

# Preparation and properties of close-packed composite materials

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Monodisperse silica particles of about 0.3  $\mu\text{m}$  diameter are suspended in methacrylate monomer using a carefully selected dispersant. Many steric dispersants are hydrocarbon chains with a reactive end-group. These are not effective as dispersants for silica in moderately polar solvents, such as esters and the methacrylate monomers. Good dispersion was obtained with a methacrylate polymer terminated by a chlorosilane end group. Settling or centrifugation of these unagglomerated dispersions gives well-packed particle beds. Polymerization of the surrounding monomer produces composite materials with high packing fractions and a high degree of regularity. Moduli and strengths of these composites are reported.

## 1. Introduction

Filled polymer composite materials are normally prepared by the dispersion of inorganic particles into a thermoplastic. Filler fractions are limited by the progressive loss of processability of the dispersion of particles, either in polymer or in liquid monomer. Maximum levels in practical use are typically about 40 wt % or 25 vol %. In principle, it should be possible to make filled composites with 74 vol % spherical monodisperse particles, but such a material would not flow. Even higher levels should be achievable with suitable size distributions [1]. There are a number of cases, such as dental composites, where particles are first dispersed into a monomer which is subsequently polymerized [2-4]. Recent interest in the production of high-strength ceramics has focused attention on the use of monodisperse sub-micrometre particles, a model for which is "Stober" silica, produced by controlled hydrolysis of silicon tetraethoxide. It would be of interest to explore the mechanical properties of ideal composite systems with known distributions of uniformly sized particles in a polymeric matrix. With this aim in view, we report here studies of the use of various dispersing agents to optimize the distribution of silica particles in methacrylate monomers, and the mechanical properties of the resulting composites.

Studies of the dispersion of oxide particles into organic liquids have identified a number of dispersants which are very effective in non-polar liquids such as toluene and hexane [5-7]. It is also relatively easy to disperse oxide particles into water and alcohols. Methacrylate monomers are liquids of intermediate polarity and it has proved quite difficult to find suitable dispersants. Accordingly we first investigated a range of polymers and short-chain molecules to find

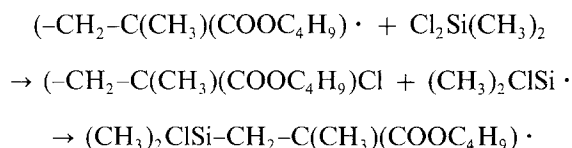
an effective dispersant. With this we were able to obtain sediments, from suspension in monomer, with a high packing density. Subsequent polymerization led to a well-packed composite material.

## 2. Experimental details

### 2.1. Dispersants

Amine, alcohol and chlorosilane dispersants were reagent-grade chemicals. A series of ethylene oxide-propylene oxide random copolymers of molecular weight 1 to  $2 \times 10^3$  with from 25 to 85 mol % ethylene oxide and one hydroxyl end-group, were obtained from the Nanjing Plastic Factory.

Silane-terminated polybutylmethacrylate (PBMAS), and polybutylacrylate were formed by free radical polymerization in toluene in the presence of 1% dimethyldichlorosilane which acts as a chain-transfer agent [8, 9]



Polymer molecular weights were 30 to  $85 \times 10^3$  by gel permeation chromatography (GPC), based on polystyrene calibration.

### 2.2. Formation of particles

Monodisperse silica particles were prepared by the Stober method [10]. Typically, 0.3M tetraethoxysilane was added with stirring to a solution of 1.1M ammonia and 2.6M water (made with 28% ammonium hydroxide). Particles of 0.2 to 0.5  $\mu\text{m}$  were formed with a polydispersity within any batch, as defined by a ratio

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TABLE I

Dispersant	Adsorption (mg g <sup>-1</sup> )	Packing (%) (gravity sedimentation)		
		Toluene	THF	Ethyl Acetate
Dodecylamine	32	30	28	
Hexadecanol	35	33	25	14
Trichloro-octylsilane (vacuum-dried silica)	30	22	45	
(air-dried silica)	14		41	
Triethoxydodecylsilane	16	10	19	

of weight average to number average particle diameter, of < 1.05.

At the end of the reaction (24 h) the mixture was acidified to remove excess ammonia, the particles were centrifuged and washed with de-ionized water. Excess water was removed by drying at 95°C for 10 h. Mild drying was used to prevent formation of any strong agglomerates.

### 2.3. Dispersion and sedimentation studies

Silica as a slurry of a few weight percent in solvent was dispersed by a 1 h treatment in an ultrasonic cleaning bath. Sediment densities were measured after either letting the particles settle under gravity, or after centrifugation. Sediment density is expressed as the mass of particles/(volume occupied by sediment × theoretical density of silica) [11].

Suspensions were normally prepared by ultrasonic dispersion of silica in a solution of dispersant, followed by reaction under suitable conditions. The particles were then centrifugally separated, washed and redispersed into the solvent or monomer under test. Amine dispersants were allowed to react with the particles for 1 h at room temperature, alcohols and polyethers were reacted for 2 h at 200°C under nitrogen [12]. Silanes were refluxed with the particles for 2 h. The extent of adsorption of dispersant was determined by thermogravimetric analysis of the dried particles up to 600°C. Blank runs for the particles alone were subtracted and the remaining weight loss attributed to the dispersant.

Composites were prepared either by polymerization after dispersion in monomer and sedimentation, or by

TABLE II

Polyether (EO:PO, mol wt)	Adsorption (mg g <sup>-1</sup> )	Packing in THF (%)
Untreated		42
25:75, 1240	50	43
40:60, 1580	48	40
50:50, 1330	39	62
65:35, 1560	34	43
85:15, 1940	31	48

monomer replacement of solvent in the sediment, and polymerization. Final volume fractions of filler were determined by thermogravimetric analysis.

Polymerization was performed by heating the sediment, containing monomer and 0.5% azoisobutyronitrile, to 60°C for 3 d, then to 100°C for 1 h. Replacement of solvent was performed by allowing the sediment to dry in air, then adding monomer, allowing it to stand and then to dry again, and then finally adding monomer containing initiator. Polymerization was carried out as above.

### 2.4. Mechanical properties

Samples were cut to cylinders of 5 mm diameter and 5 mm height and tested in compression at 5 mm min<sup>-1</sup>.

## 3. Results

### 3.1. Dispersants for silica spheres

In principle, optimum packing will occur as a result of slow settling of non-agglomerated and non-interacting particles [5]. We believe that there are few agglomerates in our silica powder because it was never subjected to high-temperature drying. Particles dispersed in a liquid will normally have an attractive interaction arising from van der Waals forces. In organic liquids, these can be overcome by steric stabilization, where a long chain molecule is attached to the surface with part of the chain dissolved in the surrounding solvent [13]. The dissolved chains set up an osmotic repulsion when particles approach. We have investigated a number of long-chain dispersants with end groups that should attach to the silica surface.

The degree of adsorption of alkyl chain compounds with a number of different end groups is shown in

TABLE III

	Adsorption (mg g <sup>-1</sup> )	Packing (%)		
		Ethylacetate	Butylmethacrylate	Toluene
Silanated polymer	37	33	47	41
Unmodified polymer	56	15		

TABLE IV

Dispersant	Sedimentation method	Voi. fraction (%)	Modulus (MPa)	Strength (MPa)	Strain to break
PBMAS	Centrifuge	52	900	30-70	0.1
PBMAS	Gravity	53	890	60	0.4
Polyether	Centrifuge	24	350		
PBMA	Centrifuge	42	600		
None	Centrifuge	43	830 (Disp. and packed in THF)		
Hexadecanol	Centrifuge	42	810		
PBMAS	Centrifuge	15	330 (Fumed silica)		
PBMA		0	230 (Unfilled)		

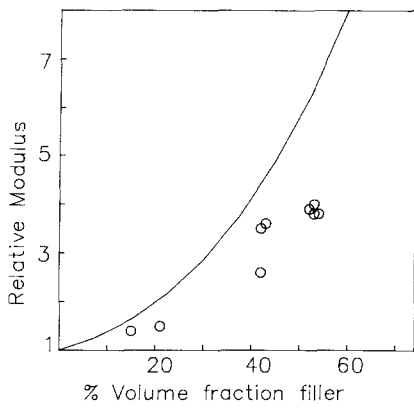


Figure 1 Elastic moduli of composites measured in compression. Curve is a modified Kerner equation for the case of packing of identical spheres, and where the modulus of the filler is much greater than the modulus of the matrix.

Table I. It can be seen that hydroxyl, chlorosilane and amino terminations are effective in bonding a chain to the silica surface. Ethoxysilane does not work well under the conditions of treatment (1 h at room tem-

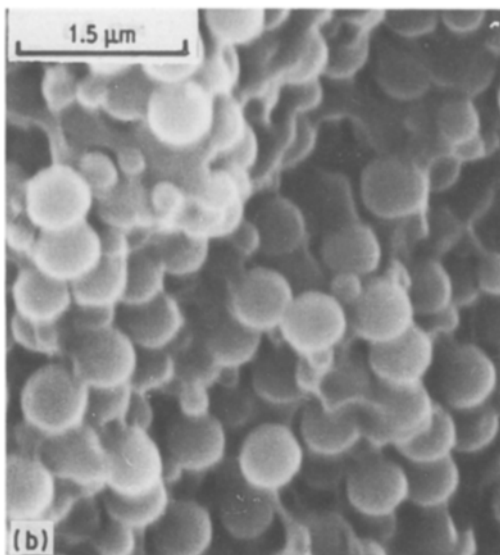
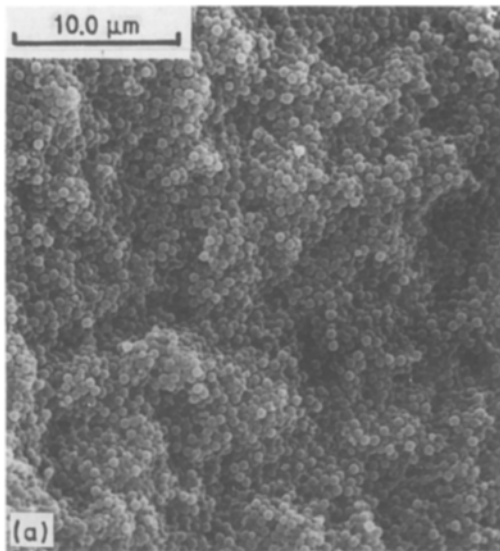


Figure 2 Fracture surface of composite of silica, dispersed with silanated polybutylmethacrylate in polybutylmethacrylate, settled under gravity.

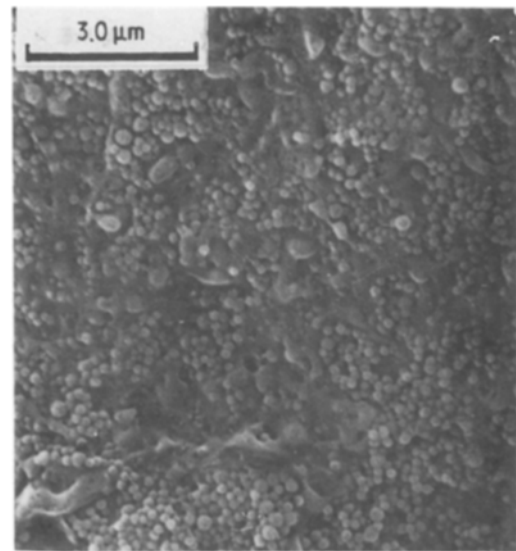


Figure 3 As Fig. 2, but without dispersant.

perature or 5 h under reflux). The chlorinated silane treatment is apparently sensitive to the water content of the particles, which presumably interferes with the surface reaction. Sediment densities in ethyl acetate and in toluene were measured for silica dispersed with a number of amines, of which only the long chain dodecylamine gave a good packing density ( $> 20\%$ ). Comparing the various long chain alkyl compounds (Table I), all except the ethoxysilane gave a good packing density in toluene and THF, but none were effective as dispersants in ethyl acetate (used as a model for methacrylate monomers).

This work was extended to studies of polyethers as dispersants. The results are summarized in Table II. The surface coverage decreased as the ethylene oxide content increased in the ethylene oxide-propylene oxide block copolymer (EO:PO). The efficiency of the polyethers as dispersants, determined by the sediment volume test, was very dependent on the suspending solvent. Good dispersion was obtained in water, ethanol and THF but results were poor in less polar

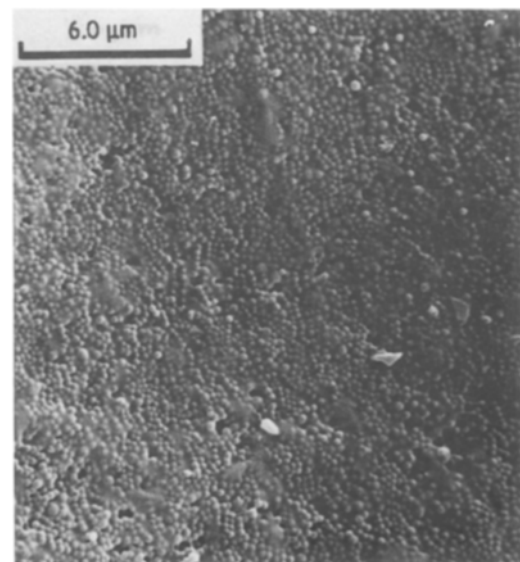


Figure 4 As Fig. 2, but with polyether dispersant.

solvents, such as methacrylates, benzene and chloroform, where the particles were either highly aggregated or gelled. This is apparently related to the relative binding energies of the solvent and polymer for the particle surface.

Silanated polybutylmethacrylate was found to be a good dispersant in several solvents, Table III, and was used for the preparation of composite materials. In THF, dispersions settled very slowly and were opalescent. Unmodified polybutylmethacrylate also bound to the particles but was not effective as a dispersant.

### 3.2. Composite materials

Our aim in this work is to prepare highly ordered composites of silica in a polymeric matrix. This was achieved by preparing a dispersion of particles in monomer which was then polymerized. Two methods were tried. Particles were dispersed in solvent, sedimented by centrifugation, followed by drying and reimpregnation with monomer. This allowed us to take advantage of the good sediment density that can be achieved with THF, but the resulting samples were weak and brittle. Better results were obtained by dispersing the silica particles, with chlorosilane-terminated polybutylmethacrylate as a dispersant, directly into butylmethacrylate monomer. Table IV shows that packing densities up to 53% could be achieved by centrifugal settling of these systems. Low packing densities were obtained using a polyether dispersant, no dispersant or unmodified polybutylmethacrylate. A commercial fumed silica also gave poor packing with the silanated polybutylmethacrylate.

The moduli of the composites increased with packing density, and fit well to the Kerner equation [1], as seen in Fig. 1. The fracture properties were studied in compression. Many of the samples showed extensive deformation without fracture. Only those with high volume fractions of particles showed definite fracture. Samples packed by gravitational settling to a high packing density, showed a much higher elongation to break than those which were centrifugally settled.

The fracture surface of a gravitationally settled sample of silica, treated with silanated polybutylmethacrylate in butylmethacrylate, is shown in Fig. 2, the packing appears very regular with no sign of polymer-rich zones or voids, in contrast to the untreated particle composite, or the polyether-treated composite (Figs 3, and 4). A polished section of a centrifugally-settled sample is shown in Fig. 5. Here some voids can be seen on the scale of one particle.

Silica-polystyrene composites were prepared in a similar way. Packing densities were rather poor at 20 to 30% and fracture surfaces showed much inhomogeneity in packing.

### 4. Discussion

We have shown that, with careful optimization of the dispersion conditions, high-quality composites can be prepared with uniform sub-micrometre particles well dispersed in a polymeric matrix. The modulus is as expected for composites with this high level of packing. Such high levels of packing could also be achieved by the use of wide size distribution particles, but the

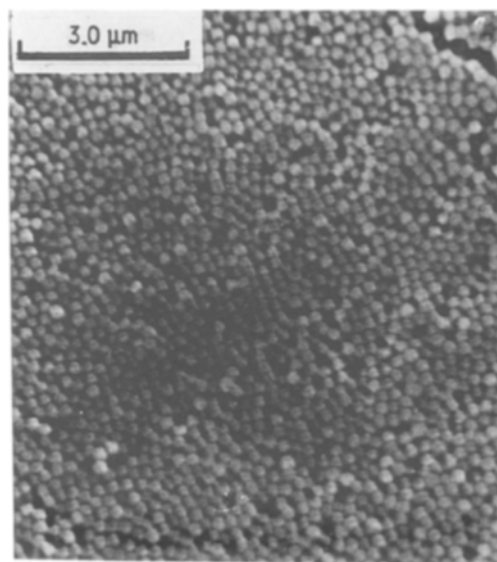


Figure 5 As Fig. 2, but centrifugally settled. Polished cross-section.

equivalent level of regularity has not been described before.

It is well known that amorphous metals are substantially harder and more brittle than the equivalent crystalline metals, because dislocation motion is much more difficult in an irregular structure. We had hoped to produce very regular and opalescent composites which could be shown to have fracture properties different from those of poorly packed and irregular samples. There is some sign of this in the higher fraction strain of the gravitationally settled samples, as compared to the centrifuged samples. This is currently being studied further.

These well-packed samples are brittle when compared to the toughness of the pure, rubbery, polybutylmethacrylate or of lightly-filled samples. This may depend on the presence of large particle-free zones in the lightly packed samples. These studies give us a method to study the effect of the quality of packing on fracture properties of composites. Hitherto, only volume fraction effects have been studied.

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