초청강연

《 PHYSICOCHEMICAL STUDIES ON POLY(VINYL ALCOHOL) HYDROGELS 》

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Polymeric hydrogel is composed of three-dimensional network from polymer chains which are insoluble in any solvent. There are basically two types of method for gel preparation.[1,2] One is the chemical crosslinking method and the other is the physical crosslinking. In the former case, functional groups on polymer chains are bound with crosslinking agent or radiation to form insoluble gels. On the other hand, the latter physical method introduces physical crosslinks between polymer chains though intermolecular force. De Gennes[2] has proposed the following three types as the structure formed by intermolecular force ; (1) helical structure from plural polymer chains, (2) crystallite, and (3) nodule from block copolymer. The gel formation from (1) has been found mostly in natural polymers such as protein and polysaccharide, whereas gel formation from the intermolecular force of (2) has been applied to the synthetic polymers, for example, poly(vinyl alcohol) (PVA),[3] polyethylene,[4] polypropylene,[5] polylactide,[6] nylon 6,[7] and ethylene-vinyl alcohol copolymer.[8]

PVA is hydrophilic crystalline polymer which has hydroxy groups. It is predicted that high ultimate strength and modulus fiber will be produced from PVA, because PVA has planar zig-zag structure similar to polyethylene. The viscosity of aqueous PVA solution is known to increase, gradually setting to a gel through hydrogen bonding among the PVA segments when left standing at room temperature.

Gelation of PVA solution has been studied by many research groups and various methods have been proposed for PVA gelation.[9~21] Recently, physical crosslinking methods without any use of chemical crosslinking agent have attracted much attention because they allow us to prepare high strength and high water content PVA hydrogels. This paper reviews a series of investigations concerning formation of PVA hydrogel by physical crosslinking without any crosslinking agent and their physicochemical properties.

1. Formation of PVA Hydrogel by Low Temperature Crystallization of Aqueous PVA Solutions.[22]

PVA hydrogels with high strength and high water content were prepared by freezing the concentrated aqueous PVA solutions below their freezing points, followed by slow crystallization of frozen polymer above their freezing points. When a 30 wt% aqueous solution of PVA with the degree of polymerization of 1750 and the degree of saponification of 99.5 mol% was frozen at −20℃ for 24 hr and then slowly thawed at 5 ℃ for 10 hr, a hydrogel was obtained, which exhibited the tensile strength and elongation became 35 kg/c m^2 and 400%, respectively, for a

PVA gel prepared by thawing the frozen solution at 20℃ for 3hr. X-ray and SEM studies revealed that the gels had a semi-crystalline and micro-porous structure.

2. Preparation of Trasparent PVA Hydrogels with High Water Content.[23-26]

The transparent PVA hydrogels with high water content and high strength were prepared by low temperature crystallization of PVA solutions in mixed solvents consisting of water and a water-miscible organic solvent. The strength and transparency of PVA hydrogel were dependent on the type of organic solvent, the mixing ratio of water/organic solvent and crystallization temperature. A mixed solvent from water/dimethyl sulfoxide(DMSO) resulted in the highest transparency and the highest tensile strength among the water/organic solvent combination studied at the lowest crystallization temperature. The tensile strength and the elongation of PVA hydrogel prepared from water/DMSO=20/80(w/w) were about 2 and 1.5 times as high as that of PVA hydrogel prepared from water alone. This result is related to the unique solvency of DMSO to PVA.

3. PVA Hydrogel as Soft Contact Lens Materials.[27-30]

A new type of soft contact lens was developed from the PVA hydrogel prepared by the low temperature crystallization technique using a water/DMSO mixed solvent. The PVA contact lens material had a water content of 78 wt% and a tensile strength of 50 kg/cm ^{2}, five times as strong as that of commercial PHEMA soft contact lens. The amount of proteins adsorbed to the PVA soft contact lens material was half to one thirtieth of that the conventional soft contact lenses. Histological and scanning electron microscopic observation of rabbit eyes which had worn the PVA soft contact lens for 12 weeks showed no difference in corneal epithelium and cell arrangement in the corneal epithelium from wearing eyes.

4. High Strength and Modulus PVA Fiber.[31,32]

Gel spinning of PVA was attempted from the PVA dope prepared from the mixture of water and DMSO. The water/DMSO=20/80(w/w) mixture and methyl alcohol were found to be the best solvent for the spinning dope and coagulant, respectively. PVA fiber with the highest strength and Young's modulus were obtained from the undrawn gel fibers when subjected to hot two-stage drawing under conditions such as to produce maximum drawability. Furthermore, higher draw ratios of PVA fiber were attained for 6 wt% dope by lowering the coagulating temperature of methyl alcohol. In the present work, the highest tensile strength(2.8 GPa) and the highest Young's modulus(64 GPa) were realized, when the spinning dope was prepared from PVA with DP of 5,000 and water/DMSO(20/80, w/w) mixed solvent to have the PVA concentration of 6 wt%, the coagulating temperature of methyl alcohol was −20℃, and two-stage drawing was carried out at 160(first) and 200℃(second). The PVA fiber prepared under this gel spinning condition could be elongated to 45 times draw ratio. The very high drawability of PVA fibers obtained from the water/DMSO(20/80, w/w) mixture dope was ascribed to the

ability of the water /DMSO mixture to promote gelation.

5. Preparation of PVA Hydrogels with Low Water Contents.[33]

PVA hydrogel with low water contents could be prepared by low temperature crystallization of PVA solution in water/DMSO mixtures, followed by high temperature annealing after drying and subsequent reswelling with water. The annealing resulted in an increase of crystallinity of PVA and also, unexpectedly, an increase of the water content of hydrogels when the degree of polymerization(DP) of PVA was 11,000. The tensile strength and dynamic modulus of PVA hydrogels increased with annealing, irrespective of DP of PVA, but always at the sacrifice of the water content of the hydrogel. In addition to the mechanical strength, the hardness and wear resistance of PVA hydrogels were improved by lowing the water content. The wear resistance of PVA hydrogels was greatly affected by DP of PVA when compared at a similar water content. The highest tensile strength(20MPa) and the highest dynamic modulus(180 MPa) were obtained when hydrogel was prepared from PVA with DP of 11,000 and annealed at 140℃ for 24 hr. The water content of this hydrogel was 16wt% and remained unchanged even if kept in water at 37℃ for 85 days. The wear resistance of this hydrogel was higher than that of ultrahigh-molecular-weight, high-density polyethylene.

6. Development of an Artificial Articular Cartilage.[34-37]

We have attempted to develop an artificial articular cartilage on the basis of a new viewpoint of joint biomechanics in which lubrication and load-bearing mechanisms of natural and artificial joints are compared. We investigated PVA-hydrogel(PVA-H) which has been recognized as a rubber-like gel and have improved the mechanical properties of this gel through a new synthetic process.

In this study we report the biocompatibility and various mechanical properties of the new, improved PVA-H from the aspect of its usefulness as artificial articular cartilage. As regards the lubrication, we measured the change of thickness and fluid pressure of the gap formed between a glass plate and the specimen under loading and found that the PVA-H had a thicker fluid film under higher pressure than polyethylene (PE). The momentary stress transmitted through the specimen revealed that PVA-H had a lower peak stress and a longer duration of sustained stress than PE, suggesting a better damping effect. The wear factor of PVA-H was approximately five times as large as that of PE. Histological findings of the articular cartilage and synovial membranes around the PVA-H implanted for 8-52 weeks showed neither inflammatory nor degenerative changes. The PVA-H artificial articular cartilage could be attached to the underlying bone using an osteochondral composite material. Although there remain still some problems to solve, PVA-H seems to be a very interesting and promising material which meets the requirements of artificial articular cartilage.

7. Development of an Artificial Intervertebral Disc.[38,39]

Spine which consists of many vertebral bodies and intervertebral discs, is required to have not only supportability but also movability. Recently in the case of disc disorders, spinal fusion is often performed. However, to recover both supportability and movability, it is desirable to develop an artificial intervertebral disc. We have been paying attention to PVA-Hydrogel as a material for artificial intervertebral disc. Accordingly, we have attempted to develop canine artificial intervertebral disc using PVA-Hydrogel, in order to develop human artificial intervertebral disc. In this study, mechanical properties of canine artificial intervertebral disc were investigated to obtain fundamental data for human artificial intervertebral disc development.

By performing axial compression and torsional tests of cadaver motion segments and those in which canine artificial intervertebral disc was implanted, their compressive and torsional stiffness were measured comparatively. As a result, compressive and torsional stiffness of test specimen I and II (L5-6) showed about 31% and 24% lower value than those of control, respectively. This decrease might be due to a combination of surgical insult to the annulus and decoritication of adjacent vertebral bobies, shape for artificial intervertebral disc. But, this problem is possible to solve by changing water content and degree of polymerization for PVA-Hydrogel.

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