Fine Colloidal Silica as Reinforcing Filler in Polyurethane Polymers

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Synopsis

Colloidal silica in the particle size range 1.4–10 nm was extracted into tetrahydrofuran (THF). Alkali silicate solutions with $SiO_2 : M_2O$ (M = Li, Na, K, Cs) ratios ranging from 3 : 1 to 20 : 1 were used as source of silica particles in the size range 1.4–4.4 nm whereas commercial silica sols were used for particles in the range 5–10 nm. Films of polyester- and polyether-based polyurethane-containing colloidal silica were prepared and their mechanical properties measured. The reinforcing effect increased with increasing silica content and showed a maximum between 1.5 and 2.5 nm for polyether-based polyurethane and between 4 and 6 nm for polyester-based polyurethane. The area under the hysteresis loops of the stress–strain curves also showed maximum in the same particle size ranges for the two types of polyurethane. Reinforcement mechanisms are discussed in terms of interactions between small particles and hard or soft segments of the polymer chains.

INTRODUCTION

Small particles of carbon black have been used as reinforcing fillers in rubber for many years and the reinforcing effect increases with decreasing particle size.[1] Silica particles in the range 10–25 nm, esterified with butoxy groups, increased the tensile strength, modulus, and shore hardness of rubber and the reinforcing effect increased with decreasing particle size.[2] It has been shown that it is possible to prepare tough elastomers by swelling polydimethylsiloxane networks with tetraethyl orthosilicate, which is then hydrolyzed *in situ* to give silica particles with average diameter of 25 nm.[3] Carbon black and silica fillers provide large reinforcement in elastomers·but the mechanism by which they do so is still poorly understood.[4] It is the purpose of this study to investigate the effect of particle size and concentration of fine colloidal silica on the mechanical properties of polyurethane.

EXPERIMENTAL

Preparation of Colloidal Silica in THF

In concentrated solutions of alkali silicates with $SiO_2 : M_2O$ (M = Li, Na, K, Cs) ratios ranging from 3 : 1 to 20 : 1, more than 90% of the silica is present as very small particles which increase from 1.4 to 4.3 nm with
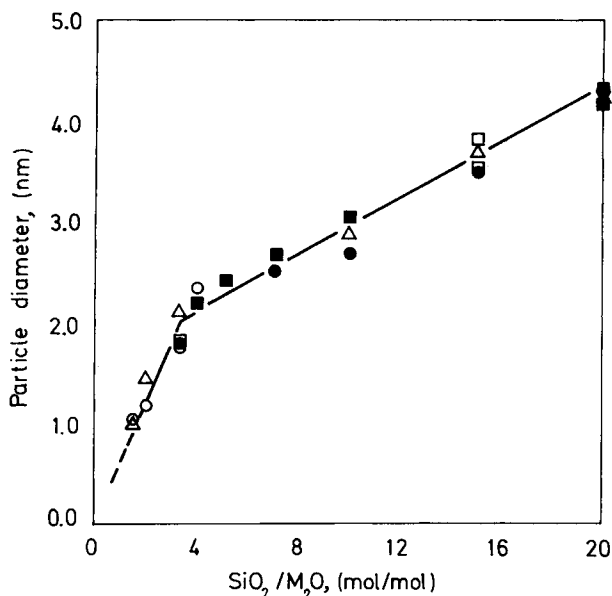
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Fig. 1. Size of colloidal particles in alkali silicate solutions as a function of $SiO_2 : M_2O$ ratio. (●) Li_2O; (○) Na_2O; (△) K_2O; (□) Cs_2O; (■) Cs_2O, 3M.

increasing ratio[5,6] (see Fig. 1). The colloidal particles were extracted into a hydrogen bonding organic solvent (e.g., tetrahydrofuran, THF), by the following procedure: 20 mL of 5M SiO_2 solution of alkali silicate, corresponding to 6 g of SiO_2, were added to 180 mL of a cooled (0–5°C) dilute solution of H_2SO_4 with very vigorous stirring. The concentration of the solution of H_2SO_4 was adjusted so that the pH, after the addition of the alkali silicate solution, was 1.7–2.0 where silicic acid polymerizes least rapidly. Then 94 g of cooled THF were added to the acid sol of polymeric silica with moderate to gentle stirring. After 5 minutes, 70 g of fine sodium chloride were added under gentle to moderate stirring. The mixture was stirred for 20 minutes and then transferred to a separating funnel. After 30 minutes the mixture separated into 2 layers and the upper organic phase containing most of the solvent and silica was recovered by driving off the lower aqueous saline layer.

For particles in the range 5–10 nm a similar procedure was used to extract particles from commercial silica sols (e.g., Ludox SM and Ludox LS from DuPont) for 8 nm and 12 nm particles, respectively.

Fine silica powder is used as filler in polymers and Aerosil from Degussa, with a surface area of 170 m^2 g^{-1} which corresponds to an ultimate particle size of 16 nm, was used as a representative of commercial fine silica fillers.

Preparation of Polymer Films

First, 10 g of Estane 5714, which is a polyether-aromatic isocyanate polyurethane, or Estane 5710 F1, which is a polyester-aromatic isocyanate polyurethane, both from Goodrich, were dissolved in 45 mL THF. Solutions of THF containing extracted colloidal silica were added dropwise under vigorous stirring to the polymer solutions to give the desired concentrations of silica (in
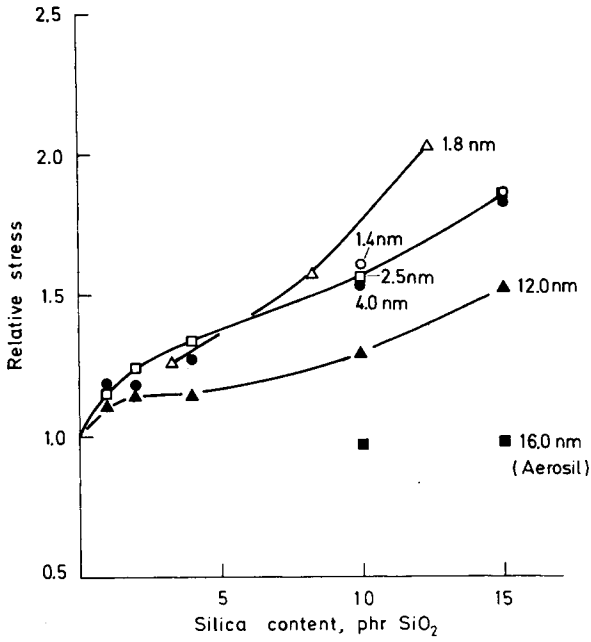
Fig. 2. Effects of particle size and SiO_2 content on relative stress of Estane 5714 at 100% stress.
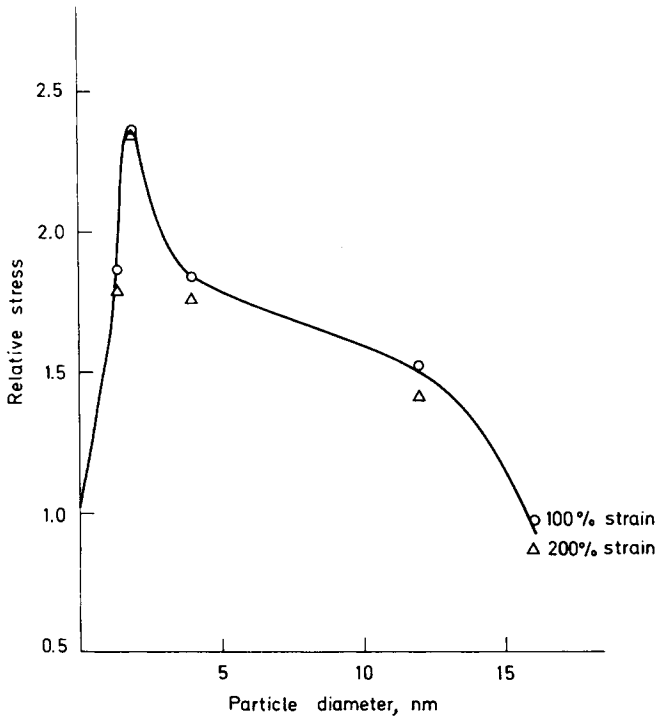

Fig. 3. Relative stress of Estane 5714 containing 15 phr SiO_2 as a function of particle size at 100% and 200% strain.

phr). The THF contents of the solutions were adjusted so that the polymer concentrations (g polymer per mL THF) became the same. Solutions containing Aerosil were prepared by adding calculated amounts of Aerosil powder to the polymer solution under vigorous stirring.

Films of the polyurethane solution were cast on Teflon-coated glass plates using a doctor blade with a slit of 1.5 mm. The films were left in room temperature for about 20 minutes, after which time they were placed in an oven at 60°C. After 1 h at 60°C a vacuum of about 1 mmHg was applied for 0.5 h. Finally, the evaporation of THF was completed at 90°C and vacuum for 45 minutes. The resulting films had a thickness of about 0.15 mm.

Mechanical Testing of Film

Film samples were conditioned at 20°C and 65% relative humidity (RH) for 24 h before testing in an Instron 1122 "Tensile Testing Machine" operated at a beam speed of 50 min/min. In order to determine the hysteresis of the stress–strain curve, the films were strained 350% at beam speeds of 50 and 500 mm/min. The beam was returned at the same speeds.

In several of the figures the term relative tensile stress is used which is obtained by dividing the tensile stress, in Newton/mm^2, of the sample containing colloidal silica by that of the film containing no silica.
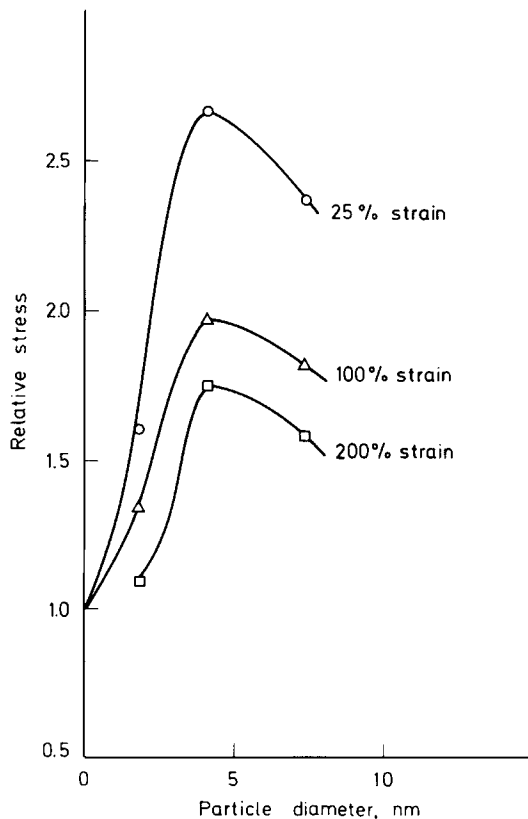

Fig. 4.   Relative stress of Estane 5710 F1 containing 17.6 phr SiO$_2$ as a function of particle size at 25%, 100%, and 200% strain.
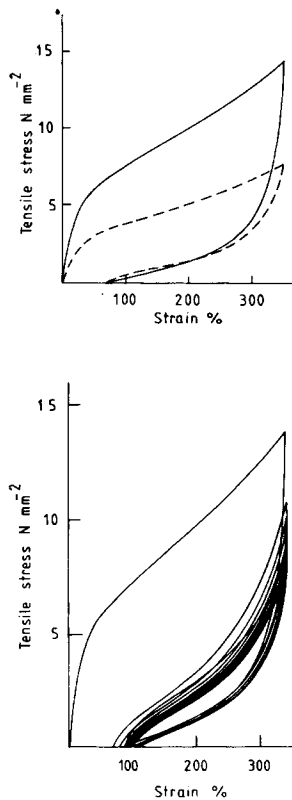
Fig. 5. Hysteresis loops of Estane 5714 (beam speed: 50 mm/min). (a) 1 cycle. (———) 12.4 phr 1.8 nm SiO_2; (---) no silica. (b) 14 cycles.

RESULTS AND DISCUSSION

Figure 2 shows that the relative stress of Estane 5714 increases with increased silica content and, generally, with decreasing particle size. Aerosil has a very modest reinforcing effect at 25% strain but actually decreases the relative stress at higher strains. Where the reinforcing effect has been studied at low silica contents, 1–5 phr SiO_2 corresponding to about 0.5–2.3 volume % SiO_2, there appears to be a rapid increase, in some cases even a tendency of a maximum, in relative tensile stress between 1 and 5 phr SiO_2. The relative tensile stress seems to vary with particle size in a somewhat irregular manner at different strains. Figure 3, however, shows that at 100% and 200% strain the relative stress shows a marked narrow maximum at particle sizes between 1.5 to 2.5 nm.

For Estane 5710 F1 the effect of particle size was investigated at two concentrations of SiO_2 only; 11.1 and 17.6 phr SiO_2, respectively. The same general trends could be observed as for Estane 5714, including some irregularities with regard to the dependence of the reinforcing effect on particle size at different strains. Figure 4 shows that relative stress goes through a maximum at particle sizes between 4.0 to 5.0 nm, compared to between 1.5 to 2.5 nm for Estane 5714.

Figure 5 shows that 15 phr of 1.8 nm SiO_2 particles greatly increase the area of the hysteresis loop of Estane 5714. The effect is very large for the first cycle
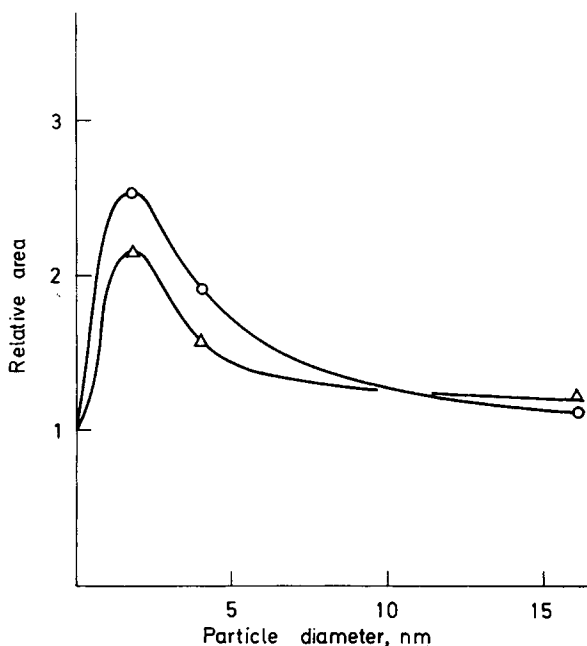
Fig. 6.   Relative area of hysteresis loop of Estane 5714 containing 15 phr SiO_2 as a function of particle size (beam speed: 50 mm/min). (○) First cycle; (△) 14th cycle.

but decreases convergingly to a value which is significantly higher than the area of the polymer film containing no silica which has undergone the same number of cycles. As for the tensile stress, a relative area of the hysteresis loop was obtained by dividing the areas of the hysteresis loop of the stress-strain curves for polymer films with and without silica.

Figures 6 and 7 show the effect of particle size on the relative area of the hysteresis loops of the stress-strain curves of Estane 5714 and Estane 5710 F1 after the first and fourteenth cycle. The areas go through maxima at about 2 nm for Estane 5714 and at about 5 nm for Estane 5710 F1 which corresponds well to the maxima observed for the relative stress observed in Figures 3 and 4.

Hysteresis loops were also obtained at beam speeds of 500 mm/min and the results were generally the same as for the lower beam speed of 50 mm/min.

The structure of polyurethane elastomers is well known and consists of hard and soft chain segments. The ordered hard segments act as bridges between the unordered soft segments.[7,8] The hard segments are typically in the range 2–4 nm whereas the mean free path of the soft segments are in the range 10–30 nm. The hard segments make up about 10–20% of the molecular weight.

In the SiO_2–polyurethane system, 15 wt% corresponds to 7 vol %. It can be shown by simple calculations that for spherical particles well dispersed in a matrix 7 vol % corresponds to a distance between particles of 1 particle diameter. In other words, the mean free paths of the particles is one particle diameter.
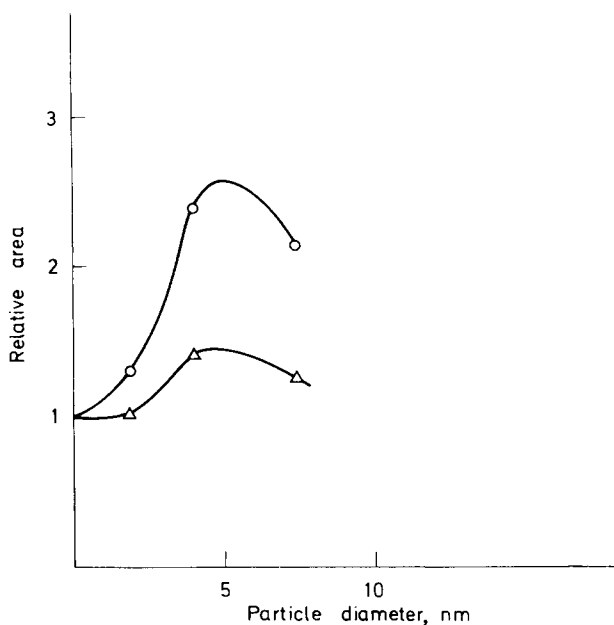
Fig. 7. Relative area of hysteresis loop of Estane 5714 F1 as a function of particles size (beam speed: 50 mm/min). (○) First cycle; (△) 14th cycle.

The pronounced maxima of the tensile strength and the area of the hysteresis loop for particles in the range 2–5 nm indicate some kind of geometrical and chemical matching of the particles to the hard segments. During the formation of the elastomeric structure from the solutions of polymer containing well dispersed silica particles, the particles may interact with the hard segments in different ways. One possibility is close association by hydrogen bonding between the silanol groups of the particle surface and the hard segments.

An additional reinforcing mechanism is bridging of hard segments by the particles. The large deformations in the first hysteresis cycle will weaken some of the interaction and alter the geometrical arrangement of the particles. The plastic deformation after completed cycling is virtually the same for polymer containing silica particles as that for polymer without silica, which may be attributed to the fact that the particles are almost one order of magnitude smaller than the size of the soft chain segments.

CONCLUSIONS

Colloidal particles in the size range 1.5–10 nm had a remarkably high reinforcing effect in polyurethane polymers.

The secant moduli at 25% and 100% strain increased by up to 250% at SiO_2 concentrations of 15 phr corresponding to about 7% by volume.

The effect of the small particles on the area of the hysteresis loop paralleled that on the secant modulus.

At 15 phr SiO_2 the effects on secant modulus and area of the hysteresis loop showed maxima at 2 nm for polyether-based polyurethane and at 5 nm for polyester-based polyurethane.

The observed effects are consistent with a reinforcing mechanism by which particles of approximately the same size as the hard chain segments can hydrogen bond to these and enhance strength by a favorable geometrical arrangement.

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