

氏名	孫 曼兮		
授与学位	博士 (工学)		
学位授与年月日	令和 03 年 03 月 23 日		
学位授与の根拠法規	学位規則第 4 条第 1 項		
研究科専攻	秋田県立大学大学院システム科学技術研究科 博士後期課程総合システム科学専攻		
学位論文題目	Development of Tough Poly(vinyl alcohol) Hydrogels and their Applications (強靱な PVA ハイドロゲルの創製およびその応用に関する研究)		
指導教員	教授 <u>邱 建輝</u>		
論文審査委員	主査 教授 <u>邱 建輝</u>		
	副査 教授 <u>尾藤 輝夫</u>	教授 <u>倪 慶清</u>	(信州大学)
	准教授 <u>中山 昇</u>		(信州大学)

## 論文内容要旨

A Hydrogel is a kind of material with a three-dimensional(3D) network structure. The hydrophilic structure of which renders them capable of holding large amounts of water in their three-dimensional networks. Hydrogel is also being used for everyday applications, such as tofu, pectin, contact lens. Moreover, there are many living things that possess supporting tissues in nature, supporting tissues play an essential role in the body, and include both hard tissues (bone) and soft tissues (tendon, ligament, skin, fascia etc.). Hydrogels have been used as one of the most common tissue engineering scaffolds over the past two decades due to their ability to maintain a distinct 3D structure, to provide mechanical support for the cells in the engineered tissues, and to simulate the native extracellular matrix. Nowadays, there are many investigations of hydrogels on many fields, e.g., biology technology, environmental science, and sensor. Literature on this material was found to be expanding, especially in the scientific areas of research.

Conventional hydrogels show weak mechanical properties which greatly limits the application of hydrogel. Most recently, the designed hydrogels, according to the energy dissipation principle,

overcome the low mechanical strength, poor toughness, and limited recoverability of common hydrogels and show excellent mechanical properties. Recently, a lot of progress has been made in the construction of high-strength hydrogels, mainly as follows ideas: 1) Increase the interaction between the chains of polymer hydrogels and develop synergistic hydrogels, such as chemical crosslinking, hydrophobic interaction, hydrogen bond crosslinking, and ionic bond crosslinking, etc., using two or more of them to construct synergistic hydrogels; 2) In terms of spatial structure, build multiple networks between polymer networks to develop toughness hydrogels; 3) The combination of the above two forms. These construction ideas are currently one of the hot spots and development trends in the preparation of high-strength hydrogels.

In order to develop high-strength hydrogels that match the mechanical strength required by the application (modulus:  $1\sim 10^2$  MPa, water content 50%~90 wt%, tensile strength  $1\sim 10^2$  MPa, compressive strength  $10\sim 10^3$  MPa). Based on the above understanding, in this study, three kinds of high-strength hydrogels were prepared through different design.

In chapter 1, the research background of hydrogel was introduced, including hydrogel types, hydrogel applications, research status of tough hydrogel and the purpose of this study.

In chapter 2, the properties of experiment materials, as well as experimental methods and characterizations were presented.

In chapter 3, a biobased monomer, i.e., epoxidized soybean oil (ESO), was used to modify Poly(vinyl alcohol) (PVA) to formulate a series of ESO-crosslinked PVA (PVA-ESO) hydrogels. Infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and thermogravimetric analyses (TGA) were used to confirm the formation of PVA-ESO copolymer. Scanning electron microscope (SEM) revealed that the formed PVA-ESO hydrogels presented a distinct porous structure while no obvious pores were observed on pure PVA hydrogel. The tensile strength of PVA-ESO hydrogels increased up to 2.4 times when compared to that of pure PVA hydrogel. Dynamic mechanical analysis (DMA) indicated that the elastic properties of PVA-ESO hydrogels are better than that of pure PVA hydrogel, which are similar to that of natural cartilage. In summary, the modification of PVA with ESO can improve the thermal stability and mechanical properties of the hydrogels due to the

improved cross-linking degree and the formed hydrophobic association.

In chapter 4, a tough double crosslinked hydrogel (DC-Gel) was obtained from PVA/Poly(acrylic acid) (PAA) by facilely visible light triggered polymerization and subsequent salt impregnation. The ionic DC-Gels have been proofed with a high toughness (up to 19 MJ/m<sup>3</sup>), recovery property, self-healing ability and conductivity. The rubber-like flexible network and homogeneous interconnected phase of the ionic DC-Gels were certificated by scanning electron microscope and thermodynamics analysis. The tensile strengths and stretches at break of the ionic DC-Gels closely depended on the acrylic acid (AA) content. Cyclic tensile test results showed that the ionic DC-Gels with the optimized AA content (PVA: AA=1:5) afforded a good comprehensive mechanical properties and recoverable energy dissipation; the resilience and stress of the hydrogel at a strain of 150% maintained over 85% and 1.8 MPa, respectively. When the ionic DC hydrogel was applied to assemble a strain sensor, the excellent resilience is beneficial for precisely and quickly distinguishing the deformation of hydrogel-based sensor. This part provides a potential approach for the development of ion hydrogels with stretchable, self-healing, high resilience and strain-sensitive properties.

In chapter 5, a composite double network ionic hydrogel (CDN-gel) was obtained by the facile visible light triggered polymerization of AA, PVA, and hydrolyzed triethoxyvinylsilane (TEVS) and subsequent salt impregnation. The resulting CDN-gels exhibited high toughness, recovery ability, and notch-insensitivity. The tensile strength, fracture elongation, Young's modulus, and toughness of the CDN-gels reached up to ~21 MPa, ~700%, ~3.5 MPa, and ~49 MJ/m<sup>3</sup>, respectively. The residual strain at a strain of 200% was only ~25% after stretch-release of 1000 cycles. These properties will enable greater application of these hydrogel materials, especially for the fatigue resistance of tough hydrogels, as well as broaden their applications in damping.

In chapter 6, general conclusions of study were summarized. The prepared hydrogels based on PVA in this study possessed thermal stability, instantaneous recovery, anti-fatigue, and high toughness.

論文提出者氏名	孫 曼兮
論文題目	Development of Tough Poly(vinyl alcohol) Hydrogels and their Applications (強靱な PVA ハイドロゲルの創製およびその応用に関する研究)
指導教員	邱 建輝
論文審査委員	主査 教授 <u>邱 建輝</u> ㊦ 副査 教授 <u>尾藤 輝夫</u> ㊦      教授 <u>倪 慶清</u> ㊦ (信州大学) 准教授 <u>中山 昇</u> ㊦ (信州大学)

## 論文審査結果要旨

本論文は、力学特性の優れたポリビニルアルコール (PVA) ハイドロゲルの開発を目的として、高性能ハイドロゲルの創製方法と性能評価を行い、その応用性も検討したものである。本論文は全 6 章で構成されている。

第 1 章は緒論として、ハイドロゲルに関する既存の研究から本研究の背景を述べ、研究の目的を示している。第 2 章では材料および試験方法として、ハイドロゲルの作製方法およびそれらの力学性能の評価方法、内部構造などの分析方法について説明している。第 3 章では、両親媒性 PVA-ESO (エポキシ化大豆油) 高分子を簡単な開環反応によって合成している。400 kPa~1.4 MPa の高い引張強さ、350~400% の破断伸びおよび 2.5 MJ/m<sup>3</sup> の靱性を示すハイドロゲルを作製しており、疎水性相互作用や水素結合などの相互作用を駆逐することで、優れた弾性特性を示し、生体材料に適用できる可能性を示すゲルを創製している。第 4 章では、簡単なワンポット可視光誘発重合とイオン結合によって、高回復性ハイドロゲルを作製している。作製したゴム状ハイドロゲルは、最大 7 MPa の高い引張強さ、500~950% の破断伸びおよび最大 1.25 MPa の弾性率を示している。また、塩化リチウム水溶液を含浸させることにより二重網目構造を持つ高靱性ハイドロゲルを可視光誘発重合により得ており、靱帯や腱、筋肉などの複雑な変形をリアルタイムでマッピングするセンサとしての利用可能性を示唆している。第 5 章では、多重犠牲結合をハイドロゲル系に導入して、高い力学性能のハイドロゲルを作製している。作製したゴム状ハイドロゲルは、引張強さが 21 MPa、弾性率が 3.5 MPa、靱性が 49 MJ/m<sup>3</sup> という優れた力学特性を有し、さらに切欠き感受性が低く、優れた振動減衰特性を有することを明らかにしている。第 6 章は結論であり、研究結果をまとめている。

本論文は、学術的および工学的価値が高く、その研究成果は、高性能ハイドロゲルへの応用および新規医用材料の開発に寄与することが期待できる。また、研究業績として、査読付国際学術論文 3 編、国際会議 1 件を公表している。

よって、本論文は博士 (工学) の学位論文として合格と認める。