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Correlation between Functionated Structure and Nanomechanical Property Profiles of Silsesquioxane Films and Bulks

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Summary: Three silsesquioxane (SSO) building blocks based on [3-(methacryloxy)-propyl]trimethoxysilane (MPMS), [(3-glycidoxy)propyl] trimethoxysilane (GPMS), (vinyl)trimethoxysilane (VMS) and modified with 15 wt-% tetraethoxysilane (TEOS) were prepared using hydrolytic condensation. The hardness, elastic modulus and harmonic contact stiffness for three films [f-MTSSO (film-MPMS-TEOS-SSO), f-GTSSO and f-VTSSO] and bulks (b-MTSSO, b-GTSSO and b-VTSSO) derived from the three SSOs were tested by instrument-indentation testing. Different profiles of nanomechanical properties of the films can be attributed to a different functionality and the functionated structure of the different SSOs. The f-MTSSO shows better mechanical properties which are higher than the other two films containing more OH or OCH_3 groups. For the f-GTSSO with a bulky organic substituent, the unsatisfactory properties resulting from ring opening during hydrolytic condensation and an incomplete crosslinking network are discussed. However, the nanomechanical properties of the three bulks are very different from the corresponding nanomechanical properties of their films: b-VTSSO possesses the best nanomechanical properties (note: not b-MTSSO) among three bulks due to the differences in reaction conditions and chain less flexibility which are also discussed.

Keywords: elastic modulus; hardness; harmonic contact stiffness; nanoindentation; silsesquioxane; thin film and bulk

Introduction

Silsesquioxanes have an inorganic silicon-oxygen core that is externally functionalized with organic groups, as building blocks for silsesquioxane nanostructural materials. A silsesquioxane nanostructure can be manufactured to contain a chemically precise number of reactive groups that impart specific functionality to these building blocks.[1] With silsesquioxane functional technology, the intrinsic properties of silsesquioxane materials can be fully controlled and hence provide enhancement to a very wide range of desirable properties.[2–5]

Functionality can fully control the structure of the silsesquioxane building blocks, leading to the corresponding properties of silsesquioxane materials. The silsesquioxane building blocks have multiple structures, and their general formulas are $T_n(OH)_x(OR')_y$ [$T = RSiO_{1.5-(x+y)/2n}$; $n = 4, 5, 6\ldots$; $x, y = 0, 1, 2\ldots$].[6] With the silsesquioxane general formula, T_n (x and $y = 0$) represents a complete structure, and when x or y is not zero, $T_n(OH)_x(OR')_y$ represents an incomplete structure, containing more OH or OR′ groups. An incomplete structure is usually formed if the group R bonded to the Si atom is a simple group such as –H, $-CH_3$, –Cl, *etc*., due to difficult interactions with each other. The more OH or OR′ groups containing in the incomplete building blocks directly influence the crosslinked networks and mechanical properties of the

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generated silsesquioxane materials. On the contrary, the presence of larger organic groups such as $-CH_2CH_2CH_2OCOC(CH_3)=CH_2$, $-CH_2CH_2CH_2OCH_2CH[O]CH_2$, $-CH_2CH_2CH_2NH_2$, *etc*., favor a complete structure leading to a narrow distribution of polyhedra[7] due to the presence of a larger organic substituent and greater interactions with each other. Therefore, the silsesquioxane building block configurations are largely influenced by the type of organic group bonded to the Si atom, taking into account a steric effect promoting intramolecular condensation.[6]

The aim of this work is to analyze the structures of the silsesquioxane films and bulks based on different building blocks with different functionality and to find the correlation between the functionality, structure and nanomechanical property (hardness, elastic modulus and harmonic contact stiffness) profiles of the silsesquioxane films and bulks.

Experimental Part

The hydrolytic condensation of trialkoxysilane, [3-(methacryloxy)propyl]trimethoxysilane (MPMS), [3-(glycidoxy)propyl]trimethoxysilane (GPMS) and vinyltrimethoxysilane (VMS), was carried out in a beakers placed in a water bath. Ethanol (99.7 wt-%) was used as a solvent, in a 3:1 molar ratio with respect to Si. The polycondensation was carried out in the presence of formic acid (88 wt-%), added in a 3: 1 molar ratio with respect to Si.[8] The reaction products (silsesquioxane, SSO) were homogeneous viscous liquids. With the standard spectroscopic techniques (FTIR, NMR and UV-MALDI-TOF MS), the structural characterizations of SSO building block based on MPMS (MSSO), GPMS (GSSO) and VMS (VSSO) were reported in the previous works.[10–12]

To modify MSSO, GSSO and VSSO with 15 wt-% tetraethoxysilane (TEOS), the hydrolytic condensation of the alkoxysilanes was carried out separately for 9 days initially and then was mixed together to react for 2 days under similar conditions as above. The MSSO, GSSO and VSSO modified with 15 wt-% TEOS will be denoted as MTSSO (MPMS-TEOS-SSO), GTSSO and VTSSO. The preparation of their films (f-MTSSO, f-GTSSO and f-VTSSO) were described in the previous works.[10–12]

For the preparation of MTSSO, GTSSO and VTSSO bulks (b-MTSSO, b-GTSSO and b-VTSSO), the same hardeners (benzoyl peroxide and ethylenediamine) as mentioned in the previous works were added to the resulting SSOs for curing the reaction. The SSOs were diluted with tetrahydrofuran (at a purity of 99.7%) in a weight ratio 5:1. The reaction was carried out in sealed beakers placed in a water bath. The temperature was held at 60 °C for 24 hours to form the bulky materials with no internal superficial cracks and bubbles followed by another 24 hours at 120 °C in an oven.

The thickness of the films, 300–450 nm, was determined by scanning electron microscopy (SEM, Hitachi S-570).

Hardness (*H*), elastic modulus (*E*) and harmonic contact stiffness (*HCS*) profiles of different films or bulks were determined using a Nano-Indenter device (XP, MTS Systems) provided with a continuous stiffness measurement (CSM) technique, similarly described in detail elsewhere.[13,14]

Results and Discussion

Hardness and Elastic Modulus Profiles

The plots of *H* or *E* vs. displacement can be divided into four regions.[10] Figure 1 shows the intrinsic *H* and *E* profiles of f-MTSSO, f-GTSSO and f-VTSSO, measured from the third region where it is actually used to calculate the average *H* and *E* of the films and bulks (seen able 1T).[10] Figure 2 shows the *H* and *E* profiles of the third region for the three SSO bulks. From Table 1, the *H/E* values are relatively smaller than those of the films due to the stronger elastic behavior of the bulk without the substrate effect.

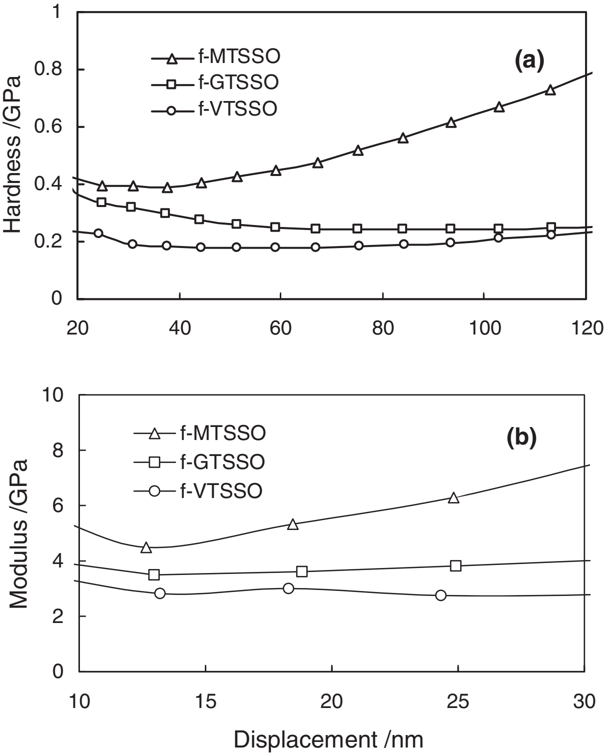

Figure 1.
The hardness (a) and the elastic modulus (b) profiles of f-MTSSO, f-GTSSO and f-VTSSO modified with 15 wt-% TEOS.

Film Functioned Structure and Nanomechanical Property

In the previous work,[12,15] a ladderlike structure (a incomplete structure, containing more OH or OR′ groups) and a cage structure (either incomplete or complete structure where there are fewer or no OH or OR′ groups) were reported and verified, respectively, for VSSO containing a smaller R ($-CH{=}CH_2$) and GSSO containing a longer R ($-CH_2CH_2CH_2OCH_2CH[O]CH_2$) connected to Si atoms by a quantum chemical calculation (QCC). For MSSO, it should have the same structural type as the GSSO, i.e. a cage structure roughly determined by a distinctive parameter which characterizes the structure of a particular SSO by the fraction of intramolecular cycles (f) present in their species.[8]

From Figure 1, the average H of three films is different due to their different terminal groups. The H of the f-MTSSO (0.39 GPa) exhibits twice more than the H of the f-VTSSO (0.18 GPa) because the organic polymerization was more effective in the former system due to the larger size of organic branches covalently bonded to the silica network.[8] Methacryloxy groups should be able to approach each other to participate in the free-radical crosslinking process. This process should be much more difficult for the short vinyl groups present in the f-VTSSO. In addition, the small group of the VTSSO causes most building blocks to possess a ladderlike structure containing more OH or OR′ groups,[12] and thus the f-VTSSO network has a lower density and a weaker H when it is crosslinked.

The f-GTSSO's, although GPMS possesses a larger organic branch and the f-GTSSO building blocks possess cage structures, H (0.24 GPa) is much smaller than the H of the f-MTSSO (0.39 GPa) which can be attributed to an incomplete crosslinking

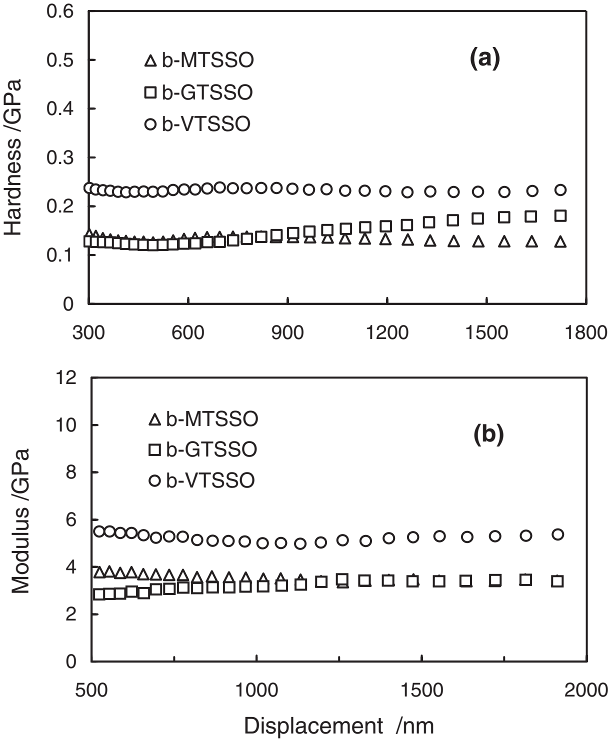

Figure 2.
The hardness (a) and the elastic modulus (b) profiles of b-MTSSO, b-GTSSO and b-VTSSO modified with 15 wt-% TEOS.

network.[15] Residual alcohol and/or H_2O (H^++OH^-) in the sol which promote the ring opening reaction,[16] producing OH termination which makes the f-GTSSO network have lower density and weaker H when it is crosslinked.

The E of the f-MTSSO (4.49 GPa) is larger than those of the f-GTSSO (3.56 GPa) and f-VTSSO (2.77 GPa), respectively, which might be explained by the stronger functionality of the methacrylpropyl groups for MTSSO during organic polymerization (a larger conversion of C=C bonds), generating a hybrid network with a higher cohesive energy density.[8] In addition, the f-MTSSO crosslinked network based on the cage-structure building blocks is much denser than the b-GTSSO and the f-VTSSO networks containing more OH or OR′ groups.[11]

Table 1.
Nanomechanical data of the SSO films and bulks modified with 15 wt-% TEOS.

SSO	Films			Bulks		
	H/GPa	E/GPa	H/E	H/GPa	E/GPa	H/E
MTSSO	0.39 ± 0.126 (24.83–44.33 nm)[a]	4.49 ± 1.456 (12.00–13.00 nm)	0.090	0.13 ± 0.032 (342–2000 nm)	3.49 ± 0.583 (493–2000 nm)	0.040
GTSSO	0.24 ± 0.043 (67.05–123.67 nm)	3.56 ± 1.174 (12.97–18.82 nm)	0.070	0.15 ± 0.055 (342–2000 nm)	3.27 ± 0.960 (493–2000 nm)	0.040
VTSSO	0.18 ± 0.028 (44.25–75.39 nm)	2.77 ± 0.743 (24.32–30.91 nm)	0.060	0.24 ± 0.141 (342–2000 nm)	5.27 ± 1.600 (493–2000 nm)	0.050

[a] Depth regions for determining intrinsic H and E values.

Bulk Functional Structure and Nanomechanical Property

Figure 1 shows that f-MTSSO possesses the best nanomechanical properties due to its functional structure. However, as seen in Figure 2, b-VTSSO possesses the best nanomechanical properties among the three bulks. Reaction conditions determine the best properties of b-VTSSO. During the preparation of b-VTSSO, the hydrolytic condensation is slower in the sealed beaker and the volatile products (methanol and water) are unable to volatilize out of the container. The OR′or OH groups containing an incomplete VTSSO can be continuously hydrolyzed and condensed at 120 °C for 24 hours, while the volatiles on the beaker wall and on the plastic film surface drop back into the sol. Thus the crosslinked network of b-VTSSO is much denser, the pores in the network become smaller and the nanomechanical properties of b-VTSSO are better than the other two bulks.

The other factor influencing the nanomechanical properties of the bulks is organic-chain flexibility. Without a stiff substrate support, the moveable behavior of the longer-linked chains in the bulks (such as b-MTSSO) becomes a significant contribution to their softness and to their poorer mechanical properties. However, the shorter-linked chains in the denser b-VTSSO are more difficult to move when forced than those in b-GTSSO and b-MTSSO. Thus the nanomechanical properties of b-VTSSO are enhanced and superior to the other two. Although the OR′or OH groups contained in GTSSO can be greatly reduced by further hydrolytic condensation under the reaction conditions of the prepared bulks, b-GTSSO still possesses the worse nanomechanical properties (similar to b-MTSSO) due to the moveable longer-linked chains in b-GTSSO without a stiff substrate support.

Harmonic Contact Stiffness (HCS)

Figure 3 show the other nanomechanical property (harmonic contact stiffness, *HCS*) profiles of three films and three bulks,

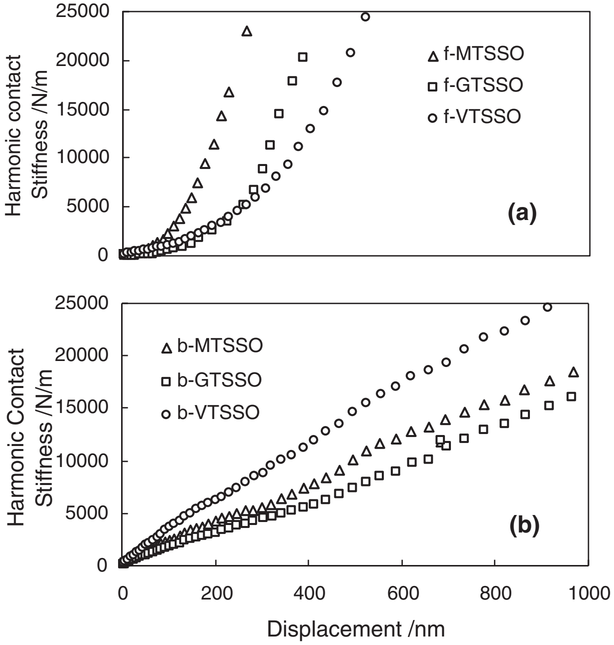

Figure 3.

The *HCS* profiles of three SSO films (a) and three SSO bulks (b) modified with 15 wt-% TEOS in a depth range of 0–1000 nm.

respectively. There are two obvious differences between the film- and bulk-*HCS* profiles: 1) a nonlinear curve for the film-*HCS* profile and an almost straight line for the bulk-*HCS* profile; 2) the film *HCS* approaches a maximum value through a shorter displacement but the bulk *HCS* approaches a maximum value in a longer displacement. These differences are caused by the substrate effect on the soft-film/hard-substrate coating system. A significant difference exists for the *HCS* values between the films and bulks: f-MTSSO has the stiffest *HCS* value among the films but b-VTSSO has the stiffest *HCS* value among three bulks (similar to the *H* and *E* of the SSO bulks) due to: 1) the reaction conditions leading to a decrease in the OR′or OH groups in b-VTSSO and to a much denser network in b-VTSSO; 2) a less chain flexibility because the shorter-linked chains in the denser b-VTSSO are difficult to move when they are forced, enhancing the nanomechanical properties of b-VTSSO.

Conclusions

Compared with the *H* and *E* profiles of films, there were no substrate effect regions in the bulk profiles.

With different functionated structures, the f-MTSSO exhibits good nanomechanical properties which are higher than the other films (f-GTSSO and f-VTSSO) due to the presence of a bulky organic substituent and the greater interactions with each other. For the f-GTSSO with a bulky organic substituent, the unsatisfactory properties can be attributed to an incomplete cross-linking network resulting from ring opening during hydrolytic condensation of the GPMS. In addition, the f-VTSSO building blocks possess the ladderlike structure (containing more OH or OR′ groups) to make the f-VTSSO network have lower density and the lower nanomechanical properties.

However, b-VTSSO possesses the best nanomechanical properties among the three bulks due to: 1) the reaction conditions leading to a decrease in the OR′or OH groups in b-VTSSO and to a much denser network in b-VTSSO; 2) a less chain flexibility because the shorter-linked chains in the denser b-VTSSO are difficult to move when they are forced, enhancing the nanomechanical properties of b-VTSSO.

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