Particle Sizes of Reinforcing Silica Precipitated into Elastomeric Networks

Inherently weak elastomers are generally reinforced by blending particulate fillers into the elastomeric polymer prior to its being cured into a network structure.[1-10] A specific, and very important, example is the mixing of high-surface silica (SiO_2) of a few hundred Å diameter into poly(dimethylsiloxane) PDMS [—$Si(CH_3)_2O$—].[1-5,8,9,11] One disadvantage of this standard approach, however, is the invariable coalescence of the filler particles into large aggregates in an essentially uncontrolled and poorly understood manner.[11] The nature and extent of such aggregation obviously would have a large effect on the mechanical properties of the elastomer thus reinforced.

It has recently been demonstrated[12] that it is possible to prepare very tough elastomers by swelling PDMS networks with tetraethyl orthosilicate (TEOS) [$(C_2H_5O)_4Si$], which is then hydrolyzed *in situ*. It was proposed[12] that the hydrolysis of the TEOS gives silica particles which provide the desired reinforcement. The present investigation tests these ideas by means of transmission electron micrographs obtained on thin slices of PDMS elastomers thus prepared. The main goals are to find evidence for such filler particles and, if present, to estimate their sizes and size distribution. Since any such particles would be formed within a polymer matrix which should impede their coalescence into undesired aggregates, the degree of dispersion of the filler particles is also of considerable interest.

EXPERIMENTAL

The network was prepared from vinyl-terminated PDMS chains having number-average molecular weights corresponding to $10^{-3}M_n = 13.0\ g \cdot mol^{-1}$. They were tetrafunctionally end-linked with $Si[OSi(CH_3)_2H)]_4$ in the usual manner,[13] and the resulting network was extracted with tetrahydrofuran and then toluene for several days to remove soluble material (found to be present to the extent of a few percent). Strips cut from the network sheet were then dried, and one was set aside as a reference material (0 wt % silica).

The other network strips were swelled with TEOS to the maximum extent attainable, which corresponded to a volume fraction of polymer of approximately 0.26. Several strips were placed into an aqueous solution containing 2% by weight of ethylamine, and the hydrolysis of the TEOS was permitted to occur at room temperature for 1.5 h. The weight of the dried strips indicated that 34.4% by weight of filler had been incorporated in this manner.

Thin films having a thickness the order of 10^3 Å were microtomed from both the filled and unfilled samples using the following technique. A piece of network approximately 1 × 1 × 4 mm was inserted into the water-filled cylindrical opening in a copper mount, and was then frozen into place. The entire assembly was cooled to approximately −126°C with vapor from a container of liquid nitrogen, and was then inserted into a similarly cooled Porter-Blum MT-2 Ultramicrotome equipped with a diamond knife. Thin slices obtained in this way were collected on copper grids, and examined in transmission using an RCA 3-G Electron Microscope with double condensor and high magnification pole piece.

RESULTS AND DISCUSSION

The electron micrographs obtained for the filled PDMS network at magnifications of 52,800 × and 118,800 × are shown in Figures 1 and 2, respectively. For purposes of comparison, the corresponding (essentially featureless) micrograph for the unfilled network at 118,800 × is shown in Figure 3. The existence of filler particles in the first network, originally hypothesized on the basis of mechanical properties, is clearly confirmed. The particles have average diameters of approximately 250 Å, which is in the range of particle sizes of fillers[9] typically

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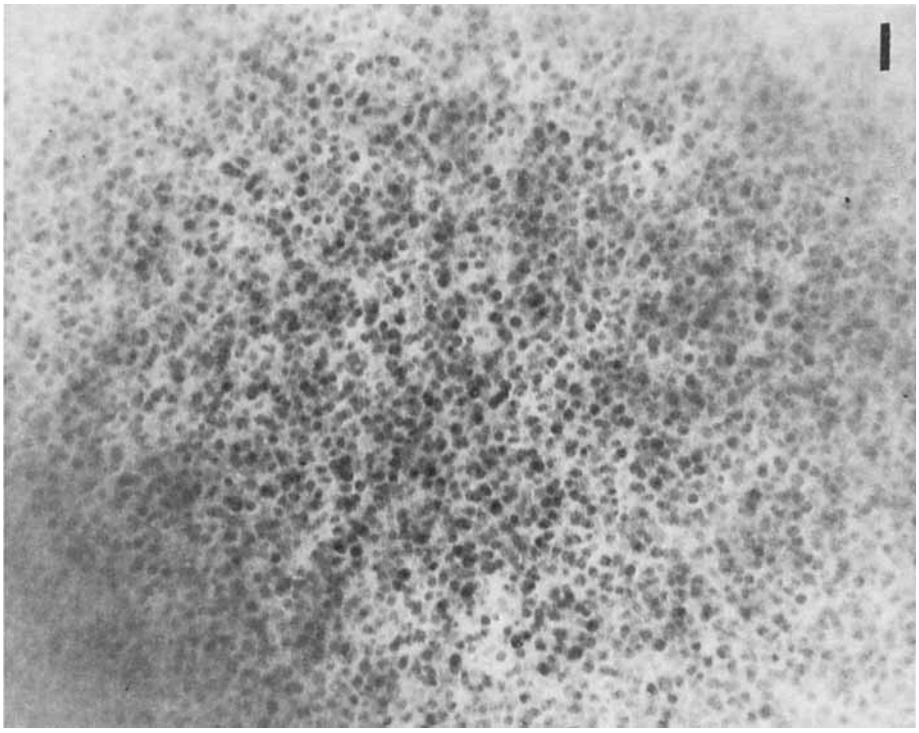

Figure 2.

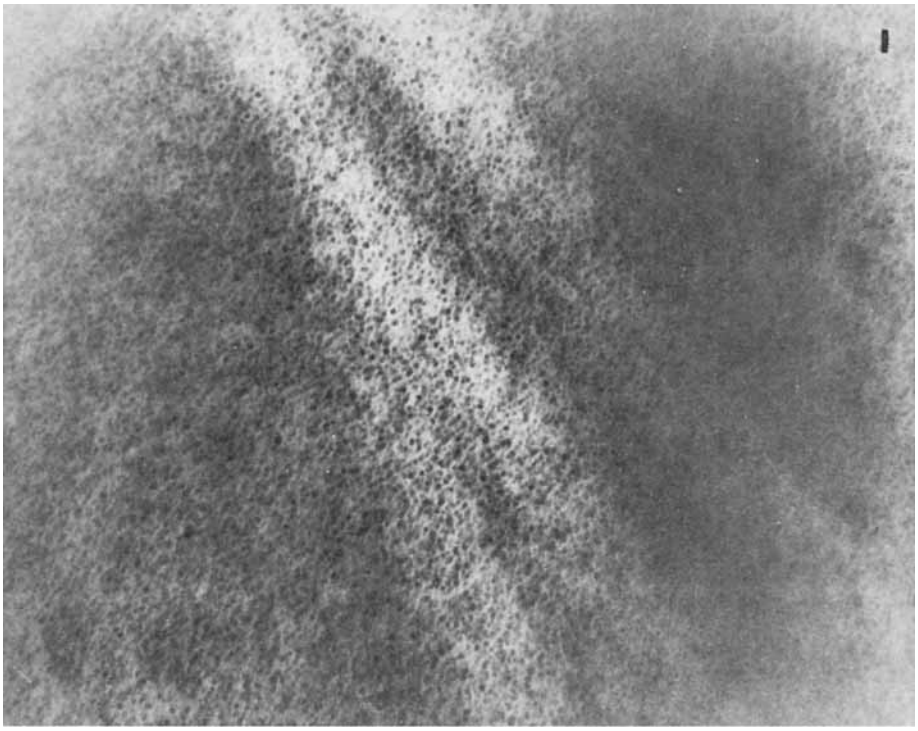

Figure 1.

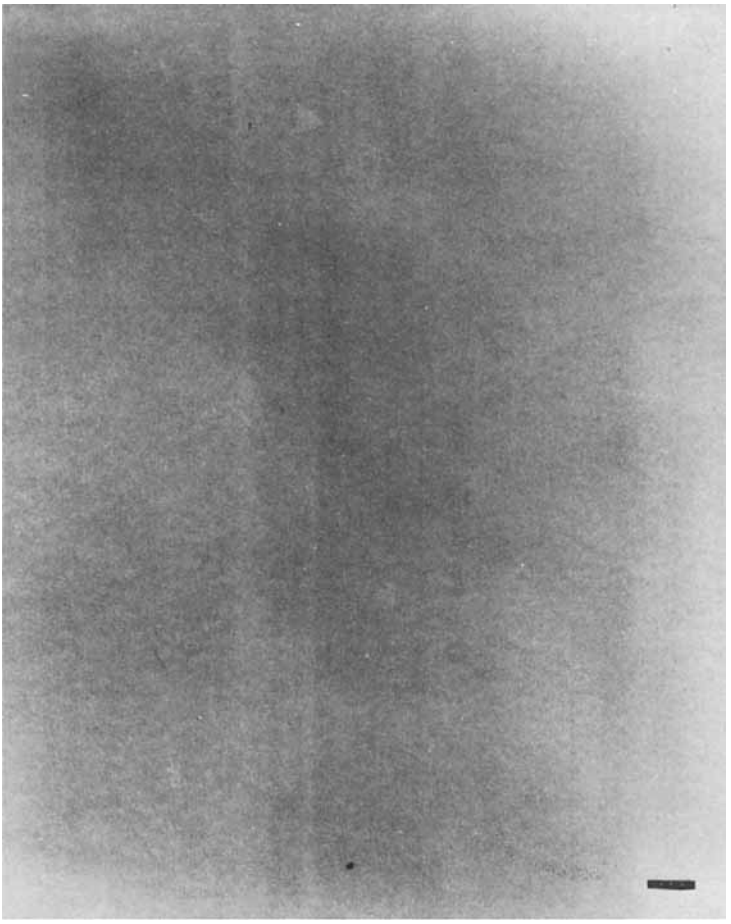

Fig. 3. Micrograph for the unfilled PDMS network at 59,400 ×.

introduced into polymers in the usual blending techniques. The distribution of sizes is relatively narrow, with most values of the diameter falling in the range 200–300 Å.

Most strikingly, there is virtually none of the aggregation of particles essentially invariably present in the usual types of filled elastomers. These materials should therefore be extremely useful in characterizing the effects of aggregation, and could be of considerable practical importance as well.

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Fig. 1. Transmission electron micrograph at a magnification of 26,400 × for the PDMS network containing 34.4 wt % filler. The length of the bar in each figure corresponds to 1000 Å.

Fig. 2. Micrograph for the same filled network at 59,400 ×.

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Y.-P. NING
M.-Y. TANG
C.-Y. JIANG
J. E. MARK

Department of Chemistry and the Polymer Research Center
The University of Cincinnati
Cincinnati, Ohio 45221

W. C. ROTH

Analytical Research Department
Dow Corning Corporation
Midland, Michigan 48640

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