RESEARCH ARTICLE

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Polydopamine as Adhesion Promotor: The Effect of Thermal Treatment on the Performance of Poly(lactic acid) (PLA)-Metal Co-molded Joints

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Molecular interactions in polymer/metal oxide interfaces are of paramount interest in polymer composite applications, including comolding of polymer-metal joints, additive manufacturing, and mold release. This study shows the potential of biomimetic polydopamine (PDA) layers to control polymer-metal adhesion covering a range from strong bonding to release for poly(lactic acid) (PLA) adhering to two metals of significant commercial importance, i.e., titanium (Ti) and stainless steel (SS). The results show that even though PLA bonds significantly weaker to Ti than to SS surfaces, both metals exhibit considerably higher and similar adhesion values following deposition of a PDA layer. In addition, a simple thermal annealing of the PDA-coated wires before the comolding process results in a sharp increase of the bonding strength at low annealing temperatures, followed by a gradual drop at higher annealing temperatures. This observation opens the possibility to provide control of adhesion in polymer-metal interfaces. As PDA forms strongly bound adhesive layers on a wide range of materials, this study proposes that the phenomenon described here can be successfully applied to surfaces other than metals, raising high expectations for future polymer composite applications.

1. Introduction

The bonding strength between polymers and metals is a very important parameter for advanced composite applications ranging from nano-composites to polymer-metal hybrid structures, including mold release technologies.[1,2] The type of polymer and/or metal determines the bonding strength of the interface.[3] Primers are often applied to alter the interfacial properties of metals, according to the needs of the respective application.[4] However, the performance of commercial primers highly depends on the metal type and often does not provide control over the interfacial bonding strength. To meet the increasing industrial requirements for substrate-independent primers that offer good control over adhesion, new coating compositions and technologies should be considered that utilize various molecular interactions.

Messersmith and coworkers,[5] inspired by mussel adhesion, polymerized dopamine in basic aqueous solutions to form polydopamine (PDA) (**Figure 1**A). During this polymerization process, a wide range of substrates immersed in the basic dopamine solution are coated with a PDA layer of thickness in the nanometer range (Figure 1B). In addition, Messersmith et al. [6] showed that a simple thermal treatment of the PDA layer can enhance its stability and mechanical properties, indicating that PDA undergoes a thermally triggered chemical transformation. The combination of substrate-independent adhesion[7] with the ability to chemically transform to a more robust layer using mild thermal treatments makes PDA a great candidate for future primer technologies.

Here, we utilize polydopamine and its thermal transformation and show that adhesion in thermoplastic polymer-metal comolded joints can be finetuned by the thermal treatment. In particular, two commercially relevant metal alloys, titanium grade 5 (Ti6Al4V) and stainless steel (SS-316), were comolded with a poly(lactic acid) (PLA) thermoplastic matrix to form pullout specimens that were used to evaluate the strength of the respective polymer-metal interfaces. Next, we applied a PDA layer on the metal surfaces. This step was followed by thermal treatment at different temperatures before the comolding process. The effect of the thermal transformation of PDA at different temperatures on the bonding strength of the polymer-metal interface was subsequently evaluated.

2. Experimental Section

2.1. Materials

Dopamine hydrochloride (M: 189.64 g mol^{-1}) and tris(hydroxymethyl)-aminomethane buffer (M: 121.14 g mol^{-1}),

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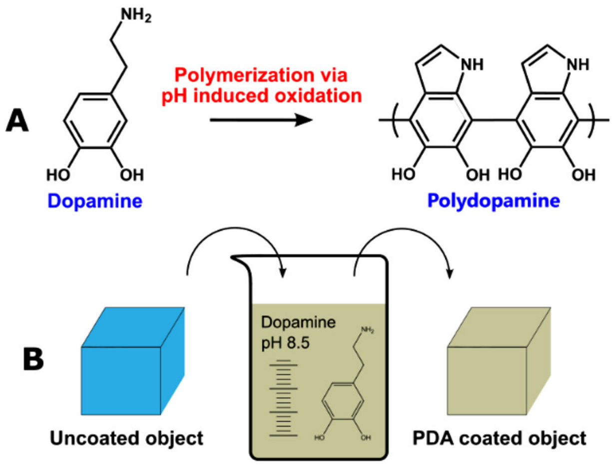

Figure 1. Oxidative polymerization of dopamine in basic aqueous solution (A) and a schematic of dip coating of an object during dopamine polymerization (B).[5]

were purchased from Sigma-Aldrich (Zwijndrecht, the Netherlands). Ingeo Biopolymer 4060D (PLA) granules were acquired from NatureWorks B.V. (Arendonk, Belgium). One millimeter diameter titanium wires (Ti6Al4V) were purchased from SELFAN Fine + Metal GmbH (Köln, Germany) and 1 mm diameter stainless steel (SS-316) wires were purchased from Kuil Nicos (Enschede, the Netherlands).

2.2. Methods

Prior to use, 9 cm long Ti6Al4V and SS-316 wires were subjected to a cleaning process.[8] The thus cleaned wires were then immersed in a freshly prepared tris buffer solution (10 mM, pH = 8.5) containing 5 mg mL^{-1} dopamine hydrochloride to form a PDA layer on their surfaces with a thickness in the nanometer range. The PDA-coated wires (i.e., SS-PDA and Ti-PDA) were then cleaned and dried under vacuum at room temperature for 24 h. The SS-PDA wires were then annealed under vacuum at different temperatures (25°C, 50°C, 100°C, 150°C, and 200°C), thus forming five groups of specimens (SS-PDA-25, SS-PDA-50, SS-PDA-100, SS-PDA-150, SS-PDA-200). The number behind the abbreviation refers to the annealing temperature. All wires (clean SS & Ti, PDA-coated SS & Ti, and SS PDA annealed) were then embedded in PLA matrices using a compression molding process (40 MPa, 180°C) to form pullout specimens that were subsequently subjected to pullout tests (10 mm min^{-1} crosshead speed) after being stored under vacuum for 24 h. The whole process is schematically summarized in **Figure 2**. For further details on the experimental methods, please refer to our previous work.[8]

3. Results and Discussion

3.1. Pullout Model for Testing, Data Analysis, and Model Evaluation

A typical pullout curve of a Ti6Al4V wire embedded in a PLA matrix is shown in **Figure 3**A. During the pullout process, a progressive detachment occurs at the Ti-PMMA interface until the “slip point” (F_s), where the interfacial debonding is complete (a to c in Figure 3A). Past this point, a sudden drop in the force is observed (F_o) and the wire is eventually removed from the PLA matrix (c to e in Figure 3A).

By obtaining F_o from the pullout curves as well as knowing the modulus (E_f) and the radius (r) of the metal wire, the energy of adhesion (G_a) can be calculated using Equation 1.[9]

$$F_o = 2\pi r^{3/2} \left(E_f G_a\right)^{1/2} \tag{1}$$

Values of F_s and F_o are plotted for various wire embedding lengths (Figure 3B) to validate the applicability of Equation 1 for the materials and experimental setup used to perform pullout tests in this work. According to the model used to derive Equation 1, for low embedded lengths, the extrapolation of F_o and F_s at zero embedded length should result in the same value.[9] In Figure 3B, by observing the blue and red dashed lines, it is apparent that the condition mentioned above is fulfilled, and thus the use of Wang’s model[9] is valid for this work. For more details on the theoretical background regarding the pullout curve analysis and validation of the model used to calculate G_a, please refer to our previous work.[8]

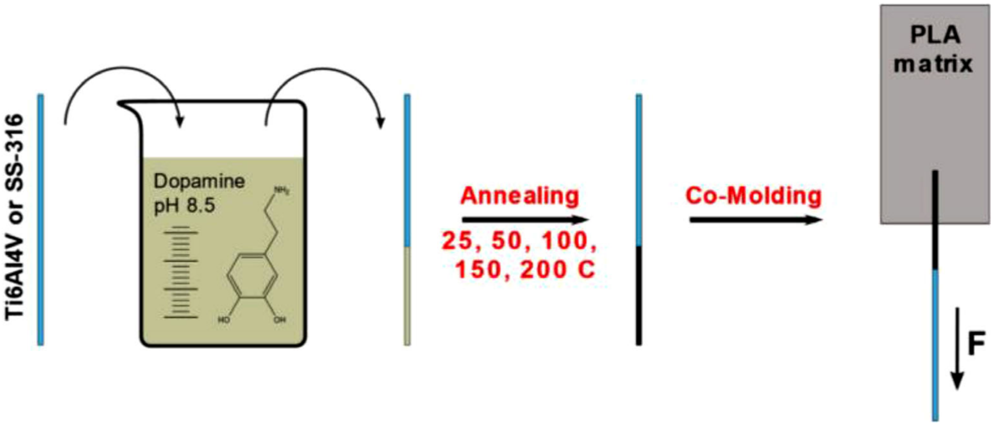

Figure 2. Schematic representation of the experimental procedure.

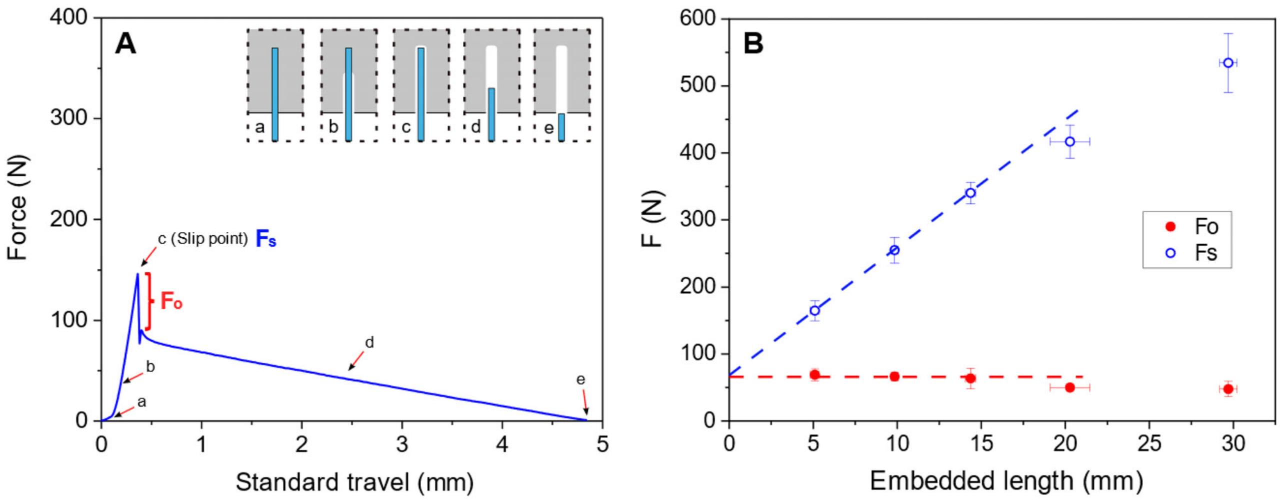

Figure 3. Typical pullout curve of a Ti6Al4V-PLA comolded specimen (A) and F_o and F_s values versus the embedded length of Ti6Al4V wires (B). The insets in (A) represent schematics of the embedded part of A Ti6Al4V wire in the PLA matrix at different stages of the pullout process.

Table 1. G_a values of pullout tests performed on metal-PLA comolded joints, using unmodified and PDA modified Ti6Al4V and SS-316 wires.

	Unmodified	PDA
Ti6Al4V	10 ± 3 Jm^{-2}	66 ± 9 Jm^{-2}
SS-316	41 ± 3 Jm^{-2}	59 ± 8 Jm^{-2}

3.2. Pullout Tests Using Unmodified and PDA Modified SS-316 and Ti6Al4V Wires

Unmodified and PDA-modified SS-316 and Ti6Al4V wires embedded in a PLA matrix were subjected to pullout tests. The results were analyzed according to the methodology described in Section 3.1 and are summarized in **Table 1**. From Table 1, it is clear that for unmodified wires, the adhesion between Ti6Al4V and PLA is significantly lower than the adhesion between SS-316 and PLA. However, after applying a PDA layer on the metal surfaces, both metal alloys exhibit similar and significantly increased G_a values. The observed enhanced adhesion is attributed to the stronger interaction of the PDA layer with the metal substrates compared to the metal PLA matrix interaction. In addition, since the adhesion values between PLA and the two PDA coated metal alloys are similar, we speculate that the interfacial failure is located between the PLA matrix and the PDA layer.

The strong interaction between PDA and metal substrates is well studied and attributed to the coordination of the catechol moieties to the metal oxide.[10] On the contrary, the thermal reactivity of PDA with other chemical species has not been investigated in detail. Regarding PDA, as reactive chemical species we identify hydroxyl groups as well as primary and secondary amines present in the formed PDA layer, while in the case of PLA, the ester groups seem to be the only reactive species. Based on this, we propose that PLA interacts with the hydroxyl groups of PDA-forming covalent bonds via transesterification reactions (**Figure 4**).

3.3. The Effect of Annealing PDA Layers Prior to the Co-molding Process

Given the similar adhesion values between the two metal alloys with PLA after their modification with PDA, the results shown in this section correspond only to PDA-coated SS-316 wires. PDA layers deposited on the SS-316 wires were annealed at different

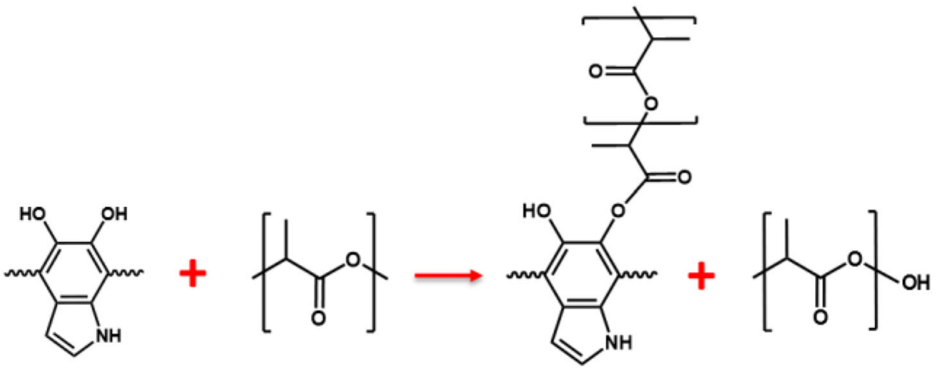

Figure 4. Proposed reaction between PLA and PDA during the comolding process at 180°C.

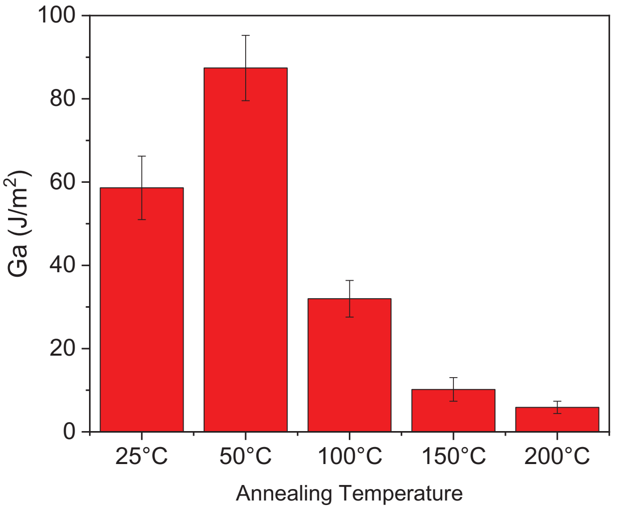

Figure 5. The energy of adhesion between PDA coated SS-316 wires and PLA for different annealing temperatures of the PDA layer prior to the comolding process.

temperatures prior to the comolding process. The produced specimens were subjected to pullout tests, and the results are shown in **Figure 5**. By annealing the PDA layer at 50°C, a significant increase in adhesion is observed, followed by a gradual decrease in adhesion for higher annealing temperatures. We propose that the initial increase of the G_a value upon thermal annealing can be explained by removing physiosorbed water from the PDA layer that could not be removed at 25°C. In that case, during the comolding process, the water molecules, when present, potentially hydrolyze part of the PLA molecules preventing them from maximizing the interaction with PDA. The decrease of G_a values for higher annealing temperatures could be explained by dehydration reactions occurring in the PDA layer that would reduce the concentration of hydroxyl groups present at the PDA surface. This reduces the number of potential interaction sites between PDA and PLA (i.e., the hydroxyl groups as depicted in Figure 4). The results shown in this work suggest that a single PDA layer on a metal surface can be used either to promote strong adhesion or provide release properties, depending on the applied thermal treatment. This process could make a strong impact on a number of composite applications. To put in context, titanium bonds weakly with PLA, hence a PDA layer can be used to promote adhesion. However, in the case of stainless steel, where bonding with PLA is strong, PDA could be used either to promote even stronger bonding or even cause release. Overall, a simple thermal treatment of PDA prior to the comolding process is shown to provide a good control over adhesion, from strong bonding to release. However, the exact molecular mechanism behind the thermal transformation of PDA that would explain these results remains to be clarified.

4. Conclusions

This study has demonstrated the potential of PDA layers to control adhesion between thermoplastic polymers and metals using PLA and two commercially relevant metal alloys (i.e., Ti6Al4V and SS-316). Adding a PDA layer to metal wires was very effective in obtaining similar and significantly higher G_a values for the PLA metal wire composites. Furthermore, a simple thermal treatment of the PDA layer before the comolding process resulted in adjustable adhesion ranging from strong bonding to release. Overall, based on the substrate independent adhesion of PDA[7] and the demonstrated control over adhesion by simple thermal processing, we propose that the results presented in this study may be implemented beyond metal substrates.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

interface, poly(lactic acid), polydopamine, polymer-metal adhesion, stainless steel, titanium

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