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A biomimetic water-resistant adhesive based on ϵ -polylysine/tannic acid complexation

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Abstract: This study investigates the potential of combining ϵ -polylysine and tannic acid to develop bio-based adhesives with enhanced water resistance. The two biomolecules exhibited complexation/precipitation in aqueous solutions with a pH range of 5-9. Water-based adhesives were prepared using complexes formed at pH 5, 7, and 9, followed by evaluating their adhesion properties in both dry and wet lap shear tests. The complexes prepared at higher pH values showed larger adhesion strength and improved water resistance. To further enhance the adhesive properties, an epoxide-based reagent was utilized to double-cross-link the complexes, resulting in a lap shear strength of ~ 2 MPa after being submerged in water for 7 days.

Keywords: bio-based adhesive, water resistance, polylysine, tannic acid, marine-inspired adhesive

1. Introduction

Extensive research is dedicated to the development of adhesives from renewable and less hazardous resources, known as bio-based adhesives.^{1,2} Several challenges need to be tackled on this path, with one notable obstacle being the poor water resistance of bio-based adhesives.³⁻⁶ Most biomacromolecules used in developing bio-based adhesives show significant water adsorption and swelling. As a result, such adhesives cannot maintain bonding in humid or wet environments, which limits their widespread use.⁷ To overcome this challenge, research is focused on exploring innovative strategies to improve the water resistance of bio-based adhesives.⁸⁻¹¹

The emulation of adhesion mechanisms found in marine organisms is being actively investigated as a promising strategy for the development of innovative adhesives.^{8,12} These organisms, e.g., sea mussels, have evolved intricate adhesion mechanisms that allow them to firmly attach to seashores and underwater environments.^{13,14} These natural adhesives, composed primarily of proteins, reveal that biomolecules with precisely optimized compositions could exhibit remarkable water resistance. Research is thus focused on (i) uncovering the underlying physicochemical mechanisms responsible for the wet adhesion of marine organisms and (ii) harnessing this knowledge to develop bio-based adhesives with enhanced water resistance.^{15,16}

Several mechanisms are suggested to play a substantial role in mussel adhesion,¹⁴ three of which have been taken as inspiration in our recent studies.^{11,17} The first mechanism revolves around the signature amino acid found in the mussel adhesive, i.e., L-3,4-dihydroxyphenylalanine (L-DOPA). The catechol moiety of L-DOPA can form various covalent/non-covalent interactions,¹⁸ enabling robust interfacial adhesion to substrates of

different chemistries,¹⁹ as well as cross-linking and curing of the adhesive proteins.²⁰ The second mechanism entails the synergistic effects of L-DOPA and lysine, or catechol–amine chemistry. This combination is proposed to facilitate catechol interaction with hydrated surfaces and regulate the cohesive strength of the adhesive through various pathways, including cation– π interactions, Michael addition, and Schiff base reactions.²¹ The third mechanism underlines the role of physical phase transitions of the mussel adhesive proteins, particularly through coacervation.²² This process leads to the formation of a condensed protein-rich phase, which exhibits a remarkable ability to spread onto underwater surfaces without dispersing in seawater.^{23,24}

Therefore, as a potential strategy in developing water-resistant bio-based adhesives, one requires catechol or catechol-like groups, amine groups, and a complex condensed phase. This study aimed to explore a potential bio-based candidate that meets these criteria, i.e., ϵ -poly-L-lysine (ϵ -PL) and tannic acid (TA). ϵ -PL is a natural polypeptide composed of lysine building blocks, which is generally recognized as safe (GRAS) and is commercially used as an antimicrobial food preservative.²⁵ TA is a natural polyphenol with 2–12 galloyl (3,4,5-trihydroxyphenyl) groups, which is also classified as non-hazardous.²⁶ One of the primary reasons for choosing these two bio-based substances was their high water solubility (unlike most polyphenols and biomacromolecules), which simplifies the preparation process. However, we hypothesized that they, combined in a complex state, could exhibit water resistance given the similarities to the mussel glue chemistry. The amine–galloyl chemistry may mimic the interactions of lysine–DOPA and their corresponding benefits for wet adhesion. Moreover, our initial evaluations showed that the two biomolecules exhibit complex interactions leading to the formation of a dense precipitated phase. This material was

anticipated to show improved water resistance as compared to an adhesive composed of biomolecules in a non-condensed state. Therefore, various ϵ -PL–TA complexes were prepared under controlled conditions, and their adhesive properties and water resistance were assessed.

2. Experimental Section

2.1 Materials: ϵ -polylysine (ϵ -PL, $\geq 95\%$) was obtained from Handary (Belgium). Tannic acid (TA, $M_w = 1701.20$ Da) and glycerol diglycidyl ether (GDE, $M_w = 204.22$ Da, technical grade) were purchased from Sigma-Aldrich. All solutions were prepared using ultrapure water (Arium® Pro) with a resistivity of $18.2 \text{ M}\Omega \text{ cm}$. pH adjustment was carried out using 10 M NaOH and 10 M HCl aqueous solutions. Other solvents used were of HPLC grade and were not subjected to further purification. Additional characterization data of reagents are available as Supporting Information (Section S1).

2.2 Preparation of ϵ -PL–TA complexes: ϵ -PL (40 wt.%) and TA (20 wt.%) solutions were prepared in water without any pH adjustment. Once fully dissolved (after 2 h), the TA solution was added to the ϵ -PL solution in a 1:1 weight ratio under stirring. The resulting mixture was found to have a pH of ~ 2.3 . The mixture solution was then subjected to different pH adjustments ranging from 3.0 to 10.0, and the resulting precipitate was collected by centrifugation ($6.5 \text{ K rpm min}^{-1}$ for 10 min). The collected ϵ -PL–TA complexes were dried in a vacuum oven (Thermo Scientific, Germany) at $30 \text{ }^\circ\text{C}$ for two days. Subsequently, the dried complexes were finely ground using an agate mortar and stored in a desiccator. Additional characterization data of the dried ϵ -PL–TA complexes are provided as Supporting Information (Section S2).

2.3 Preparation of ϵ -PL–TA adhesives: ϵ -PL–TA adhesives were prepared by mixing ϵ -PL–TA complex powder with water in a 4:6 weight ratio (adhesive water content = 60 wt.%). In a separate set of adhesives, varying weight ratios of GDE were incorporated (Supporting Information, Section S4).

2.4 Adhesion testing: The lap shear strength of the ϵ -PL–TA adhesives was evaluated using a testing system (Instron 34Sc, USA) equipped with a 2 kN load cell. Before testing, pre-cut aluminum substrates (L×W×H: 50 mm × 12 mm × 10 mm) were polished and cleaned with ethanol/acetone. The adhesive was then placed between two aluminum substrates with an overlap area of 12 mm × 12 mm and clamped together. The clamped specimens were thermally cured in an oven at 120 °C for 10 minutes. After cooling at room temperature for 1 h, the specimens were subjected to single lap shear testing at a controlled rate of 1.5 mm min⁻¹. To assess the water resistance of the adhesives, the cured specimens were immersed in water for 2 or 7 days, after which the lap shear strength was measured.

2.5 Water solubility: To test the water solubility of each ϵ -PL–TA adhesive, the wet adhesive sample was applied onto a Teflon substrate as a thin film, followed by curing for 10 min at 120 °C. The dried film was then ground into a fine powder. For each adhesive then, a given amount of the dried powder was weighed (m_d) and added to 15 ml of water, followed by vortex mixing at room temperature for 2 days, and then centrifugation (6.5 k rpm min⁻¹ for 10 min). The collected precipitate was dried until a final constant weight was achieved (m_r). The residual mass (RM) was calculated as $(m_r/m_d) \times 100$.

2.6 IR Spectroscopy: ATR spectra of specimens were collected using a VERTEX80v FTIR vacuum spectrometer (Bruker Optics GmbH), equipped with a Germanium (Ge) coated KBr beam splitter, a liquid N₂-cooled HgCdTe detector, and a thermal globar radiation source.

Dried powder specimen was placed on the Ge crystal in a single-reflection ATR accessory (PIKE Technologies, Inc, USA) installed in the sample compartment of the FTIR spectrometer. The sample spectra were recorded in blocks of 300 scans within the wavenumber range of 400 and 5000 cm^{-1} , with a resolution of 2 cm^{-1} . Using the same parameters, background spectra of the cleaned Ge crystal were collected before and after sample measurements. The data were processed and evaluated with the OPUS-7.2 software (Bruker Optics GmbH, Germany). Briefly, the absorption spectra were obtained by averaging the sample and background scans, and further adjustments were made to correct for any residual water vapor absorption from the atmosphere. Subsequently, gentle baseline corrections were then performed before final ATR corrections were applied to account for the wavelength-dependent penetration depth of the infrared probe beam. **Curve Fitting:** each spectrum was first normalized based on the absorbance of bands in two different ranges: i) 1415 cm^{-1} to 700 cm^{-1} , and ii) 1050 cm^{-1} to 700 cm^{-1} (Supporting information, Section S4). Selected bands within the range from 1250 cm^{-1} to 980 cm^{-1} were selected for dedicated curve fitting analysis in order to follow the degree of cross-linking (section 3.3).

3. Results and discussion

3.1 ϵ -PL–TA complexation: Figure 1 depicts the chemistry, preparation, and characterization of ϵ -PL–TA complexes. ϵ -PL, a cationic polypeptide, becomes less charged with pH increment ($\text{pK}_a \sim 9.4$).²⁷ TA, a polyphenol with multiple galloyl groups, undergoes two pathways with increasing pH: (i) deprotonation of hydroxyl groups, resulting in a negative charge ($\text{pK}_a \sim 6.0$),²⁸ and (ii) oxidation into quinone species. The amine and galloyl groups, as well as their corresponding forms at elevated pH, are expected to interact through a variety of physical (hydrogen bonding and ionic bonding)²⁹ and chemical mechanisms (covalent bonds through

Michael addition³⁰ and dynamic covalent bonds through Schiff base reaction^{31,32}), all of which are pH-dependent (Figure 1b).¹⁸ As a result, the net interaction between ϵ -PL and TA is expected to be pH-dependent.

Figure 1c displays the effect of pH (3-10 range) on the complexation of ϵ -PL and TA. The initial pH of the mixture containing ϵ -PL and TA in a 1:1 weight ratio was ~ 2.3 , and no cloudiness or precipitation was observed herein. However, increasing the pH resulted in complexation/precipitation, particularly within the pH range of 5-9 (as shown in Figure 1c, d). The absence of complexation/precipitation at $\text{pH} < 5$, where TA is nearly uncharged,²⁸ and at $\text{pH} > 9$, where ϵ -PL is minimally charged,³³ may suggest that ionic forces are the primary driving force behind the observed complexation/precipitation. An XPS analysis (Supporting Information, Section S2) indicated that the complexes produced at pH 5, 7, and 9 have a comparable ϵ -PL content, estimated to be ~ 50 -60%. However, given that TA can undergo oxidation at $\sim \text{pH} > 7$, the chemical structures and interactions of the complexes formed at different pH levels are expected to be different. This is evident from the color change (Figure 1c) observed in the dried complex powders, transitioning from light beige (prepared at pH 5) to dark brown (prepared at pH 9).

To explore the interactions within the complexes, additional investigation was performed using ATR analysis (Figure 1e). In particular, the absorbance of the bands related to C=O and C=N stretching in the range of 1800 - 1400 cm^{-1} was investigated. Herein, the complexes prepared at higher pH appear to contain a larger content of these functional groups. The increased content of C=O (1630 - 1570 cm^{-1}) groups can indicate a larger quinone content with increasing pH. These quinone moieties may form chemical bonds with the amine groups of ϵ -PL through Michael Addition and Schiff base reactions, producing C-N covalent bonds and

C=N dynamic covalent bonds, respectively. In Figure 1e, with pH increasing, a noticeable gain in the absorbance peak of both C-N ($1150\text{-}1050\text{ cm}^{-1}$) and C=N ($1700\text{-}1630\text{ cm}^{-1}$) bonds is also found, suggesting oxidative cross-linking reactions. Notably, the relatively larger increase in absorbance for the C=N bond, compared to C-N, as the pH increases from 5 to 9, suggests that Schiff base formation is the primary oxidative coupling reaction. A TGA analysis (Supporting Information, Section S2) also indicated increased thermal stability with increasing pH, which can further affirm chemical cross-linking at higher pH. Such chemical cross-linking of ϵ -PL and TA is expected to reduce water solubility and swelling. Consequently, ϵ -PL-TA complexes prepared at pH 5, 7, and 9 were selected for further investigation of their adhesive properties and water resistance.

3.2 ϵ -PL-TA adhesives: Figure 2 compares the lap shear strength of ϵ -PL-TA adhesives (from complexes produced at pH 5, 7, and 9). To make the ϵ -PL-TA adhesives, the dried complex was mixed with water in a 4:6 weight ratio (Figure 2a). The resulting mixture was applied onto aluminum substrates, clamped, and subjected to thermal curing. Notably, it was found that a thermal curing process of 10 min at $120\text{ }^{\circ}\text{C}$ was necessary for optimal adhesive performance (Supporting Information, Section S3). The bonded specimens were then tested either in dry state or after being submerged in water for 2 and 7 days.

The lap shear adhesion data of ϵ -PL-TA adhesives under dry and wet conditions are compared in Figure 2b. It was found that complexes produced at higher pH levels demonstrate larger dry adhesion strength (also see Supporting Information, Section S3). This finding confirms that changes in the chemical structure/interactions of the complex occur depending on the pH of the complex preparation. The enhanced adhesion strength might be due to mechanical reinforcement resulting from galloyl-amine chemical cross-linking.

The adhesives' water resistance was demonstrated to follow a similar trend, with the adhesive produced from the pH 9 complex exhibiting the highest water resistance. After 7 days of immersion in water, the adhesive specimens made from pH 5 and pH 7 complexes debonded. The adhesive made from pH 9 complex maintained some level of adhesion (0.35 MPa, ~15% of dry strength) under similar wet conditions. The increased water resistance of the complex made at pH 9 suggests higher cross-linking between ϵ -PL and TA. A comparison with the control specimen (aqueous solution of ϵ -PL (20 wt.%) and TA (20 wt.%)), indicates that complexation of ϵ -PL and TA can improve water resistance. Despite both TA and ϵ -PL being highly water-soluble, their water resistance is overall improved when they are in a complex/condensed state. Additionally, when complexation is combined with chemical cross-linking (as seen for pH 9 complex), it provides even greater water resistance.

Further confirmation of the observed trends is provided by testing the water solubility of ϵ -PL–TA adhesives (Figure 2c). Since both ϵ -PL and TA are highly soluble in water, the insoluble matter content can be attributed to the cross-linked part. The results indicate that the complexes prepared at elevated pH exhibit a larger insoluble content, providing additional evidence for chemical cross-linking between ϵ -PL and TA complexes formed at elevated pH.

3.3 Double-cross-linking via epoxide chemistry: Thus far, we have demonstrated that ϵ -PL and TA, both highly water-soluble, can be converted into a partly cross-linked and water-resistant adhesive by (i) complexation and (ii) controlling pH of complexation. However, it is worth investigating why the water resistance remains relatively low and whether it can be further enhanced. One potential reason for the relatively poor water resistance could be that the Schiff base bonds are the primary means of chemical cross-linking (as argued in relation to Figure 1e). The imine bonds are reversible in nature,³⁴ sensitive to acidic pH and moisture,³⁵

and may alone not provide a prolonged source of cross-linking and water resistance.³² Overall though, regardless of having reversible bonds or not, a secondary source of cross-linking is anticipated to further reinforce the adhesives' water resistance.

With amine and aromatic alcohol functional groups present in the complex, we investigated epoxide chemistry (Figure 3a) as a promising cross-linking approach. GDE was selected considering its ability to function as a plasticizer/cross-linker and its overall safe profile.³⁶⁻³⁸ The epoxide groups on GDE may react with (i) the hydroxyl groups on TA, resulting in the production of stable ether bonds (C-O),^{36,38,39} and (ii) the amine groups found on ϵ -PL, producing covalent C-N bonds.^{40,41}

The adhesion performance of ϵ -PL-TA adhesives, including 5 wt.% GDE (relative to the total dry content), is presented in Figure 3b. The optimal concentration of GDE was determined based on the adhesion strength and water resistance testing (Supporting Information, Section S4). The addition of GDE was observed to increase the dry lap shear strength of the complexes across all pH values. Notably, all the adhesives also exhibited enhanced water resistance. The adhesive made from pH 9 complex again demonstrated the highest water resistance, with a lap shear strength of 2.5 MPa (~70% of dry strength) after 2 days and 2.0 MPa (~55% of dry strength) after 7 days of submerging in water. Upon comparison with the control sample (aqueous solution of ϵ -PL 19 wt.%, TA 19 wt.%, and GDE 2 wt.%), the effect of complexation on water resistance is once again confirmed.

The water-solubility test was conducted to further investigate the cross-linking effect of GDE. When comparing Figure 3c with Figure 2c, it is evident that the addition of GDE leads to an increase in the insoluble content of all complexes. For instance, at pH 9, the insoluble content was increased from approximately 80% to 90%. Similarly, the ϵ -PL-TA adhesive produced

from the pH 9 complex exhibited the highest stability. Thus, it can be deduced that GDE induces a cross-linking effect that leads to a decrease in the solubility of the complex adhesive and an improvement in dry and wet lap shear strength. Notably, it appears that the highest reinforcing effect of GDE is found in the complex produced at pH 9, which may indicate that this sample has a larger net degree of cross-linking.

ATR analysis was conducted to examine the interactions of the adhesives including 5 wt.% GDE. The anticipated epoxide–hydroxyl and epoxide–amine reactions are expected to show an absorption band in the range of 1150-1050 cm^{-1} . Herein, the integrated area under the peak, as a measure of the net content of C-O and C-N groups, or as a measure of cross-linking degree, was compared for adhesives with and without GDE (Figure 4). For adhesives without GDE, it is shown that the integrated area decreases with increasing the pH of complex preparation. This may be due to the decreased number of hydroxyl groups resulting from the oxidation of TA. When adding GDE, the integrated peak area increases in general for all three complex systems, which may indicate further cross-linking. Notably, the adhesive made from pH 9 complex showed the largest relative gain in peak area (when GDE added), which may suggest a larger cross-linking effect of GDE on this complex.

Finally, dry and wet lap shear strength of the ϵ -PL–TA adhesive was compared with two commercial bio-based adhesives (UHU Glue and Pritt Glue) and several recently reported mussel-inspired bio-based adhesives (Table 1). The results show that ϵ -PL–TA/GDE exhibits higher adhesion strength in wet conditions compared to both the commercial controls and the bio-based adhesives reported in the literature, indicating the potential of this system for developing a bio-based adhesives with enhanced wet adhesion.

4. Conclusion

ϵ -PL and TA combined show promise as a compelling choice for developing bio-based adhesives with improved water-resistance. Both substances possess a relatively safe profile and readily dissolve in water. Additionally, the two components undergo complexation, which was herein demonstrated to enhance water-resistance. Particularly, this complexation process is pH-dependent, meaning that the properties of the complex, including the adhesion properties, are adjustable by pH of complex preparation. Herein, it was demonstrated that complexes prepared at higher pH values exhibit the largest dry and wet adhesion strength. Moreover, the amine- and galloyl-rich composition of ϵ -PL–TA allows for additional cross-linking strategies. Herein, we demonstrated that by utilizing an epoxide-based reagent, it is possible to further cross-link the complex and enhance the water resistance of the adhesive.

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Supplementary Information is available at:

- Characterization data of ϵ -PL and TA, XPS and TGA characterization of ϵ -PL–TA complexes, optimization of the ϵ -PL–TA adhesive composition and thermal curing

method, optimization of GDE content based on lap shear testing, and details of ATR-FTIR spectra normalization.

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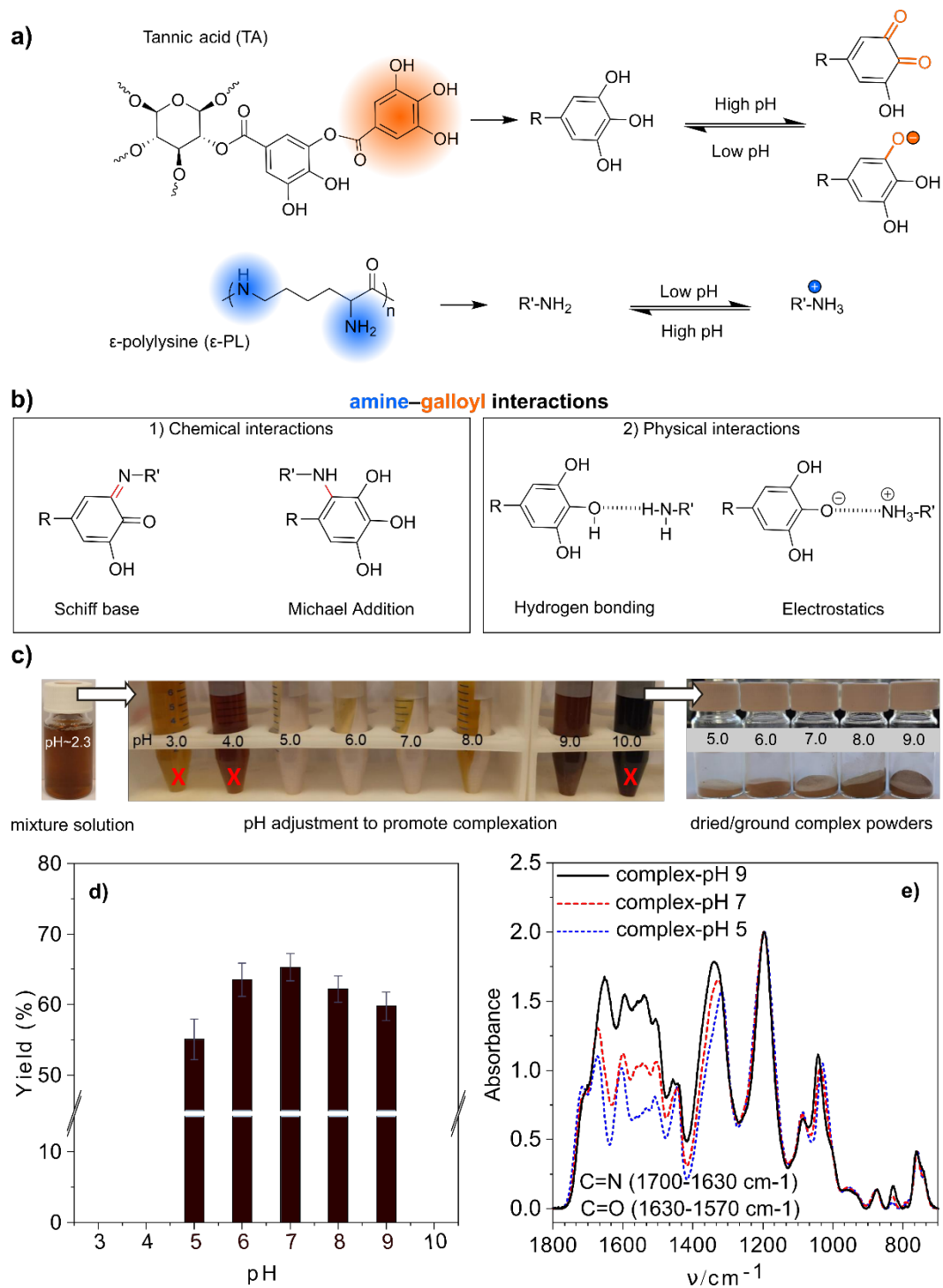


Figure 1 ϵ -PL-TA complexation: (a) chemical structures and pH-responsive behavior of ϵ -PL and TA, (b) possible chemical and physical interactions between the amine groups of ϵ -PL and the galloyl groups of TA, (c) preparation of ϵ -PL-TA complexes at different pH values, (d) yield of complexation at different pH, (e) ATR spectra of complexes (dried powder) prepared at pH 5, 7, and 9.

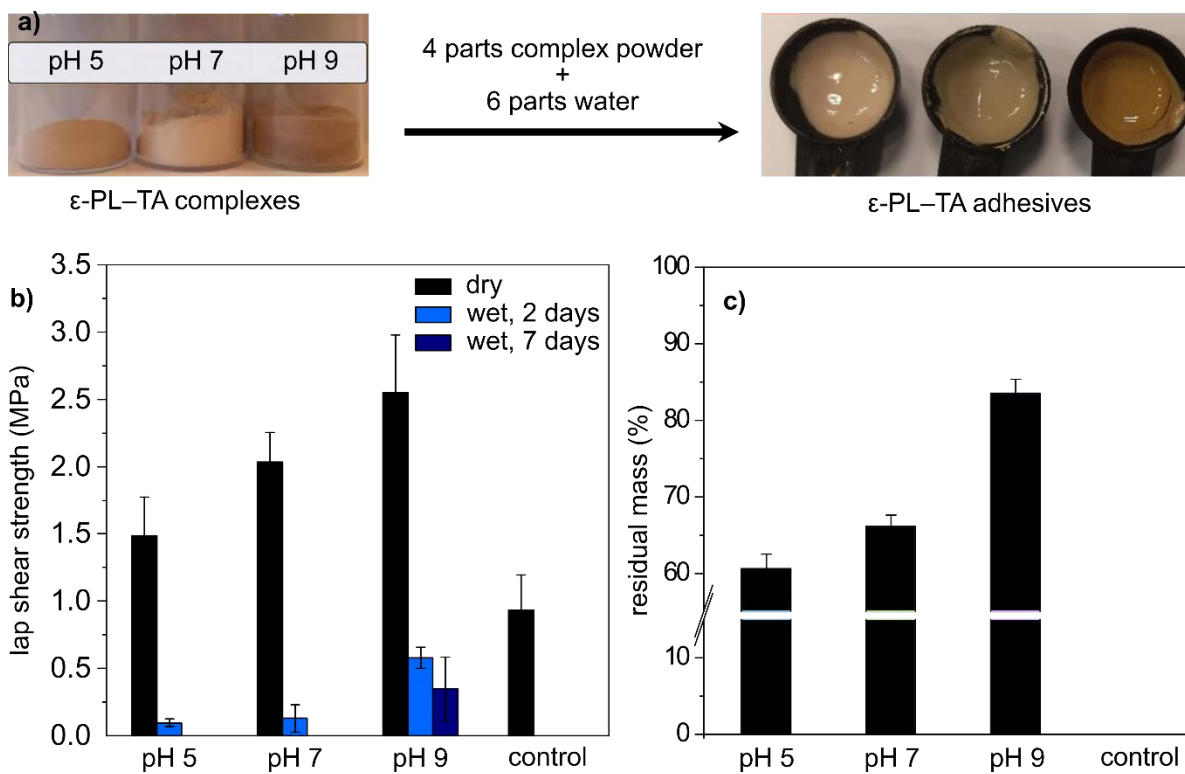


Figure 2 ϵ -PL-TA adhesives: a) preparation of ϵ -PL-TA adhesives from dried complex powders, b) lap shear adhesion strength of ϵ -PL-TA adhesives (from complexes prepared at pH 5, 7, and 9) measured dry and wet after 2 & 7 days of underwater immersion, c) insoluble matter (residual mass) of ϵ -PL-TA adhesives after 48 h of water immersion.

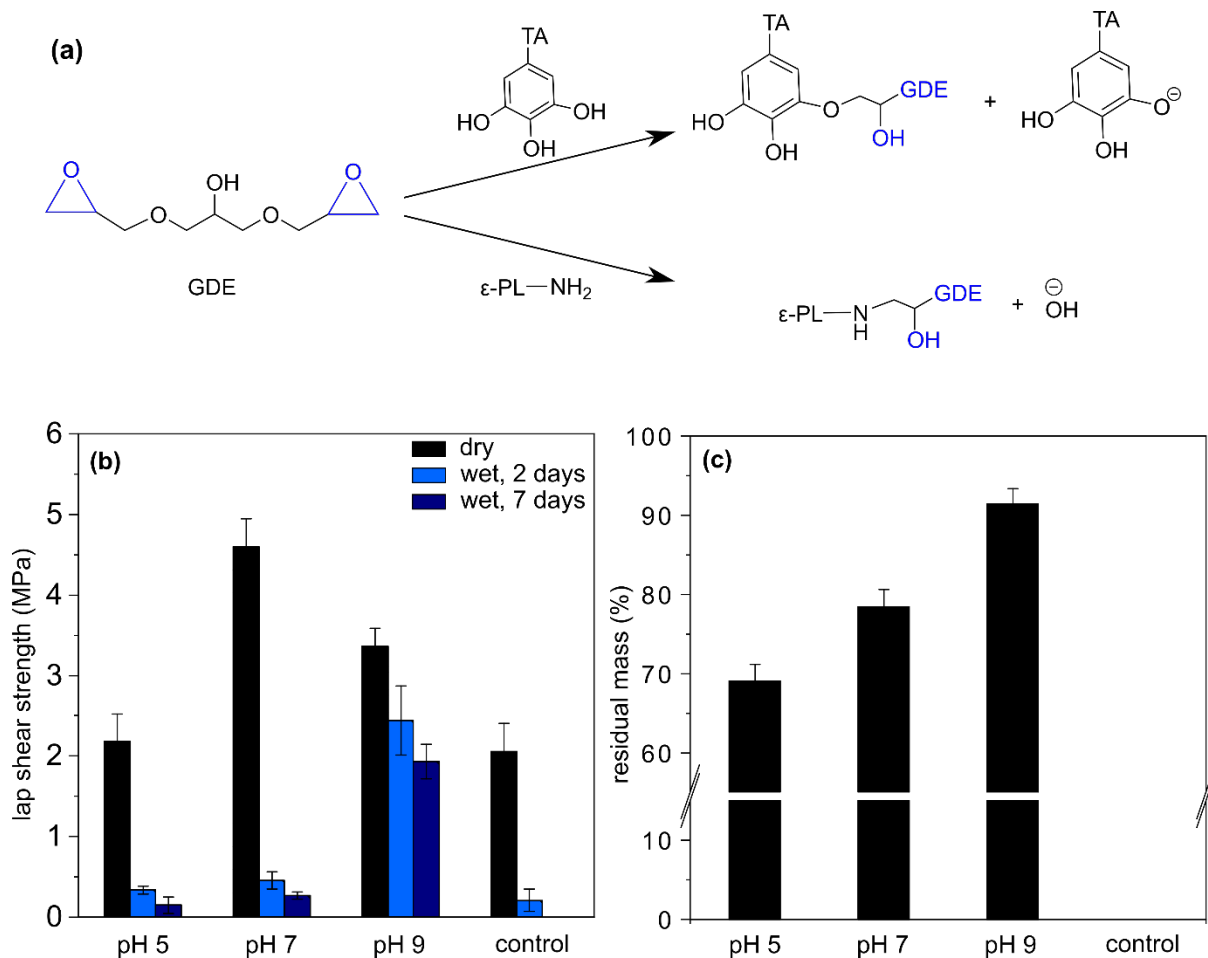


Figure 3 ϵ -PL-TA adhesives with GDE added as cross-linker: a) possible covalent cross-linking of GDE with ϵ -PL and TA, b) lap shear adhesion strength of ϵ -PL-TA adhesives with 5 wt.% GDE (from complexes prepared at pH 5, 7, and 9) measured dry and wet after 2 & 7 days of underwater immersion, c) insoluble matter (residual mass) of ϵ -PL-TA adhesives with 5 wt.% GDE after 48 h of water immersion.

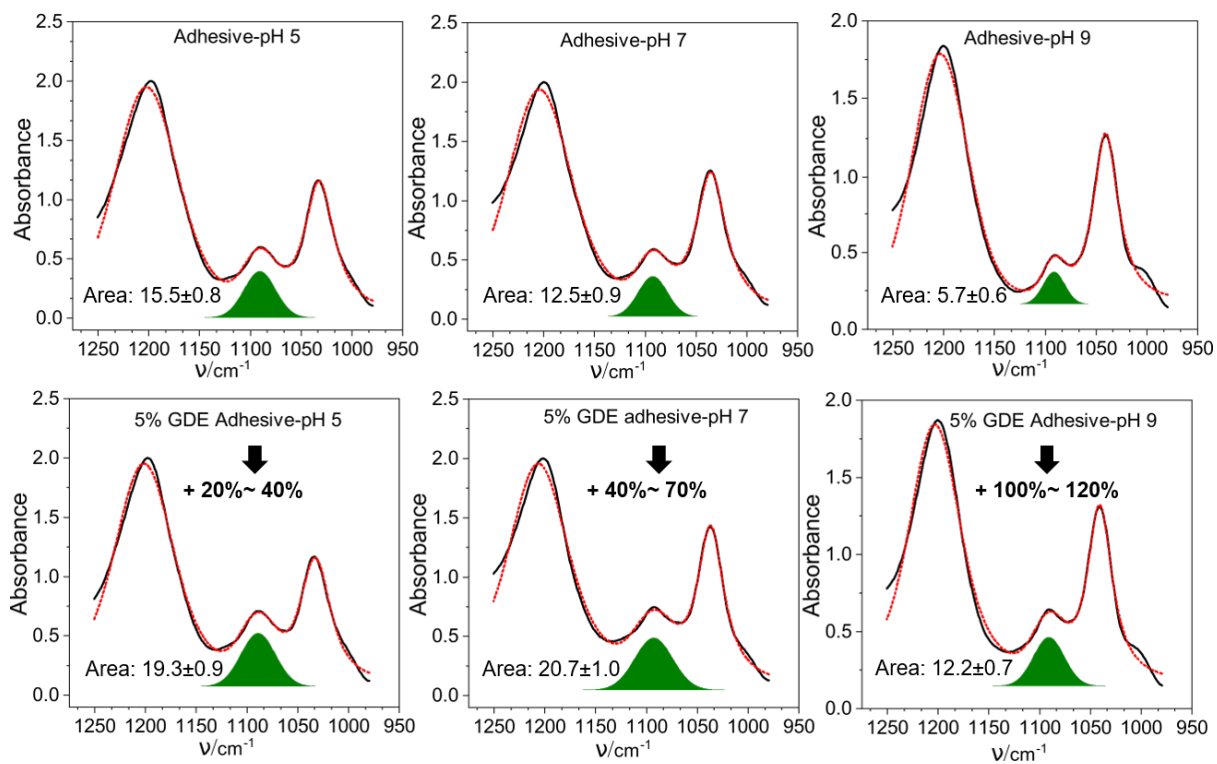
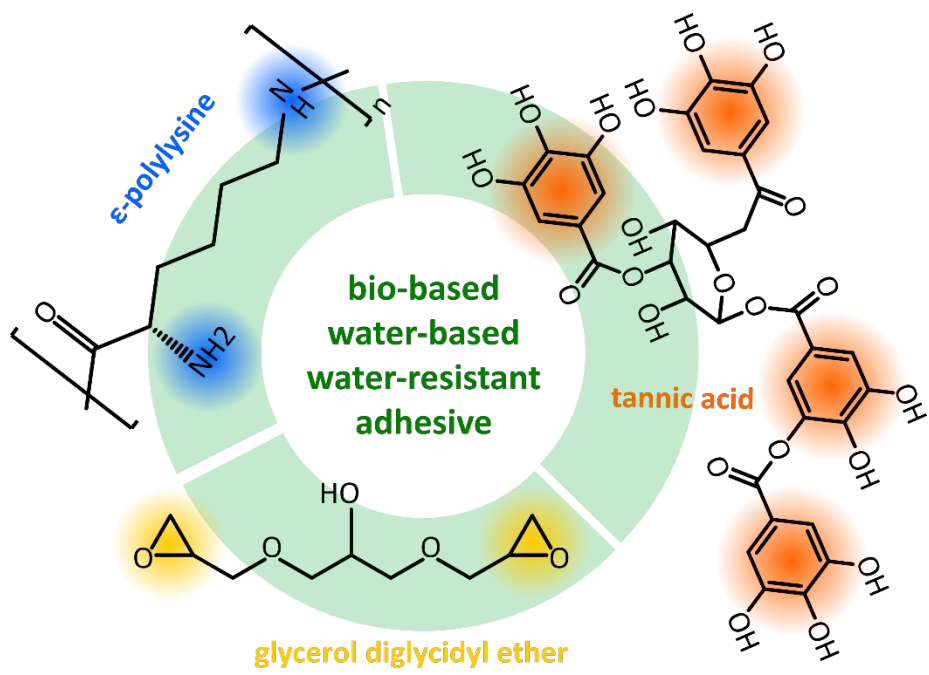


Figure 4 ATR spectra of ϵ -PL-TA adhesives with and without GDE

Table 1 Dry and wet lap shear adhesion strength of ϵ -PL-TA adhesive (from complex made at pH 9, with 5 wt.% GDE) compared with two commercial bio-based adhesives and literature.

Adhesive	Adhesion [MPa] in dry state	Adhesion in wet condition		ref
		[MPa]	Soaking time [hr]	
ϵ -PL-TA	3.36 ± 0.22	2.44 ± 0.42	48	
UHU Glue	1.04 ± 0.27	0.58 ± 0.23	48	
Pritt Glue	0.74 ± 0.3	-	48	
Zein-TA	7.5	3.5	72	¹¹
Gelatin-TA	6.3	0.3	24	¹¹
Zein-catechol	7.5 ± 0.7	0.3 ± 0.2	24	⁴²
PAE-TA	1.55 ± 0.08	0.26 ± 0.01	24	⁴³
PLA-catechol copolymers	2.6 ± 0.4	1.0 ± 0.3	24	⁴⁴



Graphical Abstract