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ORIGINAL CONTRIBUTION

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Function and performance of silicone copolymer (VII). Dispersing ability of hydrophile-grafted acrylic copolymers and the corresponding siloxane copolymers to fumed silica. The effect of pH

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Abstract Acrylic copolymers and the corresponding siloxane copolymers grafted with cationic and nonionic hydrophiles were used as dispersants to disperse fumed silica in an aqueous solution at different pH values. The dispersing ability was evaluated by viscosity and scanning electron microscopy (SEM) methods. The results showed that the dispersing abilities are functions of the dispersant concentrations and of the pH of the system. By comparing the results of SEM and viscosity methods, it can be concluded that, under comparable conditions, a suspension with a lower viscosity is more homogenously dispersed. It was also found that at pH 2 only CHE and SHE and that at pH 7 only CHE, SHE, and SQHE showed better dispersing ability. At pH 10.5, all the dispersants in this study except CQDEA resulted in a slurry of very low viscosity of 10–20 cP with 15 wt% of silica. Basically, nonionic dispersants CHE and SHE exhibit excellent dispersing ability at different pH values.

Key words Siloxane · Dispersant · Fumed silica · Slurry and viscosity

Introduction

As chemical-mechanical planarization (CMP) becomes more widely used for polishing during microcircuit manufacture, increasingly sophisticated process-control procedures are being developed and implemented. The demand for planarization of oxide layers is growing as a result of the increased degree of integration of dynamic random access memory. Regardless of the slurry type or source, the properties and the consistent quality of slurry are crucial to maximize the performance and yields of devices [1]. In the latter half of the 1980s, aqueous dispersions of fumed silica began to be used in the United States for the planarization of the oxide layer of logic devices. The applicability of fumed silica as abrasives of CMP slurry for metal (W, Al, Cu) interconnects is now being studied for future applications [2–4].

Polishing slurries commonly encounter the problems of coagulation of solid particles in the slurry and their formation during processing. A colloidal suspension with particles dispersed in a medium is thermodynamically unstable, so dispersants are normally used to stabilize the system. The main function of the dispersant is to provide the particles with an electrostatic barrier [5–8] and/or a steric barrier [9, 10] to prevent the coagulation of particles. Polymers are widely used as dispersants because they can provide a high charge density and efficient steric stabilization. Also, polymer-type dispersants do not induce the foam problem as do conventional surfactants.

In our laboratory, acrylic copolymers and the corresponding siloxane copolymers grafted with different types of hydrophiles were synthesized and their solution properties were investigated [11]. These two types of polymers were further used as dispersants to prepare a dispersion system of fumed silica in water, which is stable and essentially foam-free during the polishing process and used as a CMP slurry, resulting in excellent performance of high removal rate accompanied by a low nonuniformity [12]. In this study, the fundamental properties of a slurry of fumed silica particles dispersed in water under different pH conditions were investigated by means of viscosity and scanning electron microscopy (SEM) methods. The results were correlated with the polymer structure, and then interpreted in terms of polymer properties under different pH conditions.

Experimental

Materials

Octamethylcyclotetrasiloxane, poly(methylhydrogensiloxane), hexamethylcyclotetrasiloxane, and platinum divinyltetramethyl disiloxane (Pt catalyst) were purchased from Dow Corning. Allyl glycidyl ether (Acros), sulfuric acid (UCW), methyl methacrylate (Lancaster), methacrylic acid glycidyl ether (TCI), 1-butanethiol (R.D.H), 2,2′-azobis(isobutyronitrile) (SHOWA), diethanolamine (Lancaster), diethylamine (Alps), dimethyl sulfate (Acros), sodium hydroxide (Merck), and hydrochloric acid (UCW) were used as received. Fumed silica (Degussa, Aerosol 70) was used as supplied. The water used in these experiments was ion-exchanged and distilled to give a pH value between 6.8 and 7.2 and a conductivity of $4.4 \times 10^{-6}\ \Omega^{-1}\mathrm{m}^{-1}$.

Methods

Synthesis and characterization of the acrylic and siloxane copolymers

All the copolymers were prepared as dispersants (Scheme 1) following the same procedures and conditions as described in our previous work [11, 13].

Assessment of the dispersing abilities of the acrylic and siloxane copolymers

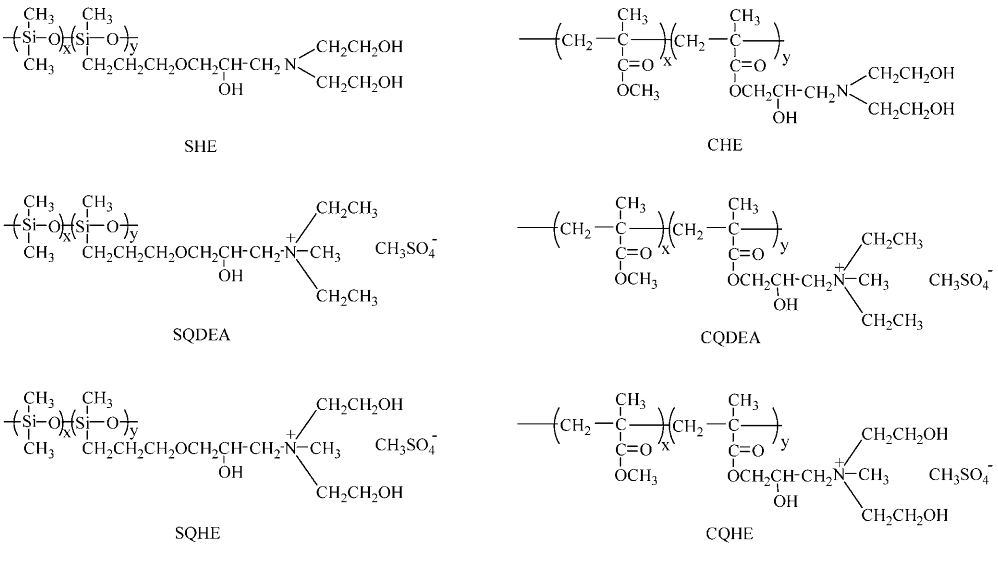
The fumed silica was dispersed in water by using different copolymers as dispersants. An amount of dispersant (weight percent based on dry fumed silica) was dissolved in water (85 g), and the pH value of the aqueous solution was adjusted with sodium hydroxide or hydrochloric acid and mixed with the fumed silica (15 g); then, zircon beads (diameter 2 mm, 50 g) were added for milling. The mixture was milled mechanically at 800 rpm for 60 min at room temperature. All the dispersed pastes prepared were evaluated by the following methods:

1. *Rheological method.* Dispersed paste (80 ml) was put in an adapter with an appropriate spindle and its viscosity was measured using a rotating cylindrical viscometer (Brookfield DVII LVT). The apparent viscosities (under a fixed shear rate) were used as a parameter to assess the dispersing ability of the dispersants. All the viscosities were measured at 25 °C.
2. *SEM.* The dispersed paste (about 1 g) was coated (about 12.5 μm wet film thickness) on a thin copper plate. After drying (1 day), a small piece of the paste (about 4 × 4 mm) was cut and put on an aluminum sheet (with a diameter of 20 mm) and electrodeposited with a layer of gold. The surface of the coating film was observed using an SEM electron probe microanalyzer (JEOL JXA-840).

Results and discussion

Rheological analysis of the silica slurry

For a solution with low solids content, the Einstein–Stokes equation [14, 15] can be used to express the viscosity of the dispersion as a function of the viscosity of the solvent (η_s) and the volume fraction of the solid. For a dispersing system with high solids content, the shear rate (γ) and the shear stress (τ) have a relationship of form $\gamma = \kappa\tau^n$ [16]. On a plot of τ versus γ of plastic flow, the intercept and the apparent viscosity (τ/γ) are useful parameters to estimate the extent of dispersion of a system. The apparent viscosity is always used to measure a non-Newtonian fluid that shows different viscosities under different shear rates [17, 18]. For a well-dispersed system, the aggregation of the particles is small, so the spindle senses a smaller hindrance from aggregates under a given shear rate and, consequently, detects a small shear stress and a lower viscosity. In contrast, the agglomerate of a poorly dispersed system forms a network that hinders the spindle and results in a higher shear stress,



Scheme 1 The structures of hydrophile-grafted acrylic copolymers and the corresponding siloxane copolymers used as dispersants

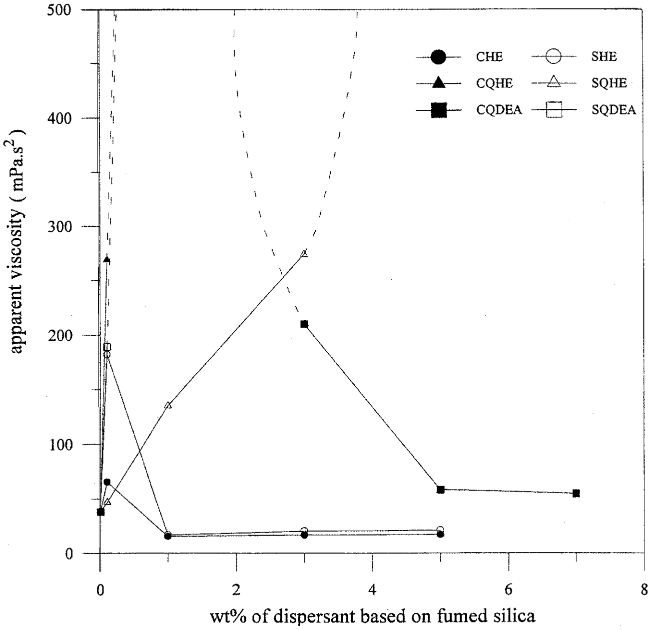


Fig. 1 Apparent viscosity as a function of dispersant concentration for fumed silica dispersed in water using various dispersants at pH 2

thereby showing a higher viscosity. In this study, a low-shear-rate viscometer (Brookfield DVII, LVT) was used to measure the apparent viscosity, $\eta_{\mathrm{app}} = \tau/\gamma$, where τ is the shear stress and γ is the shear rate.

In order to simulate the application of CMP, the dispersed systems of fumed silica in water were studied by means of a viscosity method using a hydrophile-grafted acrylic polymer as a dispersant. The isoelectric point of fumed silica is about 2.3 [19]; however, there are regions of positive charge at the edges of the fumed silica at pH < 2.3, probably owing to the protonation of Si–OH with H^+ to form Si–OH_2^+ ions. These phenomena influence the effect of dispersants in a fumed silica/water dispersed system at pH 2, 7, and 10.5. The apparent viscosity is shown in Figs. 1, 2, and 3 as a function of dispersant concentration for fumed silica dispersed in aqueous solution using these two types of copolymers as dispersants under different pH conditions. The dotted line represents the poorly dispersed system and the viscosity of the dispersed system was too high to measure. For industrial applications, a good dispersant is expected to reach a lower viscosity accompanied by a lower dispersant concentration.

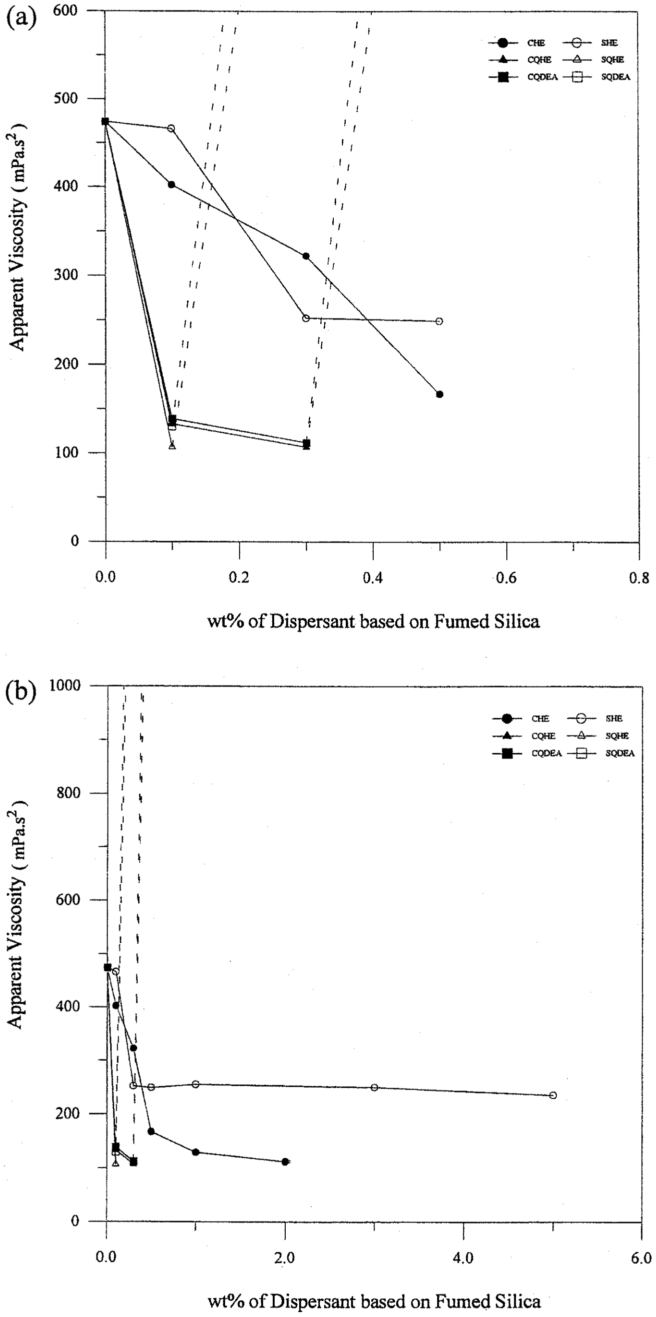


Fig. 2 Apparent viscosity as a function of dispersant concentration for fumed silica dispersed in water using various dispersants at pH 7

At pH 2 with 0.1 wt% of dispersants based on fumed silica, the viscosity of the dispersed system increases for all dispersants as shown in Fig. 1. As the concentration is higher than 0.1 wt%, the viscosity increases gradually for SQHE and increases suddenly for CQHE and SQDEA. Relative to these phenomena, the viscosity of the dispersed system for CQDEA decreases with increasing concentration and remains almost constant at concentrations higher than 5%. In the case of SHE and CHE, the viscosity decreases to an even lower value (20 cP) and remains constant when the concentration is higher than 1 wt%. It is apparent that CQHE, SQHE, and SQDEA have no dispersing ability and the interaction between the polymer backbone and the fumed silica particle surface results in a bridging effect among silica particles. Consequently, the viscosity increases owing to

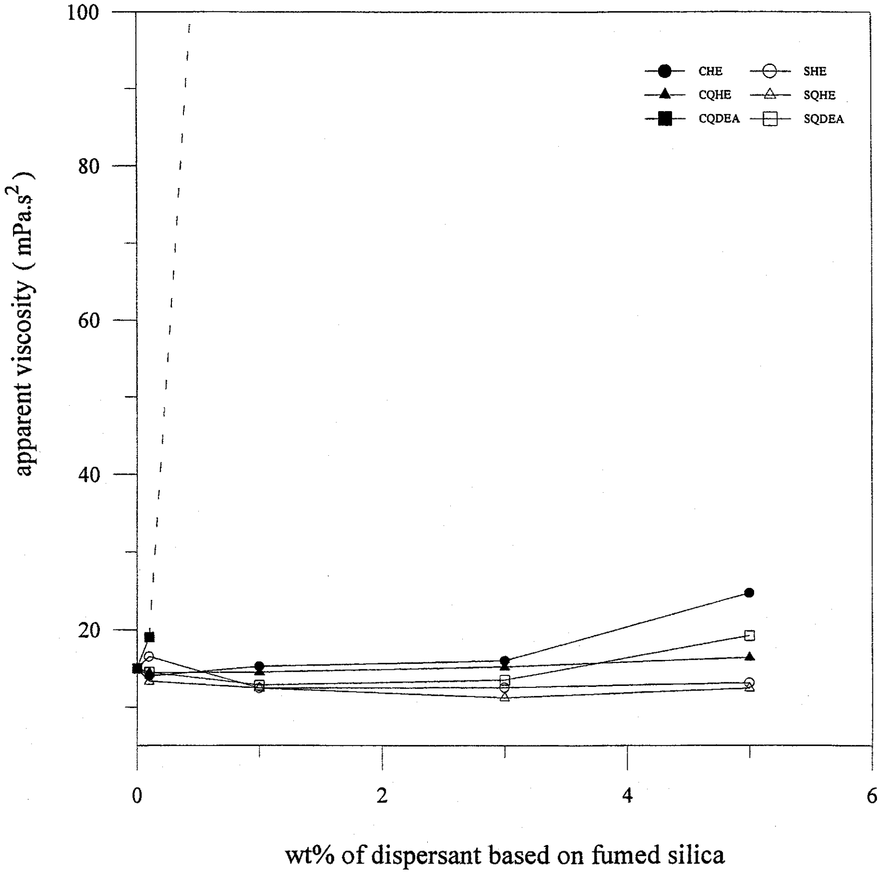


Fig. 3 Apparent viscosity as a function of dispersant concentration for fumed silica dispersed in water using various dispersants at pH 10.5

the remarkable aggregation of fumed silica particles. Reversely, the decrease in viscosity for CHE and SHE can be attributed to the adsorption of dispersants onto the fumed silica particle surfaces in the presence of protons, which promote the interaction between oxygen atoms and silica by means of protonation. After the adsorption of dispersants, the charges on the fumed silica particles increase, resulting in an increase in repulsive forces and steric hindrance between particles.

At pH 7 (Fig. 2), for SQHE, CQHE, SQDEA, and CQDEA dispersants, the viscosity decreases greatly at low concentration (0.1 wt%), but the viscosities increase suddenly at concentrations higher than 0.1 wt% for SQHE and SQDEA and at the concentration higher than 0.3 wt% for CQHE and CQDEA. However, in the case of SHE and CHE, the viscosity decreases with increasing concentration of dispersant and remains almost constant at low values of 250 and 130 cP, respectively. For a tertiary amine, the degree of protonation can be calculated from its pK_b value and is close to 100% below pH 7. Thus, the degree of protonation of tertiary amines of CHE and SHE can be assumed to be close to 100%. At this pH value, the fumed silica particles are negatively charged; therefore, the interaction occurs between the positively charged dispersants and the fumed silica particles and the accompanied adsorption of dispersants on the silica results in the decrease in viscosity. The increase in the viscosity of the dispersed system at relatively high dispersant concentration can be attributed to the bridging between the fumed silica particles. For SQHE, CQHE, SQDEA, and CQDEA, the viscosities reach lower values at relatively low concentrations, indicating that the strongly negatively charged fumed silica particles are dispersed more homogeneously owing to the repulsion.

The apparent viscosity of the dispersed system is shown in Fig. 3 as a function of the concentration of the dispersants for pH 10.5. For all the dispersants except for CQDEA, it is observed that the viscosities reach low and constant values of about 15 cP as the concentration of the dispersants becomes higher than 0.1 wt%. As the pH increases to 10.5, the fumed silica particles are highly negatively charged and well dispersed in water, resulting in a low viscosity. Only SHE and SQHE can decrease the viscosity. At a concentration higher than 3 wt%, the increase in viscosity for CHE and SQDEA owing to the bridging effect can again be observed. Compared with CHE and SQDEA, the viscosity for SQHE, CQHE, and SHE increases slightly, probably owing to less bridging. It is obvious that CQDEA has no dispersing ability, in this case owing to the occurrence of aggregation, as mentioned earlier.

Scanning electron microscopy

SEM can be used to observe the surface of the film prepared from the dispersed particles so that the dispersion state of the particles in solution can be assessed directly. The pastes of the dispersed particles were coated on metal plates for SEM observation. SEM micrographs at a magnification of 10,000× are shown in Figs. 4 and 5 for the pastes of fumed silica dispersed in water, using these two types of copolymers as dispersants; the results correspond to the different concentrations of the plot, shown in Figs. 1 and 2, at different pH values.

The two types of dispersants were used to disperse the fumed silica at a fixed concentration (0.1 wt%) below pH 2 (Fig. 4a), where the viscosity of the dispersed system is in the order CQHE > SQDEA ≈ SHE > CHE > SQHE (Fig. 1). Obviously, the degree of homogeneity of the dispersed particles is in the order SQHE > CHE > SHE ≈ SQDEA > CQHE. These two trends indicate that the paste with lower viscosity shows the more homogenous dispersion. The pastes which exhibited the lowest viscosity for each dispersant, as shown in Fig. 1, were also coated on a metal plate for SEM analysis. The results show that the pastes that reached the lower viscosity exhibited more homogenously dispersed particles (Fig. 4b), coinciding with the trend observed for the paste with 0.1 wt% of dispersant. At pH 7 (Fig. 5), it is apparent that the dispersion is better for SQHE than for SHE and CHE at a concentration of 0.1 wt%. As the concentration increases to 0.5 wt%, the particles are more homogenously dispersed, both for SHE and CHE. Those results again show that a suspension with a lower viscosity is more homogenously dispersed, in agreement with our previous work [20, 22]. At pH 10.5, the results from SEM are identical with the trends that the slurry of low viscosity

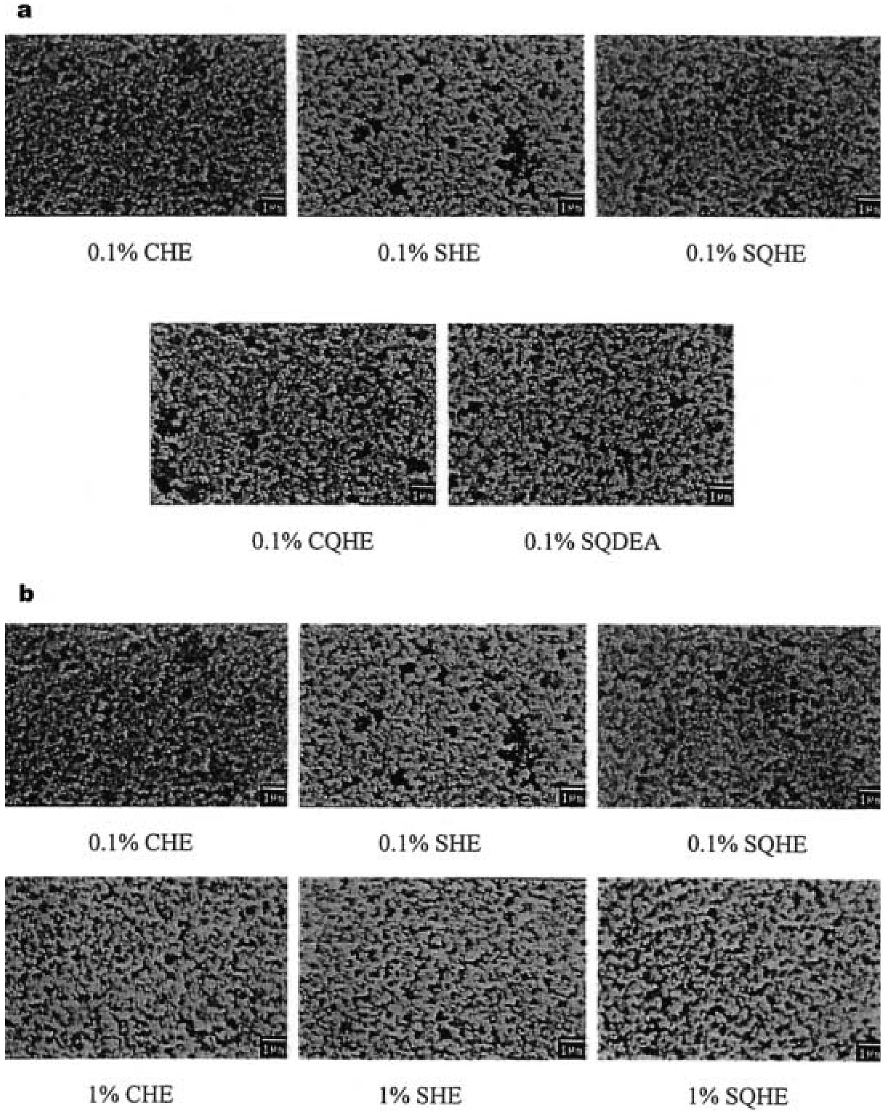


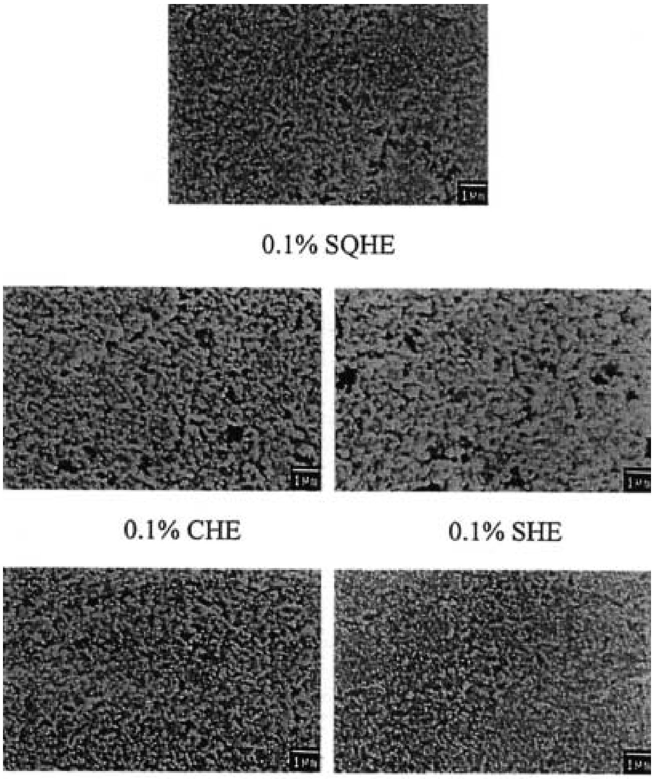
Fig. 4 Scanning electron microscopy (*SEM*) micrographs for fumed silica dispersed in water using various dispersants with different concentrations at pH 2

0.1% CHE 0.1% SHE 0.1% SQHE

0.1% CQHE 0.1% SQDEA

0.1% CHE 0.1% SHE 0.1% SQHE

1% CHE 1% SHE 1% SQHE



0.1% SQHE

0.1% CHE

0.1% SHE

0.5% CHE

0.5% SHE

Fig. 5 SEM micrographs for fumed silica dispersed in water using various dispersants with different concentrations at pH 7

shows a homogenous dispersion in SEM, as described in Figs. 4 and 5.

From the results of the viscosity method and SEM, it can be concluded that some of these two types of copolymers can act as dispersants to successfully disperse fumed silica particles in water under different concentrations and pH values, i.e., at pH 2, the copolymers grafted with diethanol amine (SHE and CHE) have the best dispersing ability; at pH 7, the cationic dispersant SQHE shows the best dispersing ability; and at pH 10.5, all the dispersants except CQDEA have dispersing ability.

Summary

Correlating the results of viscosity and SEM, it can be concluded that the dispersion exhibiting a lower viscosity can be directly observed to be more homogeneously dispersed by SEM; thus, the dispersant resulting in a lower viscosity of the dispersed system has a better dispersing ability. At pH 10.5, all the dispersants in this study except CQDEA can result in a slurry of very low viscosity at 10–20 cP with 15 wt% of silica. However, at pH 2 only CHE and SHE and at pH 7 only CHE, SHE, and SQHE can show dispersing ability. Basically, nonionic dispersants CHE and SHE can exhibit excellent dispersing abilities at all pH.

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References

1. Philipossian A, Moinpour M, Oehler A (1996) An overview of current issues and future trends in CMP consumables. Proceedings of the 1st CMP-MIC conference, Tampa, Florida. VMIC, pp 13–19
2. Hariharaputhiran M, Li Y, Ramarajan S, Bahu SV (2000) Electrochem Solid State 3:95
3. Yoshida K (2000) J Jpn Soc Tribologis 45:727
4. Ramarajan S, Li Y, Hariharaputhiran M, Her YS, Babu SV (2000) Electrochem Solid State 3:232
5. Parfitt GD (1981) Dispersion of powders in liquids, 3rd edn. Applied Science, NJ
6. Sato T, Ruth RJ (1980) Stabilization of colloid dispersions by polymer adsorption. Dekker, New York
7. Ottewill RH (1977) J Colloid Interface Sci 58:357
8. Napper DH (1983) Polymeric stabilization of colloidal dispersions. Academic, San Diego
9. Napper DH (1977) J Colloid Interface Sci 58:390
10. Heller W, Pugh TL (1960) J Polym Sci 67:203
11. Liang WJ, Kuo PL (2001) Macromol Chem Phys 202:1902
12. (a) Kuo PL, Liao CL, Ghosh SK (2001) Colloid Polym Sci; (b) Kuo PL, Hou SS, Teng CK, Liang WJ (2001) Colloid Polym Sci 279:286
13. Kuo PL, Hou SS, Teng CK, Liang WJ (2001) Colloid Polym Sci 279:286
14. Hunter RJ (1987) Foundations of colloid science, vol II. Clarendon Press, New York
15. Strivens TA (1976) J Colloid Interface Sci 57:476
16. Schroder J (1988) Prog Org Coat 15:337
17. Moriyama N (1975) Bull Chem Soc Jpn 48:1713
18. Huber O, Weigl J (1969) Papier 23:663
19. Ochiai M, Ishida M (1997) CMP science. Science Forum, Tokyo
20. Kuo PL, Chen WH, Wu CC (1996) J Appl Polym Sci 60:815
21. Kuo PL, Wey BS (1993) J Appl Polym Sci 50:95
22. Kuo PL, Wey BS, Chen WH (1993) J Appl Polym Sci 48:1953