

Tapping Mode AFM Evidence for an Amorphous Reticular Phase in a Condensation-Cured Hybrid Elastomer: α,ω -Dihydropoly(dimethylsiloxane)/Poly(diethoxysiloxane)/Fumed Silica Nanoparticles

Tomoki Ogoshi,^{†,‡} Tomoko Fujiwara,[†] Massimo Bertolucci,[§] Giancarlo Galli,[§] Emo Chiellini,[§] Yoshiaki Chujo,[‡] and Kenneth J. Wynne^{*,†}

Chemical Engineering Department, School of Engineering, Virginia Commonwealth University, 601 West Main Street, Richmond, Virginia 23284-3028, Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan, and Dipartimento di Chimica e Chimica Industriale, Università di Pisa, UdR Pisa-INSTM, Via Risorgimento 35, 56126 Pisa, Italy

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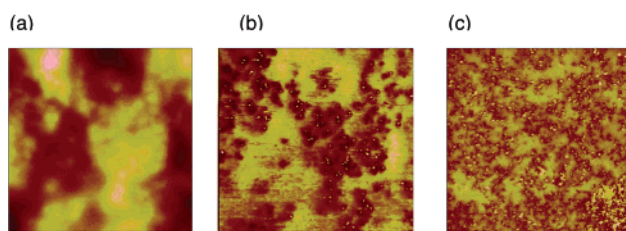
Hybrid nanocomposite materials have received much attention in recent years, opening a wide range of opportunities for new materials.¹ One nanocomposite subset includes soft hybrids based on poly(dimethylsiloxane) (PDMS).² PDMS hybrids are hydrophobic, have low-temperature elasticity ($T_g = -123$ °C), and display good hemocompatibility and biocompatibility.³ PDMS/metal oxide hybrids are prepared in situ using metal alkoxides that undergo hydrolysis and condensation reactions.⁴ We have focused on PDMS hybrid surface science, including dihydroxy-terminated PDMS ($\text{HO}(\text{Me}_2\text{SiO})_n\text{H}$) cross-linked by condensation with fluorinated alkoxy silanes⁵ or poly(diethoxy-siloxane) (PDES).⁶ These studies and those on Pt-cured divinyl PDMS revealed time-dependent surface morphologies and the *intrinsic* wetting behavior of PDMS coatings.⁷

Hydrosilylation or condensation-cured PDMS networks are weak materials usually needing fillers for good mechanical properties.⁸ The customary filler for many applications, including biomedical elastomers,³ is amorphous fumed silica nanoparticles (FSN), which consist of nanoparticles and clusters. In the present research, a modification of “technology” known since 1950⁹ was used to prepare FSN PDMS hybrids (Scheme 1). In a surface analysis by tapping mode atomic force microscopy (TM-AFM), a surprising result was observed. For certain compositions and cure conditions the near-surface fumed silica nanoparticles seemed to “disappear”. Below, we report experiments that elucidate the basis for this phenomenon. The results shed new light on structure in condensation-cured PDMS hybrid elastomers and show that nanoparticles can act as “reporters” for secondary structure buildup.

PDMS hybrid nanocomposites reported herein comprised (1) a low T_g PDMS phase cross-linked by (2) a siliceous phase (SP) generated by in situ hydrolysis/condensation of PDES, and (3) FSN, diameter ≈ 50 nm (Scheme 1). Slides were dip-coated (Supporting Information). An example composition is PDMS-14x-14%, where 14x is the ratio of Si-OEt (from PDES) to Si-OH (from PDMS) and 14% is wt % FSN. Two 3-day cure conditions were used for the hybrid PDMS nanocomposites: 25 °C (90% RH) and 100 °C (ambient humidity). The degree of condensation was apparent from TGA analysis of PDMS-14%-14x. Mass loss was observed below 200 °C for 25 °C cure, while no mass loss was observed below 200 °C for 100 °C cure (Supporting Information).

Height and phase TM-AFM images were used to examine nanocomposite near-surface topography. With “soft tapping” (setpoint ratio, $A/A_0 = 0.95$) the PDMS-14x-14% surface (25 °C cure) was smooth and relatively featureless (faint FSN, Supporting Informa-

PDMS-14x-14% 25 °C Cure



PDMS-14x-14% 100 °C Cure

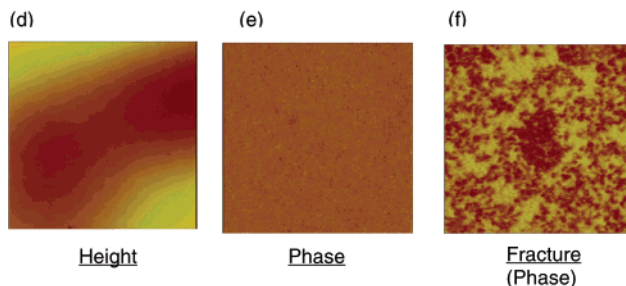
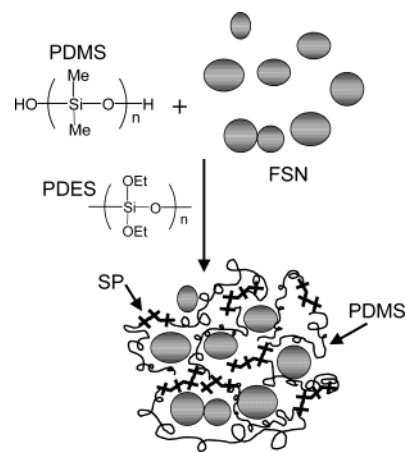


Figure 1. TM-AFM images, $A/A_0 = 0.60$, for PDMS-14x-14%. (a, b, d, e) $5 \mu\text{m} \times 5 \mu\text{m}$. (c, f) $10 \mu\text{m} \times 10 \mu\text{m}$.

Scheme 1. Hybrid PDMS Coating Preparation Utilizing PDES as the Siliceous Phase (SP) Precursor



tion). However, with harder tapping ($A/A_0 = 0.60$) near-surface FSN were readily observed because of the marked difference in Young’s modulus between FSN vs the PDMS matrix (Figure 1a,b).

Surprisingly, the near-surface image was dramatically changed after 100 °C cure. Even with hard tapping, the near-surface FSN

[†] Virginia Commonwealth University.

[‡] Kyoto University.

[§] Università di Pisa.

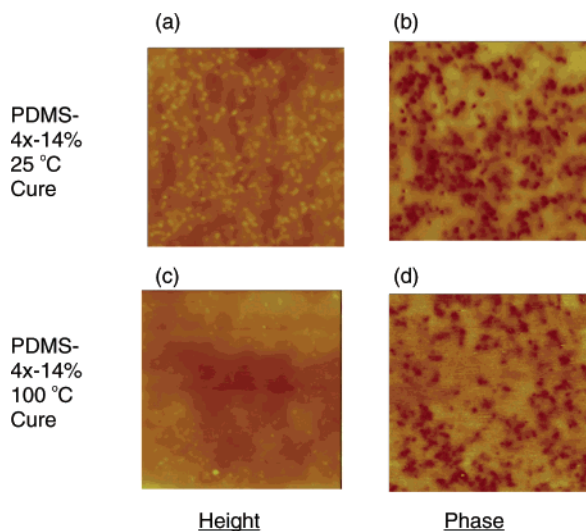


Figure 2. TM-AFM images, $5 \mu\text{m} \times 5 \mu\text{m}$, $A/A_0 = 0.60$, for PDMS-4x-14%.

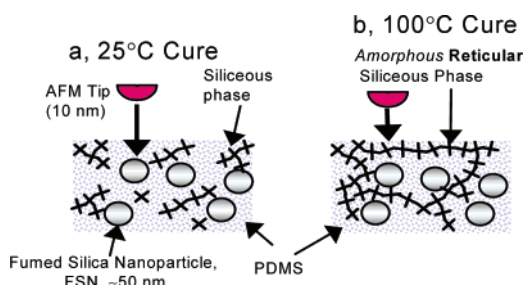


Figure 3. Model for PDMS-14x-14% cure (a) fragmented clusters after 25 °C cure and (b) formation of a rigid, amorphous, reticular siliceous phase for post 100 °C cure.

“disappeared” completely (Figure 1d,e). Experiments were carried out to clarify the origin of this change. First, images of fracture surfaces showing near-surface FSN (Figure 1c,f) were independent of cure temperature. Second, the effect of changes in composition on near-surface nanostructure was examined.

Figure 2 shows images for PDMS-4x-14%, 25 °C cure and 100 °C cure. Height and phase images demonstrate that at low volume fractions of siliceous phase the near-surface nanostructure is independent of cure temperature.

Contrasting TM-AFM results for “4x” and “14x” compositions indicate that a mechanical “nanobarrier” forms between the surface and FSN at 14x and prevents the AFM tip from imaging near-surface FSN. A schematic for “nanobarrier” formation is shown in Figure 3. After 25 °C cure (Figure 3a), fragmented SP clusters form with sizes smaller (perhaps 2–3 nm) than the tip dimensions. The small size results in a high Si–OH content shown by prior ^{29}Si NMR data.⁶ The small siliceous clusters do not impede the tip, and near-surface FSN are easily imaged.

In contrast, after 100 °C cure (Figure 3b) a rigid, amorphous, reticular siliceous phase forms between the elastomer surface and the FSN, precluding observation of near-surface FSN. The SP domains must increase to a size considerably larger than the tip

diameter. Yaghi and O’Keefe introduced the term “reticular”, meaning structurally resembling a net or network, to describe low-density (up to 49% open volume) *crystals* formed by employing rigid, linear ligands.¹⁰ This term is used here to describe an *amorphous*, rigid siliceous network. Instead of the open volume found in reticular crystals, the amorphous siliceous reticular phase is filled with the soft PDMS network and surrounds the FSN. Viewed another way, the interesting “disappearance” of the fumed silica nanoparticles means that the latter are acting as “reporters” for the formation of the rigid, amorphous, reticular, siliceous phase.

The rapid growth of the siliceous phase from clusters to reticular scale finds a well-known counterpart in the relationship of molecular weight and degree of polymerization for step growth (condensation) polymerization. In step growth polymerization, the last few percent of reaction accounts for large factors (ca. 20–200) in number average degree of polymerization.¹¹

In conclusion, the surprising “disappearance” of the near-surface SP reflecting the formation of a reticular SP has led us to undertake kinetic and compositional studies to understand the evolution of this phase and consequences in terms of properties.

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Supporting Information Available: Experimental section, TM-AFM images depending on set point ratio, composition table, and TGA values. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Wen, J.; Wilkes, G. L. *Chem. Mater.* **1996**, *8*, 1667–1681. (b) Novak, B. M. *Adv. Mater.* **1993**, *5*, 422–433. (c) Giannelis, E. P. *Adv. Mater.* **1996**, *8*, 29–35. (d) Chujo, Y.; Tamaki, R. *MRS Bull.* **2001**, *26*, 389–392. (e) Boury, B.; Corriu, R. J. P. *Chem. Commun.* **2002**, 795–802. (f) Corriu, R. J. P.; Leclercq, D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1420–1436. (g) Special issue for organic–inorganic nanocomposite materials. *Chem. Mater.* **2001**, *13*. (h) Ogoshi, T.; Itoh, H.; Kim, K.-M.; Chujo, Y. *Macromolecules* **2002**, *35*, 334–338. (i) Ogoshi, T.; Chujo, Y. *Macromolecules* **2003**, *36*, 654–660.
- (2) (a) Zhang, Z.; Sherlock, D.; West, R.; Amine, K.; Lyons, L. J. *Macromolecules* **2003**, *36*, 9176–9180. (b) Sur, G.-S.; Mark, J. E. *Eur. Polym. J.* **1985**, *21*, 1051–1052. (c) Huang, H. H.; Orlor, B.; Wilkes, G. L. *Macromolecules* **1987**, *20*, 1322–1330. (d) Julián, B.; Gervais, C.; Rager, M.-N.; Maquet, J.; Cordoncillo, E.; Escribano, P.; Babonneau, F.; Sanchez, C. *Chem. Mater.* **2004**, *16*, 521–529.
- (3) Wynne, K. J.; Lambert, J. M. *Silicones*. In *Encyclopedia of Biomaterials and Biomedical Engineering*; Wnek, G. W., Bowlin, G. B., Eds.; Marcel Dekker: New York, 2004; Vol. 1, pp 1348–1362.
- (4) Guru, M. W.; Sur, G. S.; Mark, J. E.; Schaefer, D. W.; Beaucage, G. J. *Polym. Sci., Polym. Phys.* **2003**, *41*, 1897–1901.
- (5) Johnston, E.; Bullock, S.; Uilk, J.; Gatenholm, P.; Wynne, K. J. *Macromolecules* **1999**, *32*, 8173–8182.
- (6) Uilk, J.; Bullock, S.; Johnston, E.; Myers, S. A.; Merwin, L.; Wynne, K. J. *Macromolecules* **2000**, *33*, 8791–8801.
- (7) Uilk, J.; Mera, A. E.; Fox, R. B.; Wynne, K. J. *Macromolecules* **2003**, *36*, 3689–3694.
- (8) (a) Bondurant, S.; Ernster, V.; Herdman, R. *Safety of Silicone Breast Implants*; National Academy Press: Washington, DC, 1999. (b) Rajan, G. S.; Sur, G. S.; Mark, J. E.; Schaefer, D. W.; Beaucage, G. J. *Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 1897–1901. (c) LeBaron, P. C.; Pinnavaia, T. J. *Chem. Mater.* **2001**, *13*, 3760–3765.
- (9) Dow Corning Corp. GB 652754 19510502, 1951.
- (10) Yaghi, O. M.; O’Keefe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705–714.
- (11) Chanda M. *Advanced Polymer Chemistry*; Marcel Dekker: New York, 2000.

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