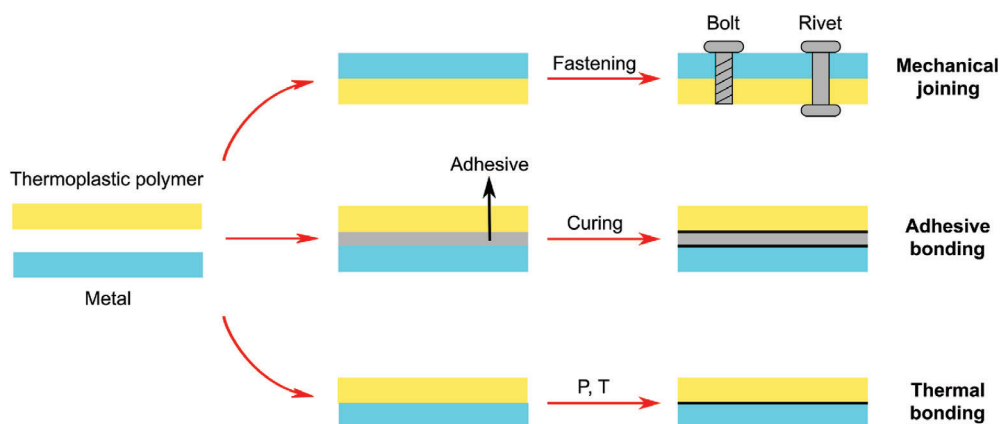

Figure 2. Schematic representation of thermoplastic polymer (TPM) and metal joining methods.

Table 1. Advantages and disadvantages of the three main categories of joining methods.

Joining method	Advantages	Disadvantages
Mechanical joining	Ease of assembly/disassembly[17,18]	Introduction of stress concentration points[24,25]
	Ease of inspection and part repair[17,18]	Local wear during drilling/puncturing[26,27]
	Tolerance of environmental effects[19,20]	Introduction of additional weight[24,25]
	Not sensitive to surface preparation[19,20]	Extensive labor for the drilling process[26,27]
	Reliability[21–23]	Disruption of fiber continuity[5,28,29]
Adhesive bonding	Good stress distribution[14,30]	Long curing cycles[13,16]
	Sealing effect[14,15] (degradation resistance)	Sensitive to surface preparation[32,33]
	Good surface finishing[6,15]	Adhesive performance depends on materials system[34]
	Allows the assembly of complex geometries[16,32]	Performance depends on the loading condition[15,36]
	No additional weight[16,31]	Unpredictable long-term performance[6,16,35]
	Fatigue resistance[6,30]	Sensitive to environmental degradation[15,16,37]
		Does not allow disassembly[6,35]
Thermal bonding	Allows the assembly of complex geometries[6,41]	Requires complex tooling[5]
	No filler materials required[6,41]	Time-consuming and costly processing optimization[14,38]
	Relatively short processing times[5,40]	Sensitive to surface preparation[43,44]
	No additional weight[5,40]	Adhesive performance depends on the materials system[14,38]
	Good stress distribution[5,42]	Unpredictable long-term performance[14,5]
	Good surface finishing[6,41]	Sensitive to environmental degradation[1,45]
	Potentially repairable structures[14,38]	
	Fatigue resistance[46,47]	

mechanical performance.[38,39] In addition, the drilling and puncturing processes, apart from the extensive labor they require, often cause local damage, potentially reducing the individual parts' lifespan.[40,41] Lastly, in the case of fiber-reinforced thermoplastics, drilling causes fiber discontinuity that, apart from lowering the load-bearing capacity of the composite, also affects other relevant properties such as electrical continuity.[42–44]

In adhesive bonding, an interlayer, e.g., epoxy or acrylic resins, is placed between the two adherents, followed by a curing process.[7] The purpose of the interlayer is to form chemical bonds with both parts and to extent bridge the interface.[8] Conversely to mechanical joining, adhesive bonding results in a more uniform stress distribution[7,45] and saves the additional weight of screws and rivets.[9,1] In addition, the presence of the adhesive also seals the joint[7,8] and often promotes improved fatigue performance.[3,45] Adhesive bonding also allows the assembly of complex geometries[9,46] and results in good surface finishing.[3,8] However, this method requires extensive surface preparation,[46,47] long curing cycles,[9,30] and the selection of the appropriate adhesive for the respective materials system due to the lack of universal adhesives.[48] Such bonded joints cannot be disassembled without being damaged, rendering inspection and part replacement challenging.[3,49] The mechanical performance of adhesively bonded interfaces shows strong dependence on the loading conditions[8,50] and are sensitive to environmental (e.g., humidity or temperature) degradation.[8,9,51] Finally, the most crucial drawback of adhesive bonding is the lack of reliability, as the long-term performance of adhesively bonded joints is unpredictable, with failure to often be sudden rather than progressive.[3,9,49]

Thermal bonding is realized by bringing in contact, often under pressure, a TPM with a metal followed by heating and then a cooling step.[49] During the heating step, the TPM melts and forms intimate contact at the boundary with the metal, while during the cooling step, the TPM solidifies to form a sta-

ble structure.[52] Joining is achieved via bonding at the TPM–metal interface that facilitates load transfer between the two materials.[53] Thermal bonding is classified based on the technique used to provide heat to the system, i.e., bulk, electromagnetic, and friction.[42] This method, similar to adhesive bonding, allows the assembly of complex structures, though at shorter processing times[10,42] and without the need for filler materials (adhesives).[3,54] In addition, the formed structures lack the additional weight and stress concentration points of mechanical joining methods and exhibit improved fatigue resistance.[10,42,55] Due to the reformable nature of TPMs at elevated temperatures, thermally joined structures can be potentially repaired by appropriate heat processes.[7,52] However, issues related to the high processing temperatures, e.g., molten resin dislocation, uneven temperature distribution, residual thermal stresses, and temperature-induced defects, resulting in time consuming and costly tooling design and process optimization.[7,42,52] Finally, similar to adhesive bonding, the joint performance is sensitive to surface preparation[56,57] and materials system,[7,52] is prone to environmental degradation,[58,59] and exhibits unpredictable long-term behavior.[7,42]

An ideal TPM–metal joining method would combine the reliability of mechanical joining in the absence of liabilities introduced by the presence of mechanical fasteners.[35–37] Fastener-free joining could be achieved by processes such as thermal or adhesive bonding. However, the lack of reliability of joints produced via these methods hinders their sole application.[3,42] Thus, to date, efficient joining of TPMs and metals without mechanical fasteners remains elusive and raises the question of whether novel technologies could achieve such a feat. In an attempt to answer this question, a focus is made on the process that is most commercially attractive for TPMs mainly (but not only) due to the faster processing times it offers,[10] i.e., thermal bonding. Thus within the framework of this thesis, by studying thermally bonded TPM–metal joints, an attempt is made to contribute to-
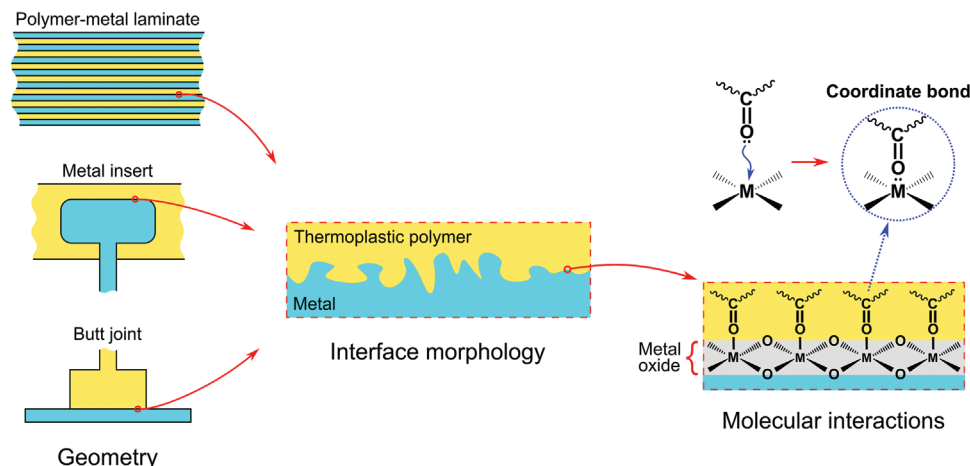
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Figure 3. Schematic representation of design parameters that affect the performance of thermoplastic polymer (TPM) metal joints produced by the thermal joining method.

ward what would be ideal, i.e., fastener-free TPM–metal efficient joining. This is realized by studying the adhesion of various TPMs with titanium, a metal alloy of industrial importance. The first step toward achieving this is understanding the bonding mechanisms that govern adhesion across different length scales and identify where there is space for further progress.

3. Bonding Mechanisms in TPM–Metal Thermally Bonded Joints Across Length Scales

Assuming optimized processing conditions, the strength of a TPM–metal joint is governed by mechanisms that occur across different length scales. The factors that affect these mechanisms can be divided into three main categories, i.e., the joint geometry, the interface morphology, and the molecular interactions at the interface (see **Figure 3**).

The TPM–metal joint geometry affects the joint strength either by potential interlocking that can be achieved by utilizing particular geometries,[11,60,61] or by its effect on the residual thermal stress distribution at the TPM–metal interface.[62,63] The morphology of the TPM–metal interface, which is determined by the metal surface morphology, affects the interfacial—and by extent, the overall joint—strength by several mechanisms/parameters. These include micro- and nano-interlocking, the TPM–metal interfacial area, and the distribution of applied thermal/mechanical stresses around the interface.[12,63] Molecular interactions between the TPM and the metal are responsible for interfacial adhesion and contribute to the overall joint strength (considering intimate, conform interfacial contact between the two constituents).[13] Of the three factors that determine the performance of a TPM–metal joint, i.e., geometry, interface morphology, and molecular interactions, within the framework of this thesis, a focus is made on the molecular interactions. This choice is motivated by the premise that the joint geometry is application-specific, while the impact of the interface morphology has been extensively studied by various methodologies.[5,59,64–66] On the other hand, engineering of molecular interactions at interfaces offers a wealth of unexplored possibilities that show potential for TPM–metal hybrid joint applications.

4. Molecular Interactions at TPM–Titanium Interfaces

Concerning molecular interactions, TPM–metal interfaces are bridged with chemical bonds formed between atoms that apart the respective TPM and metal oxide.[67] Here, it is noted that the term chemical bond is used within the context of the IUPAC definition, i.e., a lasting attraction between atoms that allows the formation of stable independent molecular entities.[68] Thus, the term chemical bond includes secondary bonds, i.e., π-stacking, dipole interactions (Van der Waals), and hydrogen bonds, as well as primary bonds, i.e., metallic, ionic, and covalent; see **Table 2** for a summary of the energy range for each bond type.

Secondary bonds are almost certainly formed in polymer–titanium oxide interfaces. However as they are intrinsically weaker, their contribution to the adhesion strength of the interface is assumed negligible within the framework of this study. This assumption is based on the fact that the interfacial work of adhesion is quantified via stable crack propagation tests. In such trials due to the localization of the applied force in a small area, strong bonding mainly depends on primary bonds.[74] In addition, a recent experimental study on polymer–metal adhesion indicated that secondary bonds are present in such interfaces. However, their contribution is minimal when compared to the formed primary bonds.[75] Thus, when considering only primary

Table 2. Typical bond energy range of chemical bonds.[69–73]

Chemical bond type	Energy (kJ mol^{-1})
Primary bonds	
Ionic	≈600–4000
Covalent	≈60–1000
Metallic	≈100–350
Secondary bonds	
Hydrogen bonds	≈10–160
Van der Waals	≈1–40
π-interactions	≈2–50

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bonds, metal oxide surfaces and polymers interact primarily via coordination bonds,[76], i.e., covalent bonds formed between two atoms with both shared electrons to originate from one of the two atoms.[77] When compared to conventional covalent bonds (where each atom provides one electron), coordinate bonds are characterized by fast and reversible formation kinetics, however, at the cost of thermodynamic stability.[78]

The focus here is to bond TPMs to titanium, so we primarily discuss interactions between TPMs and Ti oxides. Titanium oxide exists in three thermodynamically stable crystal structures, i.e., Brookite, Rutile, and Anatase.[79,80] In such surfaces, coordinate bonds are expected to form between atoms present in the TPM that possess at least one lone pair of electrons, e.g., oxygen or nitrogen, and coordination sites on the TiO$_2$ surface, i.e., exposed fivefold coordinated Ti sites (Ti$_{5c}$), or surface defects. This is assumed based on studies performed on the interaction between a broad range of organic molecules and rutile or anatase TiO$_2$ surfaces.[81] This is also reflected in experiments, as polymers with higher concentrations of oxygen groups present in their molecular structure result in enhanced adhesion with titanium and other metal oxides.[53,82,83]

Concerning molecular interactions, strong adhesion at the TPM–TiO$_2$ interface can be achieved via the formation of a high density of strong bonds. Setting aside processing, it is intuitive that the TPM molecular architecture will determine the strength and density of the chemical bonds formed at the TPM–TiO$_2$ interface. However, this is quite limiting since specific molecular architectures of TPMs do not include chemical groups that can coordinate strongly with the TiO$_2$ surface. And even if they do, the optimum conformation of macromolecules to maximize the density of coordinative groups on the surface of TiO$_2$ is hindered by steric repulsion. The above, in combination with the fact that certain applications require the use of specific thermoplastic matrices raise the need for a versatile strategy that can be utilized to promote strong adhesion between titanium and a wide range of thermoplastic matrices.

A strategy to promote adhesion at TPM–titanium interfaces is the introduction of functional molecules in the form of monolayers or thin films on the surface of titanium before the thermal joining process. The molecule selection needs to be such that strong coordination bonds can be formed with TiO$_2$, while during the joining process, they can thermally react with the TPM to form covalent bonds. In the case of thin films, it is also necessary for the layer to possess good mechanical properties to efficiently transfer load between the joined materials. Although this methodology is not novel, the molecule diversity used by the industry to date is mainly limited to silanes,[5] leaving several promising alternatives unexplored. Hence, the purpose here is to explore more options for applications related to TPM–titanium thermal joining. It is highlighted that the focus here is primarily on molecular interactions, without considering the other equally important aspects that affect the performance of TPM–metal joints, i.e., the joint geometry and morphology of the TPM–metal formed interface. Hence, in the following sections, molecules present in natural "glues" that are used by biological organisms to firmly adhere to a wide range of materials, are considered as potential candidates to promote adhesion between TPMs and metals.

5. Dopamine as Promising Adhesion Promotor at TiO$_2$–TPM Interfaces

While natural "glues" existed since ancient times, synthetic polymer-based adhesives have become prevalent in adhesion technology only during the past century. With the recent resurrection of interest in "biomimetic" materials, naturally adhering molecules, such as catechols, have become the subject of distinguished attention. Polymers containing natural phenolics (some examples shown in **Figure 4**), including "catechol polymers" and "dopamine polymers", often referred to in popular terms as "mussel-inspired polymers", have been the focus of this recent surge of activity. To a large extent, this is driven by the firm and nearly universal adhesion of "mussel proteins" on even the most notoriously difficult-to-adhere materials, such as PTFE or polyolefins.[84,85]

The choice of a building block to form an adhesive interlayer for bridging titanium–TPM interfaces is initially based on two main factors, i.e., the interaction with TiO$_2$ substrates and the chemical versatility of molecular interactions. Dopamine (marked in green in Figure 4) is a molecule with high potential due to its simple yet unique structure, combining many active groups to concerning molecular interactions in a small molecule.[17,86–88] Regarding secondary bonds, the aryl ring may interact via π–π[89–92] and π-cation interactions,[93–96], while the primary amine and hydroxyl groups may form hydrogen bonds.[97–100] Furthermore, dopamine may participate in several reactions to form covalent bonds with other chemical species. Some examples include condensation reactions,[101–104] amide bond formation,[105–108] Michael addition,[109–112] aryl coupling[113–115], and Schiff base formation.[116–118] Finally, the catechol moiety is known to form strong coordination bonds with a wide range of metal atoms.[119–123] A schematic summary of potential molecular interactions with dopamine is shown in **Figure 5**.

The chemical versatility of the dopamine molecule is thus expected to be sufficient for strong interactions with thermoplastic matrices during the thermal joining process. However, for the present study, a high density and strong interaction between dopamine and TiO$_2$ surfaces are equally important. The catechol moiety in the dopamine structure plays a vital role in this function. Due to its high significance for several applications,[124,125] the catechol-TiO$_2$ interaction has been at the center of scientific attention.[17,126] Combined near-edge X-ray absorption fine structure (NEXAFS), scanning tunneling microscopy (STM), and density functional theory (DFT) calculations have shown that catechols interact with TiO$_2$ via the adsorption and dissociation of the hydroxyl groups, which form coordination bonds with Ti$_{5c}$ atoms (see **Figure 6A**).[127–129] Experimental and theoretical studies on rutile surfaces have shown that catechol groups interact with Ti$_{5c}$ via three possible coordination geometries, i.e., monodentate, bridging bidentate, and chelating bidentate (see Figure 6B).[130–132] In particular, it has been shown that dopamine molecules coordinate on rutile TiO$_2$ surfaces in a nearly perpendicular fashion, allowing a high-density surface coverage.[130,133] Aside from the ability to achieve high surface coverages, dopamine molecules may also form strong bonds with TiO$_2$. Messersmith and co-workers, by using AFM-based single
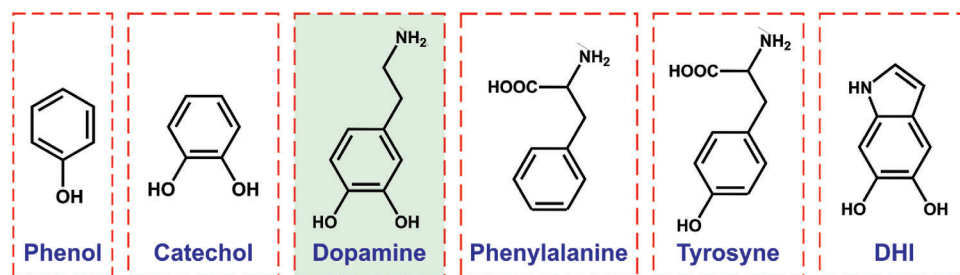
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Figure 4. Examples of phenolic molecules.

molecule force spectroscopy (SMFS), showed that the catechol-TiO$_2$ dissociation force was approximately 800 pN (Figure 6C). This value is weaker than rupture strength of C–C single covalent bonds (≈2000 pN) but significantly stronger than a hydrogen bond (few tenths of pN).[134] This signifies the unique interaction between catechols and TiO$_2$ surfaces, shown via SMFS measurements to be significantly stronger when equivalently compared to phenol or benzene chemical groups.[135] It should be considered that the coordination as mentioned above geometries and interaction strengths between catechols and TiO$_2$ is also affected by the oxide type (anatase versus rutile), crystallographic plane, and defect content of the TiO$_2$ surface.[136,128]

Thus, dopamine is an excellent candidate to promote adhesion in thermally joined titanium–TPM interfaces. This is based on three facts mentioned above, i.e., the high surface density of coordinated molecules, the strong bonding to TiO$_2$ surfaces, as well as the chemical versatility of interacting with TPMs. However, thermally induced degradation of dopamine begins at ≈210 °C,[137,138] which is a relatively low temperature concerning the typical processing temperatures TPMs require, i.e., ≈150 °C–380 °C.[139] Similar degradation patterns are also observed when dopamine is attached to aliphatic backbones.[140,141] Consequently, the application of dopamine in its pristine form cannot be applied to thermally joined interfaces due to the elevated processing tem-

peratures required by the process. A dopamine derivative with a higher degree of aromaticity than dopamine, such as PDA,[14] could pose a more thermally stable alternative. This expectation is based on the known proportionality between the degree of aromaticity and thermal stability of organic molecules and polymers.[142,143]

6. Polydopamine Coatings for Surface and Interface Molecular Engineering

The composition of foot proteins present in the byssal threads of *Mytilus* mussels has been a source of inspiration for the molecular design of synthetic adhesives.[89,144] The high content of catechol and primary/secondary amines in *Mytilus* foot proteins (Mfp) −3 and −5, present at the contact point between the byssal thread and attached surface (**Figure 7A–D**), motivated the use of simple catechol-amine molecules as building blocks for universal adhesives.[145–148] In 2007, Messersmith and co-workers[14] polymerized a catecholamine, dopamine (DA), in an aqueous solution under alkaline conditions to form PDA. The authors showed that the immersion of virtually any object in the DA polymerizing solution would result in the formation of a PDA film on its surface with a thickness of a few tenths of nanometers
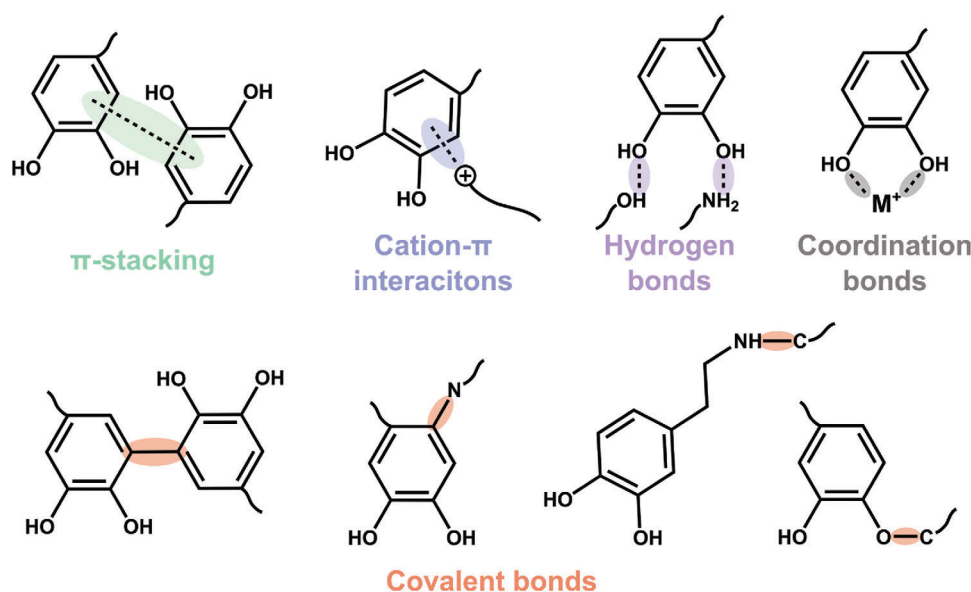

Figure 5. Possible molecular interactions of dopamine with other chemical species.

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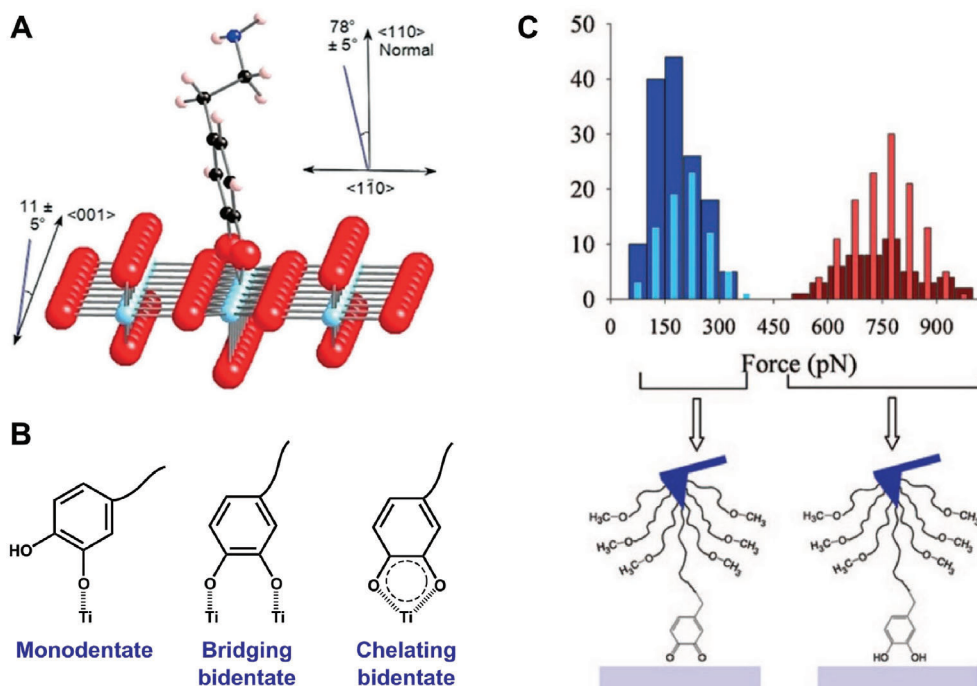Open Access

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Figure 6. A) Dopamine molecule adsorbed on fivefold coordinated Ti sites (Ti$_{5c}$); the color of the spheres represent red for oxygen, black for carbon, white for hydrogen, light blue for titanium, and blue for nitrogen. Image adapted[130] Copyright 2022, American Chemical Society. B) Possible coordination geometries of catechol-containing molecules on the surface of TiO$_2$.[130–132] C) Single-molecule force spectroscopy (SMFS) force signals between a catechol molecule and TiO$_2$ at 8.3 pH (red) and 9.7 pH (blue). Reproduced with permission.[134] Copyright 2006, The National Academy of Sciences of the USA.

(Figure 7F–H).[14] PDA offers a simple, easy-to-apply, versatile, and low cost substrate indent adhesion coating technology that is most commonly applied by a dip- or spray-coating.[149,150] This has increased interest in using PDA in a broad range of scientific and industrial fields to alter the surface chemistry of nanoparticles, fibers, and macroscale objects.[16]

Despite the increasing interest and extensive application of PDA coatings over the past 15 years, PDA's formation mechanism and chemical structure remain an open question.[18] It is widely accepted that, when using the first PDA recipe,[14] polymerization of DA is triggered when DA is oxidized by O$_2$ in alkaline conditions (TRIS buffer solution).[18] After the oxidation of DA, a number of reaction mechanisms via by both covalent and noncovalent assembly pathways, are hypothesized by various research groups.[151–155] Even though there is no definitive answer on the exact polymerization mechanism of DA, the majority of hypotheses agree that the most abundant PDA building blocks comprise of DA and dihydroxy indole (DHI). With DHI to be the product of intramolecular cyclization of DA via nucleophilic addition.[151–155] It should also be noted that other building blocks have also been reported for PDA, with some examples of the buffer used to tune pH, e.g., TRIS, covalently attached via nucleophilic addition or DHI/DA degradation products, e.g., pyrrole carboxylic acid (PCA), that are formed during the polymerization process.[18,151] Examples of proposed DA polymerization pathways can be seen in **Figure 8**. Finally, there is also no consensus on the degree of polymerization of PDA, with hypotheses to propose that PDA comprises building blocks that are noncova-

lent, oligomeric or polymeric species, or any combination of the three.[151,153,155–157]

Apart from PDA's polymerization mechanism and chemistry, the PDA film formation process is equally important. The distinction between PDA films and PDA aggregates needs to be made at this point. During the polymerization process the PDA films are formed on substrates; however, at the same time, DA polymerizes in the bulk solution forming aggregates.[152] The two processes compete as they consume the identical monomers, while at later stages of the DA polymerization process, PDA particles formed in solution are attached to the surface of the growing films, leading to their incorporation in them.[152] It is noted that even though PDA films and aggregates share the same main building blocks, they have been reported to exhibit minor chemical differences.[159] It is intuitive that the incorporation of the PDA particles affects the final surface morphology of the coatings, which alongside with the thickness, growth kinetics, and chemistry of PDA films, are vital variables when considering their technological applications.

The chemistry, thickness, growth kinetics, and surface morphology of PDA films can be tuned via several parameters. To begin with, increasing the DA concentration in the polymerization solution increases the film thickness, growth kinetics, and surface roughness.[149,160] In addition, increasing the DA concentration enhances the concentration of primary amines since, due to the slow rate of DA cyclization, dimerization of DA is favored over cyclization at high DA concentrations.[151,154] The deposition time of the films also affects the film thickness and
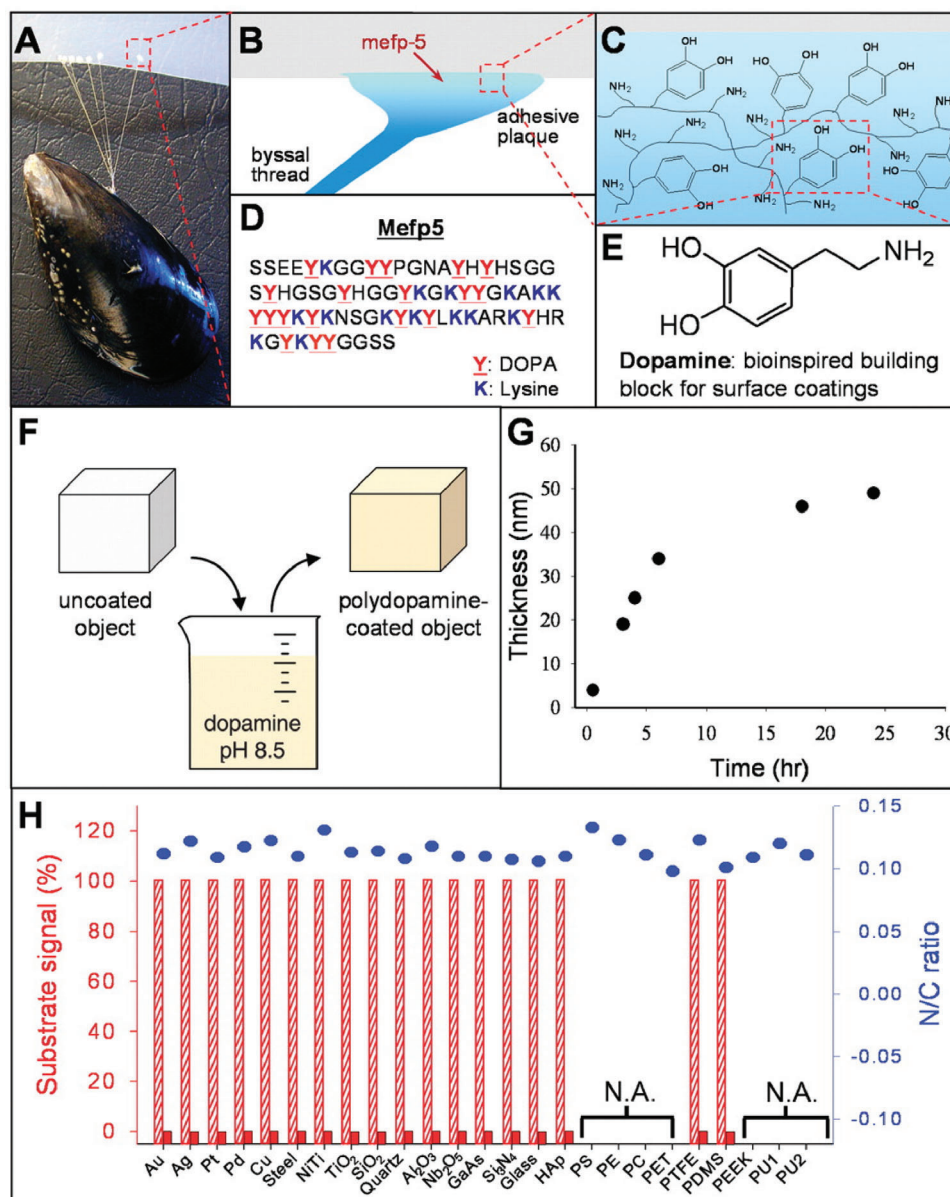
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Figure 7. Inspiration, deposition process, and application of polydopamine (PDA) coatings. Image reproduced with permission.[14] Copyright 2007, The American Association for the Advancement of Science.

surface morphology, with lower deposition times resulting in thinner films with lower surface roughness.[161,162] The low deposition times may be combined with multiple deposition cycles to enhance the thickness of the coatings while maintaining a low surface roughness.[163] The O_2 concentration is also essential as PDA films formed in pure O_2 were reported to exhibit faster growth kinetics and a smoother surface compared to PDA films created in air.[109] Thickness and film growth kinetics are also reported to increase by increasing the temperature and stirring intensity during the DA polymerization process.[164] The choice of buffer also influences the morphology of PDA films since, conversely to phosphate or bicarbonate, TRIS is reported to inhibit the formation of large aggregates that would increase the surface roughness of PDA films.[158] However, TRIS is

incorporated covalently into the PDA structure resulting in an alteration of the PDA chemistry.[18,151] Parameters such as the DA/buffer ratio and deposition time have also been shown to affect the PCA content of the coatings offering more options to alter the chemistry of PDA coatings.[151,158] Finally, the choice of solvent—other than water that is mostly used—also affects the PDA deposition process. However, this parameter becomes relevant mainly when considering nonpolar substrates,[165] fast drying of coated samples, and preventing hydrolysis effects.[18]

The first PDA recipe involved the oxidation of DA by atmospheric O_2 in aqueous alkaline solutions, resulting in a slow polymerization process.[14] However, DA oxidation can be achieved or accelerated in the absence of oxygen or acidic conditions by means, such as oxidizing agents, UV, and microwave irradiation.
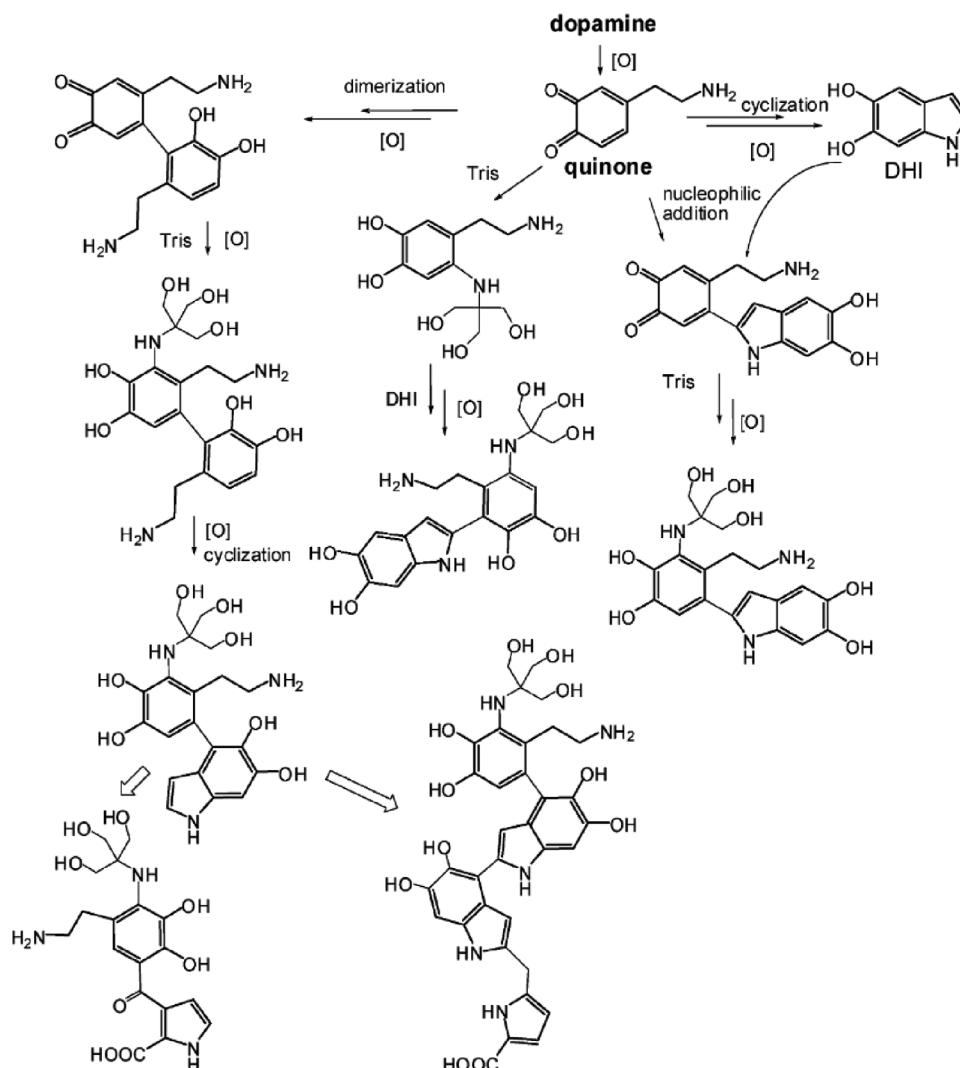
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Figure 8. Proposed dopamine oxidative polymerization pathways using TRIS as a buffer. Image reproduced with permission.[158] Copyright 2014, American Chemical Society.

Oxidizing agents such as Fe (III), NaIO$_4$, CuSO$_4$, and NAIO$_4$ have triggered DA polymerization.[150,166,167] In these reports, the chemistry of the coatings was affected by the oxidant used, and in some cases, the film formation process was substantially accelerated. UV light has also triggered the polymerization of DA and DA derivatives, providing a more precise tool to control the initiation and termination of PDA formation when DA is polymerized in acidic conditions.[168–170] Finally, microwave[171] and electrochemical[172,173] methods have been employed to initiate, accelerate and control PDA formation.

Incorporating functional molecules in PDA is yet another opportunity PDA offers to molecularly engineer surfaces and interfaces. This process is known as "co-deposition" and involves the inclusion of functional molecules in the DA polymerization solution resulting in PDA hybrid coatings.[15] By incorporating functional molecules in PDA, one may control the growth and chemistry of the formed layers, thus gaining more degrees of freedom over tuning their functionality and properties.[15,174,175] Various metal ions, organic and inorganic molecules have been success-

fully incorporated in PDA coatings via different molecular mechanisms. Thiol[176–178] and amine[179–182], containing molecules or oligomers, included in PDA via Schiff base and Michael addition reactions. Metal ions may act as coordination centers for the catechol, primary, and secondary amines in PDA.[183–185] Silanes such as aminopropyl tri-ethoxy silane (APTES)[186,187] or tetra ethyl ortho silicate (TEOS),[188–190] are reported to covalently incorporate in PDA via several reaction mechanisms. Dopamine analogs can be also copolymerized with DA via similar reaction paths as the DA homopolymerization, and in some cases, dopamine analogues can be polymerized in alkaline aqueous solutions without DA, forming PDA-analogue coatings.[177,191] Beyond the numerous possibilities to modify the chemistry of PDA via the codeposition process, the as-formed PDA (hybrid) coatings may be postmodified via "grafting to" and/or "grafting from" methods with biomolecules,[192–195] polymer brushes,[196–198] metal ions,[199,200] and other organic and inorganic functional molecules.[201–204] An overview of the codeposition process, along with the postmodification options that PDA chemistry offers to modify surfaces, is
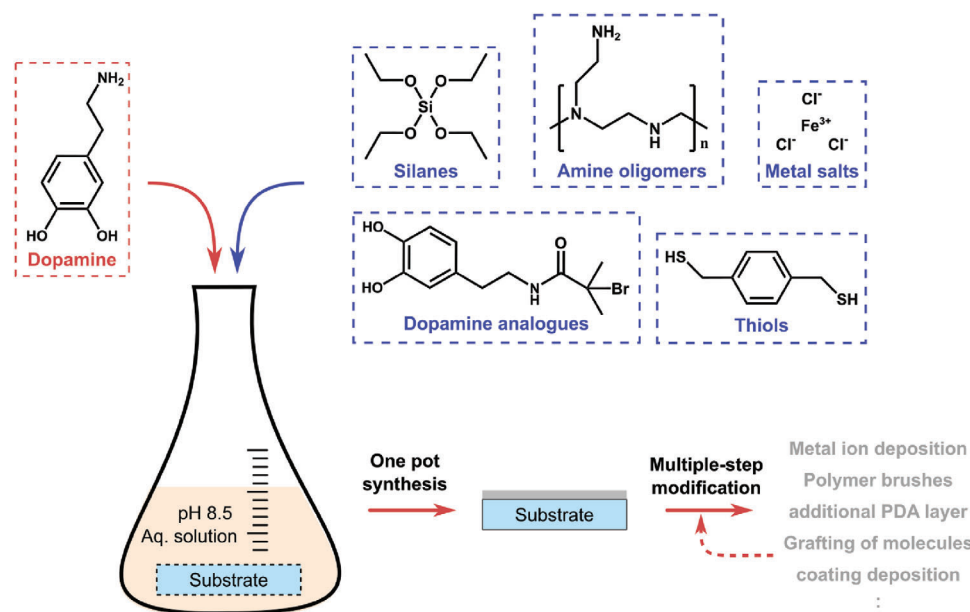
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Figure 9. Schematic overview of the surface modification strategies with polydopamine (PDA) chemistry.

schematically represented in **Figure 9**. The above remarks highlight the potential of PDA to be utilized as a versatile platform for substrate-independent surface functionalization that can be tailored to the respective application's needs.

7. PDA Application in TPM–Titanium Thermally Joined Interfaces

Regarding TPM–titanium thermally joined interfaces, PDA shows the potential to promote interfacial adhesion and stability. In principle, a PDA coating deposited on titanium should bond strongly to the substrate via the previously reported strong bonds formed between catechols in PDA and TiO_2.[134] In addition, the intrinsic reactivity[17] of PDA may result in the formation of primary bonds with the respective TPM during the thermal joining process via thermally activated reactions. If no bond formation between PDA and a particular TPM can take place during the thermal joining process, the PDA chemistry may be adjusted (see Figure 9) to facilitate bonding and even provide further functionality. Thus, based on the above, PDA coatings can be considered ideal candidates for thermally bonded interfaces. However, when focusing on the reported characteristics of PDA, two main drawbacks should be pointed out, i.e., the high surface roughness and the poor mechanical properties of the as-formed PDA coatings.[18,19] The high surface roughness is rather an advantage for thermally joined interfaces, as the high roughness is beneficial with respect to adhesion due to the enhanced TPM–metal area of contact it offers conversely to smooth interfaces. However, the mechanical performance of a candidate coating used as an adhesive interlayer for structural applications does affect significantly its applicability. Based on anecdotal[18] and experimental[20] reports, the poor mechanical properties of PDA are the main reason why such coatings failed to—hitherto— qualify as structural adhesives.

To date, studies on improving or even quantifying the mechanical properties of PDA are scarce.[19,138,185] Based on the existing reports, there are two possible options to improve the mechanical performance of PDA coatings, i.e., the incorporation of metal ions and the thermal treatment of the coatings. The latter is relevant for thermal joining of TPMs and metals, since the process takes place at elevated temperatures. Upon exposure to high temperatures PDA has been shown to thermally transform via cyclization of ethylene amine species, cross-linking reactions, and magnification of supramolecular interactions.[205] These mechanisms have been shown to enhance the mechanical properties of PDA coatings[138] at 130 °C. Further property enhancement follows an increasing trend with the annealing temperature.[185] This aligns well with the temperatures required to process thermoplastics (i.e., ≈150 °C–380 °C)[139] and potentially opens a new opportunity for PDA to be applied as a structural adhesive. Hence, the proposed concept here is to deposit PDA-based coatings on the surface of titanium and then thermally join with the TPM to form load-bearing interfaces. During the thermal joining process, the functionality of the PDA coating is to 1) react with the TPM to form covalent bonds and 2) thermally transform, enhancing its mechanical performance. Given the known strong interaction of catechols (present in PDA) with titanium oxides,[134] the coating is expected to interact with both substrate and polymer, thus effectively bridging the TPM–titanium interface with enhanced performance. Finally, the chemistry of PDA coatings is adjusted accordingly via codeposition or postmodification methodologies to promote a higher density of covalent bonds with the respective TPM, enhance the cohesive strength of the PDA interlayer, or provide functionality at the interface.

8. Concluding Remarks

Thermal bonding offers an industrially competitive methodology to join TPMs and titanium. The performance of TPM–titanium

hybrid joints relies on the TPM–titanium interfacial bonding, which is affected by the joint geometry, interface morphology, and interfacial molecular interactions. The lack of variety with respect to molecular interactions raises the need to explore new possibilities. PDA, owing to its rich catechol and primary amine chemistry, is an excellent candidate to be considered for such applications. The chemistry of PDA has an affinity for TiO_2 and provides valuable options for surface and interface engineering.[16] To date, the application of PDA within the context of load-bearing applications is hindered by the poor mechanical properties the as-formed coatings exhibit.[18] However, the unique thermal transformation PDA undergoes upon heating, which positively impacts its mechanical performance,[138] may offer a window for successfully applying PDA as a structural adhesive at elevated temperatures. Proof-of-concept regarding the applicability of PDA as a structural adhesive,[21–23] combined with the post- and comodification options PDA offers, may open new horizons for engineering interfacial adhesion and functionality in future hybrid materials.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Keywords

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