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Polymer-modified silica glasses

I. Control of sample hardness

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Summary

The functionality of divinyl-terminated poly(dimethylsiloxane) (PDMS) was greatly increased by a substitution reaction to give PDMS with triethoxysilyl chain ends. Samples having number-average molecular weights of 720 and 17.6 x 10^3 g mol^{-1}, and mixtures thereof, were added to tetraethoxysilane (TEOS) or a related silane. The functionalized PDMS-silane mixtures were hydrolyzed in the usual sol-gel technique to give polymer-modified silica glasses. The hardness of the glasses was measured, and then related to the molecular weight of the PDMS, its molecular weight distribution, the composition of the PDMS-silane mixtures, and the nature of the silane.

Introduction

The catalyzed hydrolyses of alkoxysilanes such as the symmetric molecule $Si(OR)_4$ and alkylalkoxysilanes and arylalkoxysilanes such as $R'Si(OR)_3$ have become of great interest to both ceramists and polymer chemists. In the ceramics area, for example, tetraethoxysilane (TEOS) has been hydrolyzed to a gel which can be dried and then fired into a porous silica (SiO_2) ceramic or glass (1). In the polymer area, TEOS can be used for the in-situ precipitation of reinforcing SiO_2 particles in elastomers (2,3), with substituted tri- or dialkoxysilanes used in an attempt to introduce some deformability in the filler particles (4). Also, in applications that combine both areas, Schmidt (5) has used mixtures of silanes and Wilkes and coworkers (6) have used mixtures of silanes and dihydroxy-terminated poly(dimethylsiloxane) (PDMS) [-$Si(CH_3)_2O$-] to obtain organically-modified glasses, some of which can be very interesting hybrids of polymers and glasses. One obvious goal in this polymer-ceramic area is the preparation of ceramic-type materials having decreased brittleness. In a sense this is related to attempts (7) to improve the impact resistance of (short-chain) thermosets by bonding much longer chains within the network structure.

The present investigation extends some of this work. It employs PDMS heavily functionalized with ethoxy groups (8) to maximize its bonding to silica-type phases generated by the hydrolyses of some of the silanes mentioned above. The high functionality should also suppress simple chain extension and the occurrence of dangling chains. Of particular interest in this first part of the project is control of the hardness of the polymer-modified glasses through changes in the nature of the polymer and the silane, and their proportions in the mixtures being hydrolyzed.

Some Experimental Details

The starting polymers were two samples of vinyl-terminated PDMS having number average molecular weights M_n of 392 and 17.3 x 10^3 g mol^{-1}, respectively. The monofunctional vinyl ends were converted (8) into trifunctional triethoxysilyl groups $[-Si(OEt)_3]$ by reacting the samples with a small excess of triethoxysilane, using chloroplatinic acid as catalyst, in sealed flasks at 70°C for one day. Removal of unreacted triethoxylsilane under reduced pressure gave the desired products as colorless viscous liquids. A small portion of each was characterized by standard chemical titration. The revised values of M_n were 720 and 17.6 x 10^3 g mol^{-1}, respectively.

The silanes employed were TEOS and three triethoxysilanes $R'Si(OEt)_3$, with R' being phenyl, methyl, and vinyl, respectively. In addition, some samples of hydrolyzed TEOS, designated HTEOS, were prepared by reacting TEOS with the appropriate amounts of distilled water, in isopropanol and tetrahydrofuran (THF), using acetic acid as catalyst. The reaction was conducted under agitation at 60°C for two hours. The resulting solution was washed with distilled water, dried over Na_2SO_4, and the desired product recovered by removal of the solvent by evaporation.

The short-chain PDMS was hydrolyzed in the pure state and also in a series of bimodal mixtures with the long-chain PDMS. Compositions are described in the first five columns of Table I, and the suitably averaged values of M_n are given in column six. The nature of the silane employed, and its relative amount, are given in columns seven and eight. A stoichiometric amount of distilled water, and isopropanol and THF were used as the hydrolysis medium; hydrochloric acid in a molar ratio HCl/silane = 0.045 was used as catalyst (6). The PDMS and silane were simultaneously added to this solution and then held at 80°C, with agitation, for 20 min. The resulting solutions were poured into Teflon®-lined dishes, covered, and allowed to react for 24 hrs. at room temperature (6). The samples were then uncovered and permitted to further react and to dry, for a period of at least 72 hrs. Column nine of the Table gives values of the molar ratio R/Si of alkyl groups to silicon atoms in the resulting polymer-modified glasses.

The hardness measurements were carried out using a PTC Model 307L D-Scale Durometer, which has been designed to measure the indentation hardness of plastics and similar materials. It meets or exceeds specification D2240-81 of the American Society for Testing and Materials (ASTM). As is customary, the hardness of each sample was expressed as a relative "D value", with 75 being typical for a glassy polymer.

Results and Discussion

The samples formed as described above seemed homogeneous, had very good transparency, and had no obvious flaws or cracks. The "D hardness"

TABLE I

Characteristics of the Components and the Resulting Glasses

	Polymers					Silanes		Polymer-Modified Glasses	
Exp	Wt % Short Chains[a]	Wt % Long Chains[a]	Total Wt % Polymer[a]	Mol % Short Chains[b]	M_n, g mol^{-1}	Wt % TEOS[a]	Wt % HTEOS[a]	Mol Ratio R/Si	D Hardness Values
1	52.0	0.0	52.0	100.0	720	48.0	0.0	1.00	45
2	46.2	5.8	52.0	99.5	804	48.0	0.0	1.05	50
3	41.8	10.2	52.0	99.0	889	48.0	0.0	1.10	30
4	36.4	15.6	52.0	98.0	1057	48.0	0.0	1.16	25
5	22.7	29.3	52.0	95.0	1550	48.0	0.0	1.31	20
6	17.8	2.2	20.0	99.5	804	80.0	0.0	0.52	Br[c]
7	53.5	6.5	60.0	99.5	804	40.0	0.0	1.15	18
8	71.8	8.2	80.0	99.5	804	20.0	0.0	1.36	2
9	40.1	9.9	50.0	99.0	889	0.0	50.0	1.00	50
10	52.0	0.0	52.0	100.0	720	0.0	48.0	0.92	60
11	75.0	0.0	75.0	100.0	720	0.0	25.0	1.19	11
12	80.0	0.0	80.0	100.0	720	0.0	20.0	1.25	5
13	17.8	2.3	20.0	99.5	804	0.0	80.0	0.46	Br[c]
14	44.6	5.4	50.0	99.5	804	0.0	50.0	0.97	57
15	53.7	6.3	60.0	99.5	804	0.0	40.0	1.09	40
16	71.8	8.2	80.0	99.5	804	0.0	20.0	1.33	4

[a] Relative to total weight of polymer-silane mixture. [b] Relative to total number of moles of polymer. [c] Brittle; D too large to measure.

values they exhibited are given in the final column of the Table.

The first five experiments, carried out with TEOS, were used to determine the effect of the molecular weight of the PDMS on sample hardness. The hardness values obtained are given in the first five rows of the Table and are shown in Figure 1 as a function of M_n at a constant 52 wt % PDMS. As can be seen, increase in M_n causes significant decrease in hardness. Part of the decrease in hardness could be due to an increased tendency for phase separation as the molecular weight of the PDMS increases (6). Unlike the case of elastomers at high elongations (2), the bimodal distribution of PDMS seems unimportant. It could possibly be exploited, however, in controlling the amount of PDMS dispersed in the glass phase (low M_n) and the amount forming a separate elastomeric phase (high M_n) (6).

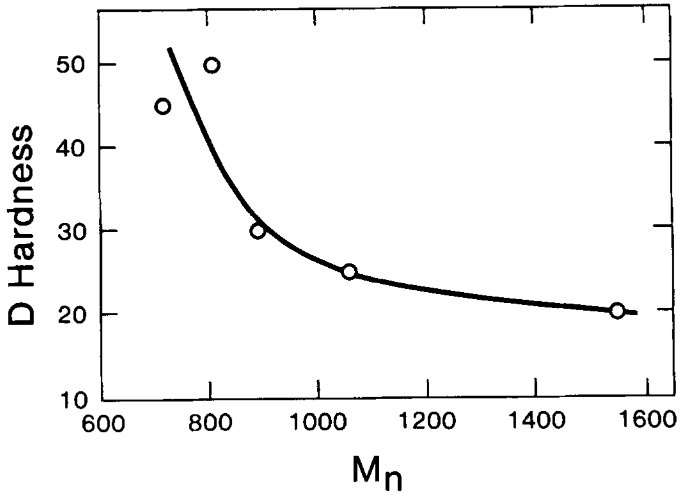

Fig. 1. The effect of PDMS molecular weight on sample hardness.

Experiments 6 through 8 establish the extent of the decrease in hardness as the total wt % PDMS is increased, when TEOS is used as the silane. The hardness obtained in experiment 9 relative to that in experiment 1 indicates that HTEOS gives samples approximately as hard as those obtained from TEOS itself. Experiments 10 through 12, also carried out using HTEOS, confirm the decrease in hardness with increase in total wt % PDMS established in experiments 2 and 6-8. The combined sets of results are shown in Figure 2.

Figure 3 shows the dependence of the hardness on the polymer content of the glass, as represented by the ratio R/Si. Samples having a hardness in the range 50-65 seemed to be the toughest, and this is seen to be achieved at values of R/Si of approximately 0.9 to 1.0.

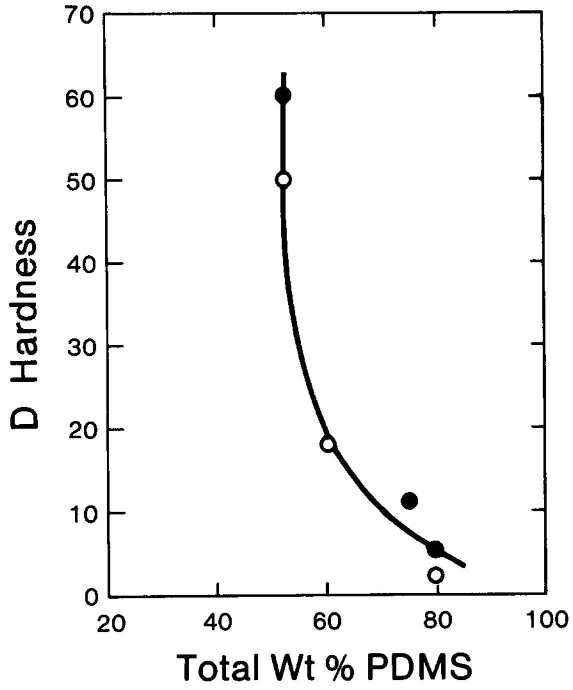

Fig. 2. The effect of total wt % PDMS on sample hardness, as obtained from experiments 2, 7, 8 (○) and 10-12 (●).

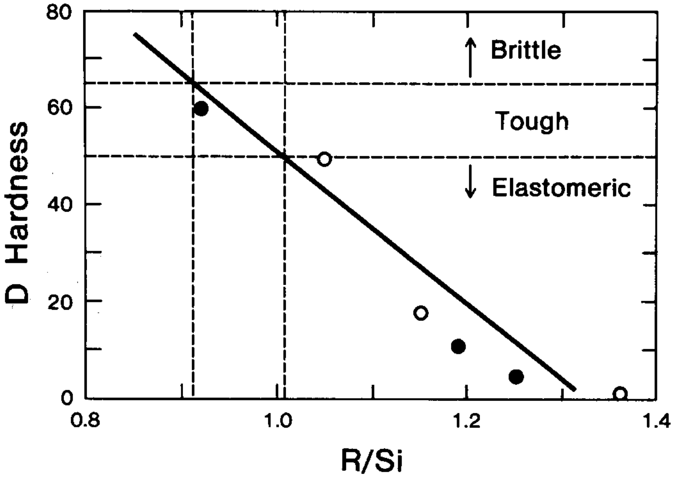

Fig. 3. The dependence of the hardness on the molar ratio of alkyl groups to silicon atoms in the glass; see legend to Figure 2.

Experiments 13-16, carried out using a bimodal PDMS distribution, confirm the decrease in hardness with increase in total wt % PDMS shown by the unimodal distributions used in experiments 10-12.

In a final series of experiments, hydrolyses were conducted on three pure samples of $R'Si(OEt)_3$, with R' being equal to phenyl, methyl, and vinyl, respectively. The first gave a brittle glass, whereas the second and third were tougher, with hardness values of 65 and 55, respectively. This clearly demonstrates the importance of the nature of the R group in the trialkoxysilanes being hydrolyzed.

Future work will correlate these results with the values of other important properties such as impact resistance, ultimate strength, and maximum extensibility.

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