High strength of poly(acrylic acid)-chitosan-silica hydrogel composites

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Abstract

In this study, poly(acrylic acid)-chitosan-silica (PAA-Ch-Si) hydrogels to be used as a substitute for articular cartilage were prepared by UV polymerization. These hydrogels formed an interpenetrating network structure through the mixing of PAA with chitosan solutions. The physical properties of the prepared hydrogels were characterized, including FT-IR, water content, morphology, mechanical strength, friction coefficient, rheological and thermal analyses. The physical properties including elastic modulus, maximum compressive strength, toughness, and cross-linking density, increased by incorporation of silica into PAA-Ch hydrogels. PAA-Ch-Si hydrogel has high water content, low friction coefficient, and high tanδ, which is feasible to be used as a substitute for cartilage repair.

1. Introduction

Joint pain is a major cause of disability in middle-aged and older people. Pain usually results from degeneration of the joint's cartilage due to primary osteoarthritis or from trauma causing loss of cartilage. Since cartilage shows very little tendency for self-repair, these injuries are maintained for years and can eventually lead to further degeneration.

Chitosan, a high molecular weight polysaccharide from chitin, is one of the most abundant biomass sources in the world. Reactive $-NH_2$ and $-OH$ of chitosan are convenient for graft polymerization of hydrophilic vinyl monomers, making this is an efficient way to acquire hydrogels with novel properties [1]. In particular, its chemical structure is analogous with diverse glycosaminoglycans found in articular cartilage. Chitosan has been widely used as a scaffold for cartilage regeneration [2].

Nano-sized silica particles were recently fused onto ceramic whiskers and used as fillers to reinforce dental resin to extend their use to large stress-bearing restorations. While plain whiskers did not significantly strengthen the resin matrix, nano-silica fusion roughened the whisker surfaces and enhanced whisker retention inthe matrix, resulting in strong composites with substantially increased strength and toughness [3].

Most of hydrogels derived from either natural or synthetic sources suffer from lack of mechanical strength. In this study, high strength poly(acrylic acid)-chitosan-silica (PAA-Ch-Si) hydrogels were prepared by UV polymerization for cartilage.

2. Materials and Method

2-1. *Materials*

Acrylic acid (AAc) monomer was purchased from Merck (Germany). *N,N'*–methylenebisacrylamide (NMBA) was purchased from Fluka (USA). The initiator, ammonium peroxodisulfate (APS), was obtained from Wako (Japan). Glutaraldehyde (GA) was obtained from Merck (Germany). Chitosan was obtained from C&B (Taiwan). Silica (colloidal, 20–30 nm) was supplied by Sunstar Chemical.

2-2. *Methods*

A series of PAA-based hydrogels were prepared by UV polymerization. To prepare PAA hydrogels, 24.71 ml acrylic acid (AAc) solution was added into 40 ml distilled water and stirred continuously; then, 0.0616 g cross-linking agent (NMBA), 0.091 g initiator (APS) and cross-linking agent (GA) were added into the above solution and stirred continuously until they were completely dissolved. The solution of the mixture was then injected into a circular glass mold with a diameter of 1.5 cm. Subsequently, the glass mold was exposed to UV light (2200 W, MHIOEBS, Hexman, Taiwan) for an hour. After polymerization, the gel was immersed into a large amount of double-distilled water for three days in order to remove the unreacted monomer. During the washing cycle, the distilled water was regularly replaced with fresh water. To prepare PAA-Ch and PAA-Ch-Si hydrogels, the desired amount of chitosan and silica was added to the above aqueous solution and the rest of the procedure was the same as above. Table 1 listed the compositions of the PAA-based hydrogels. The physical properties of the prepared PAA, PAA-Ch, PAA-Si, PAA-Ch-Si hydrogels were characterized, including mechanical strength, FT-IR, friction coefficient, swelling ratio and morphology.

Table.1 Composition of the PAA-based hydrogels prepared by UV polymerization

Sample	AAc (M)	Chitosan (wt%)	Silica (wt%)
PAA	9	—	—
PAA-Ch	9	10	—
PAA-Si	9	—	5
PAA-Ch-Si	9	10	5

3. Results and discussion

3-1. *Preparation of PAA-Based Hydrogels*

In this study, IPN systems composed of PAA, chitosan, and silica were successfully synthesized by UV polymerization. The formation of the PAA-Ch-Si network structure is illustrated in Fig. 1. The anion of PAA and cation of chitosan in solution immediately induces ionic crosslinks. The silanols condensed gradually to form a Si–O–Si inorganic network. Meanwhile, silanols can interact with –COOH groups of PAA resulting in the formation of H-bonding. After NMBA and APS were added, a PAA organic network was constructed around the silica network [4]. Glutaraldehyde reacts with chitosan and it cross-links in an inter- and intra- molecular fashion through the formation of covalent bonds mainly with the amino groups of the polysaccharide. Therefore, in the study, PAA-Ch-Si has an IPN structure between PAA and chitosan with nano-silica as a filler which is expected to have high mechanical strength.
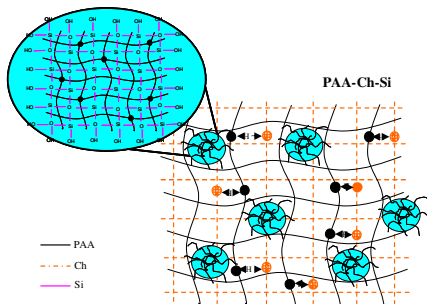

Fig.1 The formation of the PAA-Ch-Si network structure

3-2. *IR spectra of PAA, PAA-Ch, PAA-Si and PAA-Ch-Si hydrogels*

IR spectra of PAA, PAA-Ch, PAA-Si and PAA-Ch-Si are shown Fig.2. The transmittance bands at 1413-1558 cm^{-1} and 1694-1710 cm^{-1} are ascribed to COO- and C=O of the PAA hydrogel. The characteristic absorption peaks of C-H stretching of GA occur in the region of 939–1020 cm^{-1}. Absorption peaks due to Si–O–Si and Si–O stretching of silica occur in the region of 939–1020 cm^{-1}. The characteristic absorption peaks of C-O-C, NHCO and NH$_2$ stretching of the chitosan occur at 1039-1192 cm^{-1}, 1380 cm^{-1} and 1598 cm^{-1}. These characteristic absorption peaks provide evidence for the successful preparation of PAA-Ch-Si hydrogel through UV polymerization.
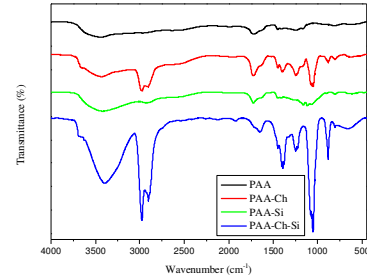

Fig.2 IR spectra of PAA, PAA-Ch, PAA-Si and PAA-Ch-Si hydrogels

3-3 *Swelling Characteristics of Hydrogels*

The swelling ratios and water contents of PAA-based hydrogels immersed in PBS at 37◦C are shown in Fig.3. The addition of silica solution into the PAA solution causes increased water content. This phenomenon is attributed to the availability of a large number of hydrophilic Si–O groups can bind to the water and form Si–OH groups from the silica in PBS as compared to those from the homo-polymer PAA hydrogel. The prepared PAA-Ch-Si hydrogel in this study were hydrophilic with water content above 80%, which are accordant with the nature of cartilage.
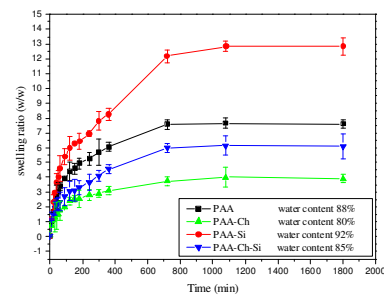

Fig.3 The swelling ratios and water contents of PAA, PAA-Ch, PAA-Si and PAA-Ch-Si hydrogels immersed in PBS at 37 ℃.

3-4. *Morphologyl of Hydrogels*

To confirm the swelling properties of these prepared hydrogels, they were freeze dried and their morphologies were observed by SEM. The pore structures of PAA and PAA-Ch hydrogels were evenly distributed to bigger extent than those of PAA-Si and PAA-Ch-Si hydrogels, as shown in Fig. 4.
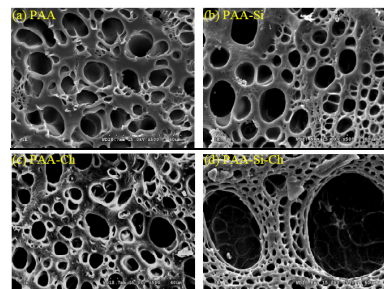

Fig.4 Scanning electron microscope of PAA, PAA-Ch, PAA-Si and PAA-Ch-Si hydrogels

3-5. *Mechanical Properties of Hydrogels*

he results of the mechanical properties indicate that the maximum compressive strength of PAA-based hydrogels increased slightly when they were interpenetrated with chitosan and silica solution, respectively. But, the maximum compressive strength of PAA-based hydrogels was significantly increased from 4.94 MPa to 42.26 MPa when both chitosan and silica were incorporated. The corresponding toughness of hydrogels also increased from 0.76 to 5.23 J and the cross-linking density increased from 0.195×10^{-5} to 2.293×10^{-5} mol/cm^3. This indicats that the prepared hydrogels became rigid with the presence of silica under static loading.

Table.2 Mechanical properties of PAA, PAA-Ch, PAA-Si and PAA-Ch-Si hydrogels

Unit / Sample	Elastic modulus (MPa)	Max stress (MPa)	Max strain (%)	Toughness (J)	Cross-link density (x10^{-5} mole/cm^3)
PAA	0.91±0.14	4.94±1.44	29.33±3.70	0.76±0.08	0.195±0.047
PAA-Ch	1.44±0.18	6.31±0.50	32.01±1.44	1.47±0.16	0.204±0.041
PAA-Si	1.49±0.16	8.92±1.22	25.92±1.43	1.99±0.68	0.764±0.15
PAA-Ch-Si	2.50±0.28	42.26±3.63	25.23±0.59	5.23±1.48	2.293±0.06

3-6. *Friction coefficients of hydrogels*

The design and production of hydrogels with low surface friction are important for the biomedical applications of these materials as substitutes for articular cartilage. As shown in Table.2, the static and dynamic friction coefficients of PAA-base hydrogel are close to that of human joints (10^{-4})[5].

Table.3 The friction coefficients of PAA, PAA-Ch, PAA-Si and PAA-Ch-Si hydrogels

Unit / Sample	First Peak Force (Kgf)	All Mean Force (Kgf)	Static friction coefficient (x10^{-4})	Dynamic friction coefficient (x10^{-4})
PAA	0.306±0.04	0.23±0.03	2.17±0.37	1.78±0.21
PAA-Ch	0.230±0.03	0.22±0.06	3.18±0.35	2.22±0.29
PAA-Si	0.279±0.08	0.31±0.03	2.44±0.81	2.37±0.42
PAA-Ch-Si	0.185±0.01	0.20±0.01	3.82±0.16	1.94±0.35

3-7. *Rheological analysis of hydrogels*

The rheological properties of the prepared hydrogels were listed in Table 3. The loss modules and tan δ of PAA-based hydrogel increased when both chitosan and silica were incorporated. Therefore, silica appears to enhance the viscoelastic properties in such a manner that it produces a soft hydrogel that can disperse the damping under dynamic loading. These properties are beneficial for hydrogels to be used as a substitute for soft tissues.

Table4. The rheological analysis of PAA, PAA-Ch, PAA-Si and PAA-Ch-Si hydrogels

Name	G'(10^{4}Pa)	G''(10^{4}Pa)	Tan delta
PAA	0.73±0.11	0.02 ±0.01	0.03 ±0.01
PAA-Ch	0.78 ±0.17	0.06±0.03	0.08±0.05
PAA-Si	0.15 ±0.07	0.07±0.02	0.47±0.25
PAA-Ch-Si	0.13±0.03	0.08±0.04	0.62±0.14

3-8. *Differential Scanning Calorimetry (DSC) Test*

All the synthesized hydrogels, before and after the washing cycles, were subjected to thermal analysis in order to verify whether any residual monomer, initiator and cross-linking agent was present after UV polymerization. A difference between the enthalpy change in the non-washing and washing cycles of the hydrogels was observed in Table 4. The residual monomer, initiator and cross-linking agent, inside the non-washed hydrogel may interfere with the flow of polymer chains at the melting temperature, thereby increasing the enthalpy change. These unreacted molecules can be removed through sequential washing cycles by using double-distilled water. As indicated in Table 4, decreasing residual activity could be detected after three washing cycles. The results of the DSC measurements used to indirectly examine the potential toxicity of the biomaterials are similar to those obtained by other works [6].

Table5. Enthalpy changes of the PAA-based hydrogels before and after washing

Name	ΔH(no wash) (J/g)	ΔH(wash) (J/g)
PAA	295±29	164±20
PAA-Ch	217±75	167±44
PAA-Si	612±98	363±65
PAA-Ch-Si	594±130	332±81

4. Conclusion

In this study, PAA-based hydrogels were successfully prepared by UV polymerization. These hydrogels formed an interpenetrating network structure through the mixing of PAA with chitosan solutions. The mechanical properties including elastic modulus, maximum compressive strength, toughness, and cross-linking density increased by incorporation of silica into PAA-Chitosan hydrogels. PAA-Chitosan-Silica hydrogel has high water content, low friction coefficient, and high tanδ, which is feasible to be used as a substitute for cartilage repair

5. References

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