ELSEVIER

Contents lists available at ScienceDirect

Materials & Design



journal homepage: www.elsevier.com/locate/matdes

Surface-patterned gallol pressure-sensitive adhesives for strong underwater adhesion

Seong-Ju Lee^a, Jong-Ho Back^{a,b}, Ji-Soo Kim^a, Mo-Beom Yi^a, Gi-Yeon Han^a, Young Do Kim^{c,*}, Hyun-Joong Kim^{a,b,*}

^a Department of Agriculture, Forestry and Bioresources, Seoul National University, Gwanak-ro 1, Gwanak-gu, Seoul, 08826, Republic of Korea

^b Research Institute of Agriculture and Life Sciences, Seoul National University, Gwanak-ro 1, Gwanak-gu, Seoul, 08826, Republic of Korea

^c Samsung Display Co., Ltd., Cheonan, 31086, Republic of Korea

ARTICLE INFO

Keywords: Adhesives Bio-inspired Polymers Pressure-sensitive adhesives Gallol Microstructures

ABSTRACT

In this study, we synthesized a gallol-functionalized PSA and generated micropatterns on its surface to improve its underwater adhesion. Compared to the adhesive-substrate interactions of benzyl and phenol-functionalized PSAs in water, Gallol PSA exhibited greater interactions with the substrate. Furthermore, the micropattern on the PSA surface provided a drainage channel for water during the bonding process so that water is not trapped at the substrate-adhesive interface. Moreover, the drainage channel allows the formation of small and uniform adhesion defects, which minimize the deterioration in adhesion caused by water. And the adhesive manufacturing process is also simple, without any gallol protection and deprotection steps, and can be achieved using the current adhesive industry infrastructure. This facile fabrication strategy and its adhesive properties could promote the commercialization of gallol-functionalized PSAs with underwater adhesion.

1. Introduction

Pressure-sensitive adhesives (PSAs) are designed to adhere to various surfaces through simple contact under light pressure. Due to their userfriendly adhesion, they are widely used in industries. Recently, there has been a growing demand for PSAs capable of maintaining strong adhesion in wet environments, owing to their potential applications in medical, electronic, and conventional marine sectors [1,2]. Nonetheless, conventional PSAs often exhibit inadequate wet adhesion, underscoring the need to develop PSAs with robust wet adhesion properties.

The presence of a thin hydration layer on substrate surfaces hampers PSA adhesion to substrates [3–5]. This issue arises due to water droplets trapped at the interface, which diminishes the contact area and leads to notable defects. Consequently, the key to achieving wet adhesion is to break down the hydration layer, enabling the adhesive to interact with the substrate surface (Fig. 1a). Moreover, the intrusion of water into the adhesive material can compromise its cohesion, causing plasticization and even hydrolysis in severe cases [6,7]. Thus, safeguarding the bulk properties of PSAs in aqueous environments is of paramount importance.

Underwater adhesives are often designed based on inspiration taken

from nature. Researchers have created drainage channels by micropatterning the adhesive surface to mimic the inner surfaces of a snail [8], frog toe pads [9], and clingfish adhesive disc [10]. This micropattern allows water to escape without being trapped at the interface during the bonding process and delays crack propagation during the debonding process [11,12]. The underwater adhesion of mussel threads in marine environments is another example. While the exact adhesion mechanism remains unclear, extensive investigation has pointed to the significant role of the catechol moiety within mussel foot proteins in both interface interactions and cohesion [13-15]. Consequently, many researchers have incorporated catechol groups into adhesive materials utilizing L-3,4-dihydroxyphenylalanine (L-DOPA). However, the relatively high cost of L-DOPA and its tendency to discolor upon oxidation present obstacles to commercialization [16]. In recent times, gallol groups have garnered attention due to its resemblance to catechol's structure. gallol plays a crucial role in the wound healing of tunicates, and it is effective for underwater adhesion like catechol (Fig. 1c). Gallic acid, a precursor to gallol, offers advantages such as affordability and greater transparency compared to L-DOPA. Additionally, triphenolic gallol groups demonstrate superior underwater adhesion compared to biphenolic catechol groups [17–20].

* Corresponding authors. *E-mail addresses:* colour.kim@samsung.com (Y.D. Kim), hjokim@snu.ac.kr (H.-J. Kim).

https://doi.org/10.1016/j.matdes.2023.112505

Received 23 August 2023; Received in revised form 15 November 2023; Accepted 15 November 2023 Available online 18 November 2023 0264-1275 /@ 2023 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC B

^{0264-1275/© 2023} The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

This study involves the synthesis of a micropatterned Gallol PSA, with a focus on exploring its underwater adhesion attributes. Design strategies at different length scales were combined to improve the underwater adhesion of PSA, and a more practical and economical approach was considered. At the molecular level, Scaffold polymer featuring an epoxy group was fabricated and subsequently modified through post-esterification with gallic acid to circumvent radical scavenging by the gallol monomer in the polymerization step [21,22]. For comparison purposes, PSAs with a structure analogous to Gallol PSA but varying in the number of hydroxyl groups on the aromatic ring were synthesized (Fig. 1b). Industrial scalability was considered during the fabrication of Gallol PSA. Hence, the protection and deprotection steps to prevent the oxidation of gallol, which would increase the cost of manufacturing, were omitted from the synthesis process. Although gallol group oxidation generally compromises adhesive performance, Gallol PSA exhibited markedly enhanced underwater adhesion in comparison to control group PSAs. Furthermore, microstructural patterning was applied to the surface of the PSA. To expedite the patterning process, patterned release films were utilized instead of the conventional molding approach, which is time-consuming. The microstructure of the PSA surface facilitated drainage during bonding, resulting in smaller and more uniform interface defects, thus further enhancing adhesion (Fig. 1d).

2. Experimental

2.1. Materials

Lauryl methacrylate (LMA, 96 %), glycidyl methacrylate (GMA, 97 %), azobisisobutyronitrile (AIBN, 12 % wt.% in acetone), gallic acid (97 %), benzoic acid (99.5 %), 4-hydroxybenzoic acid (99 %) were purchased from Sigma-Aldrich. 1-methylimidazole (1MI, 99 %), tetrahydrofuran (THF, 99 %), acetone (99.5 %) were purchased from

SAMCHUN CHEMICALS.

2.2. Polymerization of Scaffold PSA

The scaffold polymer was synthesized by free radical polymerization in THF using LMA, GMA. 100 ml of THF, AIBN (1.35 g as a solution), LMA (98.30 g, 0.39 mol), GMA (1.7 g, 0.01 mol) were mixed in a 250 ml flask using Teflon stirring bar. And the flask was filled with nitrogen gas. The polymerization was initiated by immersing the flask in an oil bath at 80 °C, and the reaction was carried out for 7 h. The polymer was then precipitated in acetone to remove unreacted monomers and others. Approximately 150 ml of THF was used to re-dissolve the polymer, and the precipitation cycle was repeated three times. After the final precipitation, the polymer was dried under a high vacuum to remove solvents. Molecular weight, monomer conversion ratio, and actual polymer composition of Scaffold PSA were characterized by GPC, ¹H NMR.

2.3. Esterification of Scaffold PSA (post-modification)

Modified PSAs were synthesized by esterifying a Scaffold PSA and three aromatic acids (benzoic acid, 4-hydroxybenzoic acid, gallic acid). Scaffold PSA (10 g, 4.5 mol% of the epoxide group in polymer backbone, 1.0 eq.) and 2 eq. of aromatic acids (0.292 g of benzoic acid for Benzoic PSA, 0.33 g of 4-hydroxybenzoic acid for Phenolic PSA, 0.407 g of gallic acid for Gallol PSA, respectively), and 1MI (0.1 wt% of Scaffold PSA) were dissolved in THF then poured into the refluxing flask. The mixture was stirred for 30 min at room temperature. Then esterification was carried out in 95 °C oil bath with constant stirring. After the reaction, the mixture was cooled to room temperature. The mixture was then precipitated in acetone to remove unreacted aromatic acids. Approximately 10 ml of THF was used to redissolve the polymer, and the precipitation cycle was repeated three times. Epoxide conversion of modified PSAs were calculated by ¹H NMR (Fig. S5, S6, S7).



Fig. 1. (a) Bonding processes of a pressure-sensitive adhesive (PSA) tape in a wet environment. (b) synthetic routes for Scaffold, Benzoic, Phenolic, and Gallol PSAs. (c) expected interaction of the Gallol adhesives in the bulk and at the interface of the substrate. (d) Effect of PSA surface structure on dehydration.

2.4. Rheological properties

Rheological properties were measured by using rheometer (ARES G2, TA Instruments) with 8 mm parallel plates. The evaluation conditions are as follows.

Modulus: 1.0 % strain, 1 Hz frequency, 5 °C/min heating rate with ranging -50 °C to 100 °C, Frequency sweep: 25 °C, 1.0 % strain, 0.01 to 1 Hz, Stress relaxation: 25 % shear strain, 1 min, 25 °C, Creep & Recovery: 1 kPa stress for 3 min, recovery for 9 min after stress removed, 25 °C.

2.5. Confocal microscopy

The surface structure of PSAs was analyzed by laser confocal microscope (VK-X3000, Keyence) equipped with laser confocal optics to measure the depth of PSA surfaces. This microscope uses both 404 nm laser light sources and white light sources to obtain height information and images.

2.6. Adhesion properties

The 180° peel strength and probe tack were measured using a Texture Analyzer (TA.XT plus, Stable Micro Systems) at 25 °C. Samples for underwater adhesion test were prepared by being immersed in deionized water.

 180° peel strength: test speed for the peel test was 5 mm/sec, and the test angle will be 180° . All measurements were repeated more than five times. And peel strength was obtained as the average force from 20 % to 80 % of the operating range.

Probe tack: A cylindrical probe (stainless steel, diameter: 5 mm) was used for the probe tack test. After contact of the probe to the surface of PSA with 100 g_f for 1 s, the probe was detached with 0.2 mm/sec. All measurements were repeated more than five times, and the average value was used.

3. Results and discussion

3.1. Design, synthesis, and characterization of Gallol PSA

We considered the following aspects during the design of the Gallol PSA: (1) The scaffold polymer has a hydrophobic structure for dehydration and water repulsion; (2) The scaffold polymer should be first polymerized and then modified with gallic acid to avoid radical scavenging by the gallol monomer [21]. (3) The scaffold and modified polymers must have sufficiently low glass transition temperatures and moduli [23] (Tg < 25 $^\circ\text{C}$ and G' < 0.1 MPa at 25 $^\circ\text{C}$) to exhibit sufficient chain mobility that enables rapid wetting of the substrate with little pressure. The G' value of 0.1 MPa is determined by the Dahlquist criterion. The Dahlquist criterion is a critical modulus mentioned by Carl Dahlquist, who worked at 3 M in 1969. Dahlquist asserted that, for a standard surface characterized by a bump radius of 5 µm and a bump height of 1 µm, PSA should exhibit a G' value below 0.1 MPa (1 Hz, 25 $^{\circ}$ C) to facilitate flow and establish effective contact. This criterion is not absolute for all situations but is a valuable rule of thumb in designing a new PSA. The glass transition temperature (Tg) was considered to ensure minimal fluidity at room temperature, considering the intended usage temperature [24].

Based on these design considerations, lauryl methacrylate (LMA) was selected as the monomer for designing a hydrophobic scaffold polymer with a low T_g and G'. LMA is hydrophobic owing to the 12 carbons in the side group, and its homopolymer has a sufficiently low T_g (-65 °C) [25]. Additionally, glycidyl methacrylate (GMA) with an epoxy group was selected as a co-monomer for the esterification reaction with gallic acid. Although LMA is rarely used as a main monomer in PSA, another reason for choosing it is that general acrylic monomers of PSA, such as butyl acrylate and 2-ethylhexyl acrylate, have significant differences in

reactivity from that of GMA; therefore, GMA is consumed faster than acrylic monomers in the initial stage of polymerization [26]. But, the combination of LMA and GMA results in a polymer with a random composition compared to the combination of general acrylic monomers due to little difference in the reactivity ratio.

Scaffold PSAs were synthesized through the free-radical polymerization of LMA and GMA using azobisisobutyronitrile (AIBN) as the initiator in tetrahydrofuran (Fig. 2). The feed ratio of LMA and GMA was adjusted from 99:1 to 90:10, followed by an assessment of the adhesive properties of the resultant polymerized Scaffold PSAs. By considering their initial stickiness and peel strength, the most suitable balance was found to be the 97:3 feed ratio of LMA to GMA, which maximized GMA content without significantly compromising adhesive properties (Fig. S10). GPC analysis of Scaffold PSA (LMA 97: GMA 3) revealed an M_n of 213 kDa (Fig. S1). The actual molar ratio of LMA to GMA determined by ¹H NMR spectroscopy was 95.5:4.5 with a conversion exceeding 96 % (Fig. S2, Fig. S3). Scaffold PSA was then reacted with gallic acid to afford Gallol PSA. Employing analogous procedures, Benzoic PSA and Phenolic PSA were synthesized by utilizing benzoic acid and 4-hydroxybenzoic acid, respectively. A minor amount of 1methylimidazole was employed as a catalyst to mitigate unintended crosslinking between secondary hydroxyl and epoxy groups [27]. After the post-esterification step, the consumption of epoxy groups in the modified polymers was measured at 4.3 %, 3.6 %, and 3.3 % for Benzoic, Phenolic, and Gallol PSA, respectively. And gelation was not observed during the post-esterification process. The reaction conditions of all three PSAs were the same, but the epoxide conversion decreased as the number of hydroxyl groups on the aromatic ring increased owing to the difficulty in proton dissociation. This post-modification method is advantageous because the molecular weights of the prepared PSAs are comparable. As the adhesive properties depend on the molecular weight, an accurate comparison of the effects of the different functional groups in the three PSAs can be achieved.

3.2. Rheological properties

The PSAs should have a low T_g and G' to establish contact with the substrate surface under weak pressure. The synthesized PSAs demonstrated a G' value of 0.1 MPa or below at a frequency of 1 Hz under room temperature conditions, coupled with a T_g below 0 °C. These attributes align with the essential criteria for establishing favorable contact, facilitated by the PSA's ability to conform to the substrates through its flow characteristics (Table 1, Fig. 3a). Incorporation of diverse functional groups led to an elevation in both the T_g and G' values; nevertheless, these values remained within the acceptable range for effective PSAs. Intriguingly, the G' values for the modified PSAs exhibited opposite trends between sub-zero temperatures and those above room temperature. In the low-temperature region, G' increased as the number of hydroxyl groups on the benzene ring decreased. The G' values for Benzoic, Phenolic, and Gallol PSAs were 8.7, 4.8, and 2.6 MPa, respectively at -20 °C. In contrast, at room temperature and higher, G' values increased with an increasing number of hydroxyl groups. The relatively large side groups of Gallol PSA increase the free volume of the polymer, thereby reducing its low-temperature G' value [28]. This unique characteristic of exhibiting a low modulus at low temperatures and maintaining the modulus as the temperature increases indicates that Gallol PSA has the potential to be applied over a broad range of temperatures without loss of adhesion strength. The tan δ data also indicate that the loss of elasticity begins at higher temperatures as the number of hydroxyl groups increases (Fig. S8).

The viscoelastic window stands out as the preeminent instrument for assessing the suitability of fabricated PSAs regarding their viscoelastic attributes. The measured G' and G'' values within the frequency range of 0.01 Hz to 100 Hz serve as predictive indicators for the conceivable applications of the PSA (Fig. 3b). With the sole exception of the Scaffold PSA, wherein no functional groups are introduced and consequently falls



Fig. 2. Synthetic routes for Scaffold, Benzoic, Phenolic, and Gallol PSAs.

Table 1				
Characterization o	f Scaffold	and	functionalized	PSAs.

Polymer	G' (MPa)		Tg	Relaxation time	Creep	Recovery
	<i>−20 °C</i>	25 °C	(°C)	(s)	(%)	(%)
Scaffold	0.4	0.01	-21.8	0.03	1,747	3
Benzoic	8.7	0.07	-8.6	0.05	44	60
Phenolic	4.8	0.09	-11.3	0.29	5.3	92
Gallol	2.6	0.10	-10.3	6.08	0.8	99

outside the low modulus region, the modified PSAs exhibit suitable G' and G'' values, rendering them suitable for general adhesive applications as well as those necessitating high shear forces (Fig. 3c).

The stress relaxation of the PSAs was characterized at a strain of 25 % (Fig. 3d). The relaxation time was defined as the time required to relax to 1/e of the initial modulus. All the PSA samples reached this value within a matter of seconds. As the modified PSAs were all derived from Scaffolds PSA with identical composition, molecular weight, and molecular weight distribution, the observed dissimilarity in relaxation characteristics can be attributed to the incorporated functional groups. Given the relatively limited introduction of functional groups in Gallol PSA, it becomes evident that the Gallol moiety exhibits more robust intermolecular or intramolecular interactions in comparison to the benzyl or phenol groups. This was corroborated by the creep recovery

results (Fig. 3e). Creep and recovery tests were performed to evaluate the degree of recovery of the PSAs upon removing the constant stress (1 kPa for 180 s). While Scaffold PSA and Benzoic PSA exhibited constrained recuperation capacity following creep deformation, Phenolic PSA and Gallol PSA demonstrated marked recovery capabilities. This observation underscores the substantial impact of the presence or absence of hydroxyl groups on the recovery process. Notably, Gallol PSA's nearly flawless recovery from deformation highlights its promising applications in contexts involving deformations, such as human joint skin and flexible electronic devices [29].

3.3. Film fabrication with surface micropatterning

Surface micropatterning on adhesives has the potential to enhance underwater adhesion greatly. This micropattern implementation establishes an interfacial drainage channel that effectively counteracts significant defects stemming from water entrapment [11,30]. Furthermore, the creation of independent and regularly spaced fibrillar bonds between the adhesive and the substrate results in heightened resistance to peeling [31,32]. This fibrillar bonding pattern offers advantages over continuous bonding, as the detachment of an individual fibril does not propagate to neighboring fibrils, necessitating the reinitiation of cracking in each fibril during detachment. Numerous studies exploring underwater adhesives have exploited this principle to achieve notable



Fig. 3. Rheological properties of Scaffold and modified PSAs: (a) modulus (G'), (b) viscoelastic window (general PSAs), (c) viscoelastic window, (d) stress relaxation, (e) creep and recovery.



Fig. 4. (a) Surface micropatterning process. (b) 3D images of the patterned PSAs obtained from confocal laser scanning microscopy (left) and Surface profiling results of the patterned PSA (right).

improvements in adhesion strength. However, the predominant molding approach employed in these studies typically demands long durations, particularly evident in the case of hydrogels where patterning may extend to up to 10 h [11,30]. To address this limitation, we employed patterned release films for rapid patterning by a continuous liquidcoating process (Fig. 4a). This technique, commonly employed in the display industry, has excellent industrial scalability owing to its patterning speed of several tens of meters per minute. Each patterned modified PSA film was prepared by coating the patterned release film with PSA, drying, lamination with 50 µm polyethylene terephthalate (PET) backing film, and subsequent delamination. The PSA surface was analyzed with a confocal microscope (Fig. 4b). Confocal microscope analysis of the PSA surface revealed the patterned structure, which comprised a cube with side lengths of approximately $\sim 175 \ \mu m$ and a height of 3.5 µm. The cumulative thickness of the patterned PSA film measured 8 µm. An 8 µm flat-surfaced PSA film was also prepared in parallel for comparative analysis of adhesion properties.

3.4. Adhesion properties

The adhesion properties of the PSAs were investigated using a 180° peel test. The PSA tapes were attached to stainless steel in air or water and then passed twice through a 2 kg rubber roller. The peel strength was measured after allowing the PSA samples to stand under ambient (drv) or underwater (wet) conditions for 24 h. The modified PSAs showed higher peel strength under dry conditions, suggesting that the modifications to the aromatic ring improved the adhesion (Fig. 5a). The modified flat PSAs (Benzoic PSA: 14.5 \pm 0.1 N/25 mm, Phenolic PSA: 15.6 ± 0.1 N/25 mm, Gallol PSA: 12.2 \pm 0.1 N/25 mm) showed over a five-fold increase of peel strength from that of Scaffold PSA (2.4 \pm 0.3 N/25 mm). All modified PSAs failed at cohesion (Fig. 5b). Notably, Gallol PSA showed the highest adhesion under underwater conditions. All PSAs except for Gallol PSA exhibited a rapid drop in adhesion strength of more than 85 % [Scaffold PSA: $0.3 \pm 0.1 \text{ N/25 mm}$ (87 % \downarrow), Benzoic PSA: 2.1 \pm 0.4 N/25 mm (86 % \downarrow), Phenolic PSA: 1.8 \pm 0.5 N/ 25 mm (88 % \downarrow)] under underwater conditions compared to that in dry



Fig. 5. (a) 180° peel strength results of flat PSAs (left) and patterned PSAs (right) on stainless steel substrates. (b) Images of the substrate surfaces after the peel test with flat PSAs (left) and patterned PSAs (right). Microscopic images of substrate surfaces after the peel test with flat Gallol PSA (left) and patterned Gallol PSA (right).

conditions. The failure mode changed from cohesive to interfacial, indicating that water weakened the interactions at the interface. Although the peel strength of Gallol PSA in water decreased by 62 % (4.5 \pm 0.5 N/25 mm) compared to that under dry conditions, the failure mode exhibited a mixed characteristic, not exclusively interfacial. This was attributed to the fact that the bonding force at the interface surpassed the cohesive force, leading to the presence of PSA residues on the substrate's surface. These fracture mode changes in the PSAs indicate that, unlike the benzoic or phenolic moieties, the gallol moiety exhibited better interactions with the substrate surface under underwater conditions. In general, adhesives that are more hydrophobic are preferred for successful dehydration [5,18,33,34]. In underwater adhesion, a critical factor is eliminating the hydration layer on the adherend's surface. The predominant approach for achieving dehydration involves the utilization of hydrophobic materials. Numerous researchers have employed strategies incorporating hydrophobic monomers, polymers, or solvents [35,36]. The hydrophobic characteristics of the adhesive deter dehydration and prevent water infiltration into the bulk, thereby safeguarding the adhesive performance from deterioration [37]. From this perspective, Gallol PSAs are at a disadvantage under dehydration. The contact angle values revealed by measurement show that Gallol PSA is more hydrophilic than other PSAs (Scaffold: 107.5°, Benzoic: 103.2°, Phenolic: 99.4°, Gallol: 98.7°). Also, It has the highest theoretical hydroxyl group content (Scaffold: OH0%, Benzoic: OH4.3 %, Phenolic: OH7.2 %, Gallol: OH13.2 %) (Fig. S12). However, despite these dehydration-related drawbacks, Gallol PSA exhibits the most robust adhesion in water. This result suggests that the gallol group possesses a distinctive structural property capable of overcoming the hindering effects of water molecules attributed to its hydrophilicity, promoting strong interactions with adherends. Additionally, it demonstrated the worst performance in the probe tack evaluation, which reflects the bonding characteristics of the adhesive on a short time scale; therefore, sufficient time is required for Gallol PSA to create strong interactions with the substrate in water (Fig. S11).

Surface patterning also effectively improved underwater adhesion (Fig. 5a). All patterned PSAs demonstrated improved underwater adhesion compared to their respective flat PSA counterparts. The failure modes of Scaffold (0.4 \pm 0.1 N/25 mm), Benzoic (4.1 \pm 0.8 N/25 mm), and Phenolic ($3.6 \pm 0.2 \text{ N/25 mm}$) PSAs remained unchanged (Fig. 5b), the surface pattern increased the interaction between the adhesive and the substrate at the interface despite the reduced contact area. Among the patterned PSAs, the Gallol PSA displayed the highest underwater peel strength of 8.8 \pm 0.4 N/25 mm, approximately double that of the flat surface. In a microscopic image showing the peeled substrate surface with patterned Gallol PSA (Fig. 5c), adhesive residues were observed within a distance of less than 100 µm, alongside traces of net-shaped drainage channels. Conversely, the flat surface showed larger adhesion defects that exceeded the size of those on the patterned surface. Therefore, drainage by the surface pattern reduces the size of the adhesion defects and improves the underwater adhesion by uniformly distributing the defects. While surface patterning had a considerable impact on enhanced underwater adhesion, no discernible trend was observed under dry conditions. Given that all PSAs displayed cohesion failure under dry conditions, the bulk cohesion exerted a more substantial influence than interfacial cohesion.

4. Conclusion

In this study, we synthesized a PSA functionalized with gallol group and introduced micropatterns on its surface to enhance its underwater adhesion capabilities. In contrast to PSAs modified with benzyl or phenol groups, Gallol PSA exhibited pronounced substrate interaction in aqueous environments. And the surface micropatterning of the PSA introduced a drainage pathway during the bonding process, effectively preventing water entrapment. This design element minimized adhesion defects by ensuring their small and consistent dimensions, thereby mitigating the deteriorating effects of water on adhesion.

Furthermore, the synthesis of Gallol PSA proved straightforward, eliminating the need for a gallol protection step. A thin and uniformly patterned PSA film was rapidly produced using a pattern liner technique. This manufacturing approach relies on simple processes including free-radical polymerization, esterification, and continuous liquid coating, all well-aligned with existing adhesive industry infrastructure and requiring no additional facilities. This pragmatic approach provides new insights into the catechol chemistry of PSAs for underwater adhesion, which has been challenging to commercialize over the past decade.

CRediT authorship contribution statement

Seong-Ju Lee: Conceptualization, Methodology, Investigation, Writing – original draft. Jong-Ho Back: Methodology. Ji-Soo Kim: Formal analysis. Mo-Beom Yi: Formal Analysis. Gi-Yeon Han: Investigation. Young do Kim: Funding acquisition, Writing – review & editing. Hyun-Joong Kim: Supervision, Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This work was financially supported by the Samsung Display Co., Ltd.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matdes.2023.112505.

References

- [1] H. Fan, J.P. Gong, Fabrication of bioinspired hydrogels: challenges and opportunities, Macromolecules 53 (8) (2020) 2769–2782.
- [2] S. Ji, C. Wan, T. Wang, Q. Li, G. Chen, J. Wang, Z. Liu, H. Yang, X. Liu, X. Chen, Water-resistant conformal hybrid electrodes for aquatic endurable electrocardiographic monitoring, Adv Mater 32 (26) (2020) 2001496.
- [3] B.P. Lee, P.B. Messersmith, J.N. Israelachvili, J.H. Waite, Mussel-inspired adhesives and coatings, Annu. Rev. Mat. Res. 41 (1) (2011) 99–132.
- [4] F. Li, J. Mo, Z. Zhang, S.Q. Shi, J. Li, J. Cao, Z. Wang, Achieving strong, stable, and durable underwater adhesives based on a simple and generic amino-acidresembling design, Mater. Horiz. 10 (8) (2023) 2980–2988.
- [5] C. Qin, Y. Ma, Z. Zhang, Y. Du, S. Duan, S. Ma, X. Pei, B. Yu, M. Cai, X. He, F. Zhou, Water-assisted strong underwater adhesion via interfacial water removal and selfadaptive gelation, Proceedings of the National Academy of Sciences 120(31) (2023) e2301364120.
- [6] P. Frantzis, Durability of adhesive joints made underwater, J. Mater. Civ. Eng. 20 (10) (2008) 635–639.
- [7] A. Narayanan, J.R. Menefee, Q. Liu, A. Dhinojwala, A. Joy, Lower critical solution temperature-driven self-coacervation of nonionic polyester underwater adhesives, ACS Nano 14 (7) (2020) 8359–8367.
- [8] Z. Geng, Z. Li, Z. Cui, J. Wang, X. Yang, C. Liu, Novel bionic topography with MiR-21 coating for improving bone-implant integration through regulating cell adhesion and angiogenesis, Nano Lett. 20 (10) (2020) 7716–7721.
- [9] H. Chen, L. Zhang, D. Zhang, P. Zhang, Z. Han, Bioinspired surface for surgical graspers based on the strong wet friction of tree frog toe pads, Acs Appl Mater Inter 7 (25) (2015) 13987–13995.
- [10] K. Tsujioka, Y. Matsuo, M. Shimomura, Y. Hirai, A new concept for an adhesive material inspired by clingfish sucker nanofilaments, Langmuir 38 (3) (2022) 1215–1222.

S.-J. Lee et al.

- [11] P. Rao, T.L. Sun, L. Chen, R. Takahashi, G. Shinohara, H. Guo, D.R. King, T. Kurokawa, J.P. Gong, Tough hydrogels with fast, strong, and reversible underwater adhesion based on a multiscale design, Adv Mater 30 (32) (2018).
- [12] Y. Zhang, S. Ma, B. Li, B. Yu, H. Lee, M. Cai, S.N. Gorb, F. Zhou, W. Liu, Gecko's feet-inspired self-peeling switchable dry/wet adhesive, Chem. Mater. 33 (8) (2021) 2785–2795.
- [13] J.H. Waite, Mussel adhesion essential footwork, J. Exp. Biol. 220 (4) (2017) 517–530.
- [14] H.G. Silverman, F.F. Roberto, Understanding marine mussel adhesion, Mar. Biotechnol. 9 (6) (2007) 661–681.
- [15] Y. Li, M. Qin, Y. Li, Y. Cao, W. Wang, Single molecule evidence for the adaptive binding of DOPA to different wet surfaces, Langmuir 30 (15) (2014) 4358–4366.
- [16] Q. Lu, E. Danner, J.H. Waite, J.N. Israelachvili, H. Zeng, D.S. Hwang, Adhesion of mussel foot proteins to different substrate surfaces, J. R. Soc. Interface 10 (79) (2013) 20120759.
- [17] K. Zhan, C. Kim, K. Sung, H. Ejima, N. Yoshie, Tunicate-inspired gallol polymers for underwater adhesive: a comparative study of catechol and gallol, Biomacromolecules 18 (9) (2017) 2959–2966.
- [18] B.H. Cheng, J.H. Yu, T. Arisawa, K. Hayashi, J.J. Richardson, Y. Shibuta, H. Ejima, Ultrastrong underwater adhesion on diverse substrates using non-canonical phenolic groups, Nat Commun 13 (1) (2022).
- [19] S.Y. Lee, J.N. Lee, K. Chathuranga, J.S. Lee, W.H. Park, Tunicate-inspired polyallylamine-based hydrogels for wet adhesion: a comparative study of catecholand gallol-functionalities, J. Colloid Interface Sci. 601 (2021) 143–155.
- [20] B. Cheng, K. Ishihara, H. Ejima, Bio-inspired immobilization of low-fouling phospholipid polymers via a simple dipping process: a comparative study of phenol, catechol and gallol as tethering groups, Polym. Chem. 11 (2) (2020) 249–253.
- [21] K. Lee, B.D.B. Tiu, V. Martchenko, K. Mai, G. Lee, M. Gerst, P.B. Messersmith, A modular strategy for functional pressure sensitive adhesives, Acs Appl Mater Inter 13 (2) (2021) 3161–3165.
- [22] S. Samanta, V.K. Rangasami, H. Sarlus, J.R.K. Samal, A.D. Evans, V.S. Parihar, O. P. Varghese, R.A. Harris, O.P. Oommen, Interpenetrating gallol functionalized tissue adhesive hyaluronic acid hydrogel polarizes macrophages to an immunosuppressive phenotype, Acta Biomater. 142 (2022) 36–48.
- [23] C. Creton, Pressure-sensitive adhesives: an introductory course, Mrs Bull 28 (6) (2003) 434–439.
- [24] G. Cyprien, Stickiness: some fundamentals of adhesion, Integr. Comp. Biol. 42 (6) (2002) 1123–1126.

- [25] S. Rogers, L. Mandelkern, Glass transitions of the poly-(n-alkyl methacrylates), J. Phys. Chem. 61 (7) (1957) 985–991.
- [26] P.K. Dhal, M.S. Ramakrishna, G.N. Babu, Copolymerization of glycidyl methacrylate with alkyl acrylate monomers, J. Polym. Sci., Polym. Chem. Ed. 20 (6) (1982) 1581–1585.
- [27] T.-N. Tran, C.D. Mauro, A. Graillot, A. Mija, Chemical reactivity and the influence of initiators on the epoxidized vegetable oil/dicarboxylic acid system, Macromolecules 53 (7) (2020) 2526–2538.
- [28] M. Mai, N. Shogo, T. Hiroki, I. Katsuhiro, Free volume and local dynamics in modulus-enhanced polycarbonate under addition of low-mass molecules, 材料 72 (1) (2023) 17–22.
- [29] L. Tae-Hyung, K. Ji-Soo, L. Jung-Hun, K. Hyun-Joong, Pressure-Sensitive Adhesives for Flexible Display Applications, in: V.-B. Rafael, H. Peng, Z. Shuye (Eds.), Hybrid Nanomaterials, IntechOpen, Rijeka, 2019, p. Ch. 5.
- [30] B. Zhang, L.H. Jia, J.R. Jiang, S.S. Wu, T. Xiang, S.B. Zhou, Biomimetic microstructured hydrogels with thermal-triggered switchable underwater adhesion and stable antiswelling property, Acs Appl Mater Inter 13 (30) (2021) 36574–36586.
- [31] M. Kamperman, E. Kroner, A. del Campo, R.M. McMeeking, E. Arzt, Functional adhesive surfaces with "gecko" effect: the concept of contact splitting, Adv Eng Mater 12 (5) (2010) 335–348.
- [32] H. Yuk, T. Zhang, S. Lin, G.A. Parada, X. Zhao, Tough bonding of hydrogels to diverse non-porous surfaces, Nat. Mater. 15 (2) (2016) 190–196.
- [33] L. Yao, C. Lin, X. Duan, X. Ming, Z. Chen, H. Zhu, S. Zhu, Q. Zhang, Autonomous underwater adhesion driven by water-induced interfacial rearrangement, Nat. Commun. 14 (1) (2023) 6563.
- [34] G. Chen, X. Guo, C. Yang, H. Zhu, Q. Zhang, S. Zhu, Superstrong Water-Resistant underwater adhesives enabled by in situ coacervation through dense hydrogen bonds, Chem. Eng. J. 460 (2023), 141691.
- [35] J. Liu, S. Wang, Q. Shen, L. Kong, G. Huang, J. Wu, Tough underwater super-tape composed of semi-interpenetrating polymer networks with a water-repelling liquid surface, ACS Appl. Mater. Interfaces 13 (1) (2021) 1535–1544.
- [36] Y. Xu, Q. Liu, A. Narayanan, D. Jain, A. Dhinojwala, A. Joy, Mussel-inspired polyesters with aliphatic pendant groups demonstrate the importance of hydrophobicity in underwater adhesion, Adv. Mater. Interfaces 4 (22) (2017) 1700506.
- [37] B. Cheng, J. Yu, T. Arisawa, K. Hayashi, J.J. Richardson, Y. Shibuta, H. Ejima, Ultrastrong underwater adhesion on diverse substrates using non-canonical phenolic groups, Nat. Commun. 13 (1) (2022) 1892.

Materials & Design 236 (2023) 112505