Brillouin spectroscopy on dried sonogels

M. García-Hernández,[a] R. J. Jiménez-Riobóo, and C. Prieto
Instituto de Ciencia de Materiales de Madrid, C.S.I.C. Cantoblanco s/n 28049-Madrid, Spain

J. J. Fuentes-Gallego, E. Blanco, and M. Ramírez-del-Solar
Dpto. de Física de la Materia Condensada, Universidad de Cádiz, Apartado 40. 11510-Puerto Real, Cádiz, Spain

(Received 10 July 1996; accepted for publication October 1996)

The elastic properties of organically modified silicates prepared by ultrasonics aided polycondensation of Tetraethoxysilane and Polidimethylsiloxane is studied by means of high resolution Brillouin spectroscopy. Our results evidence the microseparation of the organic and inorganic phases for the systems with high content of polymer. We propose a mechanical model that qualitatively explains the observed variation of the elastic constant c_{11} vs molar fraction of dimethylsiloxane in these vitreous materials and develop a structural model that accounts for the observed dynamical behavior. © *1996 American Institute of Physics.* [S0003-6951(96)01751-2]

The unique properties of organically modified silicates (ORMOSILS) as produced by the sol-gel methods have recently made the study of these materials a fast growing field.[1] In particular, the macroscopic elastic properties of rubberlike materials obtained by hydrolysis and ulterior polycondensation of organic polymers with inorganic silica based precursors have been fully explored by standard methods (basically Young's Modulus measurements) since the early work by Mackenzie *et al.*[2] However, little attention has been paid to the dynamic elastic behavior of these materials and its correlation to the macroscopically observed properties. This is a major point since a full understanding of the interplay between structural and dynamical correlations is required so as to tailor the mechanical properties of these novel materials. Brillouin scattering has proven to be an essential technique to disentangle the fundamental aspects of the viscoelastic and elastic properties of a broad range of amorphous materials.[3] To the authors knowledge, this work represents the first attempt to apply this technique to the study of dried gels. We have chosen a set of samples prepared by the sol-gel route, following the sonogel procedure.[4,5]

Tetraethoxysilane (TEOS) from Merck ($n=1.38$, $\rho=0.983\ \mathrm{g\,cm^{-3}}$) was used as an inorganic precursor and polydimethylsiloxane (PDMS), with an average MW of 550, from Hüls America Inc. ($n=1.40$, $\rho=0.950\ \mathrm{g\,cm^{-3}}$), as an organic component. HCl acid was utilized as catalyst. ORMOSILS processing was carried out aided by a high power ultrasound probe (20 kHz, 15 W).

In order to avoid macroscopic phase separation due to differences between TEOS and PDMS hydrolysis rates, TEOS was prehydrolyzed by subjecting a mixture of TEOS and acidic water (2 mol/mol TEOS) to the ultrasound radiation dose $E_s=60\ \mathrm{J\,cm^{-3}}$. Subsequently, an amount of PDMS, ranging from 0 to 40 wt % referred to TEOS, was added and an additional ultrasonic energy was applied to complete the total energy dose of $0.12\ \mathrm{kJ\,cm^{-3}}$. The resulting solution gels after a period of time, ranging from 32 min to one week when increasing PDMS content. Finally, samples were aged in the closed container for one week and dried for at least two weeks resulting in monolithic samples of ORMOSILS which are transparent for the lower doses of organic component but become milky for the higher one.

For the sake of clarity, the organic fraction in the hybrid material will be expressed in the following as the corresponding monomer molar fraction defined as (DMS) mol/(TEOS mol + DMS mol).

Two different scattering geometries were used in all cases, the so called 90A[6] and the backscattering. The light source is an $\mathrm{Ar^+}$ laser with a wavelength of 514.5 nm. The scattered light is analyzed using two Fabry–Perot interferometers mounted in tandem,[7] working in an overall six pass basis.

For the 90A geometry (right angle scattering), the phonon wave-vector does not depend on the refractive index of the sample, which is unknown for this particular set. The phonon wavelength for the scattering geometries used in this experiment are: $\Lambda^{90\mathrm{A}}=363.8$ nm and $\Lambda^{180}=(514.5/2n)$ nm and the sound velocity, v, can be calculated via

$$v=f\Lambda, \tag{1}$$

where f is the corresponding Brillouin shift in frequency units. The elastic constant can be extracted using

$$c=\rho v^2, \tag{2}$$

where ρ is the density of the material. In the case of an isotropic solid, there are only two independent elastic constants, c_{11} and c_{44}, corresponding to the pure longitudinal and pure transverse polarized modes, respectively.[8]

Figure 1 shows a typical spectrum recorded using the 90A geometry for the sample containing 41.6% molar fraction of monomer DMS as well as the corresponding one recorded in the backscattering geometry. Since an external reference was used to stabilize the tandem, the existence of ultraslow modes could not be assessed. However, the presence of any broad central mode was not detected and the presence of fast relaxations in the explored systems cannot be inferred. No transverse modes appear in the measured spectra, most likely due to the severe overdamping of the acoustic modes in these porous materials.

---

[a] On leave from Instituto de Estructura de la Materia, C.S.I.C.

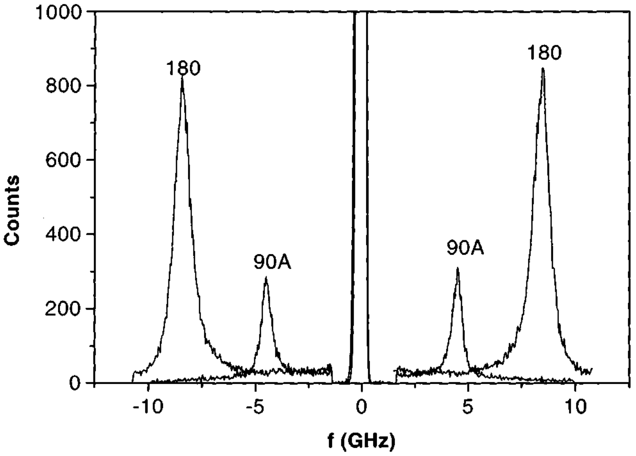

FIG. 1. Two representative spectra recorded for the sample containing 41.6% molar fraction of DMS. Labels 180 and 90A stand for backscattering and right angle geometry, respectively.

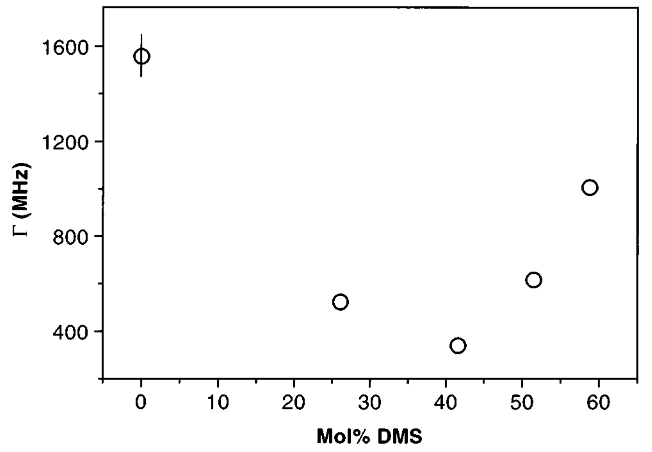

FIG. 3. DMS molar fraction dependence of the hypersonic attenuation Γ (taken as HWHM of the Brillouin peaks).

In order to evaluate the elastic constant c_{11}, shown in Fig. 2, we used density values stemming from He picnometry given by $\rho(\mathrm{gr/cm^3}) = 1.726 - 0.00945 * M$ (M being the molar fraction of DMS). We could also obtain density values for samples containing 0% and 41.6% molar fraction of DMS using C_6H_{12} picnometry. In the case of the 0% sample, both picnometries give the same density value while in the case of the 41.6% sample the C_6H_{12} picnometry gives a 15% lower value. This fact indicates a clear decrease in pore size with the inclusion of PDMS. From Fig. 2, it becomes obvious the set in of a smooth crossover in the elastic behavior of these materials between two regimes. This change is fulfilled at DMS monomer concentration around 40% and an asymptotic trend is followed at higher concentrations pointing towards the value obtained for the pure liquid PDMS.

We have also analyzed the dependence of the hypersonic attenuation (Brillouin peak widths) on the molar concentration of PDMS in the sample. These widths, Γ [measured as half-width at half-maximum (HWHM)], are related to the acoustic attenuation at these hypersonic scales and, therefore, to the phonon lifetimes τ ($\Gamma = 1/\tau$). Figure 3 shows the observed values of Γ vs molar fraction of monomer DMS as measured in the backscattering geometry. A pronounced effect of the composition of the sample on the attenuation is already apparent. We observe an initial increase of the phonon lifetime when adding small quantities of PDMS (up to 20%–40% molar on DMS) followed by a decrease of this magnitude with the PDMS content in the sample. Simultaneously, a continuous decrease in the value of the elastic constant is observed as the PDMS content raises. This behavior can be rationalized in terms of number of interphases (i.e.: porosity and microsegregation) and a physical picture of the system emerges in which two plausible PDMS forms in the sample (segmentlike and globular) coexist. For low concentration of PDMS, the inclusion of organic material in the silica network takes place quite uniformly as chains embedded in the silica matrix. The enrichment in PDMS together with the decrease in porosity of the material are reflected by a decay in the hypersonic attenuation. However, a lower pore density would imply an increase in the elastic constant which is not observed. Therefore, the measured decay (Fig. 2) can only be explained by a renormalization of the elastic properties of the gel due to the linking of PDMS to TEOS. This situation remains till the PDMS concentration is high enough to allow the globular configuration of PDMS to preferentially establish. This is consistent with the fact that at high polymer concentrations the globular form is, from the thermodynamic point of view, more stable.[9] A side product of this structural change towards some sort of microphase separation is the building up of liquidlike islands and, consequently, the lifetime of the phonons decreases while some sort of ''saturated'' value is reached for the elastic constant c_{11}. The difference in the observed linewidths at these high PDMS concentrations in relation to the measured linewidth for liquid PDMS (0.7 GHz) can be explained in terms of the porosity of the gels and severe changes in the acoustic impedances when the phonon crosses the interphase limiting the liquid islands.

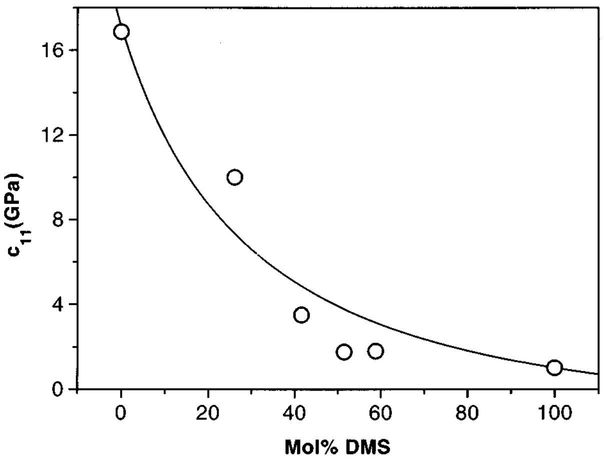

FIG. 2. Values of the elastic constant c_{11} vs molar fraction of DMS. Error bars are contained within the open symbols. The solid line is the best fit to the model described by Eq. (3).

Following the lines of the two extreme models proposed by Mackenzie,[2] we propose a mathematical model that qualitatively explains the observed elastic behavior. The main ingredient of our model is the consideration of two structurally different forms of PDMS whose relative contributions to the observed elastic behavior are normalized to the total content of PDMS in the sample. Both forms, PDMS in a segmentlike configuration within the backbone of the -SiO_{2-} network and PDMS in a quasiglobal (liquidlike) configuration, are parallel branched while being branched in series to the -SiO_2-structure. The model reads,

$$c_{11}=\frac{1}{\left[\frac{1-x}{c_1}+\frac{x}{c_2(1-x)+c_3x}\right]}, \tag{3}$$

where x is the molar fraction of DMS monomer, c_1 refers to the elastic constant of silica, c_2 and c_3 are the elastic constants of PDMS in a segmentlike and globularlike configuration, respectively. The fitted parameters in our model are c_1 and c_2, c_3 being constrained to the value of the elastic constant of liquid PDMS. This assumption is physically sound since no solid form of the polymer can be softer than the corresponding liquid and, in fact, none of the measured values for c_{11} lies below this limit. As it can be seen in Fig. 2 the model, in spite of its simplicity, describes the elastic behavior of the sonogels on semiquantitative grounds. The values of the best fit for the fitting parameters are $c_1=17.1$ GPa and $c_2=3.4$ GPa with c_3 fixed to 1.02 GPa as measured for the liquid.

The proposed picture agrees with the phenomenology reported for these materials. According to NMR data,[10] at the lowest concentrations of PDMS in the sample the probability of bonding between TEOS and PDMS in sites different from the two extremes of the PDMS chain is very high, while competing processes of autocondensation for PDMS are minimized, therefore a more efficient interbonding of the inorganic and organic components occurs.[11] As the molar fraction of PDMS increases, the probability of breaking the polymer chain by TEOS decreases and autocondensation of PDMS is more feasible. Microphase separation of both phases has been observed for closely related systems using a great variety of techniques probing either dynamical or structural aspects of these materials.[11–13]

High resolution Brillouin spectroscopy has proven to be an ideal technique to study the elastic properties of ORMOSILS. From the measured dynamic and static hypersonic properties, the elastic constant c_{11} can be extracted and a structural model can be inferred to explain the observed behavior of the phonon lifetimes.

This work has been partially supported by Junta de Andalucía (Exp No. 6015) and by CICYT (Proj No. MAT-95-0040-C02-02) and (Proj No. MAT-94-722).

[1] J. D. Mackenzie, Y. J. Chung, and Y. Hu, J. Non-Cryst. Solids **147, 148**, 271 (1992).

[2] Y. Hu and J. D. Mackenzie, J. Mater. Sci. **27**, 4415 (1992), and references therein.

[3] J. Kruger, in *Optical Techniques to Characterize Polymer Systems*, edited by H. Bassler (Elsevier Science Publishers, Amsterdam, 1989), pp. 429–534.

[4] L. Esquivias and J. Zarzycki, in *Ultrastructure Processing of Advanced Ceramics*, edited by J. D. Mackenzie and D. R. Ulrich (Wiley, New York, 1987), pp. 255–270.

[5] T. Iwamoto and J. D. Mackenzie, J. Sol-Gel Sci. Technol. **4**, 141 (1995).

[6] J. K. Kruger, A. Marx, L. Peetz, R. Roberts, and U. G. Unruh, Col. Pol. Sci. **264**, 403 (1986).

[7] J. R. Sandercock, in *Topics in Applied Physics* (Springer, Berlin, 1982), Vol. 51, p. 173.

[8] B. A. Auld, in *Acoustic Fields and Waves in Solids* (Wiley, New York, 1973).

[9] P. J. Flory, in *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, New York, 1953), Chap. 10.

[10] T. Iwamoto, K. Morita, and J. Mackenzie, J. Non-Cryst. Solids **159**, 65 (1993).

[11] H. Huang, B. Orler, and G. L. Wilkes, Macromolecules **20**, 1322 (1987).

[12] N. Micali, C. Vasi, F. Mallamace, R. Bansil, S. Pajevic, and F. Sciortino, Phys. Rev. E **48**, 4501 (1993).

[13] M. García-Hernández, R. Jiménez-Riobóo, C. Prieto, E. Blanco, and M. Ramirez-del-Solar, NMR experiments on aged ORMOSILS (unpublished).