

# Preparation and Properties of Uracil Ket One Modified Polyethylenimine Adhesive

Guoxing Lin<sup>1</sup>, Shuxi Shan<sup>1</sup>, Wenfei Wang<sup>1</sup>, Wei Cheng<sup>1</sup>, Yu Yuan<sup>2</sup>, Yuhan Li<sup>2,\*</sup>

<sup>1</sup> Luoyang Ship Material Research Institute, Luoyang, 471023, China

<sup>2</sup> College of Chemistry, Zhengzhou University, Zhengzhou, 450001, China

\*Email: liyuhan@zzu.edu.cn

---

## Abstract

In this study, 2-amino-4-hydroxy-6-methylpyrimidine (UPy) sequence was successfully introduced into polyethylenimine matrix by polymerization reaction, and UPy modified polyethylenimine supramolecular adhesive (PEI-UPy) was prepared. The successful synthesis of PEI-UPy adhesive was confirmed by FTIR test and <sup>1</sup>HNMR test. Through DSC analysis, rotary rheometer test and tensile shear strength test, it is proved that the adhesive can not only be used for bonding of various matrix materials, but also can be used as epoxy resin curing agent, and the shear strength of the adhesive on the steel plate can be increased to 6.2 MPa. The adhesive prepared in this study is reversible, and it is a kind of environment-friendly adhesive with wide application prospect.

## Keywords

Reversible Adhesive; Bonding Property; Uracil Ketone; Hydrogen Bond.

---

## 1. Introduction

With their unique ability to bond different substrates together, polymer adhesives are an effective alternative to traditional structural joining methods such as resistance welding, braze welding or other mechanical reinforcement techniques, and play a vital role in the industrial sector and in everyday life [1-2]. Traditional structural adhesives have high cohesion strength, such as epoxy resin, acrylic resin, polyurethane and other adhesives[3-4], which can form a strong bonding ability on the bonded substrate, but usually form an irreversible cross-linked network after curing, facing the problem of difficult cleaning and non-reusable. Non-structural adhesives (such as pressure-sensitive adhesives, hot melt adhesives, etc.) avoid the emission of volatile organic compounds due to their solvent-free, but they cannot be widely used because of their poor bonding strength to the bonded substance [5]. Therefore, the development of green recyclable adhesives [6-7] is of great significance for material development, environmental protection and resource conservation, while seeking mechanical properties and making them reversible.

The new reversible adhesive refers to the re-adhesive performance after bonding and disattaching, driven by itself or external conditions (temperature, light, pH, etc.), and can be used for repeated bonding. When the reversible adhesives bond the substrate, there are different driving modes, which are mainly divided into two categories according to the different reversible bonding modes, namely covalent bond and non-covalent bond link [8]. Covalent bond bonding is achieved by forming dynamic and reversible chemical bond bonding within or between molecules. Dynamic covalent bond can give strong mechanical properties to adhesives, but strong external environment stimulation is required to promote the dissociation of dynamic bond. Non-covalent bond links mainly include hydrogen bonds [9-10], metal coordination [11-12], host-guest interactions [13], and electrostatic interactions [14-15]. Polymer cross-linked networks formed through non-covalent interactions are

characterized by high thermodynamic stability, fast kinetic reversibility, and low non-covalent bond binding energy, which caused the hot melt adhesive exhibits multiple reusability and relatively mild bonding conditions.

Non-covalent bonding is a common way to develop reversible adhesives. Hydrogen bonding is directional, selective and reversible, and is formed through the interaction between proton donor and proton acceptor. The overall shear strength of reversible adhesives cannot reach the level of reactive adhesives when the interfacial bonding is only based on hydrogen bonding. How to increase the strength of hydrogen bond basic sequence in polymer networks and make them exhibit special stimulus response is particularly important for the structural design of reversible adhesives. In this paper, a reversible adhesive with high bonding strength was synthesized by grafting ethylene imine with 2-amino-4-hydroxy-6-methylpyrimidine (UPy) sequence and adjusting the ratio of raw materials. The microstructure and macroscopic properties of the synthetic material were evaluated and analyzed.

## 2. Experimental Part

### 2.1 Raw Materials and Test Instrument

**Table 1.** Main experimental materials

| Name                                 | Specification | Manufacturer                                     |
|--------------------------------------|---------------|--|
| Polyvinylimine (Mn=600)              | 99%           | Shanghai Titan Technology Co., LTD               |
| Polyvinylimine (Mn=1200)             | 99%           | Shanghai Titan Technology Co., LTD               |
| Polyvinylimine (Mn=1800)             | 98%           | Shanghai Titan Technology Co., LTD               |
| 2-amino-4-hydroxy-6-methylpyrimidine | 98%           | Shanghai Titan Technology Co., LTD               |
| Hexamethylenediisocyanate (HDI)      | 98%           | Shanghai Aladdin Biochemical Technology Co., LTD |
| N, N-dimethylformamide (DMF) 99%     | AR            | Sinopharm Group Chemical reagent Co., LTD        |

**Table 2.** Main test instruments

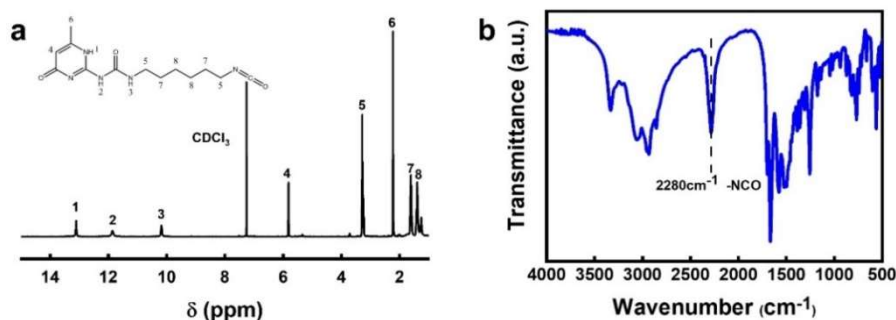
| Name   | Specification | Manufacturer                                      |
|--|---------------|---|
| Smart thermostatic heating sleeve            | DRT-SX        | Zhengzhou Great Wall Science and Trade Co., LTD   |
| Rotary vane vacuum pump                      | 2XZ-4         | Sichuan Nanguang Vacuum Technology Co., LTD       |
| Multi-function electric mixer                | DW-2          | Gongyi Yuhua Instrument Co., LTD                  |
| Electric thermostatic air drying oven        | XMTD-8222     | Gongyi Yuhua Instrument Co., LTD                  |
| Electric thermostatic vacuum drying oven     | DHG-9041A     | Shanghai Jinghong Experimental Equipment Co., LTD |
| Universal material testing machine           | TH-8100A      | Suzhou Tuobo Machinery Equipment Co., LTD         |
| Fourier infrared spectrum                    | ALPHA II      | LTD   |
| Nuclear magnetic resonance hydrogen spectrum | Advance       | Germany, Bruker Co., LTD                          |
| Tensile testing machine                      | 400MHz        | Germany, Bruker Co., LTD                          |
| Differential scanning calorimetry            | TH-8100A      | Suzhou Tuobo Machinery Equipment Co., LTD.        |
| Rotary rheometertesting machine              | DSC 204 F1    | Germany, Neutch Co., LTD                          |
|  | Physica       | Austria, Anton Paar Co., LTD                      |
|  | MCR301        |   |

### 2.2 Synthesis Method of PEI-UPy

#### (1) Synthesis of HDI-UPy

2-amino-4-hydroxy-6-methylpyrimidine (40mmol, 5.00 g) was mixed with 6 times the amount of HDI (240mmol, 40.5g) in a round-bottomed flask and stirred at 100°C under nitrogen for 24h. After the reaction is over, the filter cake is cleaned with a large amount of n-hexane to remove the unreacted

HDI. The product was dried in a vacuum oven at 50°C for 12 h to obtain white powder (11.16g, 95% yield).



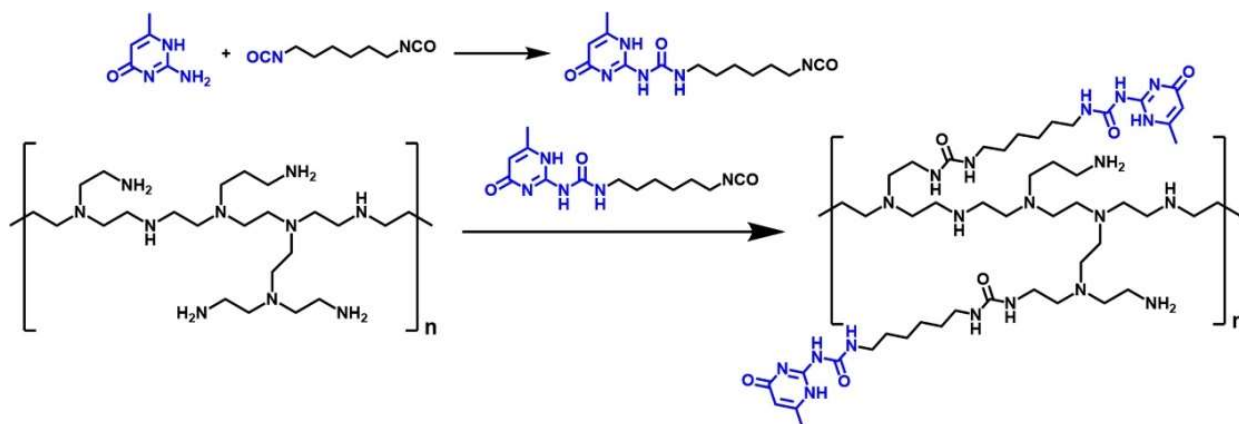
**Figure 1.** (a) <sup>1</sup>H-NMR spectrum of HDI-UPy monomer; (b) Infrared spectrum of HDI-UPy monomer

## (2) Synthesis of PEI-UPy

The experimental steps were as follows: HDI-UPy and polyethylenimine were mixed into a round-bottom flask according to different mass ratios, DMF was used as the solvent, and the mixture was stirred at 80°C under nitrogen atmosphere for several hours until the powder disappeared in the round-bottom flask and a clear and transparent solution was obtained, and the mixed solution was poured into the polytetrafluoron mold. The mold is placed in an oven at 80°C for 12h, and then dried in a vacuum oven at 80°C for 12h to remove the residual solvent, after which PEI-UPy adhesive is obtained. The raw material ratio of PEI-UPy adhesive is shown in Table 3. The resultant route is shown in Figure 2.

**Table 3.** The ratio of raw materials to synthesize PEI-UPy

| Sample          | PEI | UPy |
|-----------------|-----|-----|
| PEI-1200-25%UPy | 3   | 1   |
| PEI-1200-33%UPy | 2   | 1   |
| PEI-1200-40%UPy | 1.5 | 1   |
| PEI-1200-47%UPy | 1.1 | 1   |
| PEI-600-47%UPy  | 1.1 | 1   |
| PEI-1800-47%UPy | 1.1 | 1   |



**Figure 2.** Synthesis roadmap of PEI-UPy

### 3. Results and Discussion

#### 3.1 Characterization of PEI-UPy Adhesive

Figure 3(a) shows the FTIR spectrum of PEI-UPy adhesive, and the results are similar with different mass ratios. Taking PEI-47%UPy as an example to analyze its infrared spectrum, the infrared characteristic peak of -NCO (2280  $\text{cm}^{-1}$ ) in HDI-UPy has disappeared, indicating that HDI-UPy is completely reacted. The stretching vibration peak of C=O in the UPy sequence appears at 1561  $\text{cm}^{-1}$ , and the intensity of the absorption peak increases with the increase of UPy mass fraction. Take PEI-47%UPy as an example to analyze its nuclear magnetic hydrogen spectrum. As shown in Figure 3(b), the characteristic peaks of the UPy sequence are 10.08 ppm, 8.01 ppm and 7.18 ppm at a, b and c, respectively. The results of FTIR and  $^1\text{H-NMR}$  showed the successful synthesis of PEI-UPy adhesive.

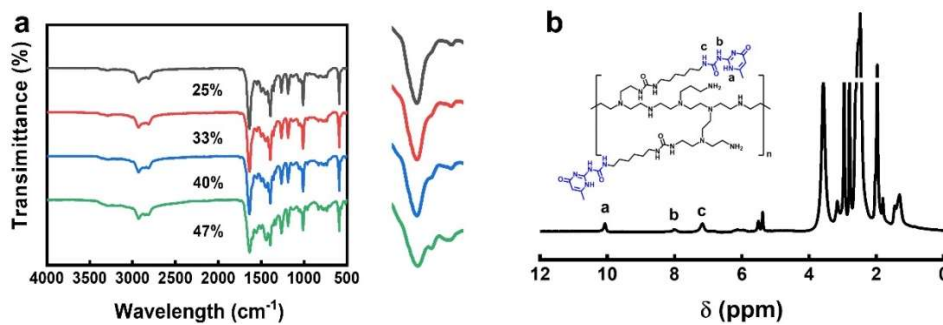


Figure 3. (a) Infrared spectrum of PEI-UPy;(b)  $^1\text{H-NMR}$  spectrum of PEI-UPy

#### 3.2 Differential Scanning Calorimetry Analysis

As shown in Figure 4, DSC tests were performed on PEI-600-47%UPy, PEI-1200-47%UPy and PEI-1800-47%UPy, respectively, to study the microstructure of adhesives through the relationship between heat flow rate and temperature. With the relative molecular weight of polyethylenimine (PEI) decreased,  $T_g$  increased significantly, the reason is the increase of hard segment proportion makes the intermolecular interaction force. In DSC curves, none of the synthesized polyethylenimine adhesives had melting endothermic peaks, indicating that PEI-UPy was in an amorphous state and was an inelastic solid at room temperature, which was conducive to achieving high strength bonding effect.

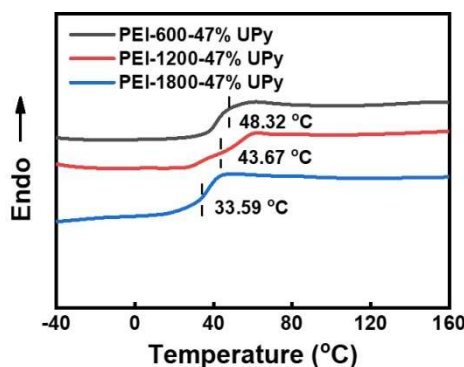


Figure 4. DSC curve of PEI-UPy

#### 3.3 Rheological Behavior Analysis

The rotational rheological test was carried out under very low strain (1%), and the viscoelastic behavior of PEI-UPy adhesive was analyzed with PEI-47%UPy as an example. The energy storage modulus reflects the rigidity of the material, and the loss modulus represents the viscosity of the material. As shown in Figure 5(a), the loss modulus of PEI-47%UPy is significantly greater than the

elastic modulus in the entire temperature scanning range, which means that the viscosity of PEI-47%UPy is its basic characteristic. Figure 5(b) shows the frequency scan curve at room temperature. In the low frequency region, the energy storage modulus is higher than the loss modulus, indicating that the current oscillation can not destroy the bulk phase structure of the associated state of the UPy sequence. With the increase of frequency,  $G'' > G'$ , which indicates that the associated hydrogen bonds in the polymer sample are broken and gradually converted from a viscoelastic solid to a viscoelasticliquid.

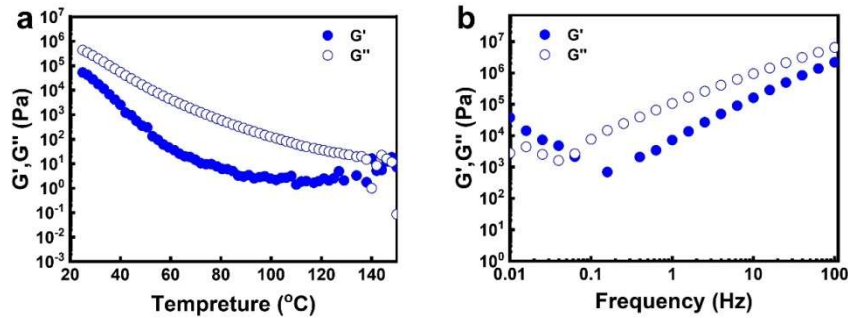


Figure 5. Rheological curve of PEI-1200-47%UPy

### 3.4 Adhesive Property Analysis

The adhesion properties of PEI-1200-47%UPy were evaluated by shear strength test. PEI-1200-47%UPy is placed between two steel plates to make a sandwich structure. The substrate and adhesive film were fixed together with clamps and placed separately in the oven at 80°C for different times. When the bonding time was increased from 5 min to 0.5 h, 1 h and 2 h, the bonding strength is increased from 0.9 MPa to 1.0 MPa, 1.25 MPa and 2.4 MPa, respectively. When the bonding time was adjusted to 4 h, the bonding strength of PEI-47%UPy decreases to 2.0MPa. The reason is that under the condition of heating, the movement of the polymer chain is accelerated, the viscosity is reduced and the fluidity is enhanced, and the glue is spilled during the extrusion process, which reduces the amount of adhesive at the bonding interface, resulting in a decrease in the bonding strength. PEI-1200-47%UPy adhesive can be heated at 80°C for 2 h to fully infiltrate the surface of the steel plate to form a good bonding effect.

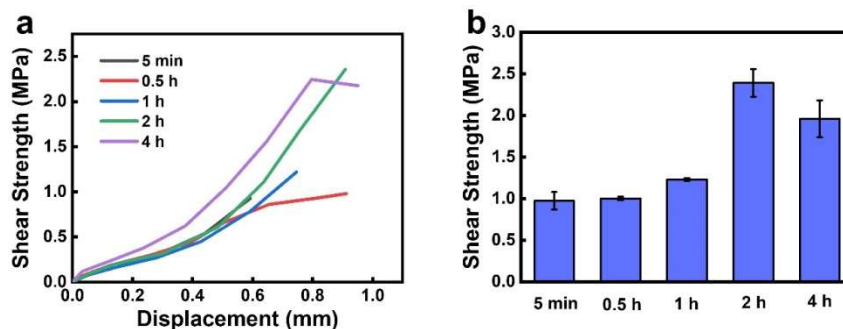


Figure 6. PEI-1200-47%UPy adhesive: (a) bonding strength-displacement curve with steel plate at different times; (b) the corresponding shear strength

In order to study the applicability of PEI-1200-47%UPy adhesive to different substrates, the lap shear experiments were carried out on different substrates. For metal materials, the adhesion strength of steel plate and aluminum alloy is 2.4MPa and 0.7MPa, respectively. For non-metallic materials, PEI-1200-47%UPy can also achieve better bonding effect, such as: epoxy resin, PET and PVC, its bonding strength is 1.7 MPa, 0.8 MPa and 0.6 MPa, respectively. A reasonable reason behind the adhesion of PEI-1200-47%UPy to different substrates is that the UPy sequence can have non-covalent interaction

with different substrates to form hydrogen bonds. As a result, PEI-1200-47%UPy adhesives show a wide range of applicability and can be tightly bound to different substrates.

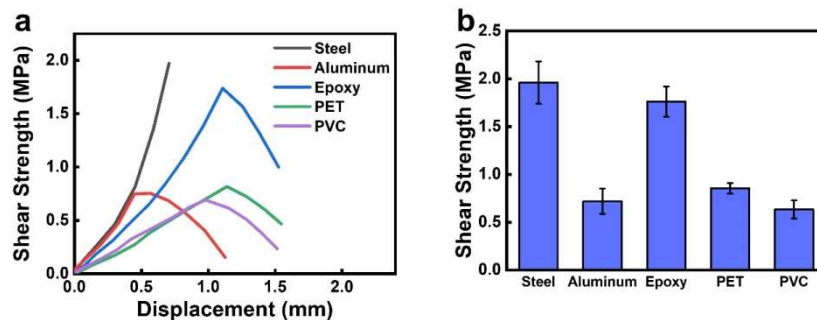


Figure 7. PEI-1200-47%UPy adhesive: (a) bonding strength-displacement curve with different substrate; (b) the corresponding shear strength

Although PEI-47%UPy adhesive can be used for bonding a variety of substrates, the bonding strength is far from meeting the needs of daily life and industrial production. PEI-1200 aliphatic polyamines can be used as curing agent of epoxy resin. A large number of active hydrogen of primary and secondary amines open the epoxy group and make the linear resin become a tough network structure. Epoxy resin 331 and PEI-1200 were evenly mixed and applied on the bonding area of the steel plate according to the mass ratio of 1.5:1, and then bonded, fixed with clamps, cured at 80°C for 2 h, and adjusted at room temperature for 24 h to perform shear strength test. The shear strength-displacement curve is shown in Figure 9. The lap shear strength of Epoxy resin 331 steel plate is 2.2MPa. Under the same conditions with PEI-1200-47%UPy curing Epoxy resin 331, due to the quadruple hydrogen bond with high cohesion energy, the lap shear strength of the steel plate will increase significantly up to 6.2MPa. It was concluded that PEI-1200-47%UPy can be used as a potential curing agent for epoxy resins.

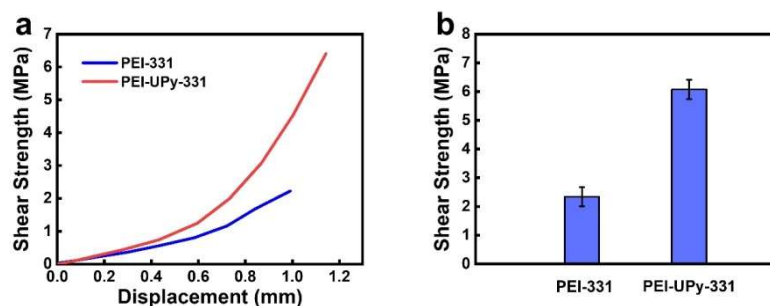


Figure 8. PEI-1200-47%UPy adhesive: (a) bonding strength-displacement curve of cured epoxy; (b) the corresponding shear strength

#### 4. Conclusion

Using 2-amino-4-hydroxy-6-methylpyrimidine (UPy) as raw materials, PEI-UPy with adhesive properties was synthesized according to different mass ratios. The synthesis step is simple, environmentally friendly, low temperature processing molding (80°C~100°C), the bonding condition is mild (80°C, 2h), and the bonding effect can be formed on a variety of substrates, such as: epoxy resin, PET and PVC. PEI-1200-47%UPy shows the best bonding performance, the bonding strength of the lapping steel plate is 2.4MPa, and it can also be used as a new epoxy resin curing agent to strengthen and toughen the effect. After curing, the shear strength of the epoxy resin adhesive on the steel plate can be increased to 6.2MPa. The adhesive prepared in this study is reversible, and it is a kind of environment-friendly adhesive with wide application prospect.

## References

- [1] Y. Ma, Z. Kou, Y. Hu, J. Zhou, Y. Bei, L. Hu, Y. Zhou, "Research advances in bio-based adhesives," *International Journal of Adhesion and Adhesives*, vol. 126, pp. 103444, 2023. <https://doi.org/10.1016/j.ijadhadh.2023.103444>.
- [2] N. T. Tran, A. J. Boyer, D. B. Knorr, "Multiple local hydroxyl groups as a way to improve bond strength and durability in structural adhesives," *The Journal of Adhesion*, vol. 98, no. 12, pp. 1834-1854, 2022.
- [3] R. Ciardiello, G. Belingardi, B. Martorana, V. Brunella, "Physical and mechanical properties of a reversible adhesive for automotive applications," *International Journal of Adhesion and Adhesives*, vol. 89, pp. 117-128, 2019. <https://doi.org/10.1016/j.ijadhadh.2018.12.005>.
- [4] Y.F. Wu, Y. Huang, "Research Progress of Room Temperature Cured Heat-resistant Adhesive," *Development and Application of Materials*, vol. 25, no. 6, pp. 88-93, 2010. DOI: 10.19515/j.cnki.1003-1545.2010.06.023.
- [5] G. Wang, Y. Liu, B. Zu, D. Lei, Y. Guo, M. Wang, X. Dou, "Reversible adhesive hydrogel with enhanced sampling efficiency boosted by hydrogen bond and van der Waals force for visualized detection," *Chemical Engineering Journal*, vol. 455, pp. 140493, 2023. <https://doi.org/10.1016/j.cej.2022.140493>.
- [6] K. Bashandeh, A. Marchert, U. Takayuki, A. A. Polycarpou, J. Meyer, P. Lan, "The effect of surface texturing on thin film reversible adhesive bond strength," *International Journal of Adhesion and Adhesives*, vol. 107, pp. 102829, 2021. <https://doi.org/10.1016/j.ijadhadh.2021.102829>.
- [7] Y. Cui, L. Yin, X. Sun, N. Zhang, N. Gao, G. Zhu, "A Universal and Reversible Wet Adhesive via Straightforward Aqueous Self-Assembly of Polyethylenimine and Polyoxometalate," *ACS Applied Materials & Interfaces*, vol. 13, no. 39, pp. 47155-47162, 2021. <https://doi.org/10.1021/acsmi.1c14231>.
- [8] M. Chen, Y. Wu, B. Chen, A. M. Tucker, A. Jagota, S. Yang, "Fast, strong, and reversible adhesives with dynamic covalent bonds for potential use in wound dressing," *PNAS*, vol. 119, no. 29, pp. e2203074119, 2022. <https://doi.org/10.1073/pnas.2203074119>.
- [9] D. W. Balkenende, R. A. Olson, S. Balog, C. Weder, L. Montero de Espinosa, "Epoxy Resin-Inspired Reconfigurable Supramolecular Networks," *Macromolecules*, vol. 49, no. 20, pp. 7877-7885, 2016. <https://doi.org/10.1021/acs.macromol.6b01491>.
- [10] D. W. Balkenende, C. A. Monnier, G. L. Fiore, C. Weder, "Optically responsive supramolecular polymer glasses," *Nature Communications*, vol. 7, no. 1, pp. 10995, 2016. <https://doi.org/10.1038/ncomms10995>.
- [11] T. Nakamura, Y. Takashima, A. Hashidzume, H. Yamaguchi, A. Harada, "A metal-ion-responsive adhesive material via switching of molecular recognition properties," *Nature Communications*, vol. 5, no. 1, pp. 4622, 2014. <https://doi.org/10.1038/ncomms5622>.
- [12] S. C. Grindy, R. Learsch, D. Mozhdehi, J. Cheng, D. G. Barrett, Z. Guan, N. Holten-Andersen, "Control of hierarchical polymer mechanics with bioinspired metal-coordination dynamics," *Nature Materials*, vol. 14, no. 12, pp. 1210-1216, 2015. <https://doi.org/10.1038/nmat4401>.
- [13] Y. Ahn, Y. Jang, N. Selvapalam, G. Yun, K. Kim, "Supramolecular Velcro for Reversible Underwater Adhesion," *Angewandte Chemie International Edition*, vol. 52, no. 11, pp. 3140-3144, 2013. <https://doi.org/10.1002/anie.201209382>.
- [14] G. G. Leisk, T. J. Lo, T. Yucel, Q. Lu, D. L. Kaplan, "Electrogelation for Protein Adhesives," *Advanced materials*, vol. 22, no. 6, pp. 711-715, 2010. <https://doi.org/10.1002/adma.200902643>.
- [15] M. Comí, G. Lligadas, J. C. Ronda, M. Galià, V. Cádiz, "Adaptive bio-based polyurethane elastomers engineered by ionic hydrogen bonding interactions," *European Polymer Journal*, vol. 91, pp. 408-419, 2017. <https://doi.org/10.1016/j.eurpolymj.2017.04.026>.