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A Curable Underwater Adhesive Based on Poly(Propylene Oxide) And Tannic Acid Coacervate

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Abstract: Coacervation of poly(propylene oxide) and tannic acid, driven by hydrogen bonding, renders a tacky viscous material that provides an underwater adhesion strength of ~ 350-550 kPa on aluminum substrates, also can bond other wet surfaces such as glass, metal, plastic, and porcelain. A curing functionality is achieved by designing a two-component system, using epoxidized poly(propylene oxide)/tannic acid coacervate as part A and amine-terminated poly(propylene oxide) as part B. Aside from underwater bonding, this adhesive can cure underwater through amine-epoxide reactions providing a commercially competitive and waterproof bonding.

Keywords: biomimicry, marine adhesives, coacervation, underwater adhesive, curable

Marine organisms have been an inspiration for designing man-made adhesives with novel functionalities such as underwater or wet bonding.[1–9] This biomimicry design is generally based on mimicking (i) the chemistry and (ii) the curing/complexation mechanisms of the marine adhesive proteins.[10–13] One promising design approach is based on polymer-tannic acid coacervation/complexation. Here, one can benefit from the galloyl-rich structure of tannic acid (TA), which allows mimicking the interactions of the catechol group found in marine adhesives. Moreover, the adhesive, being in a coacervate phase, renders reduced solubility in water and favorable wetting properties. On this basis, coacervates of TA with several polymers, including poly(N-vinylpyrrolidone)[14], polyamidoamine-epichlorohydrin[15], poly(N-hydroxyethyl acrylamide)[16], Pluronic[17], poly(vinyl alcohol)[18], poly(methyl vinyl ether-alt-maleic anhydride)[19], and poly(2-ethyl-2-oxazoline)[20] have been developed as underwater adhesives.

Commonly, such studies demonstrate the ability of the adhesive to bond surfaces underwater, providing an instant tackiness. A critical consideration is that an underwater adhesive should not only provide instant tackiness but also undergo a curing/hardening reaction so a durable water-proof bonding is obtained. Since such coacervate adhesives are often based on hydrogen bonding and ionic interactions, they are not expected to covalently cure and are thus unable to form a permanent and durable bonding.

In this study, we designed a novel underwater adhesive based on poly(propylene oxide) (PPO) and TA. This adhesive renders strong tackiness underwater, but more importantly cures underwater and provides a durable waterproof bonding. PPO is a relatively safe polyether with broad industrial uses in cosmetics, medicine, and food products. In low molecular weight forms, PPO is readily water-soluble at room temperature, which makes the preparation method much

easier compared to other reported polymer-TA coacervate systems. Notably, PPO is commercially available with different end-group functionalities, including epoxidized and aminated derivatives, which allows for designing adhesives that can undergo covalent curing reactions (detailed experimental methods available as Supporting Information, S1).

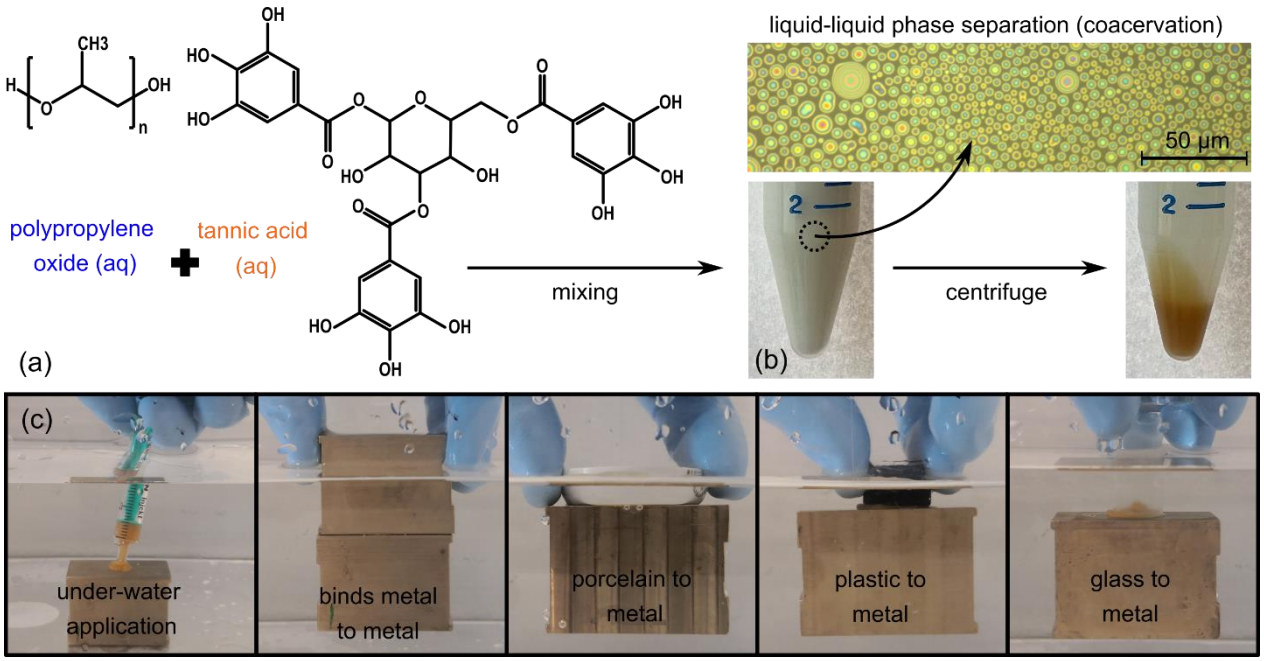

Figure 1 PPO-TA underwater adhesive: (a) Chemical formula of PPO (terminated with hydroxyl groups) and TA (*note*: commercial tannic acid has 2-10 galloyl groups; herein, the structure with 3 galloyl groups is shown as an example.), (b) Mixing the aqueous solutions of PPO and TA results in coacervation, yielding an opaque milky mixture (optical microscope image shown). The coacervate phase (i.e., underwater adhesive) can be collected by centrifugation, (c) The coacervate adhesive is easily injectable underwater and can bond various organic and inorganic materials.

PPO derivatives (i.e., with different MW and end groups) show a lower critical solution temperature (LCST) solubility behavior meaning that the solubility decreases with temperature.[21] Considering this, we chose a low molecular weight PPO (Mn ~ 400 g mol^{-1}) that can be readily

dissolved in water. The adhesive is simply prepared by mixing aqueous solutions of dihydroxyl-terminated PPO and TA (Figure 1a) of the same concentrations in a 1:1 weight ratio. Upon mixing (Figure 1b), the mixture instantly turns turbid/milky and is characterized by phase-separated droplets of the polymer-rich phase dispersed in the water-rich phase (i.e., coacervation). By centrifuging the mixture, two distinct phases are obtained, including a light orangish viscous and sticky precipitated material, i.e., the PPO-TA coacervate adhesive. The polyether backbone of PPO can form hydrogen bonds with the hydroxyl groups on tannic acid, which can herein promote liquid-liquid phase separation.[17,20] Considering that both PPO 400 g mol^{-1} and TA can be readily dissolved in water up to 40 wt.%, one can simply obtain a large amount of this adhesive at once (Supporting Information, S2). Based on a preliminary examination, a 1:1 weight ratio between PPO and TA was found to be optimal, i.e., having one component in excess seems to weaken the underwater adhesion (Table 1 and Supporting Information, S3). The PPO-TA adhesive was found to provide instant underwater bonding between different materials including metal, glass, porcelain, and plastic (Figure 1c).

Table 1 underwater adhesion force (in kPa) of PPO-TA coacervate adhesive; PPO and TA solutions of different concentrations (in wt.%) mixed in a 1:1 weight ratio (n=10)

	TA 2.5%	**TA 5%**	**TA 10%**	**TA 20%**	**TA 30%**	**TA 40%**
PPO 2.5%	218 ± 55					
PPO 5%		312 ± 84				
PPO 10%			264 ± 34	201 ± 45	237 ± 77	146 ± 41
PPO 20%			129 ± 15	228 ± 53	200 ± 25	
PPO 30%			167 ± 42	143 ± 22	234 ± 50	204 ± 38
PPO 40%				109 ± 24	189 ± 53	353 ± 36

The hydrogen bonding between PPO and TA reduces water-solubility and provides enhanced cohesiveness, but it cannot ensure a durable and permanent bonding. To examine this, two sets of adhesion testing experiments were conducted. Instant underwater adhesion strength was quantified in tensile mode between aluminum substrates (Supporting Information, S4). In brief, the adhesive was applied onto a substrate, a second substrate was brought into contact and then retracted; providing a force-distance curve from which the underwater adhesion strength (maximum measured force through retraction) was obtained (Figure 2a). To test the long-term load-bearing performance, a standard lap shear test was conducted on the samples after being underwater for two days (Figure 2b). PPO-TA adhesive showed an underwater adhesion strength of ~ 350 kPa. However, as expected, the lap shear strength after two days of being in water was found to be zero. To address this issue, we utilized the versatile chemistry of PPO derivatives, in particular, by using the epoxide- and amine-terminated PPO derivatives.

In the first attempt, diepoxide-terminated PPO (Mn ~ 400 g mol^{-1}) solution was mixed with TA solution (1:1 ratio) to make a coacervate adhesive, where one could expect covalent bonding between the epoxide groups of PPO and the hydroxyl groups of TA.[22–25] Herein, the underwater adhesion strength was found to be similar to dihydroxyl-terminated PPO adhesive. Nevertheless, no significant increment in the lap shear strength of the adhesive was found by using diepoxide-terminated PPO, which suggests insufficient covalent bonding between PPO and TA. Knowing that the reaction between epoxide and hydroxyl is catalyzed in alkaline conditions (pH > 10),[22,24] the bonded specimens were placed in alkaline solutions overnight (pH 10 and 13). Overall, no curing was found with elevated pH, i.e., the lap shear strength of specimens in pH 10 did not show any improvement, and those kept in pH 13 were debonded before testing. This observation may be

explained by the slow kinetics of the reaction (also pH increment) within the adhesive and thus hints at an inefficient cross-linking strategy.[25] Also, the alkaline pH might dissolve the adhesive before cross-linking, i.e., tannic acid can become negatively charged at high pH and thus may leak out (as seen for pH 13 specimens, where the solution turned brown and specimens were debonded).[26]

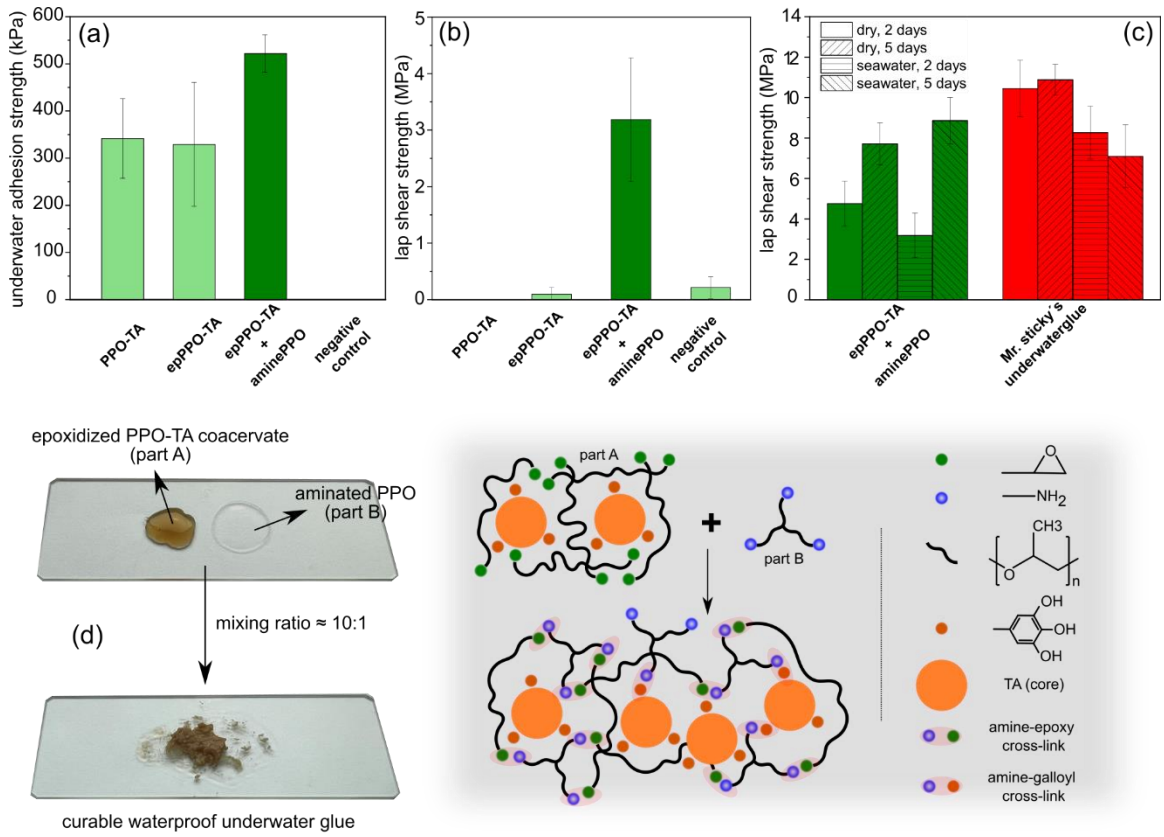

Figure 2 adhesive properties of hydroxyl-terminated PPO-TA coacervate, epoxide-terminated PPO-TA coacervate, two-component adhesive (epoxide-terminated PPO-TA coacervate + amine-terminated PPO), negative control (epoxide-terminated PPO + amine-terminated PPO), commercial benchmark (Mr. sticky's underwater adhesive); (a) underwater adhesion strength, (b) lap shear strength after 2 days curing in artificial seawater, (c) lap shear strength after 2 and 5 days curing in air and artificial seawater, for two-

component adhesive and the commercial benchmark, (d) two-component adhesive preparation and possible reaction mechanisms.

In the second attempt, triamine-terminated PPO (Mn ~ 400 g mol^{-1}) solution was mixed with TA solution (1:1 weight ratio) to utilize the possible cross-linking interactions between amine and TA in the oxidized form, i.e., quinone. However, the precipitate made by this method was found to be in the form of "heterogeneous particles/granules", not showing the fluid properties of a coacervate phase and thus not suitable as an underwater adhesive. This observation is most probably due to stronger interactions between amine and TA, which may produce a precipitated complex instead of a coacervate phase. Such interactions can be of both covalent (Schiff base and Michael addition) and non-covalent origins (hydrogen bonding and cation-π). Regardless, it is clear that the amine termini herein, compared with hydroxyl and epoxide end groups, can more strongly interact with TA.

In the final attempt, we thus designed a two-component adhesive system. The first component was made based on the coacervation of diepoxide-terminated PPO and TA. This renders part A of the adhesive that provides overall glue-like consistency and underwater bonding ability; yet, it cannot cure on its own. To make this system curable, part A was then mixed with an optimized amount of triamine-terminated PPO (part B). Herein, the amine and epoxide groups are expected to react at room temperature. Also, the amine groups should provide various interactions with TA through noncovalent (hydrogen bonding and cation−π)[4] and covalent (amine-quinone reactions via Schiff base and Michael-type addition) bonding.[27,28] The combination of these reactions (Figure 2d) is thus expected to provide a curable underwater adhesive. By varying the amount of part B, It was found that a 10:1 ratio (part A-to-part B) provides an optimum cross-

linking effect without sacrificing the underwater bonding feature (Supporting Information, S6). The two-component adhesive demonstrated an enhanced underwater adhesion strength (~ 500 kPa), which can be due to the higher viscosity/cohesiveness of the system. More importantly, the two-component adhesive could cure underwater, i.e., a lap shear strength of ~ 3 Mpa was obtained after being in the artificial seawater for two days. Notably, we also tested a mixture of diepoxide-terminated PPO and triamine-terminated PPO as the negative control sample. Herein, despite the possible crosslinking of the polymers, no underwater bonding strength was found, also the lap shear strength was negligible. This observation suggests that the presence of TA in the adhesive, and its coacervation with PPO, is essential to both underwater bonding and crosslinking/curing functionalities.

Lastly, the two-component adhesive was benchmarked against a commercial underwater epoxy adhesive, i.e., Mr sticky's underwater glue. Herein (Figure 2c), the lap shear strength of the adhesives was compared for samples cured in air and artificial seawater for two and five days. Overall, it can be concluded that the two-component adhesive shows commercial-level lap shear strength in both dry and wet states. Notably, the commercial adhesive seems to weaken with time being in water. Contrarily, our adhesive demonstrated an increased lap shear state after being in water for five days, which may be due to further cross-linking of the adhesive through galloyl (which may oxidize with time being in water) and the amine groups.

In summary, PPO-TA coacervation renders a tacky material with underwater bonding functionality. Like other coacervates driven by physical interactions (hydrogen bonding and ionic interactions), this coacervate can provide an instant tackiness underwater, but cannot produce a durable bond with load-bearing capacity. However, by using the coacervate of diepoxide-

terminated PPO and TA as part A, and triamine-terminated PPO as part B (hardener), a curable, waterproof, underwater adhesive is obtained. Functionality aside, this adhesive also has favorable environmental and health aspects, such as being partly bio-based (i.e., TA content) and relatively safe (i.e., both TA and PPO are considered relatively safe). As a future next step, cytotoxicity and tissue adhesion testing can be conducted to explore potential applications of PPO-TA coacervates as biomedical adhesives (skin adhesives, surgical adhesives, and more).[29] The environmental footprints of such an adhesive may be further minimized by using PPO derivatives obtained from renewable resources, and also by substituting the short-chain amine hardener with water-soluble natural polyamines such as polylysine. Overall, the versatile chemistry of the components and the facile preparation methods herein allow designing various adhesive systems with desired functionalities suitable for applications in underwater/offshore operations as well as biomedical engineering.

Supporting Information Description

The supporting information is available free of charge at XXXX.

- description of adhesives preparation and adhesion testing methods, demonstration of scalability of adhesive preparation, underwater adhesion test setup, adhesion strength of PPO with different molecular weights, optimization of mixing ratio of the two-component adhesive.

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