学 位 論 文 内 容 の 要 旨
Abstract of Doctoral Dissertation

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Fast Underwater Adhesion of Hydrogels by Multi-Scale Design
(マルチスケール設計によるハイドロゲルの高速水中接着)

Adhesion has long been studied, and early efforts mainly focused on the contact between stiff materials. Recently the emerging great progress on soft materials has been made, and adhesion that involves a soft material especially soft and wet materials start attracting attention. Hydrogel, one kind of typical soft and wet material, has promising applications in diverse areas, especially wet environments including tissue engineering, wound dressing, bio-medical devices, and underwater soft robotics. When it comes to adhesion in these wet environments, many of the mechanical properties which showed significant effects on the strength of adhesion, are compromised. Understanding the underwater contact behaviors of hydrogels will help design adhesives for various applications in wet or underwater environments. In this thesis, the hydrogels with dynamic bonds are chosen as underwater adhesives to be studied and designed. And the results have revealed that hydrogels with dynamic bonds can achieve outstanding underwater adhesion performance by promoting draining efficiency of water film at the contact interfaces and choosing polymers with proper dynamic bonds. The thesis consists of 6 chapters. In **Chapter 1**, general introductions are discussed. **Chapter 2**, basic concepts on adhesion and wetting behaviors of liquids are briefly introduced, and a review on the advancement on underwater adhesion is enlightened.

In **Chapter 3**, tough hydrogels adhesives with fast, strong, and reversible underwater adhesion, are developed based on a multiscale design. Realizing a tough underwater adhesive with fast and good contact as well as strong and reversible adhesion will cater to many applications such as re-usable sheets for wound dressing and anti-slippery for wall-climbing robotics. However, there are some challenges since many factors which showed significant effects on the strength of adhesion, are compromised when it comes to adhesion in these wet environments. Hydrogels usually show poor adhesion to other surfaces in their fully swollen state owing to the strong hydration ability of hydrophilic polymer strands, which prevents the formation of molecular bridges at the interface. Firstly, underwater surface contact evolution in situ is explored by a home-made set-up using critical refraction. The measurements were carried out in an aqueous solution using Shimadzu Autograph to control the approaching and retracting process. Due to the slightly difference of refraction critical angle between water and hydrogels, the contact and no contact part at the interface can be distinguished by a prism. It was found that water can be easily trapped at the interface by the flat soft gels. And the trapped water at the interfaces not only reduces the true contact area but also acts as a flaw for initiating the debonding at the interface. The result reveals that underwater contact evolution process can be well monitored by the home-made set-up, which is a helpful technique for studying the underwater contact behaviors of hydrogels. Since it has been illustrated that water at the interface needs a very long time to be drained out, and is also easily got trapped by the soft hydrogels adhesives. To address these challenges, a cling-fish inspired macro-scale surface structure and nano-scale dynamic bonds are combined. The surface structure serves to accelerate water drainage, to prevent water trapping and to delay crack propagation; the dynamic bonds of the gel serves to form reversible bridges at the interface and to dissipate a significant amount of energy in the bulk during detachment. The designed tough adhesives show outstanding adhesion performance on both soft and hard substrates including glass plate, soft gels, and tissue. The strategy of combining macroscale surface engineering and microscale dynamic bonds is applicable to various recently developed tough hydrogels based on hydrogen, ionic bonds and other dynamic bonds.

In **Chapter 5**, the matrix softness, surface structure size effect, a long time contact effect and surface hydrophobic ability are further discussed. Polyampholyte (PA) hydrgels with a single hexagonal facet on the surface were prepared. And the underwater adhesion on the flat PA hydrogels is measured by the probe tack test. Meanwhile, crack propagation during the debonding process was

record by a camera. The results show that, the underwater adhesion of the hydrogels with smaller facet (decreasing the diameter while keeping the height of the facet), is higher than the bigger one in short contact time. With the increasing of contact time, the gap between the strength become smaller. Moreover, the recorded video also showed how the crack was initiated and propagated.

Based on the results of **Chapter 3**, it can be seen that the smaller the facet is, the faster the water drainage is. In order to develop adhesives with much smaller facet as well as efficient water drainage system, in **Chapter 5**, the porous hydrogels consisting of two kind of polymers with opposite charges are prepared for studying the underwater adhesion. The porous structure of the hydrogels results from the phase separation of polyelectrolyte complexation (PEC) triggered by salts exchange. It was found that the porous hydrogels can instantly adhere to diverse substrates including metal plate, glass plate, silicone rubber, aluminium film and beef heart under water. The surface contact evolution observed clearly showed that the porous hydrogels can drain water much more efficiently than the nonporous PA hydrogels. And there is almost no water drop trapped at the interface, which reduces the flaws at the interfaces. Further study on the underwater adhesion of porous hydrogels showed that, there is a strong suction effect during the debonding process. The suction effect not only increases the adhesion strength, but also contributes to the bulk energy dissipation. To identify this effect, a series of tack tests including changing the debonding speed, size of the sample, and in viscous polyethylene glycol (PEG) solution, were conducted. All the results illustrates the suction effect during debonding process.

In **Chapter 6** the concluding remarks are included based on the overall work.