Journal Name

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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

New flexible aerogels and xerogels derived from methyltrimethoxysilane/dimethyldimethoxysilane co-precursors†

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Highly flexible aerogels have been obtained from methyltrimethoxysilane (MTMS) and dimethyldimethoxysilane (DMDMS) co-precursor systems with surfactant *n*-hexadecyltrimethylammonium chloride (CTAC) to control phase separation in a 2-step acid/base sol-gel reaction.

Since first prepared in 1931,[1] aerogels have been synthesized with various chemical compositions such as inorganic metal oxides (e.g. silica, alumina and titania)[2-4], organic crosslinked polymers (e.g. resorcinol-formaldehyde (RF))[5,6] and biopolymers (e.g. cellulose and chitosan).[7,8] In all cases, wet gels are typically prepared via liquid-phase processes and dried using a supercritical fluid such as carbon dioxide. Silica aerogels derived from tetraalkoxysilane or water glass are most extensively investigated because they have outstanding properties such as high optical transparency (> 90 %), low refractive indices (< 1.01), low thermal conductivity (< 0.02 W/mK at ambient pressure), good acoustic insulation abilities, and low dielectric constants due to their dilute nano-sized frameworks with high porosities.[2] These features have been applied to multiple fields such as heat insulators, low-*k* materials for semiconductor devices, stardust capturers for space exploration and catalyst supports.[4,9] However, since their mechanical strength is too low even against a small applied stress, the porous structure is easily collapsed and a drying gel body will exhibit shrinkage and cracks. Supercritical drying, which avoids networks collapsed by capillary force, is hence required to obtain dried aerogels.[2] This process, which needs a special condition such as high pressure and high temperature, prevents aerogels from extended applications. In recent years, there are some reports on improvements of mechanical properties.[10] One promising way is to use organoalkoxysilanes with small organic substituent groups such as methyl group to obtain organic-inorganic hybrid aerogels, but these aerogels are usually opaque because of phase separation of hydrophobic networks from polar solvent. Our group has successfully prepared low-density and transparent methylsilsesquioxane (MSQ, $CH_3SiO_{1.5}$) aerogels and xerogels from methyltrimethoxysilane (MTMS) by using surfactant and the urea-assisted acid-base two-step process to control phase separation.[11–14] Since the MSQ networks include methyl groups with high concentration and lower crosslinking density compared to silica, the wet gels and aerogels are highly flexible against compressive stress (spring-back behaviour), which allows wet gels to be dried by evaporation of solvent under an atmospheric condition. The MSQ xerogels therefore possess almost identical properties to those of corresponding aerogels obtained by supercritical drying; the xerogels exhibit high visible light transmittance and high porosity as well as high flexibility against compressive stress. However, they are still fragile against tensile and shear stresses. Some bendable aerogels are also reported by using organoalkoxysilanes as (co-)precursors. Rao et al. have reported bendable MSQ aerogels by using an acid/base two-step reaction in a water/methanol mixed solvent,[15] and Guo et al. reported highly flexible aerogels derived from bis[3-(triethoxysilyl)propyl]disulfide, tetramethoxysilane and vinyltrimethoxysilane, in which the disulphide bridges enhance elastic recovery after compression.[16] There are also reports on the polymer crosslinked aerogels, but the process needs multiple and laborious steps and porosity is partially lost though mechanical properties are highly improved.[17,18]

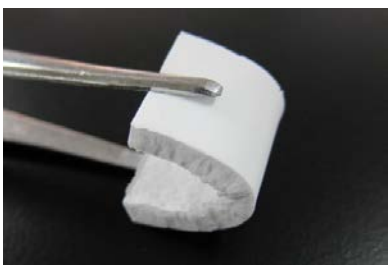

Fig. 1 Digital camera image of the flexible xerogel derived from the MTMS and DMDMS co-precursor system.

Here, we report new aerogels derived from trifunctional alkoxysilane MTMS and difunctional alkoxysilane dimethyldimethoxysilane (DMDMS) as the co-precursor. There have been a number of reports on aerogels with using tetra- and trifunctional alkoxysilane[19,20] and with tetrafunctional alkoxysilane and polydimethylsiloxane,[21,22] but few with tri- and dialkoxysilane because of their too-high phase separation tendency arising from high hydrophobicity of the network. To synthesize the methylsiloxane materials, we employed surfactant *n*-hexadecyltrimethylammonium chloride (CTAC) to control phase separation, and used the acid/base two-step sol-gel reaction utilizing acetic acid and urea as catalysts, being similar to the case of MSQ aerogels and xerogels. The synthesis process is a quite simple one-pot reaction. In the typical synthesis, 15 mL of 5 mM aqueous acetic acid, 0.80 g of surfactant CTAC and 5.0 g of urea were mixed in a glass sample tube, and then 3.0 mL of

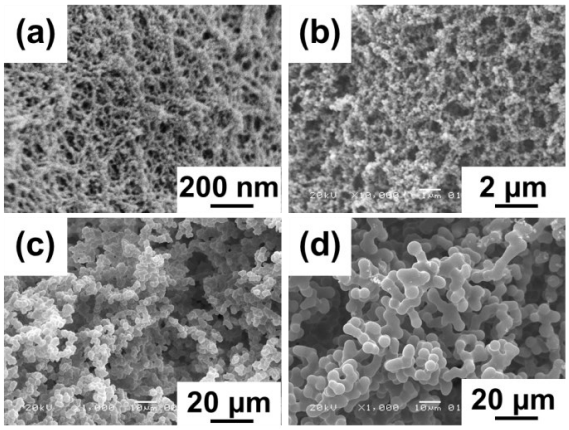

Fig. 2 SEM images of the samples prepared with varied amounts of MTMS/DMDMS: (a) 5.0 mL/0 mL (X = 0), (b) 3.8 mL/1.2 mL (X = 1.2), (c) 3.4 mL/1.6 mL (X = 1.6), (d) 2.6 mL/2.4 mL (X = 2.4).

MTMS and 2.0 mL of DMDMS were added and kept being stirred for 30 minutes for hydrolysis of these alkoxysilanes. The molar ratio of this typical starting composition is (MTMS + DMDMS):water:acetic acid:urea:CTAC = 1.0:2.4 × 10:2.1 × 10^{-3}:2.4:7.1 × 10^{-2} with MTMS:DMDMS = 5.9:4.1. After the complete mixing, the sol was transferred to a closed vessel and kept at 80 °C for gelation and aging for 2 d in the base-catalysed condition brought about by hydrolysis of urea. The typical gelation time was about 3 h. The wet gels thus obtained were soaked in water/2-propanol (volume ratio 1:1) for once and the next 2-propanol twice at each 8 h interval to wash out CTAC and other unreacted reagents. Then the half of the gel was dried from supercritical carbon dioxide at 80 °C and 14 MPa for 10 h. The remaining half of the gel was soaked in *n*-hexane, exchanging 3 times with the fresh solvent at each 8 h interval, and then slowly dried at 40 °C under ambient pressure for 1 d. In this paper, we denote the former gel as "aerogel" and the latter one as "xerogel", respectively. The digital camera image of the obtained flexible xerogel is shown in Fig. 1.

The morphology of the aerogel frameworks are significantly affected by the starting composition. Figure 2 shows the SEM images with varied ratios of MTMS:DMDMS. The total volume of MTMS (5.0 − X mL) and DMDMS (X mL) was fixed to 5.0 mL, and note that molar ratio is about the same as the volume ratio. With no DMDMS (X = 0) in the starting composition, the aerogel was transparent and the diameter of the spherical structural unit in the gel networks was about 10 nm, which is about the same material with those we have reported before.[13] As increasing the fraction of DMDMS, the aerogel became opaque and its microstructure dramatically changed predominantly due to the increase in hydrophobicity of the condensates. Where 1.6 < X < 2.4, the diameter of the framework slightly grew in size with the increasing amount of CTAC. No monolithic gelation occurred in X > 2.5, because the hydrophobicity of MTMS/DMDMS oligomers becomes too high and only hydrophobic precipitates were obtained. The change in the intermolecular structures in the networks with varied X was detected by FT-IR (Fig. S1†). The absorbance by the Si-O-Si asymmetric stretching mode of linear and branched siloxanes at 1030 cm^{-1} and of polycyclic oligomers $(CH_3SiO_{3/2})_n$ (where n = 8, 10, and 12) at 1100 cm^{-1} show that DMDMS is incorporated into

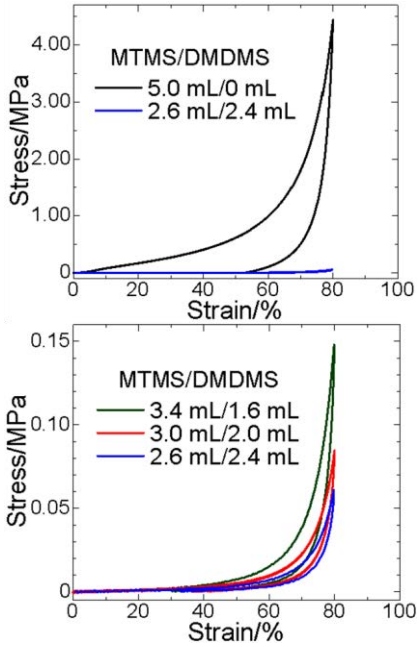

Fig. 3 Stress-strain curves obtained by the uniaxial compression tests on the flexible aerogels prepared with varied amounts of MTMS/DMDMS.

the siloxane network successfully.[23] The inclusion of DMDMS also can be confirmed by the result of thermogravimetry (TG) measurements. The larger mass decrease by the decomposition of methyl groups is observed at ~ 400 ºC in the sample richer in DMDMS (Fig. S2†). The amount of urea (U g) also affected the microstructures. Where U = 1.0, the gel was consisted of the aggregate of spherical particles. With more amount of urea, the co-continuous structure with smoother interfaces formed and became finer in proportion to U (Fig. S3†). The amount of CTAC (C g) did not clearly affect the microstructures. However, where C < 0.2, gelation did not occur but precipitation was observed due to the high hydrophobicity of MTMS/DMDMS oligomers in the polar solvent.

Mechanical property was also evaluated by uniaxial compression tests. Each sample was compressed to 80 % of its original size at the rate of 0.5 mm min^{-1}, and then unloading the stress at the same rate. With increasing X, Young's modulus drastically decreased. Where 1.6 < X < 2.4, the aerogels recovered their original shape and size almost completely after unloading the stress, and the stress of 80 % compression of the sample X = 2.4 was about 1/100 of MSQ aerogels (X = 0) (Fig. 3). Although the size of the frameworks becomes larger and the connectivity better, the aerogels become more flexible and extremely soft as X increased, because of the enhanced incorporation of DMDMS. With varied amounts of urea, the flexibility also changed. With increasing U, the aerogels became further flexible and soft (Fig. S4†), because the microstructure became finer as mentioned above. The urea concentration only changes their porous structure, and no clear difference in the molecular structure between the samples U = 1.0 and 5.0 was detected by FT-IR spectra. This means that the porous structure is determined only by the progress of phase separation and the transient structure of phase separation is frozen by gelation, which is promoted by the base catalyst (urea hydrolysate, NH_4OH). On the other hand, CTAC affected the molecular

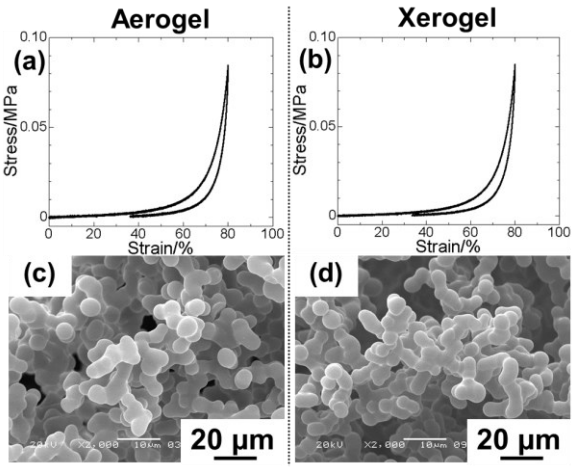

Fig. 4 Properties of the aerogel/xerogel synthesized from the same starting composition (X = 2.0, U = 5.0, C = 0.8): (a)/(b) Stress-strain curves obtained by the uniaxial compression tests, and (c)/(d) SEM images.

structure (Fig. S5†). With increasing C, Young's modulus became lower (Fig. S6†). Because there is no difference in microstructures, this difference should be caused by the change of the siloxane networks, but the further investigation is necessary for details. From these results, it is confirmed that the flexibility of MTMS/DMDMS aerogels can be extensively controlled by the starting composition. We also attempted the three-point bending test on this material, but these "marshmallow-like" aerogels were bended even by their own weight and the measurements were found to be difficult.

The flexibility of MTMS/DMDMS gels makes it possible to dry the wet gels by simple solvent evaporation under ambient pressure (the sample shown in Fig. 1 is a xerogel). In the range of the following three requirements, $1.6 < X < 2.4$, $U > 2.0$ and $C > 0.2$, xerogels can be successfully obtained without any change of the shape and size from the wet gel. We compared the xerogel with the aerogel from the same starting composition (X = 2.0, U = 5.0 and C = 0.8). Bulk densities of both gels are almost the same at about 0.11 g cm^{-1}. Together with true density (~ 1.47 g cm^{-3}) determined by helium pycnometry, the porosity can be estimated as 93 %. Fig. 4 (a) and (b) show the stress-strain curve of each gel. There is no visible difference between these gels. From SEM observations (Fig. 4 (c) and (d)), each gel is confirmed to have the identical features. In fact, we can obtain the xerogels with the identical properties even after repetitive re-wetting and re-drying. In addition, since the MTMS/DMDMS xerogels show high hydrophobicity due to the methyl groups, the gels can float on water at least a few months.

Conclusions

The highly flexible aerogels have been prepared from the mixtures of MTMS and DMDMS in the two-step sol-gel process containing surfactant CTAC. Around the ratio of MTMS:DMDMS ~ 1.5, xerogels by evaporative drying under an ambient condition can be obtained with no differences from the corresponding aerogels. These aerogels and xerogels show the perfect spring-back behaviour with a small stress (~ 0.10 MPa). The microstructure and the mechanical properties can be easily changed by varying the ratio of MTMS and DMDMS, the amount of CTAC and urea in the starting composition. Owing to the soft and elastic porous structures, these xerogels can be applied to high performance sound insulators, which we will report in the near future in detail (Fig. S7†).

Acknowledgements

The present work was supported by the Grant-in-Aid for Scientific Research (No.22750203 for K.K. and No. 20350094 for K.N.) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. Also acknowledged is the Global COE Program "International Center for Integrated Research and Advanced Education in Materials Science" (No. B-09) of the MEXT, Japan, administrated by the Japan Society for the Promotion of Science (JSPS).

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† Electronic Supplementary Information (ESI) available: FTIR, TG-DTA, SEM, and sound absorption behavior of the samples. See DOI: 10.1039/b000000x/

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