# Electron microscopy of elastomers containing *in-situ* precipitated silica

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Transmission electron microscopy is used to characterize reinforcing silica particle precipitated as filler into networks of poly(dimethylsiloxane) by the hydrolysis of tetraethylorthosilicate. Particle diameters were typically 200 Å, with relatively narrow distributions. Aggregation is generally very low but, as expectd, becomes more pronounced with increase in amount of filler. Acidic catalysts give less well defined particles than basic ones, and large catalyst concentrations give unusually small particle diameters. Permitting the particles to 'digest' in contact with water and catalyst seems to make them better defined, more uniform in size, and less aggregated.

**(Keywords: electron microscopy; elastomers; silica; poly(dimethylsiloxane))**

## INTRODUCTION

If a network of poly(dimethylsiloxane) (PDMS) $[-Si(CH_3)_2O-]$ is swelled with tetraethylorthosilicate (TEOS) and the TEOS hydrolysed, silica particles are deposited within the network structure[1-4]. The reaction is

$$Si(OEt)_4 + 2H_2O \rightarrow SiO_2 + 4EtOH \qquad (1)$$

and is catalysed by a variety of substances[2], in the vicinity of room temperature. The presence of filler particles was shown indirectly by the reinforcement observed in stress–strain measurements on the dried networks[1-4], and directly from two electron micrographs[5].

The present investigation was carried out to provide additional information on the silica generated by this *in-situ* precipitation technique. Electron microscopy is used to determine average particle diameters and their distributions, the smoothness of the particles, and the extent of their aggregation. Of primary interest is the dependence of these quantities on temperature, reaction time, the nature of the catalyst, catalyst concentration, and ageing.

## EXPERIMENTAL

### *Preparation of networks*

The networks were prepared from PDMS chains that had either vinyl groups or hydroxyl groups at both ends. All samples were tetrafunctionally end linked in the usual manner, the former type with $Si[OSi(CH_3)_2H]_4$[6] and the latter with TEOS[7]. Their values of the number-average molecular weight, which becomes the molecular weight $M_c$ between crosslinks, are given in the second column of *Table 1*. Each network was extracted for several days to remove soluble material, which was found to be present to the extent of only a few per cent.

### *Precipitation of silica*

Strips cut from the network sheets were weighed and then swelled with TEOS to the maximum extent attainable. The extent varied with $M_c$, but in all cases corresponded to a volume fraction of polymer of 0.2–0.3, which means there is a large excess of TEOS available for hydrolysis. The degree of crosslinking of the samples studied should therefore be unimportant (as should also be the nature of the functional groups originally present on the chain ends).

Each swollen strip was placed in one of several aqueous catalyst solutions, and the hydrolysis of the TEOS permitted to occur at the desired temperature for the desired period of time[2]. Details are given in columns 3–6 of *Table 1*. The final sample in the series was permitted to 'age' in contact with its catalyst solution for a period of two months. After the reaction, each strip was dried and weighed. Sample designations, based on the type of catalyst and its wt% in solution, are given in the final column of the table.

### *Electron microscopy*

A piece of each filled network approximately 1 mm × 1 mm × 5 mm was mounted in an appropriate specimen holder, which was then placed into the cryostatic chamber (Sorvall FS 1000) of an ultramicrotome (Sorvall MT 6000). The entire slicing area was taken to and then maintained at −140°C, with a controller initiating the delivery of the precise amount of liquid nitrogen and heat necessary to maintain preset temperatures in the chamber. The liquid nitrogen filling system incorporates a

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**Table 1** Conditions for network formation and silica precipitation

| | | Silica precipitation | | | | |
|---|---|---|---|---|---|---|
| | | Catalyst | | | | |
| End groups | $10^{-3}M_c$[a] (g mol$^{-1}$) | Formula | Wt% | $T$ (°C) | Reaction time (hours) | Sample designation[b] |
| Vinyl | 13.0 | $C_2H_5NH_2$ | 2.0 | 50 | 0.5 | EAM-2-1 |
| Vinyl | 13.0 | $C_2H_5NH_2$ | 2.0 | 50 | 1.0 | EAM-2-2 |
| Hydroxyl | 21.3 | $C_2H_5NH_2$ | 2.0 | 25 | 24.0 | EAM-2-3 |
| Hydroxyl | 8.0 | $CH_3COOH$ | 5.0 | 25 | 1.0 | HAC-5-1 |
| Hydroxyl | 8.0 | $K_2HPO_4$ | 5.0 | 25 | 2.0 | KPH-5-1 |
| Hydroxyl | 8.0 | $C_2H_5NH_2$ | 50.0 | 25 | 0.17 | EAM-50-1 |
| Vinyl | 7.4 | $C_2H_5NH_2$ | 2.0 | 25 | 1440.0 | EAM-2-4 |

[a] Average molecular weight between crosslinks
[b] Cat-wt%-cat-number

liquid/gas separator designed to allow only liquid nitrogen into the chamber. Specimen slices having a thickness the order of 1000 Å were obtained using a diamond knife. They were collected on carbon-coated grids, and then examined in transmission with a Hitachi HS-7 electron microscope operating at 50 kV.

## RESULTS AND DISCUSSION

The measured increases in weight of the sample strips were used to calculate values of the wt% filler introduced by the *in-situ* precipitation reaction. The results are given in the second column of *Table 2*.

The first two samples, EAM-2-1 and EAM-2-2, were prepared under conditions identical to those used in the previous study[5], except the temperature was 50°C instead of room temperature. Typical electron micrographs obtained for these two samples are shown in *Figures 1* and *2*, respectively. As in the previous case[5], the particles had a diameter of approximately 200 Å, were well defined, and were well dispersed (little aggregation). This is summarized in columns 3–6 of *Table 2*. Thus, moderate changes in temperature seem unimportant.

If very large amounts of silica are precipitated, aggregation becomes more pronounced, as should be expected. This is illustrated by sample EAM-2-3, which contains 81.5 wt% silica (~65 vol%). A typical micrograph obtained for it is shown in *Figure 3*.

The above three samples were obtained using ethylamine, a basic catalyst. The effects of changing to a highly acidic catalyst are illustrated by samples HAC-5-1 and KPH-5-1; they were prepared using solutions of acetic acid and a phosphate salt having pH's of 2.7 and 4.0, respectively. The results for the HAC sample, illustrated in *Figure 4*, show the particles to be very poorly defined. This is consistent with results[8–10] obtained for systems of interest in sol–gel–ceramics technology. It was there concluded that in the gelation process, acidic catalysts give structures that are less branched and less compact

**Table 2** Amounts and characteristics of silica precipitated

| Sample | wt% $SiO_2$ | *Figure* | Diameter (Å) | Definition | Dispersion[a] |
|---|---|---|---|---|---|
| EAM-2-1 | 10.5 | *1* | 150–225 | Good | Good |
| EAM-2-2 | 31.1 | *2* | 200–250 | Good | Good |
| EAM-2-3 | 81.5 | *3* | – | Fair | Poor |
| HAC-5-1 | 36.7 | *4* | – | Poor | Fair |
| KPH-5-1 | 38.7 | *5* | 120–200 | Good | Good |
| EAM-50-1 | 14.8 | *6* | 65–100 | Good | Good |
| EAM-2-4 | 31.0 | *7* | 200 | Excellent | Good |

[a] Lack of aggregation

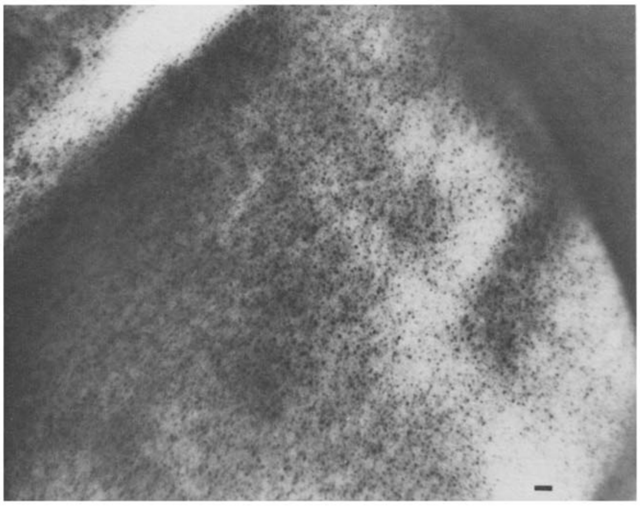

**Figure 1** Transmission electron micrograph of sample EAM-2-1 at a magnification of 60 600 ×. In this and the following Figures, the length of the bar corresponds to 1000 Å and details on the samples are given in *Tables 1* and *2*

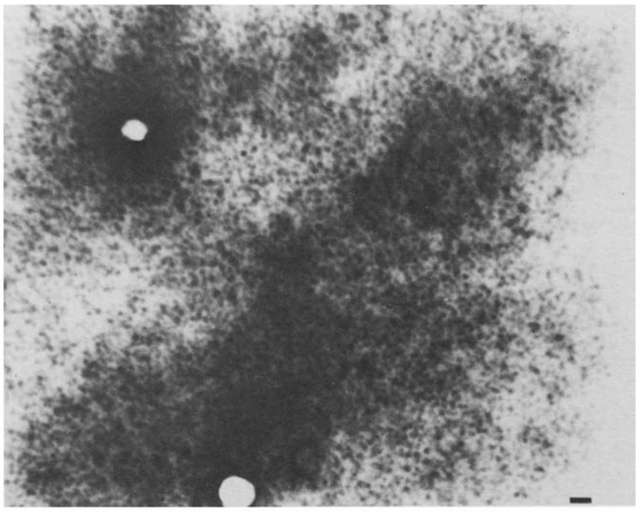

**Figure 2** Micrograph of sample EAM-2-2 at 77 550 ×

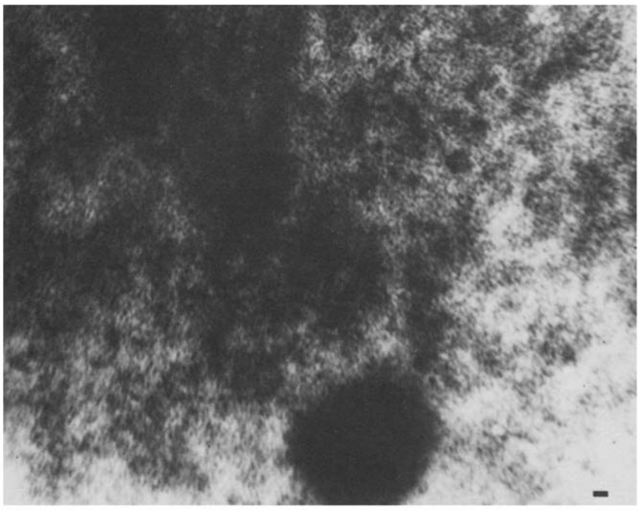

**Figure 3** Micrograph of sample EAM-2-3 at 49 830 ×

than those obtained from basic catalysts. As expected, the less acidic KPH catalyst does give better defined particles, as is illustrated in *Figure 5*.

The effect of using a very largy amount of catalyst (50 wt%) is shown by sample EAM-50-1. The particles obtained are unusually small (65–100 Å), as shown in *Figure 6*.

The final sample, EAM-2-4, was permitted to remain in contact with its aqueous catalyst solution for two months. As is illustrated in *Figure 7*, this 'ageing' or 'digestion' process did seem to make the particles better defined, more uniform in size, and less aggregated. This suggests that some reorganization is occurring, at least in some steps in the hydrolysis reaction. Additional experiments would be required, however, to confirm this tentative but very provocative result.

## ACKNOWLEDGEMENTS

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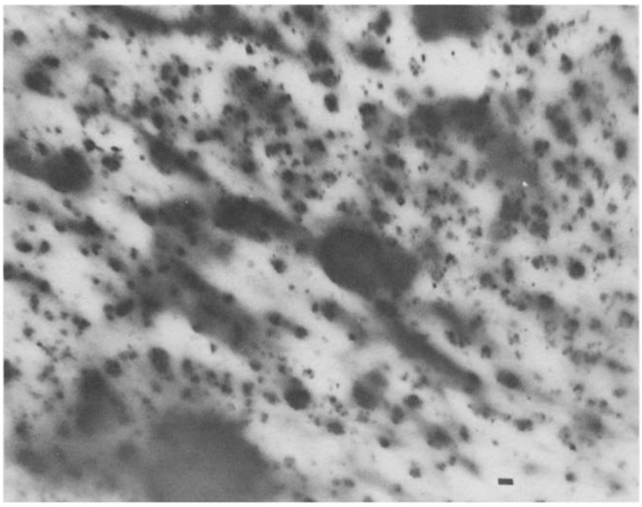

**Figure 4** Micrograph of sample HAC-5-1 at 49 830 ×

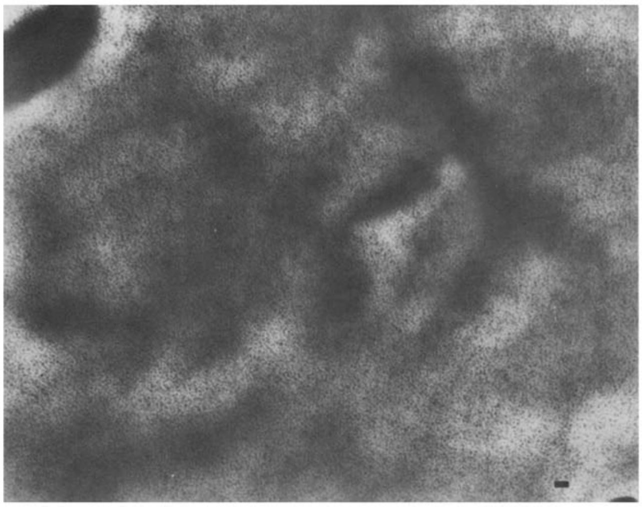

**Figure 5** Micrograph of sample KPH-5-1 at 49 830 ×

**Figure 6** Micrograph of sample EAM-50-1 at 77 550 ×

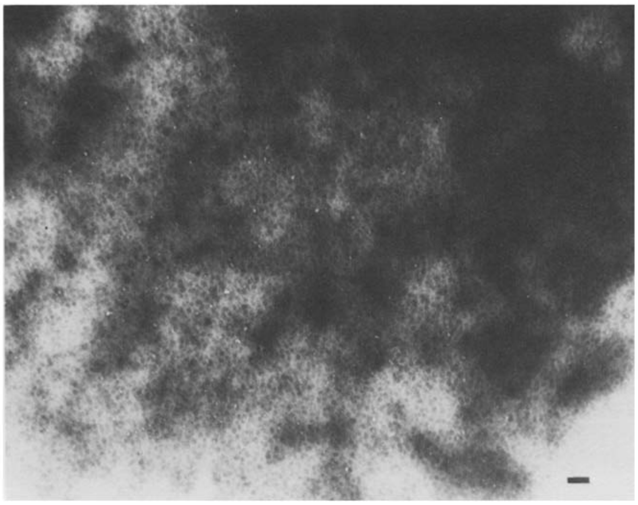

**Figure 7** Micrograph of sample EAM-2-4 at 77 550 ×

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