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Summary of Doctoral Dissertation

博士の専攻分野の名称　博士 (生命科学)　氏　名　　チャンチャル クマル ロイ
Degree requested Doctor of Life Science Applicant's name **CHANCHAL KUMAR ROY**

学 位 論 文 題 名
Title of Doctoral Dissertation

Adhesion of Polyampholyte Hydrogels
(ポリアンフォライトハイドロゲルの接着)

In last few decades, hydrogels have gained much attention as adhesive material in industrial and biomedical fields. They are the most preferred candidate for commercial water-based adhesive material, which will greatly reduce the emission of volatile organic compounds (VOC) and will incur less hazardous impact on human and climate compared to organic solvent based adhesives. As bioadhesive, hydrogel based adhesive materials have great potential due to its compatibility with living tissues, antifouling property, shock absorbing capacity and softness. However, most hydrogels have poor adhesive property with different substrates, which have greatly limited their practical applications. High dielectric screening effect of water and swelling of hydrogel are thought to be responsible for its weak adhesive property. In this dissertation, it is proposed that the adhesion problem of hydrogels can be solved by using polyampholyte system.

The polyampholytes (PAs) are the polymeric macromolecular system consisting of positive and negative monomers. When PAs are synthesized at very high concentrations, the opposite charges form dynamic ionic bonds of intra- and interchains. The interchain ionic bonds serve as physical crosslinking to form hydrogels. Owing to such dynamic ionic bonding structures, some PA hydrogels show specific properties, such as deswelling in water, strong viscoelasticity, high toughness, and self-healing. Beside these bulk properties, the dynamic ionic bonds of PA hydrogels on their surface are expected to create energetically favorable attractive interacting sites through the formation of polarization-induced ion–bond complex formation with charged or polar species of counter surfaces, which can initiate the adhesion in wet environment.

To test the idea of making adhesive hydrogels from PA systems, the author has prepared some PA hydrogels (P(NaSS-*co*-DMAEA-Q)) from their monomers; sodium 4-vinyl-benzenesulfonate (NaSS) and (2-acryloyloxyethyl)-trimethylammonium chloride quaternary (DMAEA-Q) and studied their adhesion behavior. In **Chapter 3**, adhesive behavior of P(NaSS-*co*-DMAEA-Q) hydrogel has been investigated for its biomedical use. It was observed that a neutral charged balanced PA hydrogel can join tissue, hydrogels and glass plate. Investigation of the adhesion of the PA hydrogels over different charged and uncharged hydrogels (details in full dissertation) indicates that PA hydrogel attach over the surface of biological tissues through its self-adjustable surface. A self-adjustable surface is such a surface which can offer its species for the formation of attractive interaction depending on substrate charges through dynamic reorganization process. Through the self-adjustable surface of PA hydrogel they can initiate sufficient number of adhesive interacting sites over the surface of tissue for strong adhesion.

In **Chapter 4**, it has been demonstrated that a lightly crosslinked P(NaSS-*co*-DMAEA-Q) hydrogel can form a strong adhesive joint with glass substrates. A small piece (5 cm^2) of hydrogel is enough to hold a large weight (1 kg). A systematic study has been performed to determine and compare the critical energy release rate (G_c) for adhesion of PA hydrogels. The estimated G_c, ~116 J/m^2 over glass plate is much higher than the adhesion energy of PDMS elastomers that is in the range of 10-30 J/m^2. The large value of adhesion energy appears in PA hydrogel adhesive due to strong adhesive interaction at interface and

additional viscoelastic energy dissipation in the bulk material. In dry adhesion of elastomers, G_c mostly relies upon weak non-specific van der Waals forces and the elastic deformation of the bulk material. Strong interfacial contact formation and viscoelastic energy dissipation occur in PA hydrogel adhesive due to the presence of dynamic ionic bonding of monomeric units inside the material. The ionic bonds of polymer chains can switch their ion-pair for the formation of attractive adhesive interaction sites at interface. Additionally, the exchange of their ion-pair can provide a way for sacrificing some of their bonds and dissipate energy during deformation. Further investigation has been performed to check the influence of bulk viscoelastic energy dissipation of PA hydrogel on the adhesion by observing the shear rate effect on the adhesion. The G_c of PA hydrogel is found to be increased with the increase of the shear velocity, which should be attributed to the increased energy dissipation at high velocity.

In **Chapter 5**, the adhesion behavior of a neutral PA hydrogel (P(NaSS-*co*-DMAEA-Q)) has been investigated for its industrial use. In this chapter, the preparation conditions of PA hydrogel have been explained for achieving maximum adhesion. From shear adhesion measurements over glass substrate, it was observed that the adhesion of P(NaSS-*co*-DMAEA-Q) hydrogel depends on dialysis time of the as-prepared hydrogels. The composition of the PA hydrogels plays an important role in its adhesive behavior. A neutral charged balanced PA hydrogel has better adhesion over glass substrate than charged imbalanced hydrogels. Adhesion behavior has been checked over a wide range of substrates and environmental conditions. It has been observed that P(NaSS-*co*-DMAEA-Q) hydrogel works well over hydrophilic substrates than hydrophobic substrates. A systematic study has been performed to find out the critical hydrophilicity of substrate for strong adhesion. P(NaSS-*co*-DMAEA-Q) hydrogel can attach two glass plates even in under-water. Under-water tack test over glass substrate has been performed to check the influence of environmental condition on the adhesion behavior of PA hydrogels. The results indicate that PA hydrogel can work as adhesive over a wide range of pH and temperature. Although it has been observed that presence of salt weakens the adhesive strength of PA hydrogels, but it can works well in sea water condition.

Finally in **Chapter 6**, we proposed a strategy to develop sticky and tough supramolecular hydrogels. The idea is to use polymer that form abundant of dynamic bonds, such as ionic bond, hydrogen bond, etc. The dynamic bonds have several effects on the mechanical properties of the gel. They will serve as sacrificial bonds and enhance the toughness of the gel by dissipating energy at deformation. At the interface, they will form physical adsorption by switching the bond pair from intra-gel to interface. Presence of dynamic bonds also suppresses the swelling of the gel, which favors the polymer strands adsorption on surface. As a result, such kind of hydrogels will exhibit excellent adhesion along with a high toughness.

In brief, in this dissertation the factors involving the strong adhesion of hydrogels have been identified through the systematic study of the adhesion behavior of P(NaSS-*co*-DMAEA-Q) hydrogels and a novel strategy for developing supramolecular adhesive hydrogels has been provided to implement hydrogel-based adhesive materials practically in different branches of material science.