

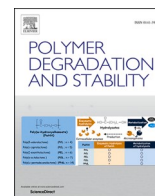


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Schiff base crosslinked poly(γ -glutamic acid) composite films with high mechanical strength and remoldability

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ABSTRACT

With growing concerns over the environmental impact of traditional thermoset materials, the development of green and sustainable alternatives has emerged as a key research priority. In this study, we report a novel approach for fabricating recyclable poly(γ -glutamic acid) (γ -PGA)-based films via dynamic covalent Schiff base crosslinking. γ -PGA was first functionalized with hydrazide groups via reaction with adipic dihydrazide (P-ADH) and subsequently crosslinked with acetoacetylated poly(vinyl alcohol) (AAPVA) under mild, catalyst-free conditions to form an acylhydrazone crosslinked network, resulting in a high-performance, recyclable thermoset film. The resulting films demonstrated excellent mechanical properties (a tensile strength of 123.5 MPa and Young's modulus of 4.4 GPa), high optical transparency, UV-shielding capability, and solvent resistance. Notably, dynamic crosslinks enable acid-triggered cleavage, allowing for the recovery of macromolecular components and their reprocessing into new films, thereby demonstrating exceptional chemical recyclability and reusability. This work presents a promising strategy for enhancing the performance and sustainability of γ -PGA-based materials and highlights their potential as viable alternatives to conventional plastic thermosets.

1. Introduction

In recent years, the persistent accumulation of plastic waste in natural ecosystems has become a global environmental concern. The low degradation efficiency of conventional plastics poses a major barrier to pollution mitigation [1]. To address this issue, the scientific community has been actively investigating sustainable carbon-based feedstocks and advancing green synthesis strategies for the development of high-performance bio-based materials, with the ultimate goal of replacing petroleum-derived plastics [2].

Poly(γ -glutamic acid) (γ -PGA) is a water-soluble, biodegradable synthetic polypeptide composed of naturally occurring D- and L-glutamic acid units linked via amide bonds between the α -amino and γ -carboxyl groups [3]. This biopolymer is primarily produced through microbial fermentation by *Bacillus subtilis* or *Bacillus natto* and is well known for its excellent biocompatibility and environmental sustainability [4]. Due to these attributes, γ -PGA has been widely applied in fields such as biomedicine, agriculture, food, and environmental engineering [5]. In recent years, increasing emphasis on green and sustainable development, γ -PGA has attracted increasing interest as it advances toward industrial-scale production and shows strong potential as a

renewable alternative to petroleum-based plastics [6]. The presence of abundant carboxyl ($-\text{COOH}$) functional groups along the molecular backbone offers versatile reactive sites for chemical modification [7,8]. Various functional moieties such as allyl glycidyl ether, glycidyl methacrylate, cysteamine hydrochloride, furfurylamine, and tyramine have been grafted onto γ -PGA to tailor and improve its material properties [9–11]. However, despite these advantages, the high hygroscopicity and poor film-forming ability of γ -PGA remain significant limitations, especially in applications requiring structural integrity, such as packaging materials.

To address these limitations, the construction of stable covalently crosslinked networks has emerged as an effective strategy to enhance the performance of γ -PGA [12]. For example, Yu et al. [13] designed a covalent crosslinking system between γ -PGA and chitosan oligosaccharide embedded in bacterial cellulose, which simultaneously improved the mechanical strength and effectively regulated the swelling behavior. In another study, Chen et al. [14] developed an adhesive hydrogel by crosslinking γ -PGA with amino-functionalized poly(ethylene glycol)-grafted poly(glycerol sebacate), which exhibited excellent wet adhesion and dynamic mechanical stability. These studies collectively demonstrate that the formation of covalently crosslinked structures can

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significantly improve the mechanical properties and functional stability of γ -PGA-based materials, offering promising potential for applications in biomedical and functional packaging.

However, poor film-forming ability remains a significant obstacle, limiting both processability and practical performance. Incorporating a polymer with superior film-forming properties and chemical reactivity has been recognized as an effective strategy to address this challenge [15]. Poly(vinyl alcohol) (PVA) is a nontoxic and water-soluble polymer that is widely used in medical dressings, food packaging, and biodegradable films [16]. Owing to its excellent chain flexibility and film-forming capability, PVA can promote the formation of dense film structures and enhance interfacial cohesion, thereby improving the mechanical strength, durability, and surface uniformity of the resulting composite films [17].

Although conventional covalently crosslinked networks are effective in enhancing material strength and stability, their irreversible nature often compromises sustainability and raises concerns regarding secondary environmental pollution [18]. In recent years, covalent adaptable networks (CANs) based on dynamic covalent chemistry have received increased attention [19,20]. By incorporating reversible covalent bonds, these networks maintain their structural integrity while introducing desirable features such as degradability and recyclability, which are particularly advantageous for the development of bio-based functional materials [21,22]. Among the various dynamic covalent strategies, the Schiff base reaction has emerged as a powerful and widely adopted click chemistry approach owing to its mild reaction conditions, metal-free catalysis, and compatibility with aqueous environments [23]. Recent studies have demonstrated the potential of this reaction for the fabrication of high-performance and sustainable polymeric materials. For instance, Khin et al. [24] developed a bio-based packaging film through Schiff base crosslinking between gelatin and dialdehyde cellulose in aqueous solution, achieving excellent tensile strength (49.4 ± 4.5 MPa), water resistance, and gas barrier performance. Similarly, Zhou et al. [25] designed a sustainable konjac glucomannan-based bioplastic using dynamic imine bond formation, which enabled hot-press processability, thermally triggered self-healing, and recyclability. These studies highlight the significant potential of Schiff base chemistry for advancing green synthetic strategies for high-performance degradable film materials and offer valuable insights into the design of next-generation sustainable polymer networks.

In this study, we report a novel recyclable thermoset film based on γ -PGA and PVA. The material was fabricated through a Schiff base reaction under mild conditions between hydrazide-functionalized γ -PGA (P-ADH) and acetoacetylated PVA (AAPVA), leading to the formation of a stable acylhydrazone ($-C=NNH-$) crosslinked network. This dynamic covalent structure endows the resulting bio-based thermoset film with excellent mechanical strength, ultraviolet (UV)-shielding ability, and chemical recyclability. The mechanical properties of these films were systematically evaluated and compared with those of several representative commercial packaging materials. The results demonstrated that the γ -PGA-based films exhibited superior overall performance, confirming the feasibility and effectiveness of acylhydrazone crosslinking for the development of sustainable functional films. This work provides an effective strategy for enhancing the performance of γ -PGA-based materials and offers a promising foundation for designing next-generation, environmentally friendly, and recyclable bio-based plastic alternatives.

2. Materials and methods

2.1. Materials

Acetoacetylated polyvinyl alcohol (AAPVA, degree of hydrolysis: 99 %, Mw $\approx 44,000$ g mol⁻¹, acetoacetyl substitution degree: 5 %) was kindly supplied by The Nippon Synthetic Chemical Industry Co., Ltd. (Tokyo, Japan) and used without further purification. Poly(γ -glutamic

acid) (PGA, Mw = 1.6×10^5 g mol⁻¹) was provided by Kookmin University (Seoul, Korea). The reagents 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC), N-hydroxysuccinimide (NHS), adipic dihydrazide (ADH), and 4-amino-L-phenylalanine monohydrate (4-amino-Phe) were purchased from Tokyo Chemical Industry (Tokyo, Japan). Additionally, 2-morpholinoethanesulfonic acid (MES) was procured from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Synthesis of P-ADH

To synthesize P-ADH, 5.2 g of PGA was completely dissolved in 500 mL MES buffer (0.1 mol/L, pH 5.5). Subsequently, 4.6 g EDC and 2.76 g of NHS were added and allowed to react for 15 min to activate the carboxyl groups. Then, 3.5 g of ADH was added, and the reaction was carried out under continuous stirring at 25 °C for 24 h. Upon completion, the reaction mixture was subjected to dialysis using a membrane with a molecular weight cut-off of 1×10^4 , first against a 0.1 mol/L NaCl solution for 3 days, followed by deionized water for 4 days. Finally, the purified P-ADH was obtained as a white, spongy solid by lyophilization.

2.3. Fabrication of the P-ADH/AAPVA films

The P-ADH/AAPVA films were prepared using the solution casting method. Initially, AAPVA was dissolved in 20 mL of deionized water at 90 °C and then cooled to room temperature. Separately, P-ADH was dissolved in 20 mL deionized water at room temperature. The AAPVA solution was gradually poured into the P-ADH solution, followed by continuous stirring to ensure homogeneity. The resulting mixture was transferred into a Petri dish ($\Phi 100$ mm) and dried in an oven at 40 °C for 2 days. The resulting films were designated as AAPVA, P-ADH, PGA/P-3, P-ADH/P-1, P-ADH/P-3, and P-ADH/P-5, as detailed in Table S1.

2.4. Measurements

The ¹H nuclear magnetic resonance (¹H NMR) spectra of the samples were obtained using JNM-ECS400 (400 MHz, JEOL Ltd., Japan). The Fourier transform-infrared (FT-IR) spectra of the materials in the 500–4000 cm⁻¹ wavenumber range were measured using a Nicolet iS5 FTIR spectrometer (Thermo Fisher Scientific, Waltham, USA). The chemical compositions and structural features were confirmed using X-ray diffraction (XRD; SmartLab, Rigaku Co. Ltd., Japan) and X-ray photoelectron spectroscopy (XPS; KRATOS ULTRA2, Shimadzu Co. Ltd., Japan). The mechanical properties of the films were investigated using a universal testing machine (EZ Graph, Shimadzu Co., Japan). A dynamic mechanical analyzer (DMA 7100, TA Instruments, USA) was used to determine the thermomechanical properties of the films. The transparency of the films was measured in the wavelength range 200–800 nm using an ultraviolet spectrometer (U-2810, Hitachi, Japan). The morphologies of the films were observed using scanning electron microscopy (SEM; SU5000, Hitachi High-Technologies Corp., Japan). Water contact angles were measured using a Drop Master DM300 (Kyowa Interface Science, Japan). Detailed evaluations of the swelling ratio, stability, and degradability of the P-ADH/AAPVA films are provided in Supporting Information.

3. Results and discussion

3.1. Synthesis and characterization of P-ADH/AAPVA films

In this study, a covalent adaptive network was constructed based on hydrazide-modified γ -polyglutamic acid (P-ADH) and acetoacetylated polyvinyl alcohol (AAPVA), leading to the synthesis of a sustainable, chemically degradable, and high-performance film material. The fabrication strategy involved chemical modification of γ -PGA followed by dynamic covalent crosslinking reactions with AAPVA (Fig. 1).

P-ADH was synthesized via EDC/NHS coupling using the synthetic

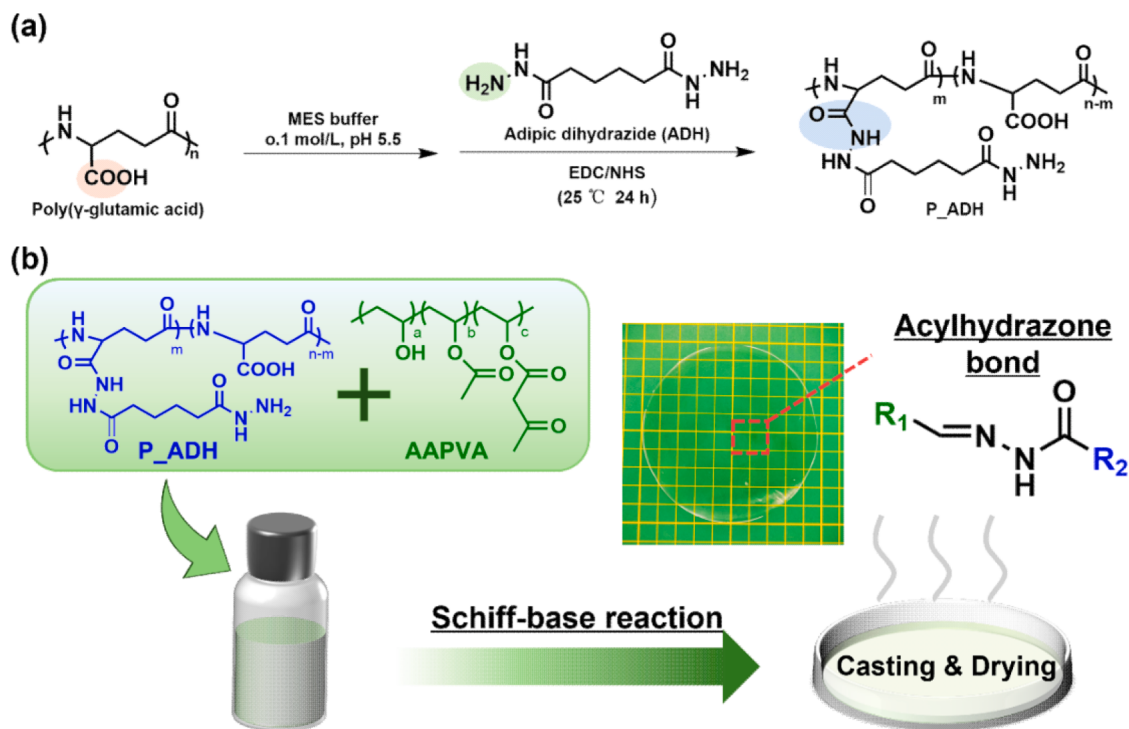


Fig. 1. (a) Schematic illustration of the chemical synthesis route of P_ADH; (b) Fabrication process of the P_ADH/AAPVA film.

pathway illustrated in Fig. 1a. The chemical structure and degree of substitution of the P_ADH polymer were characterized using ^1H NMR and FT-IR (Fig. S1). In the ^1H NMR spectrum, a new proton signal was

observed at 1.46 ppm, corresponding to the methylene protons in ADH, confirming the successful conjugation of ADH with γ -PGA [26,27]. In the FTIR spectrum, the overlapping vibrations of $\text{C}=\text{O}$, amide I, and

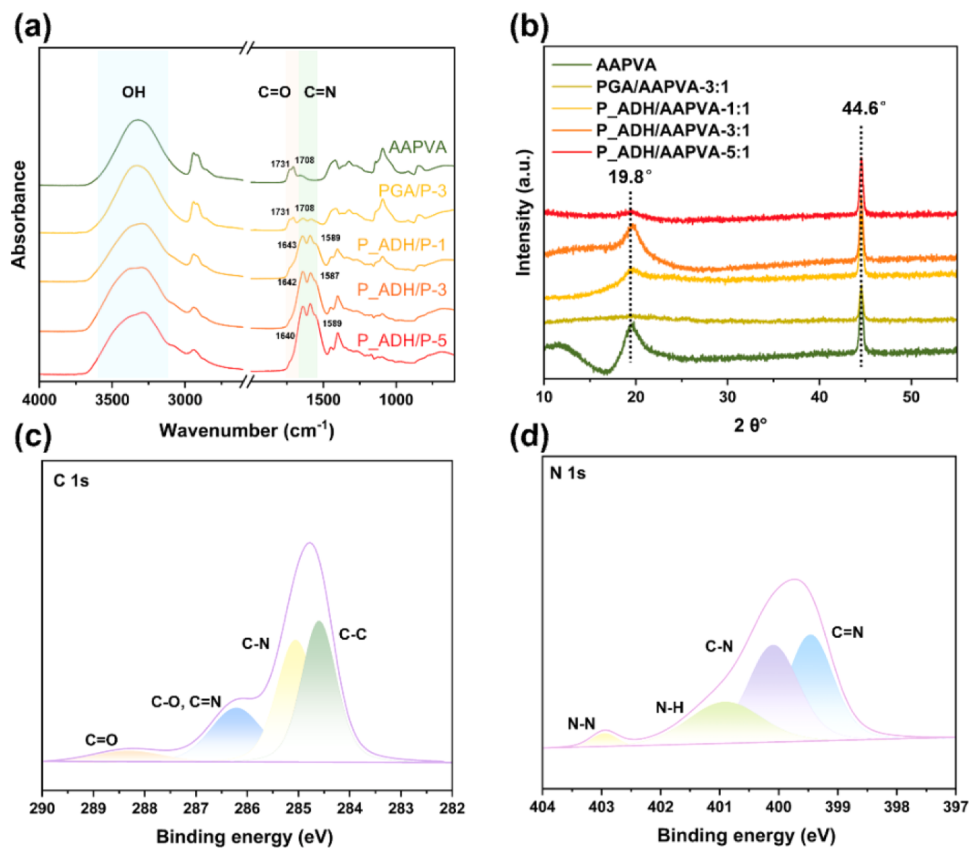


Fig. 2. (a) FT-IR spectra of AAPVA and composite films; (b) XRD patterns of AAPVA and composite films; High-resolution XPS spectra of the P_ADH/P-3 film: (c) C 1s and (d) N 1s.

amide II groups from γ -PGA and ADH resulted in the emergence of new peaks at 1545 cm^{-1} and 1631 cm^{-1} [28,29]. The degree of substitution of P_{ADH} was determined to be 12 % by comparing the integral area of the methylene protons in ADH (4H) with the α -protons of γ -PGA (1H) at 3.96 ppm.

Subsequently, P_{ADH} and AAPVA were crosslinked via a Schiff base reaction to form the P_{ADH}/AAPVA films. The FTIR spectra of the P_{ADH}, AAPVA, PGA/P-3, and P_{ADH}/AAPVA films are shown in Fig. 2a. The characteristic peaks observed at 1735 cm^{-1} – 1705 cm^{-1} correspond to the acetoacetyl groups in AAPVA [30,31]. After crosslinking, these peaks disappeared in the P_{ADH}/AAPVA films, while a new peak appeared at 1640 – 1643 cm^{-1} , corresponding to the C=N bond of the hydrazone linkage [32]. Additionally, the hydroxyl absorption band in the P_{ADH}/AAPVA films shifts to a lower wavenumber than that of AAPVA, indicating the presence of hydrogen bonding interactions [33,34]. The XRD patterns of the AAPVA and modified films are shown in Fig. 2b. The pristine AAPVA film exhibited a broad crystalline peak at $2\theta = 19.8^\circ$, attributed to intra- and intermolecular hydrogen bonding within AAPVA chains [35]. As the P_{ADH} content increased and acylhydrazone bonds were introduced, the formation of hydrogen bonds was reduced, disrupting the crystalline structure and resulting in a reduced peak intensity in all P_{ADH}/AAPVA films. Furthermore, the chemical structures of the films were confirmed using XPS (Fig. 2c, and d, and Fig. S2), using the P_{ADH}/P-3 film as a representative sample. The appearance of new peaks at 286.3 eV (C=N) in the C 1s spectrum and 399.5 eV (C=N) in the N 1s spectrum provides strong evidence for the successful formation of acylhydrazone linkages within the crosslinked network [25,36].

3.2. Mechanical properties of P_{ADH}/AAPVA films

The mechanical properties of P_{ADH}/AAPVA films with different compositions were evaluated via tensile testing (Table S2). Compared to the pure AAPVA film ($46.79 \pm 5.82\text{ MPa}$), P_{ADH} film (61.43 ± 2.16

MPa), and unmodified γ -PGA/AAPVA blend film ($5.422 \pm 2.44\text{ MPa}$), the P_{ADH}/AAPVA series exhibited significantly enhanced tensile strength (Fig. 3a, b, and c). This improvement is attributed to the formation of acylhydrazone bonds within the polymer network, where both covalent crosslinking and hydrogen bonding contribute to the increased rigidity and reinforcement. The Young's modulus of the P_{ADH}/P-3 film ($4.4 \pm 0.02\text{ GPa}$) was comparable to those of the P_{ADH}/P-1 and P_{ADH}/P-5 films. However, its tensile strength increased significantly to $123.5 \pm 2.32\text{ MPa}$, which was substantially higher than that of the P_{ADH}/P-1 ($91.81 \pm 3.91\text{ MPa}$) and P_{ADH}/P-5 ($95.37 \pm 13.4\text{ MPa}$) films, representing improvements of 34.5 % and 29.5 %, respectively. This enhancement was likely due to the optimal crosslinking density in the polymer matrix, indicating that either an excess or deficiency of P_{ADH} can compromise the mechanical properties by disrupting the formation of an efficient crosslinked structure. The notable reduction in the elongation at break was attributed to restricted chain mobility following the formation of hydrazone linkages. Fig. 3d and S3 present a comparative analysis of the Young's modulus and tensile strength of the P_{ADH}/P-3 film in relation to bio-based plastics, petroleum-based plastics, previously reported PVA-based composite films, and Schiff base-crosslinked films. Common bioplastics such as PBS, PLA, and PHB exhibit tensile strengths of approximately 34, 70, and 43 MPa, respectively, which are markedly lower than those of the P_{ADH}/AAPVA films. Notably, the Young's modulus of the P_{ADH}/P-3 film significantly exceeds that of these bioplastics and is comparable to petroleum-based polyurethane (PU, $\approx 4.3\text{ GPa}$). These results demonstrate that the P_{ADH}/P-3 film exhibits mechanical performance on par with or superior to that of conventional plastics, highlighting its potential as a sustainable alternative.

The dynamic mechanical and thermal properties of the films were further investigated using Dynamic Mechanical Analysis (DMA). Variations in storage modulus (E') and loss factor ($\tan \delta$) with temperature are depicted in Fig. 3e. The storage modulus of the P_{ADH}/AAPVA films was significantly higher than those of pure AAPVA and physically

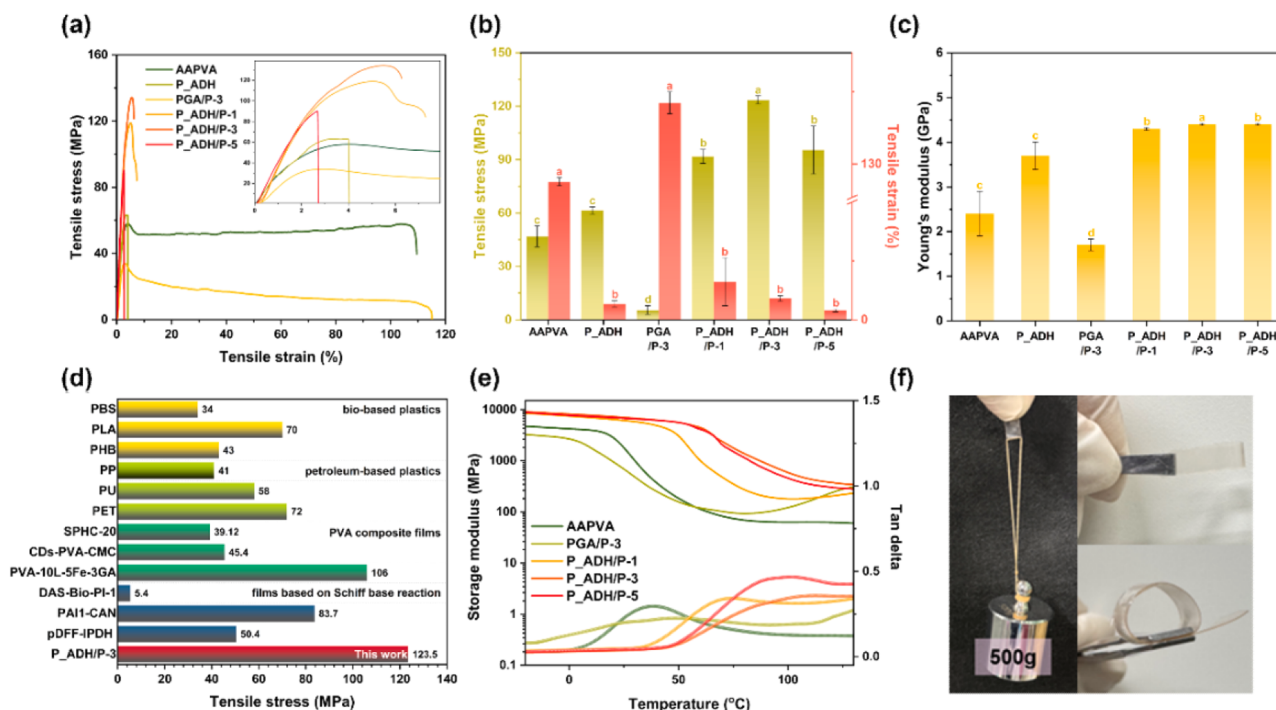


Fig. 3. (a) Tensile stress–strain curves of different P_{ADH}/AAPVA film materials; (b) Tensile stress and tensile strain of different P_{ADH}/AAPVA films; (c) Young's modulus of different P_{ADH}/AAPVA films; (d) Comparison of Tensile stress among bio-based plastics [37–39], petroleum-based plastics [40], previously reported PVA-based composite films [41–43], Schiff base crosslinked films [44–46], and the P_{ADH}/P-3 film; (e) Variation of storage modulus and $\tan \delta$ with temperature; (f) Photographs of the P_{ADH}/P-3 film lifting a 500 g weight and undergoing various deformations; Samples labeled with different letters indicate significant differences between groups ($P < 0.05$).

blended PGA/P-3 films, indicating enhanced mechanical rigidity. As the temperature increased, the storage modulus gradually decreased, suggesting the activation of the dynamic exchange of acylhydrazone bonds, which facilitated polymer chain mobility within the P_{ADH}/AAPVA network. The glass transition temperatures (*T_g*) of P_{ADH}/P-1, P_{ADH}/P-3, and P_{ADH}/P-5 films were determined to be 68.3 °C, 106.2 °C, and 96.4 °C, respectively, correlating with the acylhydrazone crosslinking content. Furthermore, the P_{ADH}/P-3 film (approximately 100 μm thick and 1 cm wide) was able to lift a 500 g weight (Fig. 3f), demonstrating its excellent mechanical strength, flexibility, and ductility. These findings underscore the superior mechanical performance of P_{ADH}/AAPVA films, making them promising candidates for high-performance, sustainable material applications.

3.3. Optical properties of P_{ADH}/AAPVA films

The UV–visible transmittance spectra of various films in the 200–800 nm wavelength range, along with their transparency values at 600 nm, are presented in Fig. 4a and b and Table S3. Optical photographs of the films are provided in Fig. S4. The results indicate that the pure AAPVA and P_{ADH} films exhibited high transparency but limited UV-blocking capability. In contrast, the P_{ADH}/P-3 film demonstrates an ~85.8 % transmittance at 600 nm with an optical transparency of 0.76 ± 0.16 , while blocking UV light in the 200–320 nm range, thereby exhibiting excellent UV-shielding performance. This improvement was attributed to the dense cross-linked structure and the presence of C=N bonds within the polymer network, which effectively absorbed UV radiation and minimized undesired reflection and scattering, resulting in a uniform refractive index and improved optical clarity [47]. Although the AAPVA/P-1 and AAPVA/P-5 films also maintained high transparency (~85.4 % and 87.9 %, respectively), their UV-shielding performances were comparatively lower. The surface and cross-sectional SEM images (Fig. S5) the P_{ADH}/AAPVA films exhibited smooth surfaces and densely packed microstructures, which contributed to their excellent optical appearance. To further illustrate the high transparency of the films, an AAPVA/P-3 film was placed over half of the image and remained clearly visible throughout the film (Fig. 4c). Overall, the combination of superior optical transparency and outstanding UV-blocking capability highlights the significant potential of the P_{ADH}/AAPVA films for applications in food packaging, biomedical devices, and other advanced material fields.

3.4. Stability and recyclability of P_{ADH}/AAPVA films

In addition to their exceptional mechanical properties and high transparency, water stability and chemical resistance are critical for the practical application of plastic alternatives. Owing to the abundance of hydrophilic functional groups in both AAPVA and P_{ADH}, these

materials inherently exhibit high water affinity and are readily soluble in water, limiting their practical applications. As shown in Fig. 5a and b, AAPVA exhibits a higher water contact angle than the other films because of the presence of acetoacetyl groups; however, it also displays an extremely high-water absorption rate of 3222 %. In contrast, the P_{ADH}/AAPVA films benefited from the densely crosslinked surface formed via Schiff base reactions, which significantly improved their water resistance. After 90s, the water contact angles of the P_{ADH}/P-1, P_{ADH}/P-3, and P_{ADH}/P-5 films were 44.4°, 46.9°, and 40.9°, respectively, with water absorption rates of 988 %, 877 %, and 1685 %. Notably, the water absorption rate of the P_{ADH}/P-3 film was reduced by 72.8 % compared to that of AAPVA, and its structural integrity was retained even after three months of immersion, demonstrating that the dense network structure and chemical modification improved water resistance. In contrast, the P_{ADH} and PGA/P-3 films dissolved completely in water after 24 h of immersion (Fig. S6). Furthermore, the water content analysis confirmed that the films maintained low moisture retention during routine storage, ensuring their functional stability (Table S4). The P_{ADH}/P-3 film also demonstrated excellent chemical resistance, retaining its original color, shape, and mechanical integrity even after three months of immersion in various commercially available organic solvents without visible deformation or degradation (Fig. 5c). The TGA and differential thermal gravimetry (DTG) curves (Fig. S7) revealed three distinct stages of mass loss occurring at 30–180 °C, 220–380 °C, and 380–500 °C, corresponding to the evaporation of absorbed and bound water, thermal degradation of P_{ADH} and AAPVA molecular chains, and decomposition of the dynamic hydrazone cross-linked network, respectively. These results confirmed that the P_{ADH}/AAPVA films possessed excellent thermal stability, ensuring their safety and reliability at elevated temperatures.

Unlike conventional non-recyclable thermoset materials, the P_{ADH}/AAPVA film series demonstrates excellent chemical recyclability owing to the dynamic and reversible nature of the acylhydrazone bonds [48]. To verify this property, a representative P_{ADH}/P-3 film was immersed in a 1 M HCl/H₂O solution and stirred at 50 °C for 24 h. As shown in Fig. 6a, the film completely degraded under these conditions. This degradation was attributed to the acid-catalyzed hydrolysis of the acylhydrazone bonds within the dynamic crosslinked network, leading to the breakdown of the film structure. The degradation solution was purified and freeze-dried to obtain a white solid powder. The recycled product was structurally characterized using ¹H NMR and FTIR spectroscopy (Fig. 6b and c). The ¹H NMR spectrum confirmed the presence of α (3.97 ppm), β (1.76–1.88 ppm), and γ (2.20 ppm) protons, indicating that the structural features of γ-PGA in the recycled P_{ADH} were retained. In addition, a signal at 1.46 ppm, corresponding to the methylene protons in ADH, was still observed, suggesting that the P_{ADH} structure remained largely intact. The FTIR spectrum of the newly formed film from recycled P_{ADH} showed the reappearance of the

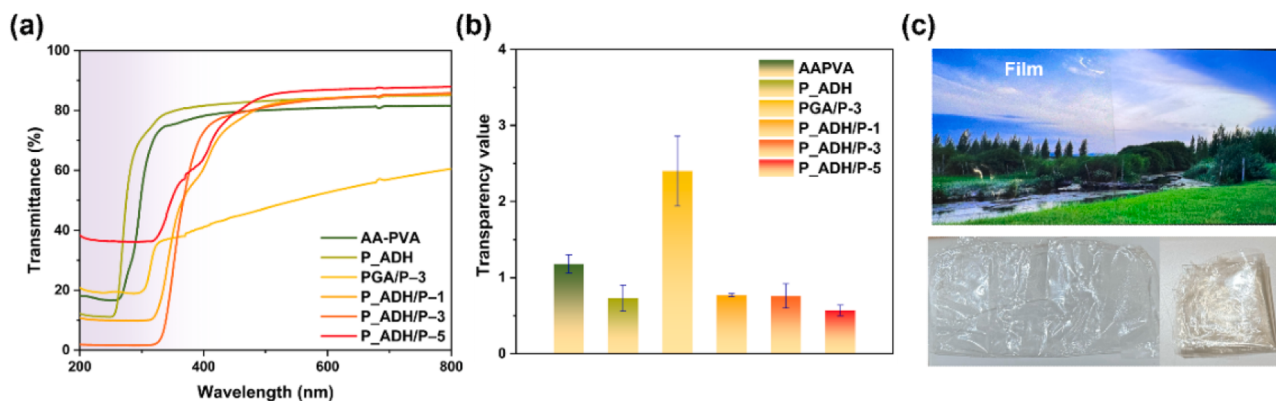


Fig. 4. (a) UV–visible transmittance spectra of different P_{ADH}/AAPVA films; (b) Transparency value of different P_{ADH}/AAPVA films at a wavelength of 600 nm; (c) Photographs of transparent P_{ADH}/P-3 film and large-scale P_{ADH}/P-3 film.

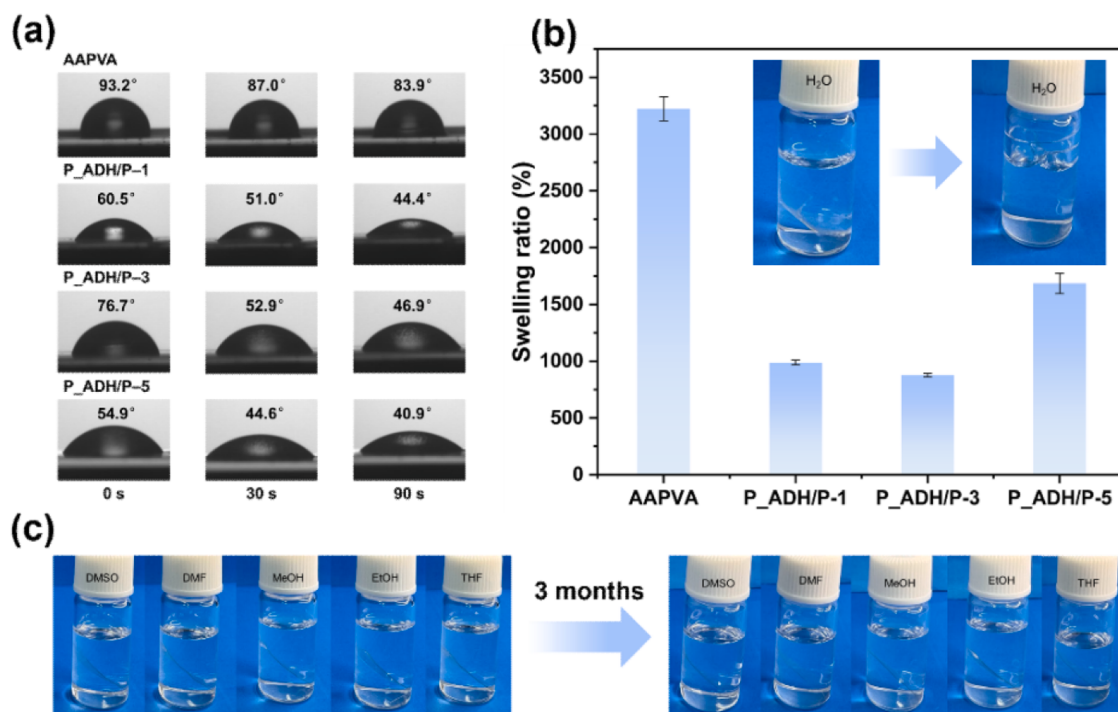


Fig. 5. (a) Water contact angles of P_ADH/AAPVA films; (b) Swelling ratio of P_ADH/AAPVA films; (c) Chemical stability of P_ADH/AAPVA films after immersion in organic solvents for three months.

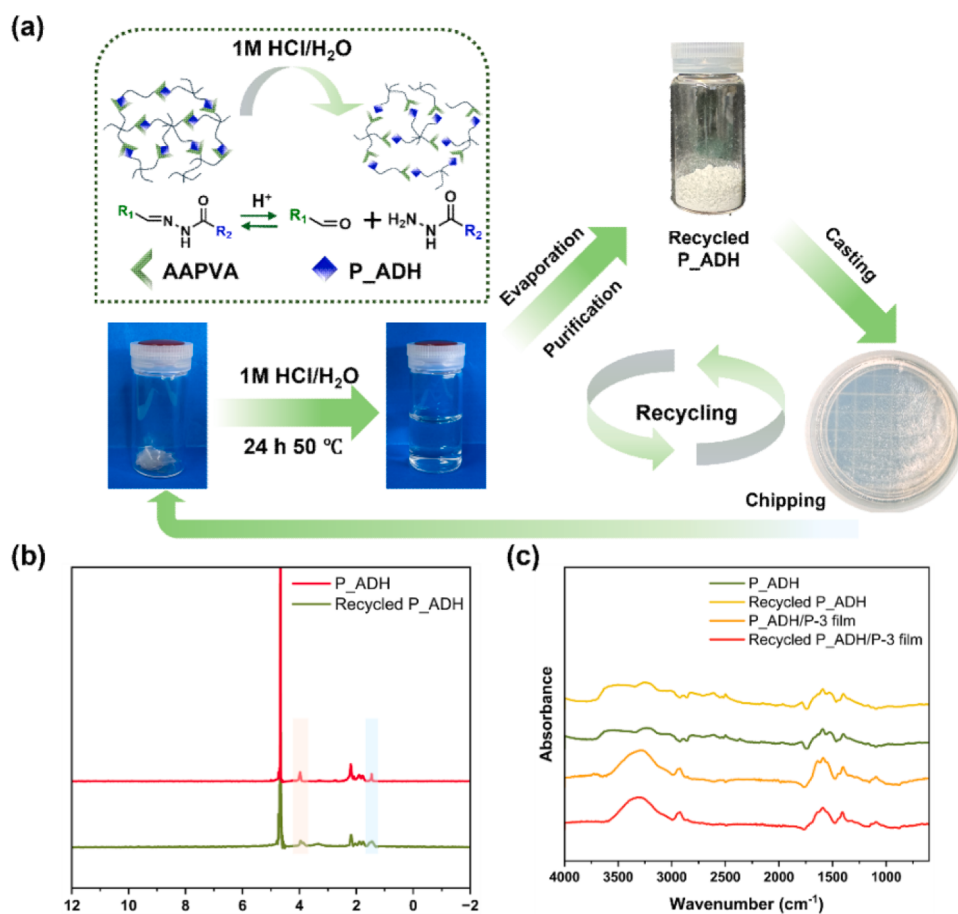


Fig. 6. (a) Chemical degradation and recycle of P_ADH/P-3 films in 1 M HCl/H₂O solution; (b) ¹H NMR spectra of P_ADH and recycled P_ADH; (c) FT-IR spectra of P_ADH, recycled P_ADH, P_ADH/P-3 film and recycled P_ADH/P-3 film.

characteristic C=N stretching band at 1640–1643 cm⁻¹, while the peak associated with the acetoacetyl group disappeared, confirming successful reconstruction of the acylhydrazone crosslinked network. Notably, the regenerated film retained approximately 30 % of its original tensile strength, which is comparable to those of some commercial plastic films (Fig. S8), demonstrating the practical feasibility of this recyclable system. Overall, the P-ADH/AAPVA films exhibited outstanding chemical recyclability owing to the reversible nature of the dynamic acylhydrazone bonds, offering an effective strategy for the development of degradable and recyclable high-performance bio-based thermoset materials.

4. Conclusion

In this study, γ -PGA was functionalized with ADH to produce P-ADH, which was subsequently crosslinked with AAPVA via a Schiff base reaction to form films containing dynamic acylhydrazone linkages. Among the various formulations, the P-ADH/P-3 film exhibited the highest tensile strength (123.5 ± 2.32 MPa) and Young's modulus (4.4 ± 0.022 GPa), along with a Tg of 106.2 °C, indicating mechanical robustness comparable to that of conventional high-performance plastics. In addition to their excellent mechanical performance, the P-ADH/AAPVA films exhibited outstanding optical transparency. Notably, the P-ADH/P-3 film exhibited UV-blocking capabilities, demonstrating its effectiveness as a UV-shielding material. These films also displayed excellent water resistance and chemical stability while maintaining their structural integrity when exposed to common organic solvents. Owing to the dynamic acylhydrazone bonds within the crosslinked network, the P-ADH/P-3 film was fully degraded in 1 M HCl/H₂O solution, confirming its chemical recyclability. The recovered P-ADH was reused to fabricate a new film, illustrating the circularity of the material system. Collectively, these attributes underscore the strong potential of the P-ADH/AAPVA films for smart packaging and other renewable materials, thereby advancing the development of sustainable polymer alternatives.

CRedit authorship contribution statement

Ying Yao: Writing – original draft, Methodology, Investigation, Conceptualization. **Yu-I Hsu:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Hiroshi Uyama:** Writing – review & editing, Supervision, Funding acquisition.

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.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.polydegradstab.2025.111450](https://doi.org/10.1016/j.polydegradstab.2025.111450).

Data availability

No data was used for the research described in the article.

References

- [1] P. Stoett, V.M. Scrich, C.I. Elliff, M.M. Andrade, N. de M. Grilli, A. Turra, Global plastic pollution, sustainable development, and plastic justice, *World Dev.* 184 (2024) 106756, <https://doi.org/10.1016/j.worlddev.2024.106756>.
- [2] G.R. Mong, H. Tan, D.D. Chin Vui Sheng, H.Y. Kek, B.B. Nyakuma, K.S. Woon, M.H. D. Othman, H.S. Kang, P.S. Goh, K.Y. Wong, A review on plastic waste valorisation to advanced materials: solutions and technologies to curb plastic waste pollution, *J. Clean. Prod.* 434 (2024) 140180, <https://doi.org/10.1016/j.jclepro.2023.140180>.
- [3] L. Wang, S. Chen, B. Yu, Poly- γ -glutamic acid: recent achievements, diverse applications and future perspectives, *Trends Food Sci. Technol.* 119 (2022) 1–12, <https://doi.org/10.1016/j.tifs.2021.11.009>.
- [4] V. Mohammadzadeh, N. Rahiman, H. Cabral, S. Quader, M.R. Zirak, M. E. Taghavizadeh Yazdi, M.R. Jaafari, S.H. Alavizadeh, Poly- γ -glutamic acid nanoparticles as adjuvant and antigen carrier system for cancer vaccination, *J. Control. Rel.* 362 (2023) 278–296, <https://doi.org/10.1016/j.jconrel.2023.08.049>.
- [5] B.S. Saharan, N. Kamal, P. Badoni, R. Kumar, M. Saini, D. Kumar, D. Sharma, S. Tyagi, P. Ranga, J. Parshad, C. Goyal, R. Kumar, M. Nehra, C.S. Sethi, J.S. Duhan, N.K. Mandal, Biopolymer and polymer precursor production by microorganisms: applications and future prospects, *J. Chem. Technol. Biotechnol.* 99 (2024) 17–30, <https://doi.org/10.1002/jctb.7524>.
- [6] M. Cai, Y. Han, X. Zheng, B. Xue, X. Zhang, Z. Mahmut, Y. Wang, B. Dong, C. Zhang, D. Gao, J. Sun, Synthesis of poly- γ -glutamic acid and its application in biomedical materials, *Materials* 17 (2024) 15, <https://doi.org/10.3390/ma17010015>.
- [7] I.-L. Shih, Y.-T. Van, M.-H. Shen, Biomedical applications of chemically and microbiologically synthesized poly(Glutamic Acid) and poly(Lysine), *Mini Rev. Med. Chem.* 4 (2004) 179–188, <https://doi.org/10.2174/1389557043487420>.
- [8] D. Dahiya, R. Chettri, P.S. Nigam, Chapter 25 - biosynthesis of polyglutamic acid (γ -PGA), a biodegradable and economical polyamide biopolymer for industrial applications, in: S. Das, H.R. Dash (Eds.), *Microbial and Natural Macromolecules*, Academic Press, 2021, pp. 681–688, <https://doi.org/10.1016/B978-0-12-820084-1.00026-0>.
- [9] N. Yang, Y. Wang, Q. Zhang, L. Chen, Y. Zhao, γ -polyglutamic acid mediated crosslinking PNIPAAm-based thermo/pH-responsive hydrogels for controlled drug release, *Polym. Degrad. Stab.* 144 (2017) 53–61, <https://doi.org/10.1016/j.polydegradstab.2017.07.028>.
- [10] R. Yang, X. Wang, S. Liu, W. Zhang, P. Wang, X. Liu, Y. Ren, X. Tan, B. Chi, Bioinspired poly (γ -glutamic acid) hydrogels for enhanced chondrogenesis of bone marrow-derived mesenchymal stem cells, *Int. J. Biol. Macromol.* 142 (2020) 332–344, <https://doi.org/10.1016/j.ijbiomac.2019.09.104>.
- [11] M. Wei, Y.-I. Hsu, T.-A. Asoh, M.-H. Sung, H. Uyama, Injectable poly(γ -glutamic acid)-based biodegradable hydrogels with tunable gelation rate and mechanical strength, *J. Mater. Chem. B* 9 (2021) 3584–3594, <https://doi.org/10.1039/D1TB00412C>.
- [12] I. Bajaj, R. Singhal, Poly (glutamic acid) – an emerging biopolymer of commercial interest, *Bioresour. Technol.* 102 (2011) 5551–5561, <https://doi.org/10.1016/j.biortech.2011.02.047>.
- [13] C. Yu, Z. Han, H. Sun, J. Tong, Z. Hu, Y. Wang, X. Fang, W. Yue, S. Qian, G. Nie, Balancing mechanical property and swelling behavior of bacterial cellulose film by in-situ adding chitosan oligosaccharide and covalent crosslinking with γ -PGA, *Int. J. Biol. Macromol.* 267 (2024) 131280, <https://doi.org/10.1016/j.ijbiomac.2024.131280>.
- [14] K. Chen, Z. Wu, Y. Liu, Y. Yuan, C. Liu, Injectable double-crosslinked adhesive hydrogels with high mechanical resilience and effective energy dissipation for joint wound treatment, *Adv. Funct. Mater.* 32 (2022) 2109687, <https://doi.org/10.1002/adfm.202109687>.
- [15] B.D.S. Silva, C.J. Ulhoa, K.A. Batista, M.C. Di Medeiros, R.R. da, S. Filho, F. Yamashita, K.F. Fernandes, Biodegradable and bioactive CGP/PVA film for fungal growth inhibition, *Carbohydr. Polym.* 89 (2012) 964–970, <https://doi.org/10.1016/j.carbpol.2012.04.052>.
- [16] H. Deng, J. Su, W. Zhang, A. Khan, M.A. Sani, G. Goksen, P. Kashyap, P. Ezati, J.-W. Rhim, A review of starch/polyvinyl alcohol (PVA) blend film: a potential replacement for traditional plastic-based food packaging film, *Int. J. Biol. Macromol.* 273 (2024) 132926, <https://doi.org/10.1016/j.ijbiomac.2024.132926>.
- [17] X. Huang, F. Wang, W. Hu, Z. Zou, Q. Tang, H. Li, L. Xu, Smart packaging films based on corn starch/polyvinyl alcohol containing nano SIM-1 for monitoring food freshness, *Int. J. Biol. Macromol.* 256 (2024) 128373, <https://doi.org/10.1016/j.ijbiomac.2023.128373>.
- [18] S. Maes, N. Badi, J.M. Winne, F.E. Du Prez, Taking dynamic covalent chemistry out of the lab and into reprocessable industrial thermosets, *Nat. Rev. Chem.* 9 (2025) 144–158, <https://doi.org/10.1038/s41570-025-00686-7>.
- [19] Z. Lei, H. Chen, S. Huang, L.J. Wayment, Q. Xu, W. Zhang, New advances in covalent network polymers via dynamic covalent chemistry, *Chem. Rev.* 124 (2024) 7829–7906, <https://doi.org/10.1021/acs.chemrev.3c00926>.
- [20] Z. Liu, Y. Tang, Y. Chen, Z. Lu, Z. Rui, Dynamic covalent adhesives and their applications: current progress and future perspectives, *Chem. Eng. J.* 497 (2024) 154710, <https://doi.org/10.1016/j.cej.2024.154710>.

- [21] Y. Jia, J. Qian, S. Hao, S. Zhang, F. Wei, H. Zheng, Y. Li, J. Song, Z. Zhao, New prospects arising from dynamically crosslinked polymers: reprogramming their properties, *Adv. Mater.* 36 (2024) 2313164, <https://doi.org/10.1002/adma.202313164>.
- [22] Z. Wang, C. Xu, L. Qi, C. Chen, Chemical modification of polysaccharides for sustainable bioplastics, *TRECHEM* 6 (2024) 314–331, <https://doi.org/10.1016/j.trechm.2024.04.009>.
- [23] M. Ismael, B. Parveen, S.S. Dogar, K. Aftab, K. Abbas, K.S. Munawar, Comparing green and conventional methods for Schiff base synthesis and unveiling environmental stability applications: a review, *J. Coord. Chem.* 77 (2024) 921–959, <https://doi.org/10.1080/00958972.2024.2362344>.
- [24] M.N. Khin, M. Easani, T. Aziz, A. Shami, N.K. Alharbi, F. Al-Asmari, L. Lin, Schiff's base crosslinked gelatin-dialdehyde cellulose film with gallic acid for improved water resistance and antimicrobial properties, *Food Hydrocoll.* 166 (2025) 111331, <https://doi.org/10.1016/j.foodhyd.2025.111331>.
- [25] H. Zhou, X. Zhang, G. Zhou, M. Demir, Z. Lei, W. Zhang, X. Wang, Water-mediated synthesis of full-biomass vitrimer with enhanced moldability, recyclability, and biodegradability, *ACS Sustain. Chem. Eng.* 12 (2024) 6952–6959, <https://doi.org/10.1021/acssuschemeng.3c08467>.
- [26] S. Yan, T. Wang, L. Feng, J. Zhu, K. Zhang, X. Chen, L. Cui, J. Yin, Injectable In situ self-cross-linking hydrogels based on poly(l-glutamic acid) and alginate for cartilage tissue engineering, *Biomacromolecules* 15 (2014) 4495–4508, <https://doi.org/10.1021/bm501313t>.
- [27] G. Liu, L. Wang, Y. He, L. Wang, Z. Deng, J. Liu, D. Peng, T. Ding, L. Lu, Y. Ding, J. Zhang, P. Liu, K. Cai, Polydopamine nanosheets doped injectable hydrogel with nitric oxide release and photothermal effects for bacterial ablation and wound healing, *Adv. Healthc. Mater.* 10 (2021) 2101476, <https://doi.org/10.1002/adhm.202101476>.
- [28] X. Ma, T. Xu, W. Chen, H. Qin, B. Chi, Z. Ye, Injectable hydrogels based on the hyaluronic acid and poly (γ -glutamic acid) for controlled protein delivery, *Carbohydr. Polym.* 179 (2018) 100–109, <https://doi.org/10.1016/j.carbpol.2017.09.071>.
- [29] Z. Zheng, J. Sun, J. Wang, S. He, Y. Huang, X. Yang, Y. Zhao, C.-Y. Yu, H. Wei, A negative feedback bionic hydrogel reverses damaged cartilage microenvironment and induces targeted BMSCs differentiation for cartilage regeneration, *Chem. Eng. J.* 473 (2023) 145228, <https://doi.org/10.1016/j.cej.2023.145228>.
- [30] J. Tie, H. Liu, J. Lv, B. Wang, Z. Mao, L. Zhang, Y. Zhong, X. Feng, X. Sui, H. Xu, Multi-responsive, self-healing and adhesive PVA based hydrogels induced by the ultrafast complexation of Fe³⁺ ions, *Soft Matter* 15 (2019) 7404–7411, <https://doi.org/10.1039/C9SM01346F>.
- [31] X. Sun, T. Fujimoto, H. Uyama, Fabrication of a poly(vinyl alcohol) monolith via thermally impacted non-solvent-induced phase separation, *Polym. J.* 45 (2013) 1101–1106, <https://doi.org/10.1038/pj.2013.18>.
- [32] J. Ren, X. Dong, Y. Duan, L. Lin, X. Xu, J. Shi, R. Jia, D. Wu, X. He, Synthesis and self-healing investigation of waterborne polyurethane based on reversible covalent bond, *J. Appl. Polym. Sci.* 139 (2022) 52144, <https://doi.org/10.1002/app.52144>.
- [33] Z. Fu, S. Guo, C. Li, K. Wang, Q. Zhang, Q. Fu, Hydrogen-bond-dominated mechanical stretchability in PVA films: from phenomenological to numerical insights, *Phys. Chem. Chem. Phys.* 24 (2022) 1885–1895, <https://doi.org/10.1039/D1CP03893A>.
- [34] R. Li, K. Zhang, G. Chen, B. Su, M. He, Stiff, self-healable, transparent polymers with synergetic hydrogen bonding interactions, *Chem. Mater.* 33 (2021) 5189–5196, <https://doi.org/10.1021/acs.chemmater.1c01242>.
- [35] H. Liu, H. Yang, K. Zhu, F. Peng, L. Guo, H. Qi, Facile fabrication of a polyvinyl alcohol-based hydrophobic fluorescent film via the Hantzsch reaction for broadband UV protection, *Mater. Horiz.* 9 (2022) 815–824, <https://doi.org/10.1039/D1MH01783G>.
- [36] Y. Zhao, Y. Huang, W. Hou, T. Zhang, Y. Zhang, Y. Wang, X. Bai, High-performance vitrimer films containing acylhydrazone dynamic covalent bonds, *J. Polym. Sci.* 61 (2023) 3266–3275, <https://doi.org/10.1002/pol.20230353>.
- [37] S.A. Acharjee, B. Gogoi, P. Bharali, V. Sorhie, B.W. Alemtoshi, Recent trends in the development of polyhydroxyalkanoates (PHAs) based biocomposites by blending with different bio-based polymers, *J. Polym. Res.* 31 (2024) 98, <https://doi.org/10.1007/s10965-024-03947-z>.
- [38] J.-M. Raquez, Y. Habibi, M. Murariu, P. Dubois, Polylactide (PLA)-based nanocomposites, *Prog. Polym. Sci.* 38 (2013) 1504–1542, <https://doi.org/10.1016/j.progpolymsci.2013.05.014>.
- [39] M.J. Mochane, S.I. Magagula, J.S. Sefadi, T.C. Mokheba, A review on green composites based on natural Fiber-reinforced polybutylene succinate (PBS), *Polymers* 13 (2021) 1200, <https://doi.org/10.3390/polym13081200>.
- [40] J.E. Puskas, Y. Chen, Biomedical application of commercial polymers and novel polyisobutylene-based thermoplastic elastomers for soft tissue replacement, *Biomacromolecules* 5 (2004) 1141–1154, <https://doi.org/10.1021/bm034513k>.
- [41] H. Wang, X. Liu, M. Wu, Y. Huang, Construction of multiple crosslinked networks for the preparation of high-performance lignin-containing cellulose nanofiber reinforced polyvinyl alcohol films, *Int. J. Biol. Macromol.* 259 (2024) 129061, <https://doi.org/10.1016/j.ijbiomac.2023.129061>.
- [42] F. Liu, X. Zhang, X. Xiao, Q. Duan, H. Bai, Y. Cao, Y. Zhang, M. Alee, L. Yu, Improved hydrophobicity, antibacterial and mechanical properties of polyvinyl alcohol/quaternary chitosan composite films for antibacterial packaging, *Carbohydr. Polym.* 312 (2023) 120755, <https://doi.org/10.1016/j.carbpol.2023.120755>.
- [43] M. Hou, B. Xia, R. Qu, J. Dong, T. Li, S. Wang, Y. Wang, W. Dong, Preparation of the double cross-linking carbon dots-polyvinyl alcohol-carboxymethyl cellulose composite film for food active packaging application, *Int. J. Biol. Macromol.* 273 (2024) 132939, <https://doi.org/10.1016/j.ijbiomac.2024.132939>.
- [44] X. Li, C. Liu, X. Quan, Y. Zhang, S. Wang, S. Zhao, J. Yang, Y. Feng, W. He, K. Guo, Mechanically strong, reprocessable and chemically recyclable furan-based poly (acylhydrazone)s materials with hydrogen-bonding networks, *Eur. Polym. J.* 221 (2024) 113584, <https://doi.org/10.1016/j.eurpolymj.2024.113584>.
- [45] C. Bao, J. Liu, Y. Yin, J. Liu, Z. Xin, Reprocessable and chemically recyclable poly (acylhydrazone-imine) covalent adaptable networks with enhanced mechanical strength and creep resistance, *Polym. Chem.* 15 (2024) 172–180, <https://doi.org/10.1039/D3PY01054F>.
- [46] X. Zhang, H. Zhang, G. Zhou, Z. Su, X. Wang, Flexible, thermal processable, self-healing, and fully bio-based starch plastics by constructing dynamic imine network, *Green Energy Environ.* 9 (2024) 1610–1618, <https://doi.org/10.1016/j.gee.2023.08.002>.
- [47] X. Zhu, C. Zhou, Z. Pan, J. Yuan, M. Pan, Multifunctional waterborne polyurethane with robustness, adhesiveness, and self-healability based on a dual cross-linked network containing multiple dynamic bonds, *ACS Appl. Polym. Mater.* 6 (2024) 13389–13400, <https://doi.org/10.1021/acscpm.4c02212>.
- [48] H. Ding, J. Wang, P. Yu, H. He, H. Wang, W. Zhang, L. Wang, Y. Lei, B. Yu, Rapidly recyclable, monomer recovery and flame-retardant bio-based polyimine networks, *Chem. Eng. J.* 481 (2024) 148024, <https://doi.org/10.1016/j.cej.2023.148024>.