

Mechanical and Structural Characterization of Poly(dimethylsiloxane) in the Presence of Reinforcing Filler Particles

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ABSTRACT. Three tetralkoxysilanes $Si(OR)_4$, namely tetramethoxy, tetraethoxy and tetrapropoxy silanes were hydrolyzed into networks of polydimethylsiloxane $[Si(CH_3)_2]_x$ to precipitate reinforcing particles of SiO_2 . All of the organofunctional silane compounds used showed a significant capacity to hydrolyze. Tetraethoxysilane (TEOS) was found to be the most efficient in this regard. However, the rate of hydrolysis lead to a different amount of filler precipitation among different samples. Tetrapropoxysilane (TPOS) yielded the highest amount of filler precipitation and tetramethoxysilane (TMOS) yielded the least. Although TEOS gave less amounts of filler precipitation as compared to TPOS, the particles precipitated from TEOS were more uniform, as SEM showed, and hence gave a better reinforcing mechanical behavior.

KEY WORDS: Poly(dimethylsiloxane) PDMS; *in-situ* precipitation; reinforcement; electron microscope; filler particles; silicon dioxide.

Introduction

It has been shown that most applications of elastomeric materials require reinforcing with relatively large amounts of finely divided fillers^[1, 2]. The ones employed are almost invariably particulate and have the specific effects of improving mechanical properties such as ultimate strengths, toughness, and abrasion resistance. Such applications include the addition of carbon black to natural rubber and Cis-diene polymers, and silica to poly (dimethylsiloxane) (PDMS) elastomers^[1-10].

There have been a series of previous investigations^[11-18] indicating the feasibility of precipitation silica (SiO_2) into a polymer or cross-linked elastomer by the method of catalyzed hydrolysis of an alkoxy silane or silicate.

In this report, three tetralkoxysilanes, *i.e.*, tetraethoxysilane (TEOS), tetrapropoxysilane (TPOS), and tetramethoxysilane (TMOS) were hydrolyzed in our laboratory to yield precipitates of silica particles (SiO_2) in a cross-linked PDMS. The aim of this study is to explore if the different tetraloxysilanes used in this study have the same or different reinforcement properties by measuring stress-strain isotherms in elongation. The order of effectiveness of these different silanes is determined. It is our goal to understand how the structure of these sources of the filler particles affect the reinforcement properties utilizing scanning electron microscope and x-ray diffraction methods.

Experimental

Preparation of Elastomers

Hydroxyl terminated polydimethylsiloxane of a number average molecular weight $18,000 \text{ g mole}^{-1}$ was end-linked with tetraethoxysilane in the undiluted state^[19-22]. The resulting network sheets were extracted using tetrahydrofuran and ethanol.

Precipitation of Silica

The extracted PDMS sheets were cut into strips. The weight of each strip was recorded and then placed into either TEOS, TPOS, or TMOS until swollen, for different times.

Each swollen strip was then immersed in 2 wt. % diethylamine catalyst solution for 24 h. The strips were dried in air for 24 h and then under vacuum until a constant weight is achieved. The amount of SiO_2 precipitated in each strip was then determined.

Stress-strain Isotherms

Strips having a cross sectional area A^* of approximately 2.5 mm^2 were cut from the PDMS sheets containing silica particles from the different sources. The central portion was marked off on each strip and its length L_i was measured with a cathetometer. The strips were mounted between two clamps; the lower one was fixed and the upper one was movable. The strips were then attached to a stress gauge^[23]. This assembly was surrounded by a double wall glass jacket, the temperature of which was controlled by means of water circulated from a thermostat. The stress-strain isotherms were obtained for all PDMS strips at identical conditions. The force exhibited by the elongated network was taken at

equilibrium value. The strain was characterized by the elongation $\alpha = L/L_i$, where L and L_i are the lengths of the central portion of the sample in the deformed and undeformed states, respectively.

Scanning Electron Microscopy (SEM)

A high resolution scanning microscope JSM-840 was utilized in this study. A sample area of 1 cm \times 0.5 cm was attached to the sample holder with a double-sided adhesive tape. Carbon conductive paint was applied along one of the edges and the samples were coated with a thin layer of gold in a sputter coater. The SEM was operated at 7 kV accelerating voltage for observation.

X-ray Diffraction

The samples were analyzed using a Philips model PW 1370/10 x-ray diffractometer. A diffraction pattern was generated for each sample by a scanning diffractometer under the following conditions:

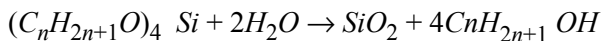
CU broad-focus tube at 45 kV and 30 milliamperere. It has auto divergence slit and no scatter slit, whereas the receiving slit is 0.2 mm.

Both monochromator and spinner used were operative during the measurements. Scanning speed and interval of data collection was 0.01 degree (two theta)/sec. angle scanned ranged between -3 and 70 degrees (two theta). The diffraction pattern was matched by patterns of different standards prepared by the Joint Committee of Powder Diffraction Data Services (JCPDS) in an attempt to determine the size of the precipitated silica.

Results and Discussions

Stress-strain Isotherms

All of the silane compounds used showed a significant tendency to hydrolyze according to the reaction.



The efficiency of the hydrolysis was variable among the samples; Table 1 shows the amounts of precipitated filler. The differences in the precipitated silica are presumably due to the different rates of hydrolysis. These data were utilized in the calculation of the reduced stress^[24-27] $[f^*]$ for unswollen samples as follows:

$$[f^*] = f^*/(\alpha - \alpha^{-2}) \quad (1)$$

For the swollen sample, the following equation was used:

TABLE 1. Details of precipitation reaction and stress-strain measurements results.

Precipitation reaction			Ultimate properties		
Silane source	Time left in silane (h)	Wt. % SiO_2 precipitated	α_r	$E_r \times 10^4$ Jmm^{-3}	$F^* \times 10^2$ Nmm^{-2}
None	–	0.0	2.55	1.27	3.00
TEOS	1	24	2.37	1.96	3.90
	6	33	3.20	1.84	3.65
	12	36	3.97	1.45	3.24
TPOS	1	30	2.30	1.35	2.50
	6	44	2.95	1.12	1.78
	12	45	3.46	0.92	1.36
TMOS	1	14	1.90	0.97	1.50
	6	16	1.60	0.73	1.45
	12	18	1.40	0.68	1.30

α_r is the elongation at the rupture point.

E_r is the energy required to reach the rupture point.

$$[f^*] = f^* - V_2^{1/3} (\alpha - \alpha^{-2}) \quad (2)$$

where α is the elongation, V is the volume of the swollen sample.

The most efficient organofunctional silane compound was found to be TEOS and the efficiency was recorded in the following order: TEOS > TPOS > TMOS. The highest modulus value observed was obtained by using TMOS as the silane source. The values of the ultimate properties, specifically the ultimate strength and maximum extensibility, are given in Table 1. The precipitation time was kept the same for all silane sources, and was ranged from 1-12 hours for each of them, therefore the ultimate properties are related to the amount of precipitated silica particles which can be related to time. The more time the sample was left in the silane source the more precipitated silica particles and this results in a better ultimate properties. It is noticed that the best sample resulted from the use of TEOS and TMOS.

Scanning Electron Microscopy

Electron microscope photographs Figure 1(A-D) showed that in the case of TEOS, the participated particles are uniform and homogeneously distributed throughout the polymer matrix and this is what lead to a higher elongation value. In the case of TMOS, the particles appear to be aggregating and not

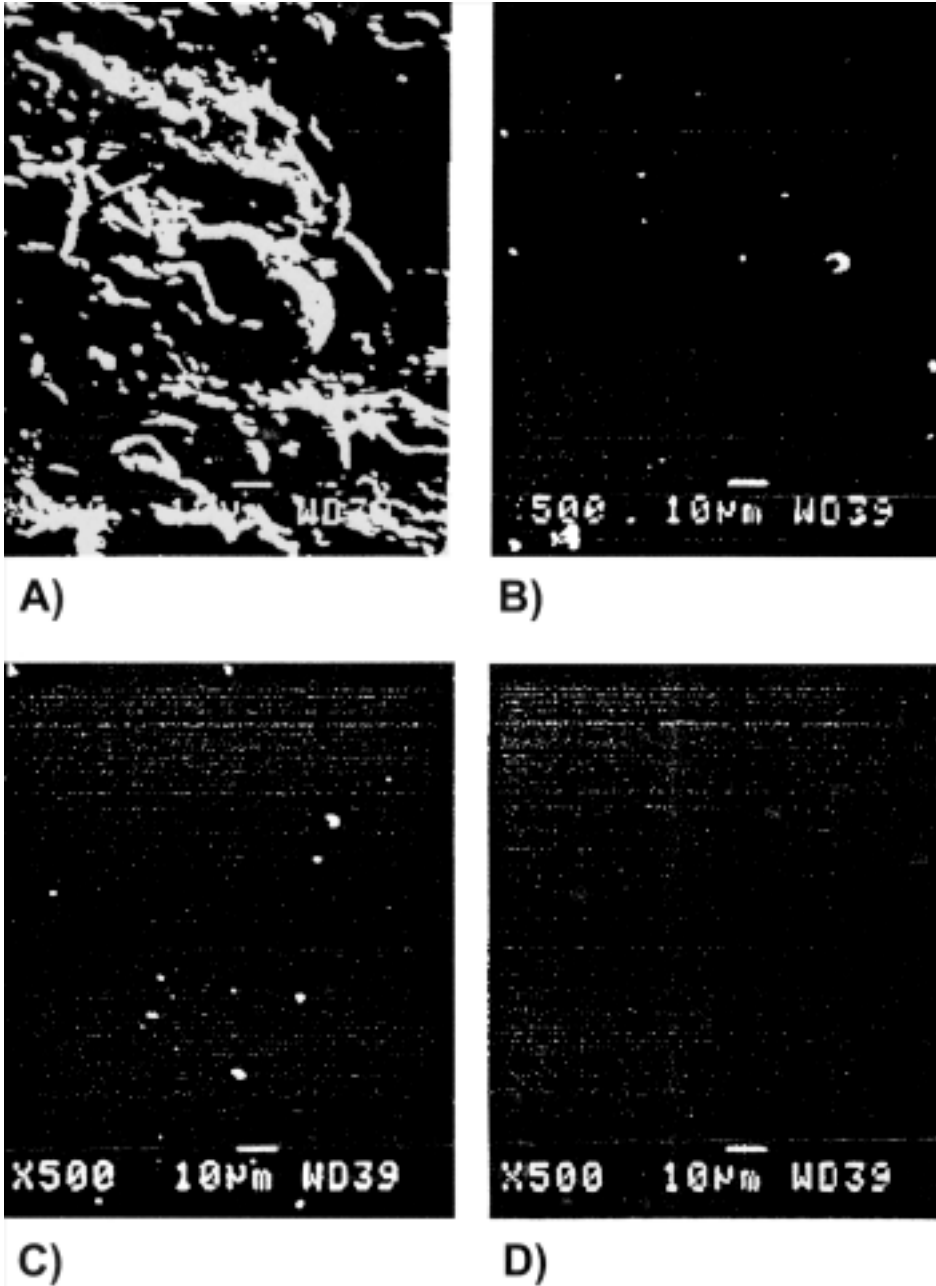


Fig. 1. Scanning electron micrographs of PDMS containing SiO₂ A) 18 wt. % from TMOS, B) 33 wt. % from TEOS, C) 45 wt. % from TPOS, D) pure pdms (magnification is 3000).

homogeneously distributed throughout the polymer matrix. This is presumably due to the fast hydrolysis rate of TMOS as compared to the other two silanes, which are more bulky and hence have a slower rate of hydrolysis.

X-ray Diffraction Analysis

X-ray diffraction analysis results suggest that the silica precipitated is invariably the amorphous variety and there is not a well defined structure that can be visualized as can be shown in Figure 2(A-D). This suggests that the precipitated particles are of no specific structure and hence no x-ray diffraction pattern can be obtained .

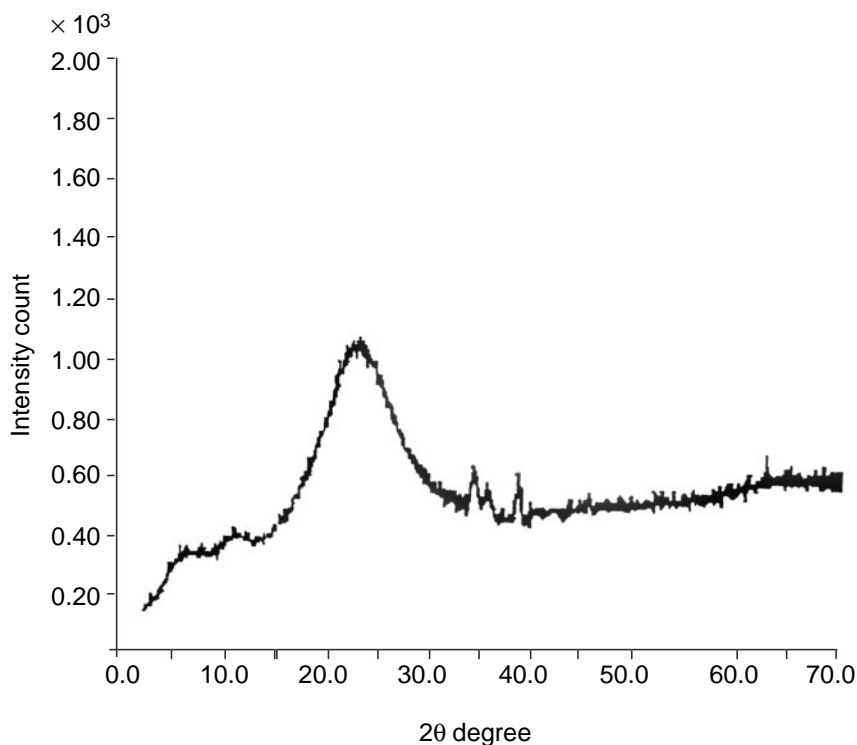


FIG. 2. A typical x-ray diffraction pattern obtained for PDMS containing silica particles.

Conclusions

The mechanical properties of polydimethylsiloxane (PDMS) showed an improvement after the precipitation of the silica particles. This improvement can be noticed from the ultimate properties of the polymer after it was treated. The difference in the

amounts of silica particles precipitated from different sources is probably due to the length of the hydrocarbon chain and hence to the rate of hydrolysis.

Scanning electron microscopy showed a difference in the homogeneity of the particles precipitated from the different sources. This is probably due to the rate of hydrolysis.

Silica particles with homogeneous distribution can therefore increase the polymer toughness, and hence can be considered as a suitable reinforcing particles.

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الخواص الميكانيكية والتركييبية لمركب بولي داي ميثايل سيلوكسان المقوّى

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الرياض - المملكة العربية السعودية

المستخلص. في هذا البحث تمت عملية ترسيب لمركب ثاني أكسيد السليكون في شرائح من البوليمر المسمى بولي داي ميثايل سيلوكسان بغرض تحسين المواصفات الميكانيكية لهذا البوليمر. مصادر هذا المركب الذي تم ترسيبه مركبات سيليكات عضوية اختلفت في نوع سلسلتها الهيدروكربونية، (رباعي ميثايل، رباعي إيثايل، رباعي بروبايل) السيليكات العضوية. جميع هذه المصادر كانت ذات قابلية جيدة لعملية الترسيب، إلا أن رباعي بروبايل السيليكات العضوية أعطى أكبر نسبة من المركب الذي تم ترسيبه بينما كان رباعي ميثايل السيليكات العضوية الأقل نسبة.

وعلى الرغم من أن الكمية المترسبة من المصدر رباعي بروبايل السيليكات العضوية كانت أكبر، إلا أن الكمية المترسبة من المصدر رباعي إيثايل السيليكات العضوية كانت أكثر تجانساً في توزيعها وأعطت بالتالي خصائص ميكانيكية للبوليمر أفضل من غيرها.