

Controlled structure copolymers for the dispersion of high-performance ceramics in aqueous media

Maria Vamvakaki,^a Norman C. Billingham,^{*b} Steven P. Armes,^b John F. Watts^c and Stephen J. Greaves^c

^aDepartment of Chemistry, University of Cyprus, PO Box 20537, 1678 Nicosia, Cyprus

^bSchool of Chemistry, Physics and Environmental Science, University of Sussex, Falmer, Brighton, UK BN1 9QJ. Tel: +44 1273 678313; Fax: +44 1273 677196;

E-mail: n.billingham@sussex.ac.uk

^cSchool of Mechanical Engineering and Materials Science, University of Surrey, Guildford, Surrey, UK GU2 5XH

Received 22nd February 2001, Accepted 25th July 2001

First published as an Advance Article on the web 7th September 2001

Statistical copolymers of a methoxy oligo(ethylene glycol) methacrylate (OEGMA) and either 2-(dimethylamino)ethyl methacrylate (DMA) or methacrylic acid (MAA) have been examined as dispersants for barium titanate powder in water and water-isopropyl alcohol mixtures. The dispersing efficiency of the polymers was assessed using gravitational sedimentation and by measuring the particle size distributions of the dispersed powders by disk centrifuge photosedimentometry (DCP). OEGMA copolymers with MAA were very efficient, causing the mean particle size of the dispersed powder to decrease by an order of magnitude in the presence of dispersant. In contrast, OEGMA-DMA copolymers were completely ineffective. The best MAA copolymers gave higher dispersion efficiency over a wider pH range (pH 1 to 10) compared to a typical commercial dispersant Darvan-C, which was efficient only above pH 7.

X-Ray photoelectron spectroscopy, zeta potential measurements, infra red spectroscopy and DCP studies all show that the acid-containing copolymers bind strongly to the barium titanate surface *via* the carboxylic acid groups resulting in good quality dispersions. There were no changes in the dispersion quality due to desorption of the dispersant even after extensive washing and drying of the copolymer-coated particles. The dried particles showed complete redispersion in water even after washing and drying, again indicating strong binding of the copolymer to the oxide surface.

1 Introduction

In recent years there has been rapid development in the use of high-performance metal oxide ceramics, both in mechanical applications and in the electronics industry, notably as dielectric materials in capacitors. The need for multi-layer ceramic capacitors in microelectronic devices has resulted in a continuous demand for size reduction, which implies thinner dielectric layers and very high relative permittivities. One of the most popular materials for these applications is barium titanate, BaTiO₃.^{1,2}

Thin layers of BaTiO₃ and other ceramics are usually prepared by dispersion of ceramic powder in a medium containing a suitable binder. The dispersion is formed by tape casting into a thin layer which can be subjected to successive solvent removal, binder removal and firing or sintering treatments to give the final ceramic. Ceramic powders are generally agglomerates, which has a major influence on the quality of the product obtained by tape casting.³ The packing of agglomerates in the ceramic green tape is poor, resulting in low density sintered materials. Ceramic parts of high density and strength are obtained only from a well-dispersed powder whose particles pack efficiently, leading to a very high density, uniform and void-free green state. A densely packed tape will sinter to a fired ceramic with near-perfect (>98%) packing, essentially free of cracks and cavities. Such ceramics have much improved mechanical and electrical properties, which are essential for their use as high technology materials. Thus, good dispersion of the primary particles in the early stages of processing is crucial to the quality of the final ceramic.

Stable dispersions are achieved by using a dispersing agent to provide a steric barrier to particle flocculation.⁴ Natural products like fish oil,⁵ as well as titanates,⁶ silanes,⁷ and aromatic carboxylic acids⁸ were the first dispersants reported for ceramic materials. The main disadvantage of the natural dispersants was the variability of their composition. To avoid such variations the use of polymeric dispersants in non-aqueous media has been reported extensively.⁹⁻¹² The type of dispersant used depends on the surface properties of the particles and the solvent medium. Al-Lami *et al.*¹³ were the first to report the use of near-monodisperse methacrylate-based statistical copolymers containing carboxylic acid groups, along with their block analogues, for the dispersion of alumina particles in organic solvents such as toluene, acetone, ethyl alcohol and isopropyl alcohol. Good packing densities were achieved using low molecular weight statistical copolymers. Methacrylic ester polymers have the advantage of their ability to degrade cleanly with minimum carbonaceous residues in the final ceramic.

Other amphiphilic near-monodisperse, diblock copolymers of methacrylic acid¹⁴ have also been tested as dispersants for alumina in toluene, while poly(vinyl butyral) is the most common dispersant used commercially for BaTiO₃ particles in organic media.¹⁵

Most studies of ceramic dispersion have used an organic solvent as the dispersion medium. Lately, due to environmental concerns replacement of organic solvents by aqueous media has attracted much attention. Dispersion studies in aqueous media are less common, with polyelectrolytes being the most widely reported dispersants.¹⁶⁻²⁶ In such systems, particle

stabilisation is very sensitive to changes in the dispersion pH and salt concentration²⁷ which affect the degree of ionisation and the charge repulsion, responsible for the electrostatic stabilization mechanism operating in these dispersions.

Recent synthetic advances have led to controlled structure copolymers becoming more accessible. Their main advantage is that they consist of at least two different types of comonomer unit, one acting as the particle binding groups while the others serve as dispersion stabilisers. Living polymerisations provide materials of controlled molecular weight, polydispersity, composition and architecture. The adsorption of such controlled structure, monodisperse block copolymers, obtained by anionic polymerisation, onto TiO₂ and SiO₂ particles has been investigated by Hooegeven *et al.*^{28,29} The particle stabilisation was examined as a function of pH, salt concentration and copolymer composition. Another Dutch group has investigated the dispersion of BaTiO₃ particles in water using poly(vinyl alcohol-methacrylic acid) block and statistical copolymers.³⁰ A steric stabilisation mechanism was suggested for the block copolymers, whilst an electrosteric mechanism was invoked for their statistical analogues. The presence of carboxylate groups increased the affinity of the copolymers for the BaTiO₃ surface compared to the PVA homopolymer suggesting that the adsorption of PMAA onto the particle surface is stronger than that of PVA. However, controlled structure copolymers have been relatively little studied in aqueous ceramic processing and more work is required to elucidate the structural features of the copolymer dispersant critical for efficient dispersion.

In an effort to obtain a better understanding of copolymer-stabilized aqueous ceramic dispersions we here report a study of the dispersion efficiency of methacrylate-based polymeric dispersants for BaTiO₃ in aqueous media.

Since BaTiO₃ is an amphoteric material, all of the polymers were based on a methoxy-capped oligo(ethylene glycol) methacrylate (OEGMA), with either methacrylic acid (MAA) or dimethylaminoethyl methacrylate (DMA) as comonomer, to provide acidic or basic surface-binding sites. The successful dispersants were also examined as a function of the medium pH and compared to a commercial analogue Darvan-C[®].

2 Experimental

2.1 Materials

The polymeric dispersants (see Fig. 1 and Table 1) were synthesized by Group Transfer Polymerisation as described elsewhere.³¹ Copolymers with DMA were prepared directly from the monomer mixtures. Copolymers with MAA were prepared by copolymerising OEGMA with 2-tetrahydropyranyl methacrylate (THPMA), followed by removal of the tetrahydropyranyl groups by acid hydrolysis to give a range of copolymers with carboxylic acid groups.

The commercial dispersant (Darvan-C[®], RT Vanderbilt Inc.) was obtained from Cookson Technology Centre in aqueous solution and was used as received. The ceramic powder was

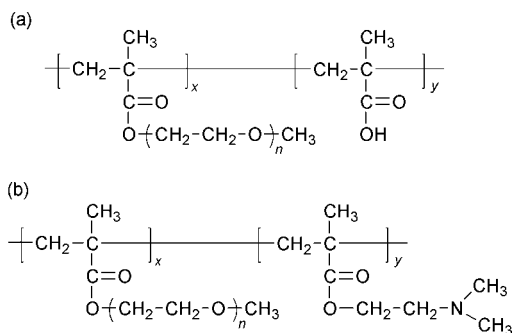


Fig. 1 Structures of the copolymer dispersants (a) OEGMA-*stat*-MAA and (b) OEGMA-*stat*-DMA. For all OEGMA polymers $n \approx 6$.

Table 1 Compositions and number average molecular weights of the polymeric dispersants and packing density of BaTiO₃ in 78:22 (v/v) H₂O-isopropyl alcohol mixture containing 2 wt% dispersant

Copolymer	OEGMA content/mol% ^a	M_n^b	Packing density (%)
None			16.3
OEGMA	100	9900	16.1
PMAA	0	4200	26.3
OEGMA- <i>stat</i> -DMA	32	24300	16.1
OEGMA- <i>stat</i> -THPMA	60	8200	14.2
OEGMA- <i>stat</i> -THPMA	60	8200	48.3 ^c
OEGMA- <i>stat</i> -MAA	13	7700	46.7
OEGMA- <i>stat</i> -MAA	20	12300	39.1
OEGMA- <i>stat</i> -MAA	31	12000	45.3
OEGMA- <i>stat</i> -MAA	40	10600	46.7
OEGMA- <i>stat</i> -MAA	52	6900	46.7
OEGMA- <i>stat</i> -MAA	61	10000	46.7
OEGMA- <i>stat</i> -MAA	71	6300	46.7
OEGMA- <i>stat</i> -MAA	72	10600	46.7
OEGMA- <i>stat</i> -MAA	81	8500	36.2
OEGMA- <i>stat</i> -MAA	90	5000	34.5
Darvan-C ^{®d}	0	28400 ^e	41.5

^aDetermined by ¹H NMR. ^bDetermined by GPC with PMMA standards. ^cAfter storage at room temperature for 3 weeks. ^dCommercial dispersant [poly(ammonium methacrylate)]. ^eDetermined by aqueous GPC with PEO standards.

BaTiO₃ (Tamtron X7R 302H, TAM Ceramics Inc.) obtained from the Cookson Technology Centre. A specific surface area of 3.3 m² g⁻¹ was measured by BET (N₂ adsorption at 77 K), using a Quantachrome Nova 1000 apparatus. The mean particle density, measured by helium pycnometry (Micromeritics AccuPyc 1330), was 5.85 g cm⁻³. An average particle radius of 0.15 μm was calculated from the specific surface area assuming non-porous, spherical particles. Unless otherwise stated, the BaTiO₃ powder and all chemicals were used as received.

2.2 Gravitational sedimentation

Gravitational settling experiments were carried out by adding a known weight of the ceramic powder to a solution of the dispersant in stoppered 25 ml graduated cylinders. 0.170 g of copolymer (2 wt% based on ceramic powder) was dissolved in the appropriate solvent or solvent mixture, and the ceramic particles (8.40 g) added. The slurry was agitated manually before being allowed to stand at room temperature for up to three weeks (depending on the efficiency of the dispersant). The sediment volume was monitored as a function of time and the final bed volume determined to calculate the packing density. The final sediment density is expressed as a fraction of the theoretical density of a barium titanate single crystal (5.85 g cm⁻³).

2.3 Particle sizing by disc centrifugation

2.3.1 X-Ray disk centrifuge. A Brookhaven Instruments X-ray disc centrifuge (XDC) was used to measure the size and degree of dispersion of the BaTiO₃ particles. A BaTiO₃ dispersion in a 78:22 v/v% H₂O-isopropyl alcohol solvent mixture prepared using 2 wt% 71-29 OEGMA-*stat*-MAA copolymer was compared to a BaTiO₃ slurry in the same solvent mixture with no added dispersant. A 0.75% suspension of the particles was prepared in each case. 12 ml of the dispersion was injected into the disk cavity. The reference sample was analysed in gravitational mode with a run time of 15 min, whilst the stabilised dispersion was analysed in centrifugal mode at 602 rpm with the detector scan in x-mode (data collected at fixed time intervals).

2.3.2 Disc centrifuge. Disc centrifuge photosedimentometry (DCP) was performed with a Brookhaven Instruments centrifuge. 1% (v/v) dispersions were prepared in water and agitated gently prior to analysis. 16 ml of suspension was injected into the disk cavity. Each sample was run in centrifugal mode at 602 rpm with the detector in the f-mode (scan off mode; calculation at fixed Stokes diameters). The measured density of 5.85 g cm^{-3} for BaTiO_3 was used for these measurements.

2.4 Transmission electron microscopy

Transmission electron microscopy (TEM) studies were made using a Hitachi 7100 instrument at a beam potential of 100 kV. A 1 wt% suspension of each dispersion was prepared in a 78:22 v/v% water-isopropyl alcohol mixture and allowed to evaporate overnight on a 3 mm carbon-coated copper grid.

2.5 Zeta potential measurements

Zeta potentials were measured using a Malvern Zetamaster ZEM5002, both before and after copolymer adsorption. A small amount of the BaTiO_3 powder (with or without the adsorbed copolymer) was dispersed in water and the pH adjusted using 0.1 M HCl or KOH for the acidic and basic solutions respectively.

2.6 Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS)

Diffuse reflectance infrared spectra were obtained using a Perkin-Elmer 1720 spectrometer equipped with a Harrick DRIFTS accessory. The dispersions were prepared by a procedure similar to that described for the sedimentation experiments. Once the final bed volume was determined, the solvent was decanted and the sediment subjected to three further centrifugation-redispersion cycles using fresh solvent. The washed dispersions were dried in a vacuum oven for 24 h at room temperature. Part of the dried sediment was ground in a mortar to break down agglomerates then mixed uniformly with dry powdered KBr (10% BaTiO_3 -90% KBr). This mixture was poured into the DRIFTS sample holder and a razor blade drawn across the top to remove excess powder. 100 scans were averaged for each spectrum using pure KBr as the reference.

2.7 X-Ray photoelectron spectroscopy (XPS)

Samples were prepared following the procedure described for the sedimentation experiments. Part of the sediment was washed three times with fresh solvent as described for the DRIFTS analysis, while another portion was analysed without washing. XPS measurements were carried out using a VG ESCALAB Mk. II spectrometer interfaced to a VGS 5000S data system based on a DEC PDP 11/73 computer. The samples were mounted on a specimen stub using double-sided adhesive tape and excess powder shaken off. The X-ray source ($\text{AlK}\alpha$ 1486.6 eV, which corresponds to a sampling depth of 2-5 nm) was operated at a power of 450 W. The spectrometer was operated in the fixed analyser transmission mode at a pass energy of 50 eV for the survey spectra and 20 eV for the high resolution spectra. The base pressure in the vacuum chamber was of the order of 10^{-8} mbar. A single scan was adequate for good quality survey spectra, while 7 scans were collected for the core-line high resolution spectra. Core-line spectra were obtained for C, O, Ba and Ti. The duration of each scan was 200 ns with a step of 0.1 eV for C and 0.2 eV for other elements. The total acquisition time for each sample was 20-30 min. Peak-fitting and corrections for sample charging used the standard VGS 5000S software.

3 Results and discussion

3.1 Gravitational sedimentation

Gravitational sedimentation of flocculated particles is rapid, giving a porous, poorly packed sediment and a clear supernatant. Since the final sediment is loosely packed, it is easily redispersed with mild agitation. In contrast, a colloiddally stable dispersion settles much more slowly, forming a denser, and much less porous sediment. From the final bed volume the packing density of the sediment can be calculated as a fraction of the bulk density of the ceramic. A high packing density is thus characteristic of a colloiddally stable dispersion.

We have tested a range of statistical copolymers containing MAA, with acid content varying from 10 to 90 mol%, as dispersants for BaTiO_3 by comparing the final packing densities. OEGMA-DMA statistical copolymers and OEGMA and PMAA homopolymers were also examined. Sedimentation experiments were carried out in either water or a 78:22% (v/v) water-isopropyl alcohol mixture. The use of isopropyl alcohol in tape-casting formulations alleviated problems of foaming and slow evaporation rates in pure water. Sedimentation experiments in pure water and in water-isopropyl alcohol mixtures gave similar results, suggesting that the small amount of isopropyl alcohol has no effect on the dispersion stability.

Table 1 shows the results of gravitational sedimentation. Dispersions with OEGMA and MAA homopolymers sedimented completely in 24 h to give packing densities little better than the unstabilised powder and sediments which were easily redispersed by gentle agitation. In contrast, the OEGMA-MAA copolymers are effective dispersants. The initial sediment is formed within about two weeks but smaller particles remain in suspension, resulting in a cloudy supernatant for up to four weeks. The final sediments were very difficult to redisperse in water.

The dispersion efficiency of the OEGMA-*stat*-MAA copolymers is insensitive to the copolymer composition. Only polymers with MAA contents below 20 mol% gave poor packing densities, suggesting that there were insufficient acid residues for strong adsorption onto the particle surface. In all other cases, stable dispersions with packing fractions of around 47% were obtained. OEGMA-*stat*-DMA copolymers gave dispersions similar to those in the absence of dispersant. Unstable dispersions were obtained in both pure water and the water-isopropyl alcohol mixture, suggesting that the tertiary amine groups are much more weakly adsorbed than the MAA residues. Protonation of the DMA amine groups (pH adjusted to 3, 4 and 5 using HCl), did not improve the dispersion quality, suggesting that strong adsorption of the MAA residues occurs *via* carboxylate formation rather than an acid-base interaction.

As expected, both binding and stabilizing units in the same polymer chain are needed for stable dispersions. OEGMA is weakly adsorbed, whilst the MAA homopolymer, which is strongly adsorbed, lacks efficient stabilizing groups at the pH (~5.5) examined. This result is also consistent with the poor dispersion properties of the commercial dispersant Darvan-C below pH 8, discussed below. Although the range examined is limited, the results indicate that any effect of molecular weight is small.

The precursor OEGMA-*stat*-THPMA copolymer (see Table 1) was also examined. The initial dispersion was worse than that in the absence of a dispersant, indicating some flocculation by the copolymer. However, the quality of the dispersion improved with time and, after about three weeks, it reached the values for the OEGMA-*stat*-MAA dispersants. This is probably related to the slow deprotection of THPMA in water even in the absence of acid.³²

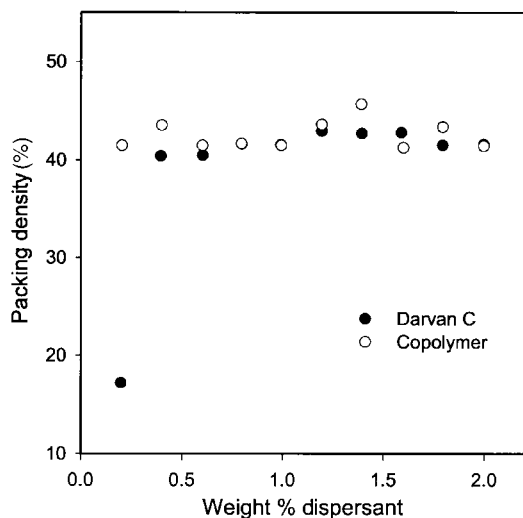


Fig. 2 Packing density of BaTiO₃ in 78:22 water-isopropyl alcohol mixture at different concentrations of 72-28 OEGMA-*stat*-MAA as the dispersant.

3.2 Effect of dispersant concentration on packing density

To minimize the amount of the dispersant required, we investigated the effect of varying dispersant concentration. The amount of dispersant was varied from 0.2 to 2.0 wt% of BaTiO₃. All experiments used a 72-28 OEGMA-*stat*-MAA copolymer in 78:22 water-isopropyl alcohol. The packing densities were directly compared to a commonly used commercial dispersant, Darvan-C, which is a polydisperse poly(ammonium methacrylate) and the results are shown in Fig. 2. The OEGMA-*stat*-MAA copolymer and the commercial dispersant were identical over the whole concentration range, except that the OEGMA copolymer was efficient at concentrations as low as 0.2% where Darvan-C gave an unstable dispersion.

3.3 Effect of pH on dispersion quality

An important parameter in aqueous formulations is the effect of pH, since pH changes often cause dispersion failure, due to changes in the ionisation of either the particle surface, the dispersant or both.¹⁹⁻²² Many industrial formulations are prepared at around neutral pH, but an ideal dispersant will be efficient over a wide pH range.

The 72-28 OEGMA-*stat*-MAA copolymer was tested in

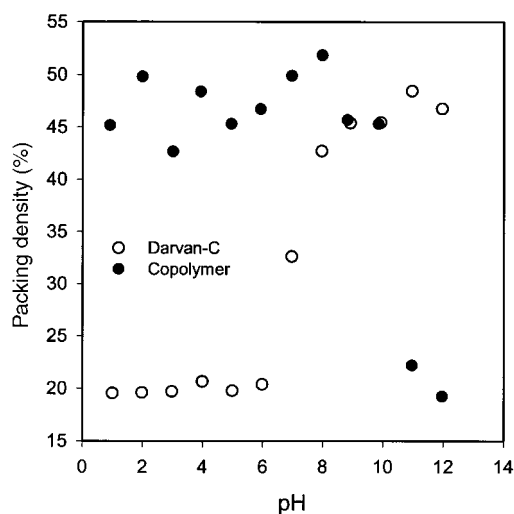


Fig. 3 Packing density of BaTiO₃ in water at different pH, using 2 wt% 72-28 OEGMA-*stat*-MAA as the dispersant.

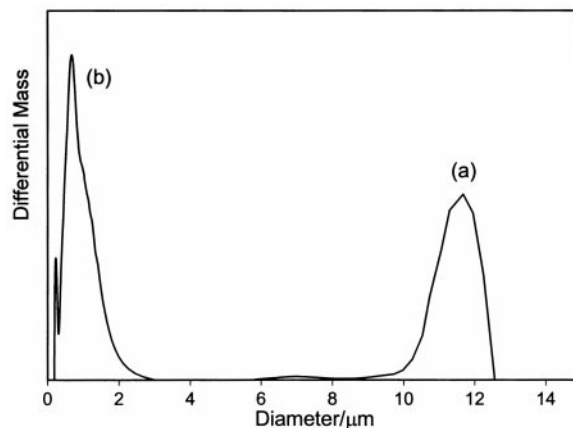


Fig. 4 Differential mass distributions obtained by XDC for (a) untreated BaTiO₃ and (b) BaTiO₃ dispersed with 72-28 OEGMA-*stat*-MAA.

sedimentation experiments in water over the pH range 1-12 and compared to the commercial dispersant (Fig. 3). Darvan-C functions well only in the pH range 8-12. In contrast, the OEGMA-MAA copolymer is very efficient over a much wider pH range (pH 1-10), although its performance drops rapidly at pH values above 10. Hence, one advantage of our dispersants is that tape fabrication does not require precise control of pH.

3.4 Particle sizing

We assessed the size distributions of aqueous BaTiO₃ dispersions using disc centrifuge photosedimentometry (DCP). High polydispersity and particle agglomeration prevented DCP analysis in the absence of dispersant. Instead this suspension was analysed by X-ray disc centrifugation (XDC) and compared to an aqueous dispersion of BaTiO₃ stabilized by the OEGMA-*stat*-MAA (72:28) copolymer. A mean diameter of 11.4 ± 0.5 μm was found for the untreated powder in water, while the copolymer dispersed particles had a mean diameter of 0.94 ± 0.40 μm (see Fig. 4). This is in good agreement with the packing densities obtained by sedimentation.

The efficiency of the 72-28 OEGMA-*stat*-MAA dispersant was measured over the pH range 1-12 and Table 2 summarizes the median particle diameters, *d*₅₀, compared to those using the commercial dispersant. The OEGMA-*stat*-MAA dispersant out-performs Darvan-C from pH 1 to 11, except at pH 3

Table 2 Effect of pH on the dispersion efficiency^a of the 72-28 OEGMA-*stat*-MAA copolymer dispersant and Darvan-C for BaTiO₃ in water

pH	72-28 OEGMA- <i>stat</i> -MAA		Darvan-C	
	Initial dispersion <i>d</i> ₅₀ /μm ^a	Redispersion after wash-dry cycle <i>d</i> ₅₀ /μm	Initial dispersion <i>d</i> ₅₀ /μm	Redispersion after wash-dry cycle ^b <i>d</i> ₅₀ /μm
1	0.93	0.81	1.99	—
2	0.89	1.20	1.95	—
3	1.28	1.63	1.53	—
4	0.67	1.98	1.71	—
5	0.76	1.54	1.72	—
6	0.62	0.94	1.50	—
7	0.63	0.89	1.13	0.91
8	0.63	0.85	1.04	0.83
9	0.78	0.87	0.98	0.91
10	0.77	0.90	1.01	0.83
11	0.79	1.22	0.97	0.75
12	2.39	—	0.99	0.75

^a*d*₅₀ is the median particle diameter as determined by DCP. ^bData for redispersed samples were obtained only for dispersions giving satisfactory initial dispersion.

where anomalous values are obtained, possibly because this is near the isoelectric point of BaTiO₃. The particle size is typically two to three times smaller than that with Darvan-C, which is only efficient at pH 8–12, where it is highly ionised.

These dispersions were washed with fresh water, centrifuged, dried under vacuum and redispersed, while keeping the pH constant. The new dispersions were then re-analysed. After washing and redispersing the particles, the copolymer dispersant is still better than Darvan-C from pH 1 to 7. Darvan-C out-performs the OEGMA-*stat*-MAA dispersant only at pH 11 and 12. However, at around neutral conditions (pH 6 to 8), the copolymer dispersant is superior to Darvan-C.

3.5 Transmission electron microscopy

TEM has been used to obtain the mean particle size for the untreated BaTiO₃ powder compared to the copolymer dispersed particles. Particle agglomerates in the absence of a dispersant confirm the poor dispersibility of the virgin powder in mixed aqueous media. The effectiveness of the OEGMA-MAA copolymer is verified by the significantly higher degree of dispersion observed by TEM (see Fig. 5). Although the particles are rather polydisperse and have ill-defined morphology, the mean TEM particle diameter agrees reasonably well with that obtained by DCP.

3.6 Surface charge of BaTiO₃ particles

BaTiO₃ shows variable electrophoretic behaviour, depending on the BaO:TiO₂ balance at the particle surface. The isoelectric point of our particles was determined by zeta potential measurements and they were found to have a small positive charge at low pH and an isoelectric point at pH 3 (Fig. 6). Isoelectric points from pH 4.5 to pH 10 have been reported,^{33,34} due to variable amounts of residual barium carbonate on the oxide surface. Lower isoelectric points indicate TiO₂-rich surfaces. The very low isoelectric point of the powder used here is attributed to a surface deficiency in barium oxide, in agreement with XPS results (see later) which gave a barium-titanium ratio lower than unity. Traces of other oxides (*e.g.* Nb₂O₅ and Co₃O₄) may also lower the isoelectric point.

Above pH 3, the particles have a net negative charge. From the results of DRIFTS and XPS analysis (see later) we suggest that the acidic dispersants adsorb onto the particle surface as polycarboxylate salts. An obvious question is why the acidic copolymer dispersants are efficient above pH 5, where both the particles and the dispersant are negatively charged. These observations can be explained by examining the variation of

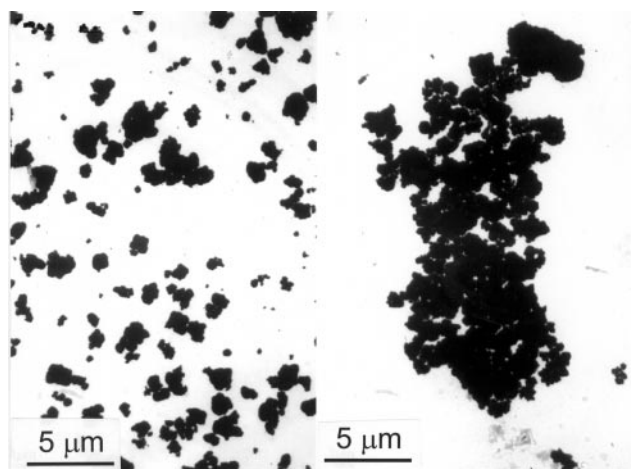


Fig. 5 Transmission electron micrographs of BaTiO₃ dried from dispersions in 78:22 v/v% water–isopropyl alcohol: (a) a flocculated suspension in the absence of a stabiliser and (b) a stable dispersion using 72–28 OEGMA-*stat*-MAA as the dispersant.

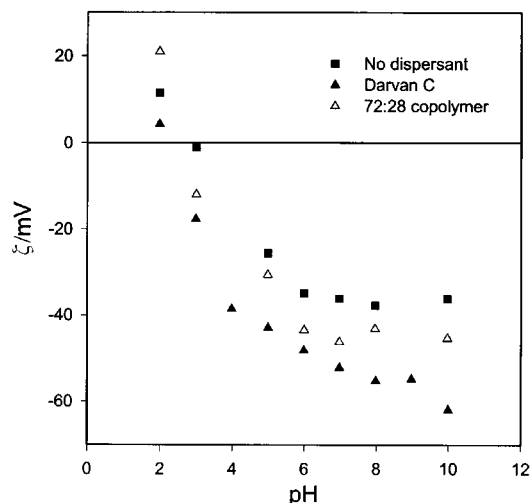


Fig. 6 Zeta potential as a function of pH for untreated BaTiO₃ particles and particles stabilised with 72–28 OEGMA-*stat*-MAA or Darvan-C.

zeta potential with pH for the copolymer-coated particles (see Fig. 6). Zeta potentials similar to those obtained for the pure powder are observed, suggesting that copolymer adsorption has little or no effect on the surface charge. Thus binding presumably does not occur on the anionic surface sites of the BaTiO₃ but is consistent with reaction of the polymer with other surface sites to form carboxylate salts. A similar adsorption mechanism was proposed by Hoad to explain the high dispersion efficiency of related acidic terpolymers for alumina particles in non-aqueous media.³⁵ This is consistent with the strong binding affinity of the copolymers for the particle surface and their resistance to desorption.

3.7 DRIFT spectroscopy

The interaction between the adsorbed copolymers and the BaTiO₃ was investigated by DRIFT spectroscopy. The spectra of the OEGMA-*stat*-MAA copolymers (before adsorption) show a shoulder in the ester carbonyl absorption at *ca.* 1700 cm⁻¹ due to the methacrylic acid residues. When the copolymers are adsorbed, a new intense band is observed at 1569 cm⁻¹ (see Fig. 7b). This peak is not found in the spectra of either the unbound copolymer (not shown) or the uncoated particles (Fig. 7a). It is assigned to the carboxylate anion formed on adsorption of the copolymer. This assignment is supported by a strong absorption band in this region in the

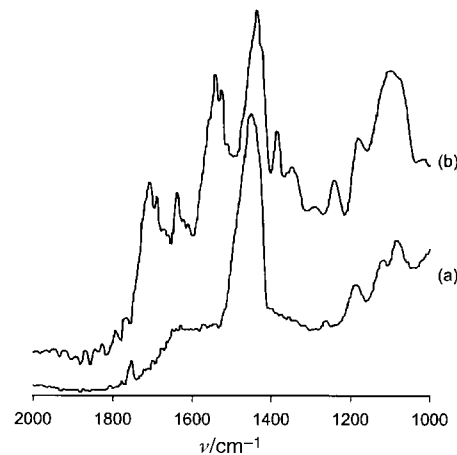


Fig. 7 DRIFTS spectra of untreated BaTiO₃ (lower curve, a) and BaTiO₃ coated with 72–28 OEGMA-*stat*-MAA (upper curve, b).

DRIFT spectrum of poly(methacrylic acid)-coated BaTiO₃ (not shown). No 1569 cm⁻¹ band is observed from the surface-bound OEGMA homopolymer, which contains no acid residues.

3.8 XPS measurements

XPS was used to determine the surface composition of the BaTiO₃ particles and to confirm the presence of the adsorbed copolymer. Spectra were recorded before and after washing, drying and redispersing the stabilized particles to investigate the copolymer resistance to desorption. Dispersions of BaTiO₃ using OEGMA and PMAA homopolymers and two statistical OEGMA-*stat*-MAA copolymers (containing 69 mol% and 29 mol% MAA residues respectively) were analysed. Control experiments on the BaTiO₃ and the corresponding dispersants were also carried out.

Peaks corresponding to barium, titanium, oxygen and carbon were observed in the survey spectra of both the virgin BaTiO₃ and the stabilized particles. The appearance of the barium and titanium peaks in the survey spectra of the polymer-coated particles suggested a patchy or thin coating of stabilizer, since a thick, uniform layer of (co) polymer would result in reduced intensities for barium and titanium. As expected, only peaks corresponding to carbon and oxygen were observed in the survey spectra of the copolymers.

Leadley *et al.*³⁶ studied the interaction of poly(methyl methacrylate) with metal oxide surfaces and suggested that base-catalysed hydrolysis of the ester groups on the particle surface generates carboxylate anions. A C1s peak at 288 eV was assigned to the carboxylate anion. In our samples (Fig. 8), the MAA homopolymer gave a partially resolved C1s peak at *ca.* 289 eV. This peak also appeared in the C1s spectrum of the PMAA-stabilised BaTiO₃, shifted to a slightly lower binding

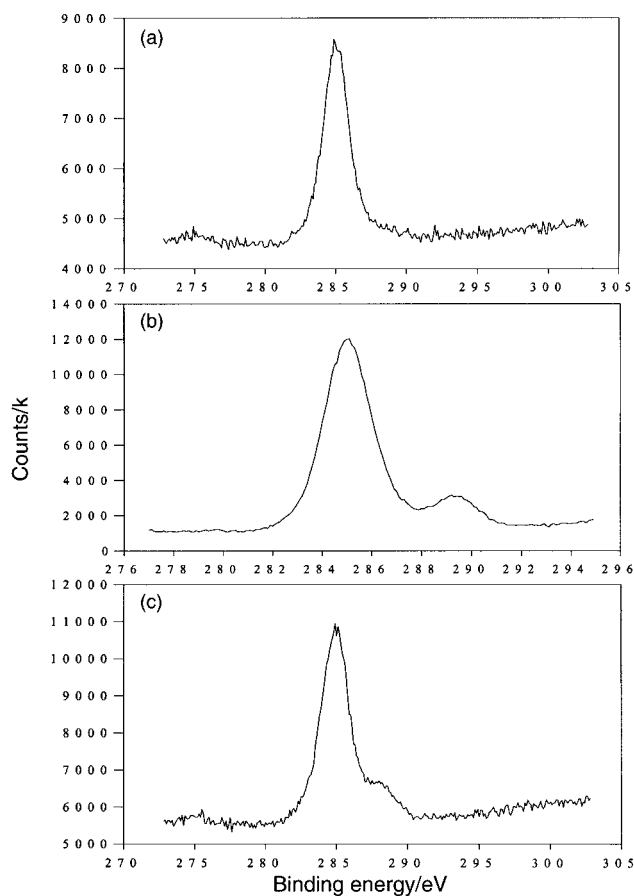


Fig. 8 C1s core line spectra of (a) untreated BaTiO₃; (b) PMAA homopolymer dispersant; (c) PMAA-coated BaTiO₃ particles.

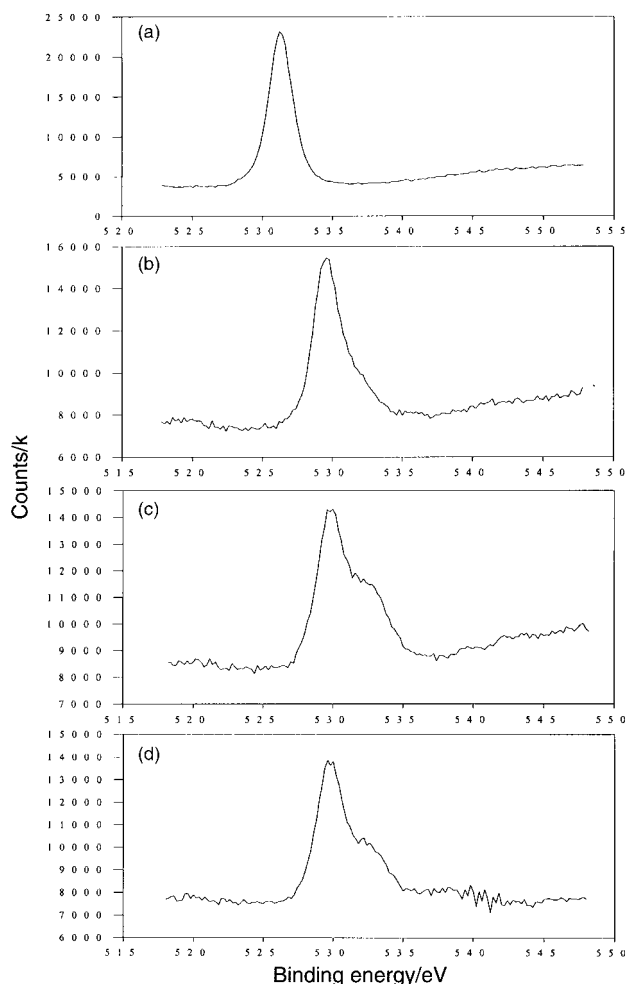


Fig. 9 O1s core line spectra of (a) untreated BaTiO₃; (b) 71–29 OEGMA-*stat*-MAA dispersant; (c) 71–29 OEGMA-*stat*-MAA-coated BaTiO₃ particles; (d) 71–29 OEGMA-*stat*-MAA-coated BaTiO₃ particles after washing.

energy (288 eV). We attribute this peak to the carboxylate anion. It disappears from the spectra of PMAA-stabilised BaTiO₃ particles after washing, showing that the PMAA homopolymer readily desorbs, and indicating only a weak interaction at the BaTiO₃ surface.

In principle, the C1s core-line carbon signals from the copolymer-coated particles might be due to the carbon atoms of the copolymer, to BaCO₃ impurities or to hydrocarbon contamination. The spectrum of the virgin powder showed weak carbon peaks, which are attributed to hydrocarbon contamination.³⁷ Thus, the C1s signal could not be used to determine the surface concentration of the copolymer unambiguously.

The O1s spectra of virgin BaTiO₃, the 71–29 OEGMA-*stat*-MAA copolymer and the copolymer-coated BaTiO₃ are compared in Fig. 9. The shoulder at higher binding energy in the O1s spectrum of the copolymer-stabilized powder (absent in the spectrum of the virgin particles) is attributed to the oxygen atoms of both the OEGMA and the MAA units of the copolymer. This result verifies the adsorption of the copolymer on the particle surface. Moreover, the continued presence of the shoulder in the O1s spectrum of the washed and dried copolymer-coated sample suggests strong binding of the dispersant and confirms its resistance to desorption (see Fig. 9d).

Similar results were obtained for the 31–69 OEGMA-*stat*-MAA-stabilised BaTiO₃. This copolymer was also resistant to desorption. Thus the XPS data are consistent with the results

obtained by gravitational sedimentation studies, zeta potential measurements and DRIFTS.

The OIs spectra of the homopolymer analogues adsorbed onto the BaTiO₃ were also recorded. Adsorption of the PMAA homopolymer was verified by the appearance of a second shoulder (qualitatively different to that observed for the copolymer-dispersed particles), overlapping with the powder OIs peak and resulting in a broad band extending to higher binding energies compared to the OIs spectrum of the virgin BaTiO₃. This broad band disappears after washing the dispersion, suggesting successful removal of the PMAA from the particle surface. This observation is consistent with the failure of this homopolymer as a dispersant. Similar results were obtained for the OEGMA homopolymer: a peak characteristic of the homopolymer was observed in the OIs spectrum of the OEGMA-stabilised particles and disappeared on washing.

The XPS data confirm adsorption of all the homopolymers and copolymers onto BaTiO₃. The two homopolymers are only weakly bound and are desorbed easily. In contrast, the copolymers resist desorption, suggesting much stronger affinity for the particle surface. These observations are consistent with their excellent dispersion performance.

4 Conclusions

The dispersion properties of tailor-made, hydrophilic statistical copolymers for BaTiO₃ were evaluated by gravitational sedimentation tests in aqueous media. OEGMA-*stat*-MAA copolymers gave high dispersion efficiency in both water and water-isopropyl alcohol mixtures, whilst the OEGMA-*stat*-DMA analogues did not give stable dispersions. Copolymers containing 30 to 90 mol% OEGMA gave good quality dispersions in aqueous-based solvent mixtures.

The dispersion of the particles was assessed by measuring their particle size distributions by XDC and DCP. In the presence of dispersant a much smaller mean particle size (0.94 µm) than that of the original agglomerated particles (11.4 µm) was obtained. The acidic residues were shown by DRIFTS to be in the form of carboxylate anions at the particle surface, which explains the strong anchoring properties of the acidic copolymers and their high dispersion efficiency. XPS studies confirmed the presence of the dispersants on the particle surface, even after extensive washing of the copolymer-coated particles. DCP showed no changes in the dispersion quality due to desorption of the dispersant and/or incomplete redispersion after passing through a dry stage.

The interaction of the acidic residues and neutral OH sites on the particle surface is further supported by the zeta potential measurements. Neither the isoelectric point (pH 3) of the BaTiO₃ powder nor the zeta potential values are significantly affected by copolymer adsorption. The anionic surface charges on the particles above pH 3 do not interact with the polymer. Presumably it is the neutral sites on BaTiO₃ particles which form ion-pairs with the copolymer, resulting in a similar overall surface charge before and after copolymer adsorption.

The dispersion efficiency of the acid copolymers results from both steric and electrostatic contributions to stabilization. At high pH, the OEGMA groups provide the required steric barrier, while those carboxylate anions which are not adsorbed contribute an electrostatic interaction, leading to electrostatic stabilization. At low pH, the electrostatic contribution diminishes since the acid groups are protonated. However, the PEG chains continue to provide the steric barrier which maintains the stabilization of the particles. In contrast, Darvan-C is an efficient dispersant for ceramic particles only at high pH,^{22,23} when stabilization is due to the repulsive forces between the extended negatively charged copolymer chains. At low pH, the reduced steric barrier and the rather flat

conformation of the copolymer on the particle surface result in flocculation, since the copolymer chains are neutralized under these conditions.

Overall, it is clear that the OEGMA-*stat*-MAA dispersants are superior to Darvan-C over the pH range examined, with the latter being an efficient dispersant only at high pH. Both dispersants promote efficient redispersion at pH 7 to 10. However, while Darvan-C is preferred at pH 12, the OEGMA-*stat*-MAA copolymers out-perform it at pH 6–7, which is likely to be a more convenient pH range for aqueous-based formulations.

Acknowledgements

We thank the University of Sussex and Cooksons Research Ltd for funding a DPhil studentship for MV. We also thank TAM Ceramics Ltd for donating the ceramic powder and Laporte Performance Chemicals Ltd for donating the OEGMA monomer.

References

- 1 P. Ward, in *Ceramics Technology International*, ed. I. Birkby, Sterling International, New York, 1994, p. 78.
- 2 P. Ward, *Electron. Eng.*, 1993, **65**, 39.
- 3 J. S. Abel, G. C. Stangle, C. H. Schilling and I. A. Aksay, *J. Mater. Res.*, 1994, **9**, 451.
- 4 R. Moreno, *Am. Ceram. Soc. Bull.*, 1992, **71**, 1521.
- 5 P. D. Calvert, E. S. Tormey and R. L. Pober, *Am. Ceram. Soc. Bull.*, 1986, **65**, 669.
- 6 P. D. Calvert, R. R. Lalanandham and D. R. M. Walton, in *Adhesion aspects of polymeric coatings*, ed. K. L. Mittal, Plenum, New York, 1983, p. 457.
- 7 S. V. Prasad and P. D. Calvert, *J. Mater. Sci.*, 1980, **15**, 1746.
- 8 S. Mizuta, M. V. Parish and H. K. Bowen, *Ceram. Int.*, 1984, **10**, 43.
- 9 E. A. Baker and D. J. Wluka, US Patent 3912677, 1975.
- 10 M. W. J. West, US Patent 4755563, 1988.
- 11 J. D. Schofield, US Patent 4954177, 1988.
- 12 G. H. Armstrong, L. Johnson and A. A. Parker, *J. Appl. Polym. Sci.*, 1994, **52**, 997.
- 13 H. S. Al-Lami, N. C. Billingham and P. D. Calvert, *Chem. Mater.*, 1992, **4**, 1200.
- 14 J. Rudolph, J. Patzsch and W. H. Meyer, *Colloid Surf., A*, 1994, **86**, 299.
- 15 S. Bhattacharjee, M. K. Paria and H. S. Maiti, *J. Mater. Sci.*, 1993, **28**, 6490.
- 16 L. Bergstrom, E. Blomberg and H. Guldborg-Pedersen, *Novel Synth. Process. Ceram.*, 1999, **159–1**, 119.
- 17 R. J. Thompson, N. R. Gurak, P. L. Josty, V. G. Xanthopoulos and J. P. Russell, US Patent 4968460, 1990.
- 18 R. P. Higgs and D. M. Ansari, US Patent 5880177, 1990.
- 19 J. Cesarano and I. A. Aksay, *J. Am. Ceram. Soc.*, 1988, **71**, 1062.
- 20 J. Cesarano, I. A. Aksay and A. Bleier, *J. Am. Ceram. Soc.*, 1988, **71**, 250.
- 21 Pradip, R. S. Premachandran and S. G. Malghan, *Bull. Mater. Sci.*, 1994, **17**, 911.
- 22 Z. C. Chen, T. A. Ring and J. Lemaitre, *J. Am. Ceram. Soc.*, 1992, **75**, 3201.
- 23 R. S. Premachandran and S. G. Malghan, *Powder Technol.*, 1994, **79**, 53.
- 24 D. H. Lee, R. A. Condrate and J. S. Reed, *J. Mater. Sci.*, 1996, **31**, 471.
- 25 N. G. Hoogeveen, M. A. C. Stuart and G. J. Fleer, *J. Colloid Interface Sci.*, 1996, **182**, 133.
- 26 N. G. Hoogeveen, M. A. C. Stuart and G. J. Fleer, *J. Colloid Interface Sci.*, 1996, **182**, 146.
- 27 F. S. Ortega, P. Sepulveda, V. C. Pandolfelli, M. M. Yokosawa and E. Frollini, *Adv. Powder Technol.*, 1999, **299–3**, 104.
- 28 N. G. Hoogeveen, M. A. C. Stuart and G. J. Fleer, *Colloid Surf. A-Physicochem. Eng. Asp.*, 1996, **117**, 77.
- 29 N. G. Hoogeveen, M. A. C. Stuart and G. J. Fleer, *Faraday Discuss.*, 1994, 161.
- 30 A. W. M. Delaat, A. W. Debruijn and G. L. T. Vandenheuvel, *Colloid Surf. A-Physicochem. Eng. Asp.*, 1994, **82**, 99.
- 31 M. Vamvakaki, N. C. Billingham and S. P. Armes, *Polymer*, 1999, **40**, 5161.

- 32 J. Kearns, C. Mclean and D. H. Solomon, *J. Macromol. Sci., Pure Appl. Chem.*, 1974, **A8**, 673.
- 33 A. W. M. Delaat and G. L. T. Vandenhevel, *Colloid Surf. A-Physicochem. Eng. Asp.*, 1995, **98**, 53.
- 34 W. H. Shih, D. Kisailus and Y. Wei, *Mater. Lett.*, 1995, **24**, 13.
- 35 O. J. Hoad, DPhil Thesis, University of Sussex, 1993.
- 36 S. R. Leadley and J. F. Watts, *J. Adhes.*, 1997, **60**, 175.
- 37 D. Briggs and M. P. Seah, in *Practical Surface Analysis Vol. 1 Auger and X-ray photoelectron spectroscopy*, ed. D. Briggs and M. P. Seah, Wiley, London, 1983, p. 128.