Effect of Copper Adsorption on the Mechanical Properties of Chitosan Beads

Tomoyo Mitani, Takashi Kawakami, Makoto Morishita, Yasumasa Adachi, Hiroshi Ishii

*Department of Chemical Science and Engineering, Tokyo National College of Technology,
1220-2, Kunugida, Hachioji, Tokyo 193-0997, Japan*

ABSTRACT: The effect of copper adsorption on the mechanical properties of chitosan beads was investigated by measurement of creep modulus with a dynamic mechanical analyzer. Creep modulus changed drastically at a critical copper adsorption amount of 0.4 mol/mol of glucosamine unit. Creep modulus increased with increasing amount of copper up to 0.4 mol/mol, but decreased steeply as the amount of copper increased beyond 0.4 mol/mol. The variation in creep modulus with copper adsorption is discussed in terms of two models that describe the binding mode of transition metal to chitosan; the bridge model and the pendant model. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2988–2991, 2003

Key words: creep; gels; mechanical properties; strain; structure

INTRODUCTION

Chitosan is a biopolymer obtained by alkaline deacetylation of chitin, which is a major component of crustacean shells. Chitosan is a superior adsorbent of transition metals, such as copper, zinc, nickel, and manganese.[1] The amino and hydroxyl groups in the glucosamine residue appear to serve as the binding sites for metals.[2] However, the detailed mechanism by which transition metals are adsorbed by chitosan is not known because of the complexity of the gel network and the flexibility of the polymer chains of chitosan. Elucidating the interesting characteristics of chitosan, including transition metal adsorption, requires further investigation from various viewpoints.

Some polymers are known to exhibit significant changes in mechanical properties, on addition of a small amount of ionic compounds,[3,4] due to the introduction of structural changes. Because the conformation of chitosan is affected by reaction with anions and cations,[5,6] measurement of the mechanical properties of chitosan after adsorption of transition metals is expected to furnish valuable information for understanding the structure and properties of chitosan. Few papers have been published on the mechanical properties of chitosan,[7,8] although a number of studies have been conducted on the characteristics of the adsorption of transition metals and organic compounds to chitosan and the resultant chemical modification of chitosan.[9–15] In particular, experimental studies on the mechanical properties of chitosan after adsorption of transition metals have not been reported.

The objective of this work is to investigate the effects of copper adsorption on the mechanical properties of swollen chitosan beads. Among transition metals, copper is adsorbed to chitosan beads in the largest amount.[11] Therefore, when copper is used as the adsorbate, remarkable changes in the mechanical properties of chitosan can be expected.

EXPERIMENTAL

Preparation of chitosan beads

Chitosan was purchased from Katakura Chikkarin (Japan) as a flaked material with a deacetylation percentage of ~84%. Swollen chitosan beads were prepared from 7 wt % chitosan flakes dissolved in 7% acetic acid. The resultant viscous solution was deaerated under vacuum, and dropped into an alkaline coagulating solvent (H_2O–MeOH–NaOH = 5:4:1 w/w) to thereby prepare highly swollen chitosan beads of 2.5 mm average diameter and average water content of 92% (w/w). The beads were collected and washed thoroughly with distilled water.

Preparation of copper-adsorbed chitosan beads

About 1 g of swollen chitosan beads and 20 mL of aqueous solution containing a prescribed amount of copper sulfate were shaken overnight in a stoppered glass flask that was immersed in a thermostat-equipped water bath maintained at 30 ± 0.1°C. Copper-adsorbed chitosan beads were stored in distilled

Correspondence to: T. Mitani (mitani@tokyo-ct.ac.jp).

water at room temperature until subjected to the mechanical test described later.

Cross-linking of chitosan beads

Chitosan beads (100 mL) were placed in a three-way flask containing 100 mL of distilled water. Next, 200 mL of an aqueous solution containing 30 g of 25% glutaraldehyde solution was added in a dropwise manner, and the solution was stirred overnight. The beads were washed thoroughly with distilled water to remove solvent. Infrared (IR) analysis showed that the degree of cross-linking for the glucosamine unit was ~40%.

Measurement of creep modulus

The creep moduli of the untreated chitosan beads and copper-adsorbed chitosan beads were measured with a Perkin-Elmer DMA7 dynamic mechanical analyzer. One bead was placed in a measuring cup and compressed by a probe with a 1.5 cm diameter. All tests were conducted while the beads were immersed in water to avoid drying of swollen beads in an open system. The compression test consisted of three steps. In the first step, the bead was fixed loosely with a force of 1 mN; in the second step, the bead was compressed with 500 mN for 1 min; and in the third step, the bead was compressed again with 1 mN for another 1 min. Variation of strain was measured by the reduction of bead diameter with time, and creep modulus was calculated as stress divided by strain. The diameter of the cross section over which the compressing probe contacts a bead was assumed to be 2 mm for all beads.

Determination of copper content in copper-adsorbed chitosan beads

After undergoing the mechanical test, copper-adsorbed beads were dried at 110°C for 2 h, decomposed by heating with a mixture of HCl and HNO_3, evapo-
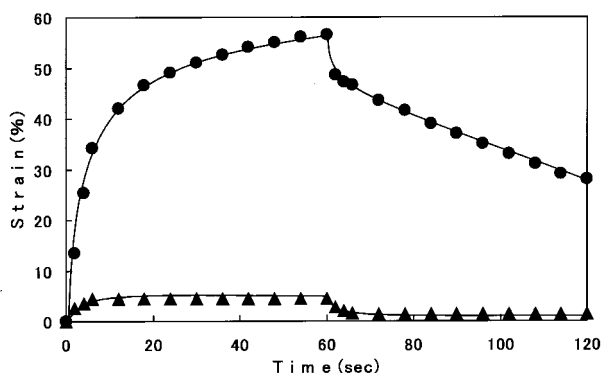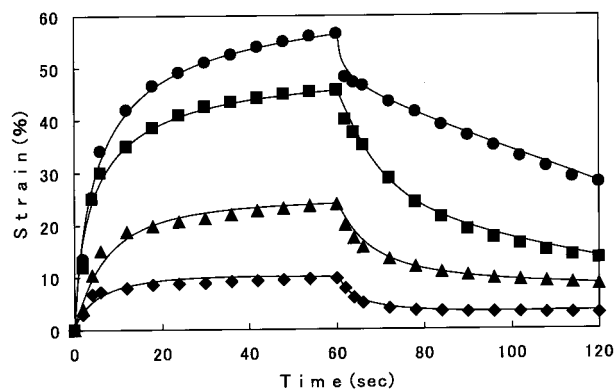

Figure 2 Variation in strain for copper-adsorbed chitosan beads. Key: (●) untreated; (■) 0.04 mol Cu/mol; (◆) 0.38 mol Cu/mol; (▲) 0.45 mol Cu/mol.

rated to dryness, and dissolved with 0.1 M HCl to make the total volume 25 mL. Copper content was determined by a Seiko SAS 7500 atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

The time course change of strain when chitosan beads were subjected to steady compressive forces (500 mN for the first 1 min and 1 mN thereafter) is shown in Figure 1. For untreated beads under 500 mN compressive force, strain initially increased steeply and thereafter showed the tendency of approaching a constant strain, suggesting typical creep deformation for a viscoelastomer.[16] After the force was changed to 1 mN, strain decreased almost linearly. For glutaraldehyde-bridged beads, strain reached a plateau within 8 s under 500 mN compression force. After the force was changed to 1 mN, the strain reached a constant value almost immediately. Compared with untreated beads, glutaraldehyde-bridged beads are characterized by lower strain by an order of magnitude, particularly under a compression force of 500 mN. This result is attributable to the bridging with glutaraldehyde that strengthened the chitosan beads against the force of compression.

The change in strain with time of copper-adsorbed chitosan beads is shown in Figure 2. The copper concentration is expressed as the adsorption amount per glucosamine unit of chitosan. The ranking of the magnitude of strain is as follows: untreated beads > 0.04 mol/mol copper-adsorbed beads > 0.45 mol/mol copper-adsorbed beads > 0.38 mol/mol copper-adsorbed beads. It is apparent from Figure 2 that strain varies with the adsorbed copper concentration. To clarify the effect of copper adsorption on the mechanical properties of chitosan beads, creep moduli are plotted as a function of the amount of adsorbed copper in Figure 3. The plotted creep moduli are values obtained under 500 mN of force for 1 min. Creep modulus increases
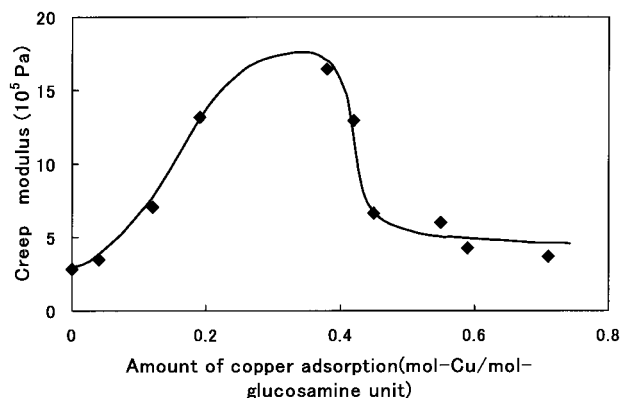

Figure 1 Variation in strain for (●) untreated chitosan beads and (▲) glutaraldehyde-bridged chitosan beads.

Figure 3 Relationship between creep modulus and amount of copper adsorption.
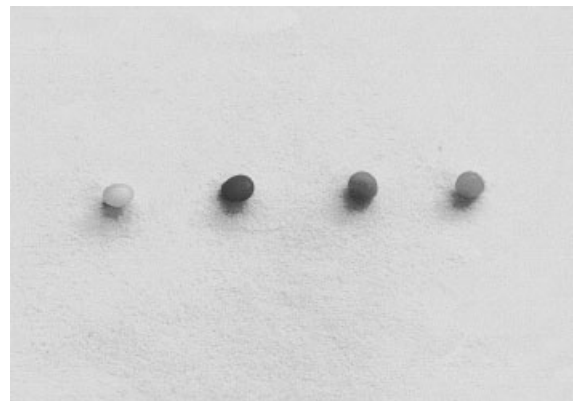

Figure 4 Color change with amount of copper adsorption: from left to right, 0.04, 0.38, 0.42, and 0.45 mol Cu/mol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

with increasing amount of copper up to 0.4 mol/mol, indicating that copper adsorption improves the mechanical strength of chitosan beads. Kubota[17] also reported that chitosan membranes containing transition metal ions become very rigid and sturdy. The increase of mechanical strength induced by copper binding can be said to be a common property of chitosan regardless of its form, bead or membrane.

The maximum creep moduli for three beads (i.e., untreated beads, copper-adsorbed beads, and glutaraldehyde-bridged beads), as determined under application of 500 mN of force for 1 min, are given in Table I. The creep modulus of copper-adsorbed beads is eight times that of untreated beads and about one-half that of glutaraldehyde-bridged beads. Copper adsorption to chitosan beads increases the creep modulus by the same order as covalent bonding (i.e., bridging with glutaraldehyde).

As shown in Figure 3, when the amount of adsorbed copper exceeds 0.4 mol/mol, creep modulus drops sharply and eventually reaches $\sim 4 \times 10^5$ Pa, which is close to the value for untreated beads. The decrease in creep modulus corresponds to an increase of strain, and therefore we can say that adsorption of copper beyond 0.4 mol/mol increases elasticity.

These results suggest that copper adsorption beyond 0.4 mol/mol leads to some change in the chemical structure of the chitosan molecule. Moreover, as shown in Figure 4, with increased adsorption of copper, chitosan beads change in color from dark blue to pale blue, which may constitute evidence supporting the change of the binding mode of copper to chitosan.

TABLE I
Creep Moduli of Chitosan Beads

Species of chitosan beads	Creep modulus (10^5 Pa)
Untreated	2.0
Copper-adsorbed (0.4 mol Cu/mol)	16
Glutaraldehyde-bridged	35

Copper was found to be uniformly distributed throughout the chitosan beads.

Although the binding mechanism of transition metals to chitosan is still under discussion, two coordination modes have been proposed; they are, the bridge model and the pendant model.[18–20] Variation in strain with increasing copper adsorption amount can be explained by these two models. In the bridge model, inter- and intramolecular crosslinking between chitosan is assumed to occur with the intervention of copper ions. As a result of crosslinking, resistivity against deformation is increased. Thus, when adsorbed in amounts up to 0.4 mol/mol, copper crosslinks to the molecular chain of chitosan. In this case, as Inoue et al.[2] have pointed out, not only amino groups but also hydroxyl groups in the chitosan molecule may serve as binding sites to copper.

The bridge model cannot explain the decrease in creep modulus with increasing copper adsorption; according to the bridge model, mechanical strength should continue to increase with increasing copper adsorption. The decrease in creep modulus is associated with a different binding mechanism of copper to chitosan. Therefore, the binding mode of copper is thought to change to the pendant mode at copper adsorption amounts >0.4 mol/mol.

In the pendant model, a copper ion is assumed to be linked to an amino group as if the copper ion was suspended from the amino group like a pendant. The mechanical strength for the pendant model is weaker than that for the bridge model, because only one binding site exists. Therefore, the decrease in creep modulus can be explained by the change in binding mode from the bridge model to the pendant model.

CONCLUSIONS

The mechanical properties of untreated chitosan beads and copper-adsorbed chitosan beads were investi-

gated by measurement of creep modulus. The strain–time curve of untreated chitosan beads shows typical behavior for a viscoelastomer. For copper-adsorbed chitosan beads, creep modulus increases with increasing amount of copper adsorption up to 0.4 mol/mol. However, when the copper adsorption amount exceeds 0.4 mol/mol, the creep modulus drops sharply and approaches a constant value. As the amount of adsorbed copper increases, chitosan beads change in color from dark blue to pale blue, suggesting a change in copper adsorption mode. The creep modulus of 0.4 mol/mol copper-adsorbed beads is eight times that of untreated beads. The change in creep modulus at the copper adsorption beyond 0.4 mol/mol can be explained by a change in copper binding mode from the bridge model to the pendant model.

References

1. Muzzarelli, R.A.A.; Chitin; Pergamon: Oxford, 1977.
2. Inoue, K.; Baba, Y.; Yoshizuka, K. Bull Chem Soc, Jpn 1993, 66, 444.
3. Kim, J.S.; Kim, H.S.; Nah, Y.H.; Eisenberg, A. Polym Bull 1998, 41, 609.
4. Lee, D.H.; Kim, J.W.; Suh, K.D. Colloid Polym Sci 1999, 277, 265.
5. Ogawa, K.; Oka, K.; Miyanishi, T.; Hirano, S. Chitin, Chitosan, and Related Enzymes; Zikakis, J.P., Ed.; Academic Press: Orlando, FL, 1984; p 327.
6. Jing, S.B.; Yamaguchi, T. Bull Chem Soc Jpn 1992, 1866.
7. Andrady, A.L.; Xu, P. J Polym Sci, Part B: Polym Phys 1997, 35, 517.
8. Nishio, T.; Matsui, R.; Nakamae, K. J Polym Sci, Part B: Polym Phys 1999, 37, 1191.
9. Koyama, Y.; Taniguchi, A. J Appl Polym Sci 1986, 31, 1951.
10. Maghami, G.G.; Roberts, G.A.F. Macromol Chem 1988, 189, 2239.
11. Mitani, T., Moriyama, A.; Ishii, H. Biosci Biotechnol Biochem 1992, 56, 985.
12. Mitani, T.; Yamashita, T.; Okumura, C.; Ishii, H. Biosci Biotechnol Biochem 1995, 59, 927.
13. Ishii, H.; Minegishi, M.; Lavitpchayawong, B.; Mitani, T. Int J Macromol 1995, 17, 21.
14. Inoue, K.; Ohto, K.; Yoshizuka, K.; Yamaguchi, T.; Tanaka, T. Bull Chem Soc Jpn 1997, 70, 2443.
15. Wan Ngah, W.S.; Isa, I.M. J Appl Polym Sci 1998, 67, 1067.
16. Morrison, F.A. Understanding Rheology; Oxford University Press: New York, 2001; p 146.
17. Kubota, N. J Appl Polym Sci 1997, 64, 819.
18. Yaku, F.; Muraki, E.; Tsuchiya, K.; Shibata, Y.; Koshijima, T. Cell Chem Technol 1977, 11, 421.
19. Schlick, S. Macromolecules 1986, 19, 192–195.
20. Domard, A. Int J Biol Macromol 1987, 9, 98.