ORMOSIL Thin Films: Tuning Mechanical Properties via a Nanochemistry Approach

Giovanni Palmisano,[†] Eric Le Bourhis,[‡] Rosaria Ciriminna,[†] Davide Tranchida,[§] and
Mario Pagliaro*,[†]

*Istituto per lo Studio dei Materiali Nanostrutturati, CNR, via Ugo La Malfa 153, 90146 Palermo, Italy,
Laboratoire de Métallurgie Physique, CNRS UMR 6630, Université de Poitiers, 2 bd Marie et Pierre
Curie, 86962 Futuroscope-Chasseneuil Cedex, France, and Dipartimento di Ingegneria Chimica dei
Processi e dei Materiali, Università degli Studi, Viale delle Scienze, 90128 Palermo, Italy*

The mechanical properties (hardness and elastic modulus) of organically modified silicate thin films can be finely tuned by varying the degree of alkylation and thus the fraction of six- and four-membered siloxane rings in the organosilica matrix. This opens the way to large tunability of parameters that are of crucial practical importance for films that are finding increasing application in numerous fields ranging from microelectronics to chemical sensing.

Introduction

Thin films of organically modified silicates (ORMOSILs) are commercially used in chemical sensing as sensors of unprecedented sensitivity[1] and in microelectronics as dielectric materials[2] and will soon find ubiquitous diffusion as ideal OLEDs in electronic devices.[3] Similar thin functional coatings are potentially extremely important to industry since a small amount of hybrid (organic−inorganic) material imparts improved new properties at low cost.

In general, trifunctional alkoxysilanes and silicon alkoxides are excellent cross-linkers and upon sol−gel polycondensation usually lead to hybrid materials with a high Young's modulus ($E > 10$ GPa) and a high (or even no) glass transition temperature (T_g). A major limitation to applicability, however, often resides in their poor mechanical behavior, so the possibility to tune the mechanical properties of these materials remains a major goal of current research in materials chemistry. Considerable work has been devoted to the study of organosilica and especially epoxy- and methacrylate-modified silica gels,[4] but only one recent study[5] addressed the behavior of alkyl-modified ORMOSIL soft coatings of methyltrimethoxysilane (MTMS) filled with colloidal SiO_2 or alumina particles on glass substrates, correlating the

response with coating thickness. Interestingly, without organic modification a brittle behavior was reported.

Using a nanochemistry approach[6] typical of the sol−gel synthesis of nanostructured materials, we show how to achieve fine-tuning of the mechanical properties of extremely smooth sol−gel coatings by varying the organic modification of the ORMOSIL matrix. An explanation of the drastic variation in mechanical response based on insight into the structural changes in the organosilica molecular structure is thus proposed, providing information that will be useful in guiding future preparation of efficient coatings for a multiplicity of industrial applications.

Experimental Section

Film Preparation. A series of thin films was obtained by spin-coating 1 mL of different sol precursor solutions obtained by stirring a solution with the composition specified in Table 1 in a closed vessel. Acidic hydrolysis lasted from 1 to 6 h (time increasing with alkylation percentage).

The films were spin coated over untreated glassy microscope slides using a Chemat Technology KW-4A spin coater. The spin-up speed was set at 1000 rpm (for 18 s) and the spin-off speed at 3000 rpm for a subsequent 60 s. The films thereby obtained were first dried at room temperature for 1 h, after which they were dried at 60 °C in a Chemat Technology oven for 24 h. The resulting films were uniform and homogeneous (Figure 1). Scanning electron microscopy (SEM) pictures were taken with an SEM Philips 515 microscope.

Nanoindentation. A reference microscope slide (substrate) was added to the series showing that all films are actually softer than the slide. All the resulting films were tested using a nanoindenter from CSM Instruments (Peseux, Switzerland) and, to test at very small loads, a nanoindentation system assembly of an atomic force microscope SPM P47 Solver (NT-MDT, Moscow, Russia) with the standard head replaced with a Triboscope indentor system (Hysitron Inc., Minneapolis, MN). Both the instruments were equipped with a Berkovich indenter, with an equivalent semiopening angle of 70.3°.

* To whom correspondence should be addressed. E-mail: mario.pagliaro@ismn.cnr.it.

† CNR.

‡ Université de Poitiers.

§ Università degli Studi di Palermo.

(1) By the U.S.-based company Ocean Optics Ltd., which commercializes an easy-to-use hand-held optical sol−gel oxygen sensor (named FOXY-LITE) with a response time of less than 1 s using a fluorescent ruthenium complex immobilized in a silica sol−gel matrix at the probe's tip; Tang, Y.; Tehan, E. C.; Tao, Z.; Bright, F. V. *Anal. Chem.* **2003**, *75*, 2407.

(2) Hatton, B. D.; Landskron, K.; Whitnall, W.; Perovic, D. D.; Ozin, G. A. *Adv. Funct. Mater.* **2005**, *15*, 823.

(3) Veinot, J. G. C.; Marks, T. J. *Acc. Chem. Res.* **2005**, *38*, 632.

(4) To ensure formation of small, highly porous organosilica particles made of flexible chains as discussed in the following review: Mammeri, F.; Le Bourhis, E.; Rozes, L.; Sanchez, C. *J. Mater. Chem.* **2005**, *15*, 3787.

(5) A drastic increase of hardness as a function of the penetration depth was reported for the thinnest coatings (0.5 μm), while the hardness response was almost a plateau for the 4 μm thick film within the investigated range. Under elevated load the thinnest films showed only delamination and chipping, while the thickest films showed first radial cracks that were followed by delamination and chipping: Malzbender, J. J.; den Toonder, J. M.; Balkenende, A. R.; de With, G. *Mater. Sci. Eng., R* **2002**, *36*, 47.

(6) In the same logic as Geoffrey Ozin and André Arsenault's book *Nanochemistry: A Chemical Approach to Nanomaterials* (Royal Society of Chemistry: Cambridge, U.K., 2005) the word "nanochemistry" here refers to a basic chemical strategy for making nanomaterials using molecular- or nanometer-scale building blocks (with a wide range of shapes, compositions, and surface functionalities) that are further chemically processed to organize into structures serving as tailored functional materials. See also the recent theme issue on hybrid sol−gel materials: *J. Mater. Chem.* **2005**, *15*, 35−36.

Table 1. Composition of the Precursor Solution Yielding Thin Films upon Sol−Gel Polycondensation[a]

	Si0Me	Si5Me	Si25Me	Si50Me	Si75Me	Si100Me
degree of alkylation (%)	0	5	25	50	75	100
TMOS vol (μL)	500	475	375	250	125	0
MTMS vol (μL)	0	24	120	240	359	479
CH$_3$OH vol (μL)	461	461	461	461	461	461
H$_2$O vol (μL)	329	329	329	329	329	329
HCl (10^{-2} M) vol (μL)	34	34	34	34	34	34

[a] Molar ratios Si:H$_2$O:MeOH:H$^+$ = 1:6:4:10^{-4}. TMOS = tetramethyl orthosilicate, and MTMS = methyltrimethoxysilane.
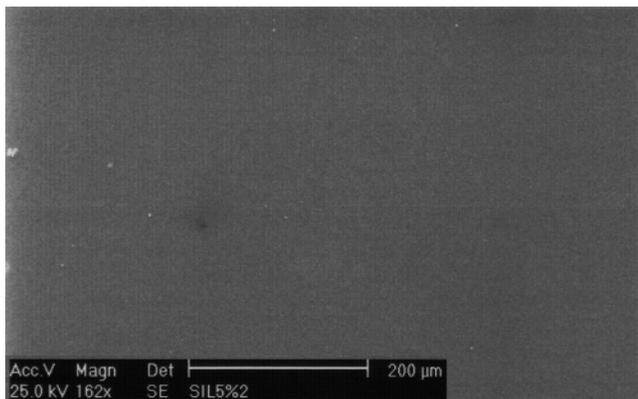
Figure 1. High-resolution SEM picture of a 5% methyl-modified thin film showing excellent homogeneity.

Figure 2. Loading curves for ORMOSIL thin films with varying degree of alkylation of the silica matrix.

Loads ranged between 30 and 2500 μN, and the loading rate was in the range 7−100 μN/s, measuring thermal drift and correcting accordingly for each indentation.

Indentations were performed in load-controlled mode after collection of images of the area to be indented, to check the surface roughness in the selected area. Following the procedure introduced by Oliver and Pharr,[7] the machine compliance and the area function, i.e., the relation between contact depth and contact area, were first calibrated.[8]

Results and Discussion

Hardness in this work represents the mean contact pressure, i.e., the ratio of the applied load and the resulting contact depth. The elastic modulus is calculated by the Oliver and Pharr procedure, which allows one to evaluate the so-called reduced elastic modulus E_r by fitting the unloading curve with a power-law relation.

In particular, following the equations derived by Sneddon describing the elastic contact between a rigid indenter and an elastic half-space, this is accomplished after evaluation of the derivative of the latter curve at the point of maximum penetration depth through the following equation:[7]

$$S = \frac{dF}{dh}\Big|_{h=h_{max}} = 2\beta E_r \left(\frac{A_c}{\pi}\right)^{1/2} \qquad (1)$$

where S is the contact stiffness, F is the applied load, h is the penetration depth, and A_c is the contact area. The correction factor β is a pure geometric correction factor, which takes into
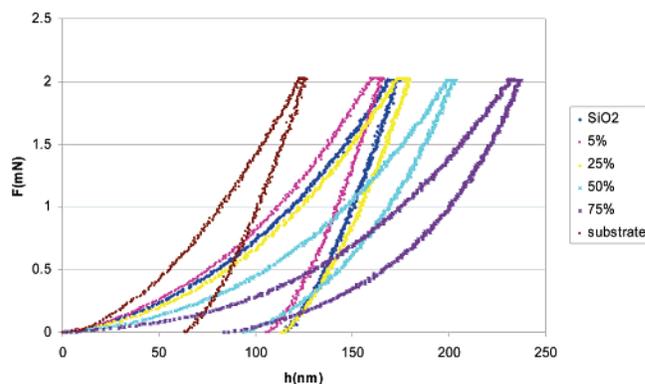
account that the indenter is not a perfect cone (King determined, by FEM simulations, for the Berkovich indenter a β value of 1.034).[9]

On the basis of this approach, and also taking into account the limitations pointed out by Chaudri on the use of the concept of the reduced elastic modulus,[10] the indenter was assumed to be rigid with respect to our films, so the original relation by Sneddon can be applied:

$$E_{film} = (1 - \nu^2)E_r \qquad (2)$$

The Poisson ratio ν was assumed equal to 0.3 for the films in this work.

Curves in Figure 2 clearly show drastic differences among the samples. As expected, the maximum penetration increases with the degree of alkylation, from about 150 nm for unmodified SiO$_2$ to almost 250 nm for the 75% methyl-modified silica film. All the films were mechanically stable. Hence, the time dependence was checked for all the films and was found *not* to affect the response as shown by the overlapping curves in Figure 3, comparing for instance the response of Si100Me with two different loading rates and the force curves shown in the inset of Figure 3 where the Si50Me ORMOSIL film was tested at 7 and 70 μN/s loading rates.

The elastic moduli represented in Figure 3 vary with the nanoindentation depth, indicating a clear substrate effect which is usually reported for a penetration depth on the order of 10% of the film thickness.[11]

Remarkably, the nanoindentation measurements are reproducible, which is often not the case for thin polymer films, as shown by the 15 force curves (for the same film, with <2% variation in the measured values) at varying loads between 30 and 2000 μN (Figure 4).

(7) Oliver, W. C.; Pharr, G. M. *J. Mater. Res.* **1992**, *7*, 1564.
(8) The area function, i.e., the relation between contact depth and contact area, was calibrated by performing several indentations on fused silica with the penetration depth in the range of 10−300 nm, with good reproducibility. The reduced elastic modulus of fused silica (E_r = 69.6 GPa) was used as input to evaluate the contact area at each contact depth, and the plot was fitted with the Oliver and Pharr dependence, obtaining the area function.

(9) King, R. B. *Int. J. Solids Struct.* **1987**, *23*, 1657.
(10) Chaudri, J. *J. Mater. Res.* **1999**, *16*, 336.
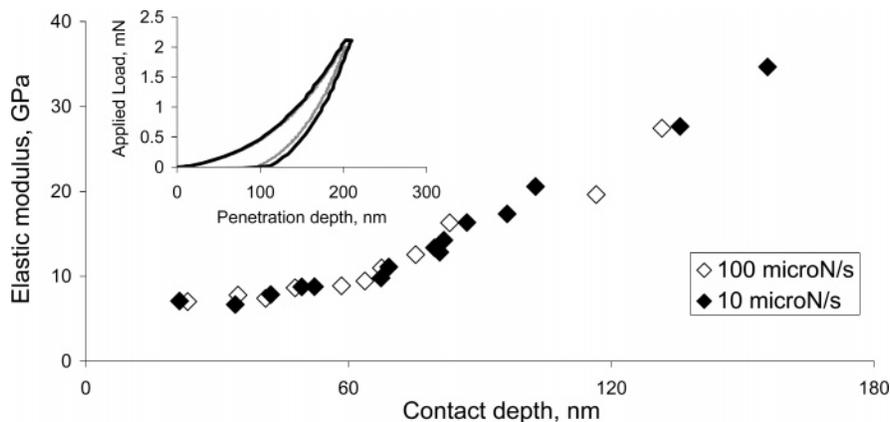(11) Fischer-Cripps, A. C. *Nanoindentations*, Springer-Verlag: New York, 2002.

Figure 3. Elastic modulus of the Si100Me film undergoing nanoindenation at different speeds and, in the inset, loading curves for the Si50Me film at different speeds (black line, 7 mN/s; gray line, 70 mN/s).
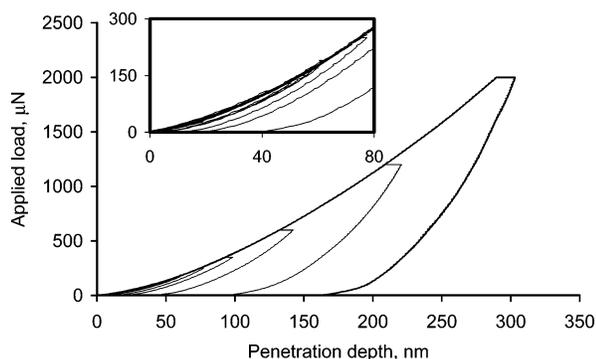

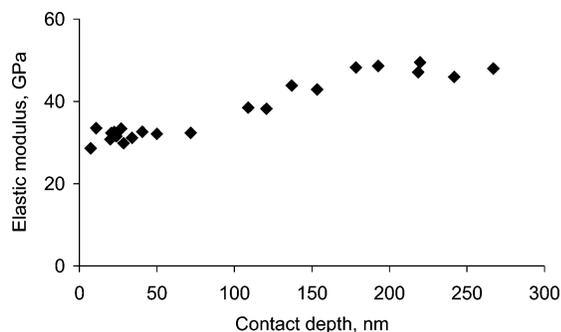**Figure 4.** Loading−unloading force curves at varying loads between 30 and 2000 μN for the Si50Me film.

Figure 5. Variation of the elastic modulus versus contact depth for the Si5Me film.

Figure 6. At 2 mN nanoindentation of the film surface (here shown for the SiMe25 sample) with deep tip penetration masks the measurements due to the effect of the substrate. (a) and (b) show two different views.

However, a plateau appears pointing at a shallow contact depth, i.e., on the true nanometer scale, as shown in Figure 5 for the Si5Me sample; it is worth stressing that similar results were observed for all films. Collecting images of the residual imprint on the nanoindented film at 2 mN (Figure 6), one can easily find that the resulting penetration depth is too large with respect to the thickness of a film obtained by spin-coating.

Furthermore, to apply the Oliver and Pharr (O&P) approximation, measurements at high loads become problematic since the exponent in the nanoindentation unloading curve, to measure the Young's modulus of materials on a nanometer scale, must be smaller than 2.[12] As well rendered by Figure 7 in our ORMOSIL films at high loads such a slope becomes larger than 2, making the application of the O&P model conceptually wrong.

Taking these subtle effects into consideration, and thus limiting measurements at lower loads, intrinsic hardness and elasticity
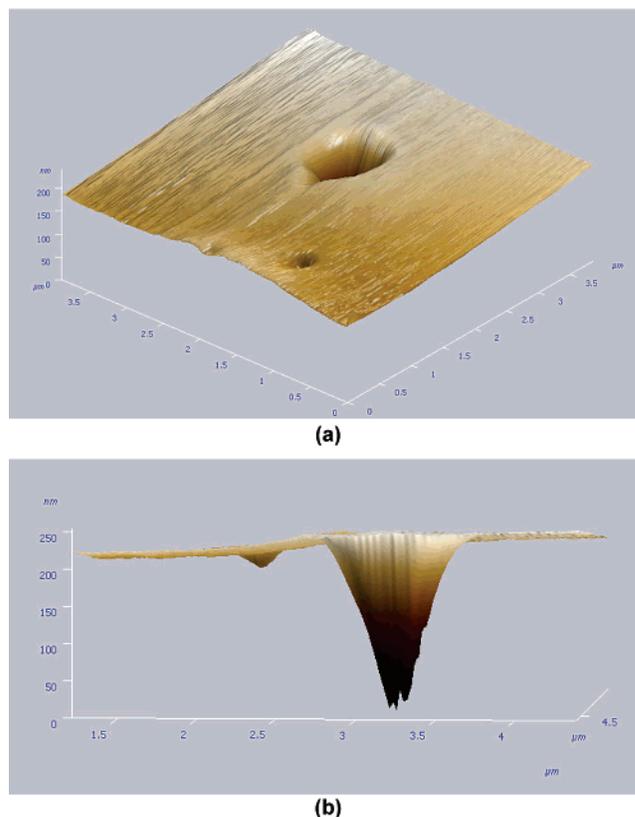
(12) Tranchida, D.; Piccarolo, S. *Macromol. Rapid Commun.* **2005**, *26*, 1800.

values for the ORMOSIL films are given in Table 2 and plotted in Figure 8 as a function of the degree of alkylation of the silica matrix (values are averages of 15 different tests for each sample).

Trends in Figure 8 reveal valuable information. The hardness values are well below 10 GPa and show substantial variation when the degree of alkylation reaches a relatively large value of 50%, when a neat decrease in hardness from 4.2 (for unmodified silica) to 2.5 GPa is observed. The modulus values, on the other hand, are large and sharply decrease until an 8.6 GPa minimum is attained for the 100% methylated film.

These results correlate surprisingly well with a molecular structural feature of ORMOSIL recently discovered by a detailed DRIFT structural analysis[13] that shows how in the absence of MTMS the SiO_2 structure is dominated by four-membered
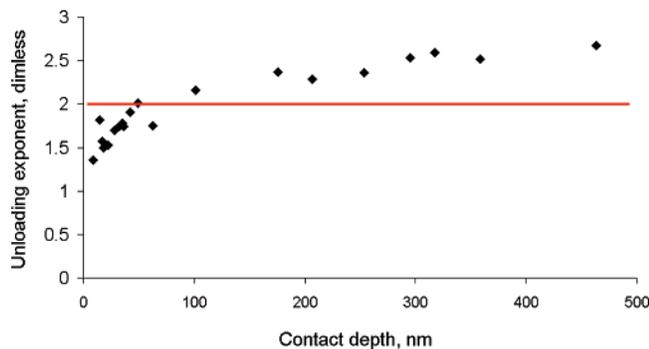
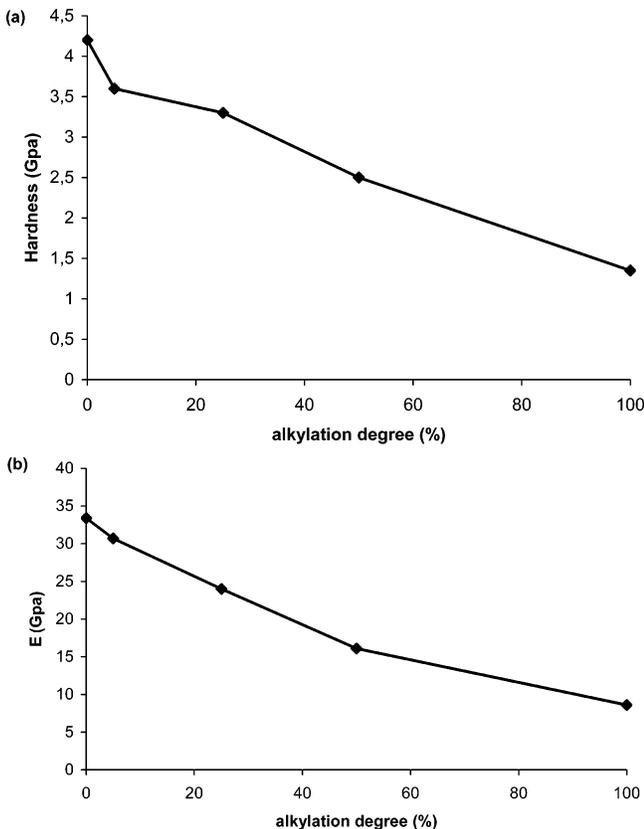**Figure 7.** Variation of the unloading exponent (*b*) versus contact depth.

Figure 8. Hardness (a) and elastic modulus (b) as a function of the degree of alkylation of the silica matrix in ORMOSIL thin films.

Table 2. Hardness and Elastic Modulus Values for Silica and ORMOSIL Thin Films

sample	H (GPa)	E (GPa)	sample	H (GPa)	E (GPa)
Si0Me	4.2	33.4	Si50Me	2.5	16.1
Si5Me	3.6	30.7	Si100Me	1.35	8.6
Si25Me	3.3	24			

siloxane rings (Figure 9 and Table 3), but a spectacular increase in the fraction of six-membered rings to 20%, 56%, 84%, and 97% is observed as the MTMS content increases to 25%, 50%, 75%, and 100%.

Such a large variation in the ORMOSIL structures is well reflected in their mechanical properties. Hence, stiffness—the resistance of the resulting elastic structure to deflection by an applied force—correlates inversely with the presence of $(SiO)_6$ rings in the organosilica matrix (Figure 10), which is ex-
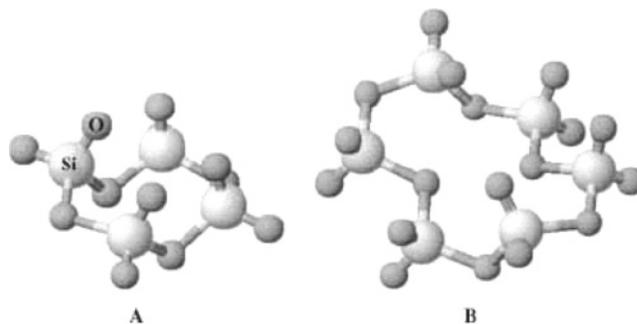

Figure 9. Schematic diagram of the more common types of primary cyclic arrangements of the structural units, SiO$_4$, in xerogels: (A) four-membered siloxane ring $(SiO)_4$ and (B) six-membered siloxane ring $(SiO)_6$.

Table 3. Relative Percentage of Four- and Six-membered Rings As Obtained by Deconvolution of the DRIFT Spectra[a]

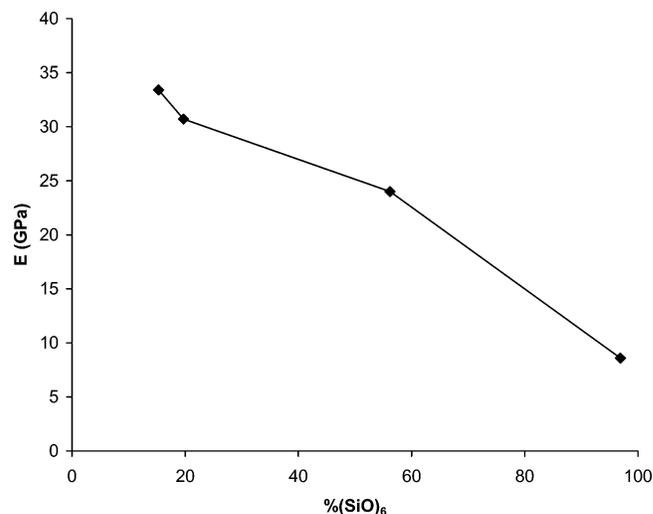|	Si0Me	Si25Me	Si50Me	Si100Me
$[(SiO)_6]$ (%)	15.3	19.7	56.2	96.9

[a] Values taken from ref 13.

Figure 10. Correlation between the elastic modulus and the percentage of $(SiO)_6$ rings in the organosilica matrix.

plained by the larger, less tensioned structure of the six-membered rings constituent of the organosilica (and not by variation in the degree of cross-linking, which besides modest alkylation is known to be poorly affected by an increasing degree of alkylation).[14]

On the other hand, the lower differences in the ORMOSILs' hardness values reflect exactly the absence of significant differences in the degree of cross-linking between ORMOSIL and unmodified silica xerogels mentioned above.[14] Finally, another structural characteristic of relevance to this study is that the material's external surface is depleted of silanol groups, leading to low optical loss in the near-infrared, which is an essential requirement for optical applications such as waveguides; moreover, in such coatings strong chemical adhesion between the glass substrate hydroxyls and the film occurs, limiting delamination.[4]

(13) Fidalgo, A.; Ciriminna, R.; Ilharco, L. M.; Pagliaro, M. *Chem. Mater.* **2005**, *17*, 6686.

(14) For example, in an ORMOSIL derived by pure MTMS, the degree of cross-linking amounts to 90%, pointing to extended connectivity among the siloxane units: Reetz, M. T.; Zonta, A.; Simpelkamp, J.; Rufinska, A.; Tesche, B. *J. Sol-Gel Sci. Technol.* **1996**, *7*, 35.

Conclusions

The rich structural diversity and the versatile chemistry of sol−gel-assembled ORMOSILs[15] enable the opportunity for tailoring of the mechanical properties of thin films made of organosilica. The work reported in this paper demonstrates the possibility of finely tuning their mechanical response by adjusting the organic content of the organosilica matrix. Good correlation exists between the variation of both the hardness and the elastic modulus with the fraction of six-membered siloxane rings in the silica matrix.

(15) Pagliaro, M.; Ciriminna, R.; Wong Chi Man, M.; Campestrini, S. *J. Phys. Chem. B* **2006**, *110*, 1976.