

Synthesis of translucent chitosan aerogel and its hydrophobic modification

Satoru Takeshita,* Satoshi Yoda

National Institute of Advanced Industrial Science and Technology (AIST)

*s.takeshita@aist.go.jp

ABSTRACT

We report a supercritical drying synthesis of a new type of aerogels constructed with trimethylsilylated chitosan nanofibers. The chitosan organogel was prepared by cross-linking gelation followed by solvent exchange. The organogel was treated with hexamethyldisilazane and then supercritically dried to obtain the aerogel. The key point for successful supercritical drying of trimethylsilylated chitosan organogel is using an aprotic system, acetone/CO₂, for the drying solvent.

INTRODUCTION

Biobased polysaccharide aerogels have been one the emerging materials in the aerogel research from their unique physicochemical properties in contrast to inorganic aerogels, which lead to wide potential applications including biomedical scaffolds and mechanically tough thermal insulators [1]. We recently developed translucent chitosan aerogels consisted from cross-linked chitosan nanofibers [2]. This aerogel shows mechanical toughness, translucent appearance, low thermal conductivity, and strong hydrophilicity, and would be a suitable candidate for translucent thermal insulators. In order to increase the feasibility of this material for practical uses, hydrophobic modification is required to improve the humidity stability. In this work, we report our recent progress in synthesis of the chitosan aerogels and their hydrophobic modification using hexamethyldisilazane (HMDS) [3].

MATERIALS AND METHODS

The hydrophobic chitosan aerogels were prepared by cross-linking gelation and supercritical drying as described in Ref. [3]. First, cross-linked chitosan hydrogel was prepared by mixing aqueous acetic acid solution of chitosan (5 g L⁻¹) and aqueous

formaldehyde solution (36.5 wt%) at the volume fraction of chitosan : formaldehyde = 4 : 1 and aged at 60 °C overnight. The obtained hydrogel was solvent exchanged by immersing in methanol for 2 days and then in acetone for 2 days with a constant change of the solvent. After the solvent exchange, the chitosan organogel was treated in HMDS/acetone solution with a certain HMDS concentration, 0–20 vol%, to obtain trimethylsilylated chitosan organogel. Finally, the trimethylsilylated organogel was washed in acetone at least in 2 days and then supercritically dried in acetone/CO₂ system to obtain the aerogel. For comparison purpose, we also prepared aerogels by using methanol as a washing solvent and methanol/CO₂ system for supercritical drying solvent.

RESULTS AND DISCUSSION

As shown in FT-IR spectra in Fig. 1, the aerogel prepared by acetone/CO₂ supercritical drying shows the characteristic peaks from Si–C vibrations at 1253, 867, and 843 cm⁻¹ and CH₃ bending at 754 cm⁻¹ [4]. On the other hand, these peaks completely disappear in the aerogel prepared by methanol/CO₂ supercritical drying. In contrast to HMDS-treated silica aerogels, the trimethylsilyl groups introduced on OH groups of chitosan chains are not stable in acidic environments such as CO₂/alcohol under high pressure [5]. Judging from these results, an aprotic system, such as acetone/CO₂, is necessary as the supercritical drying solvent of trimethylsilylated chitosan aerogels.

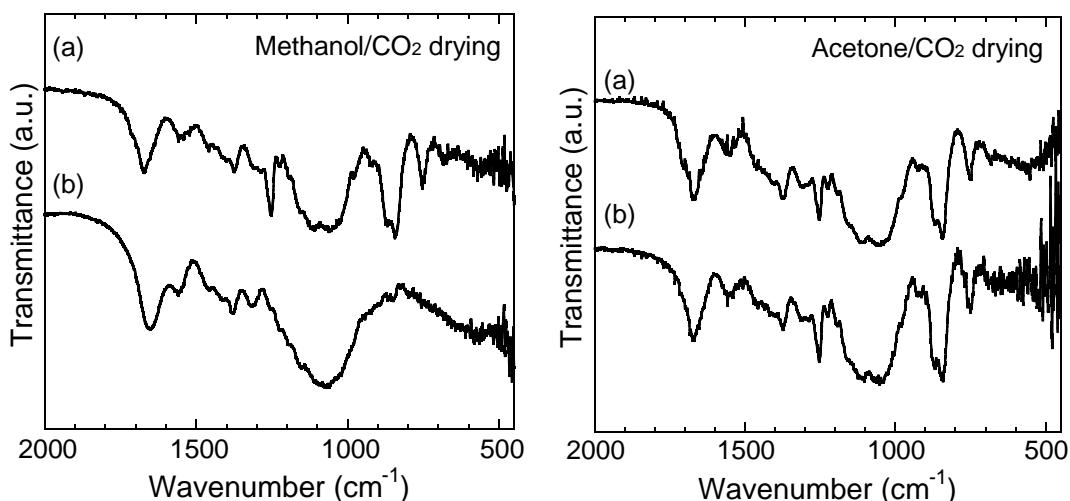


Figure 1. FT-IR spectra of samples supercritically dried in (left) methanol/CO₂ and (right) acetone/CO₂ systems (a) before and (b) after the supercritical drying. HMDS concentrations: (left) 20 vol% and (right) 0.5 vol%. Right figure is adapted from Ref. [3] with permission from The Royal Society of Chemistry.

According to SEM observation, the trimethylsilylated chitosan aerogels prepared in acetone/CO₂ system consist of three-dimensional networks of chitosan nanofibers, which

is similar to the unmodified chitosan aerogel prepared in methanol/CO₂ system [1]. The unmodified aerogel (Fig. 2, left) shows high hydrophilicity, where the water droplet immediately penetrates the aerogel monolith and causes the shrinkage of the aerogel. On the other hand, trimethylsilylated aerogel (Fig. 2, right) shows water repellent behavior originating from hydrophobic nature of introduced trimethylsilyl groups.

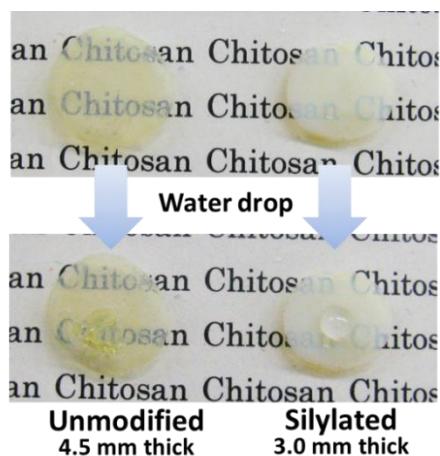


Figure 2. Typical photographs of unmodified chitosan aerogel [2] and trimethylsilylated (HMDS concentration = 0.75 vol%) chitosan aerogel before and after water dropping.

CONCLUSION

We have developed a facile method to prepare hydrophobic aerogels made of trimethylsilylated chitosan nanofibers. The trimethylsilyl groups introduced on OH groups of chitosan easily detach under acidic environments such as methanol/CO₂ supercritical drying. Acetone/CO₂ system is a suitable alternative solvent because it does not produce any protons, and hence acetone/CO₂ supercritically dried chitosan aerogel shows good hydrophobicity owing to trimethylsilyl groups.

REFERENCES

- [1] DE FRANCE K. J., HOARE T., CRANSTON E. D., *Chem. Mater.*, Vol. 29, 2017, p. 4609.
- [2] TAKESHITA S., YODA S., *Chem. Mater.*, Vol. 27, 2015, p. 7569.
- [3] TAKESHITA S., YODA S., *Nanoscale*, Vol. 9, 2017, p. 12311.
- [4] KURITA K., HIRAKAWA M., KIKUCHI S., YAMANAKA H., YANG J., *Carbohydr. Polym.*, Vol. 56, 2004, p. 333.
- [5] WEST K. N., WHEELER C., MCCARNEY J. P., GRIFFITH K. N., BUSH D., LIOTTA C. L., ECKERT C. A., *J. Phys. Chem. A*, Vol. 105, 2001, p. 3947.