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# Acid and base effects on the morphology of composites formed from microemulsion polymerization and sol–gel processing

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Phase behaviour studies were performed for microemulsions, containing organic monomers (methyl methacrylate and acrylic acid), inorganic monomer (tetraethoxy silane (TEOS)), a cross linking agent (ethylene glycol dimethacrylate) and water, stabilized by a cationic surfactant, cetyltrimethylammonium bromide. Single phase transparent microemulsions were formed over a considerable portion of the composition domain. The effects of an acid, hydrochloric acid (HCl), and a base ($NH_4OH$) on the gel times were studied and the catalytic action of acid and base on the overall sol–gel reaction was analysed. Organic/inorganic polymer composites were obtained from the hydrolysis and polycondensation reactions of TEOS (sol–gel process) and polymerization of organic monomers and inorganic monomer containing microemulsions. Scanning electron microscopy was used to examine the surface morphology of the composites. For the acid and base studies a precursor microemulsion with pH 7.0 exhibiting closed-cell microstructure upon polymerization was selected. The morphology was examined for polymerized microemulsions with the same base composition but with varying HCl to TEOS ratios or $NH_4OH$ to TEOS ratios. Pore continuity and morphology are strongly influenced by the presence of acid or base. Both the HCl and $NH_4OH$ containing precursor microemulsions led to open celled porous composites.

## 1. Introduction

Morphology control in the production of oxides formed from sol–gel synthesis is of great interest for many uses of silica [1]. The sol–gel process is a common route to make prepolymers with suitable viscosities that are useful in various coating techniques such as dipping and spraying [2–4]. Further, this process is a relatively new method for preparing ceramic composites [4]. Although the sol–gel process is advantageous in obtaining potentially higher purity and homogeneity products at lower processing temperatures compared with traditional glass melting or ceramic powder methods, the shrinkage and densification of the gel layer during drying or sintering leads to cracks with layer thicknesses more than a few micrometres [2, 5]. Chujo and Saegusa [6] found that the introduction of organics causes a decrease of the network connectivity and increases the relaxation ability which can help in overcoming these problems. Yamauchi *et al.* [7] and Arriagada and Osseo-Asare [8] found that it is possible to obtain nanometre-sized, monodisperse, spherical particles of hybrid silica solids by the hydrolysis of TEOS (tetraethoxy silane) in oil-in-water (o/w) or water-in-oil (w/o) microemulsions stabilized by a suitable surfactant. The characterization studies done by Palani Raj *et al.* [9] on the microemulsion system methyl methacrylate (MMA), acrylic acid (AA), and water stabilized by using surfactant, sodium dodecyl sulfate (SDS) revealed that a porous organic polymer can be obtained by polymerizing the Winsor-IV regions (single phase bicontinuous, w/o or o/w microemulsions).

Microemulsions are isotropic, thermodynamically stable mixtures of oil, water and surfactant [10, 11]. In our earlier work [12], we studied the phase behaviour of a microemulsion system containing two organic monomers (MMA and AA) an inorganic monomer (tetraethoxy silane, TEOS) and water, using cetyltrimethylammonium bromide (CTAB) as the surfactant. We investigated the possibility of preparing precursors for obtaining microporous composites formed by the hydrolysis, polycondensation reaction of the sol–gel process coupled with polymerization of an organic monomer containing microemulsion system. We obtained products with a controlled microstructure, a high thermal stability and homogeneity. The principle variable studied was the water to TEOS ratio. This work extends our prior efforts by examining the effects of an acid (HCl) or base ($NH_4OH$) on the microstructure of the porous composites.

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The general reaction of the sol–gel process to form highly porous silica oxide ($SiO_2$) involves at least hydrolysis, polycondensation and densification steps. [4, 13–16]

$$n\mathrm{Si(OC_2H_5)_4} + 4n\mathrm{H_2O} \xrightarrow{\text{Cat}} n\mathrm{Si(OH)_4} + 4n\mathrm{C_2H_5OH}$$

(Hydrolysis) (1)

$$n\mathrm{Si(OH)_4} \xrightarrow{\text{Cat}} n(\mathrm{SiO_2})\ (\mathrm{gel}) + 2n\mathrm{H_2O}$$

(Polycondensation) (2)

$$n\mathrm{SiO_2(gel)} \xrightarrow{\Delta T} n\mathrm{SiO_2}\ (\mathrm{glass}) \quad \text{(Densification)} \quad (3)$$

There are many parameters that affect the microstructure of the precursors formed by the sol–gel process and polymerization of microemulsions. Among them the $r$ ratio, (acid to TEOS molar ratio) and the $r'$ ratio (base to TEOS molar ratio), the $R$ ratio (water to TEOS molar ratio), gelation time, temperature, nature and concentration of electrolyte, nature of solvent and type of alkoxide are the variables of major importance [3, 13–17].

This study was focused on controlling the morphology of these composites using an acid or base without changing the water content in the precursors. Inorganic and organic based polymer composites were formed by polymerizing the precursor microemulsions whilst varying the acid to TEOS ratio ($r$) or the base to TEOS ratio ($r'$). The effects of the acid or base on the gel times and the microstructure of the porous composites were examined.

## 2. Experimental procedure

Tetraethoxy silane (TEOS), acrylic acid, (AA), methyl methacrylate (MMA) were used as received from Aldrich and were of a purity greater than 98 wt %. The water was triple distilled. Cetyltrimethylammonium-bromide, (CTAB), 95 wt % purity, was used as received from Aldrich. Hydrochloric acid, (HCl) with a normality of 12.1 and ammonium hydroxide ($NH_4OH$) with a normality of 14.8 were used as received from Fisher Scientific.

Samples for the phase behaviour and characterization studies were prepared by weighing or pipetting the required amounts of various components, into clean glass tubes, which were then sealed. The amount of CTAB used for the stabilization of the microemulsion was always 15 wt % of the total sample prepared. Acrylic acid, methyl methacrylate solution was prepared in the ratio of 3:1 by weight. The phase behaviour studies were performed at $25 \pm 0.1\,^{\circ}\mathrm{C}$ and atmospheric pressure.

The viscosity measurements were performed using a Brookfield LVT digital viscometer which had a small sample adapter with the provision to control the sample temperature. The sample temperature was maintained at $25 \pm 0.1\,^{\circ}\mathrm{C}$ and the measurements were obtained at a shear rate of $79.2\ \mathrm{s^{-1}}$. The same instrument with various lower shear rates was used for examining the effect of acid and base on the gelation rate. A 10 g sample containing 20 wt % 3:1 AA:MMA mixture, 20 wt % water and 60 wt % of TEOS was prepared and to this a fixed amount of acid or base was added. Samples with HCl to TEOS molar ratios ($r$) of 0.01, 0.10, 0.15, 0.20 and 0.25 were prepared and their viscosity recorded as a function of time. The time for the viscosity of the sample to reach 100 P was considered to be the gelation time. The same procedure, with $NH_4OH$ to TEOS molar ratios ($r'$) of 0.01, 0.1, 0.15, 0.2 and 0.25 was used to examine the effect of $NH_4OH$ on gelation time.

As outlined in our earlier paper [12], samples for polymerization were prepared by purging the microemulsion samples with dry nitrogen gas at a rate of $0.56\ \mathrm{L\ h^{-1}}$ at atmospheric pressure for 15 min. A cross linking agent, ethylene glycol dimethacrylate (EGDMA), and an initiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA) of 99 wt % purity or above were obtained from Aldrich. The amount of DMPA used to initiate the free radical polymerization reaction was 0.02 g for a 10 g microemulsion. The amount of EGDMA used was always 8 wt % of the MMA and AA present. The samples were thoroughly mixed and equilibrated in a constant-temperature bath at $25 \pm 0.1\,^{\circ}\mathrm{C}$ for 24 h. This was sufficient time for the hydrolysis reaction between the TEOS and water to take place and gel the samples. Gelled samples were subjected to photopolymerization by vertically placing the sample tubes in a reaction cell. The cell was made of Pyrex glass and was maintained at a controlled temperature by circulating water from a refrigerated circulator through it. The samples were irradiated using a 500 W quartz-halogen lamp. The polymerization was carried out for 1 h at $25 \pm 0.1\,^{\circ}\mathrm{C}$. The experimental set up is shown in Fig. 1. Visible light polymerization of the precursor microemulsions was performed only after the gelation (hydrolysis and polycondensation) of the sample because simultaneous hydrolysis, polycondensation and photopolymerization of the precursors lead to unreacted or unpolymerized monomer species in the final product.

Pore continuity information was obtained from drying rate curves using a DuPont Instruments TGA

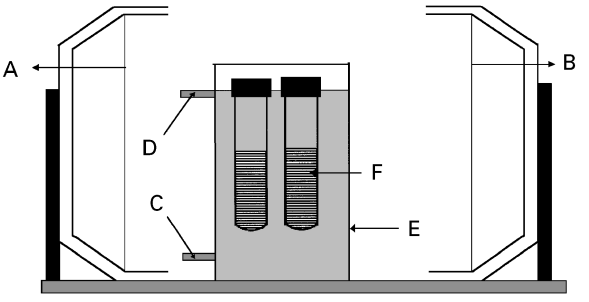


*Figure 1* Polymerization reactor for composite synthesis. A and B, visible light sources; C, cooling water circulation inlet; D, cooling water circulation outlet; E, polymerization reactor; F, precursor microemulsion.

2100 thermogravimetric analyser. A composite sample with a known size was cut and then dried in a stream of nitrogen gas at a temperature of 70 °C for 300 min. The stream temperature was then raised to 100 °C at a ramp rate of 1 °C $min^{-1}$. and the drying process was continued for a further 30 min. The plot of drying rate versus free moisture content was produced following the procedure described in the literature [18–20]. The shape of the drying rate curves when considered along with the scanning electron microscopy (SEM) micrographs provides an indication of the pore continuity.

The surface morphology of the sample was examined using an ISI SX-40 scanning electron microscope. The samples were dried at room temperature for 7 days before being analysed using the SEM technique.

## 3. Results and discussion

The phase diagrams of the microemulsion system, TEOS, AA, MMA and water, using CTAB (15 wt % of the total sample prepared) as the surfactant, equilibrated at 25 ± 0.1 °C observed 24 and 120 h after sample preparation are shown in Figs 2 and 3. The phase diagram after 24 h showed six detectable regions, A–G. Apart from the regions A and F, which were two-phase samples with the bottom phase being gelled and the top phase as either a clear transparent solution (region A) or a single phase opaque solution (region F) all the other regions were found to be single phase transparent gels or solutions. The phase diagram after 120 h shows the same regions with the exception that the gelled regions after 24 h were extended into the solutions regions and thus the solution regions are decreased. This is due to the hydrolysis and polycondensation reaction of TEOS. On the whole, from the phase behaviour studies it was observed that a large area of single phase microemulsions was obtained.

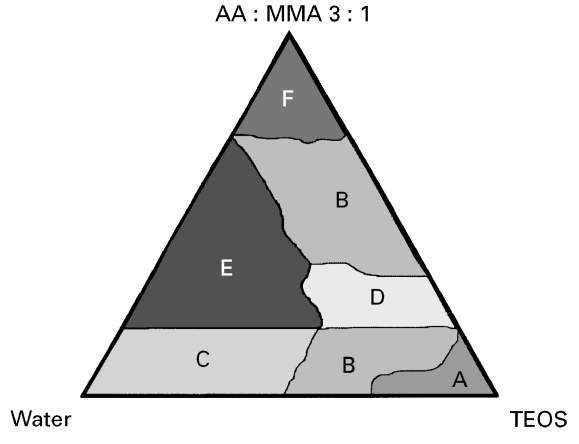


*Figure 2* Ternary-phase diagram for the TEOS/AA/MMA/water/CTAB microemulsion system observed 24 h after sample preparation, equilibrating at 25 ± 0.1 °C and 1 atmospheric pressure. The system contained 15 wt % CTAB. Compositions are on a weight per cent basis. Domains: A, two- phase bottom gelled top transparent solutions; B, single phase translucent gels; C, single phase slight precipitate transparent solutions; D, single phase transparent gel; E, single phase transparent solution; F, single phase opaque solution.

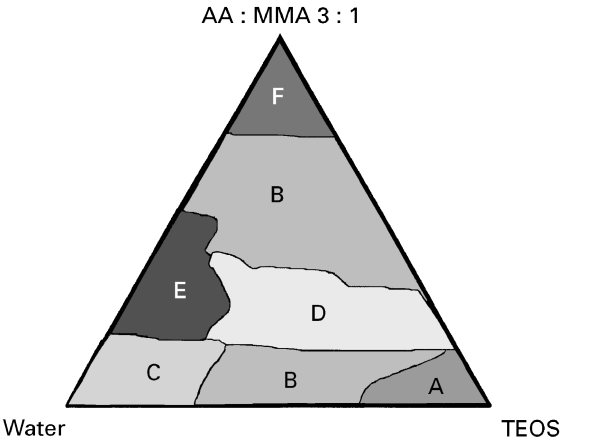


*Figure 3* Ternary-phase diagram for the TEOS/AA/MMA/water/CTAB microemulsion system observed 120 h after sample preparation, equilibrating at 25 ± 0.1 °C and 1 atmospheric pressure. The system contained 15 wt % CTAB. Compositions are on a weight per cent basis. Domains: A, two- phase bottom gelled top transparent solutions; B, single phase translucent gels; C, single phase slight precipitate transparent solutions; D, single phase transparent gel; E, single phase transparent solution; F, single phase opaque solution.

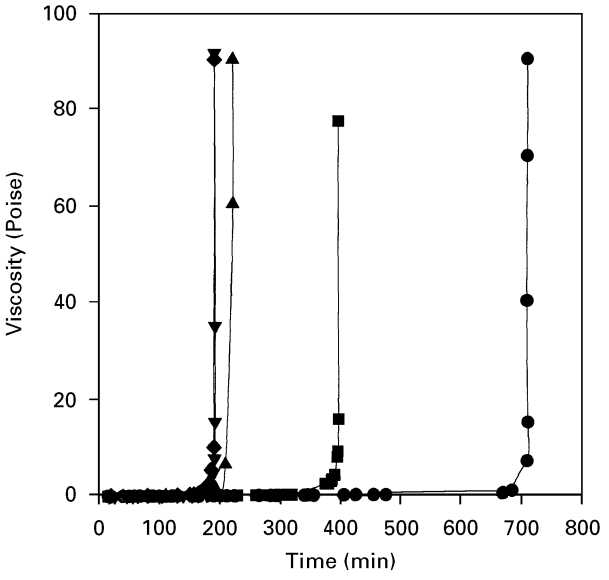


*Figure 4* Acid concentration effect on gelation time for the acid catalysed microemulsion system TEOS/AA/MMA/water/CTAB. Compositions of sample: 60 wt % TEOS, 20 wt % AA and MMA (3:1) and 20 wt % water. System contained 15 wt % CTAB. HCl used was 12.1N and HCl to TEOS molar ratios were (*r*), (●) 0.01, (■) 0.1, (▲) 0.15, (▼) 0.2 and (◆) 0.25.

Samples were prepared and the gel times determined as described above. The results are shown in Figs 4 and 5. As the *r* and *r*′ ratios increases, the gel time decreases from 716 to 196 min and from 196 to 62 min for the acid and base cases respectively. It was found that the gel time decreases for both the acid and base cases as the *r* or *r*′ ratio increases; indicating that both the acid and base catalyse the hydrolysis and polycondensation reactions in proportion to the *r* or *r*′ ratio. It was also observed that the gel time using the base as a catalyst was shorter than that observed for acid catalysis.

Acid and base catalytic effects on gel time have been examined in many publications in the literature

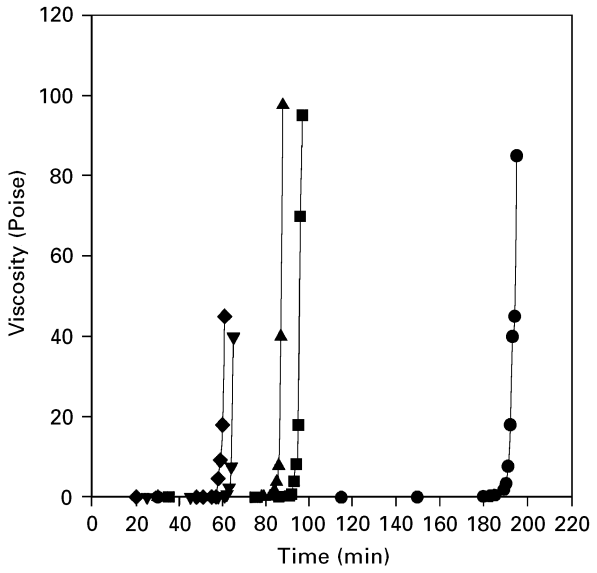


*Figure 5* Base concentration effect on gelation time for the base catalysed microemulsion system TEOS/AA/MMA/water/CTAB. Compositions of sample: 60 wt % TEOS, 20 wt % AA and MMA (3:1) and 20 wt % water. System contained 15 wt % CTAB. $NH_4OH$ used was 14.8 N and $NH_4OH$ to TEOS molar ratios were ($r'$), (●) 0.01, (■) 0.10, (▲) 0.15, (▼) 0.2 and (◆) 0.25.

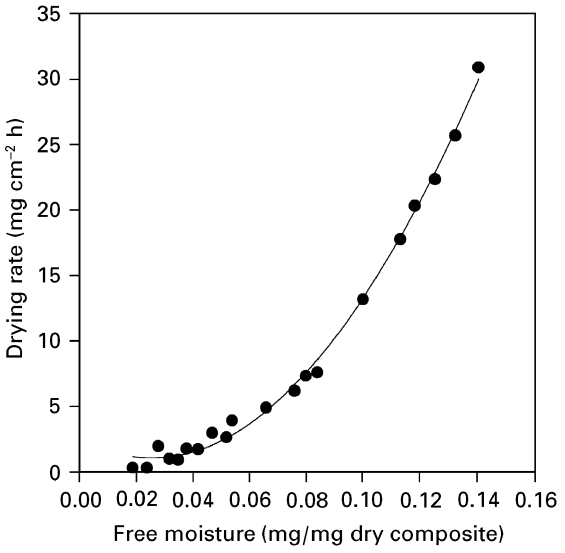


*Figure 6* Drying rate curve for the composite obtained from neutral precursor microemulsion with a composition: 60 wt % TEOS, 20 wt % AA and MMA (3:1) and 20 wt % water using 15 wt % (total sample weight) CTAB. EGDMA used is 8 wt % of the combined weight of MMA and AA in the sample.

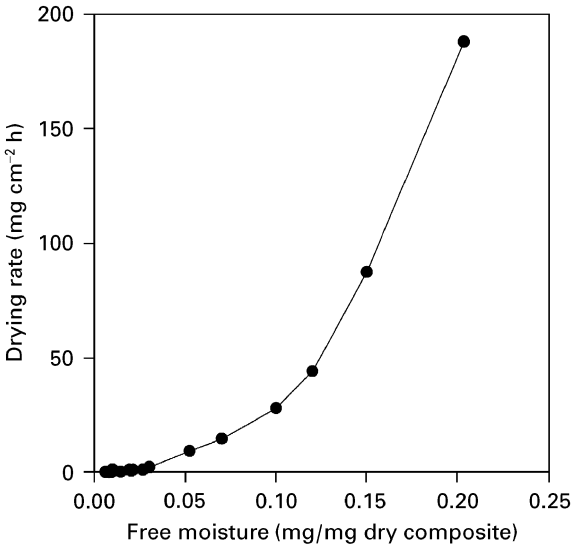


*Figure 7* Drying rate curve for the composite obtained from precursor microemulsion ($r$ ratio 0.25) and a composition: 60 wt % TEOS, 20 wt % AA and MMA (3:1) and 20 wt % water using 15 wt % (total sample weight) CTAB. EGDMA used is 8 wt % of the combined weight of MMA and AA in the sample.

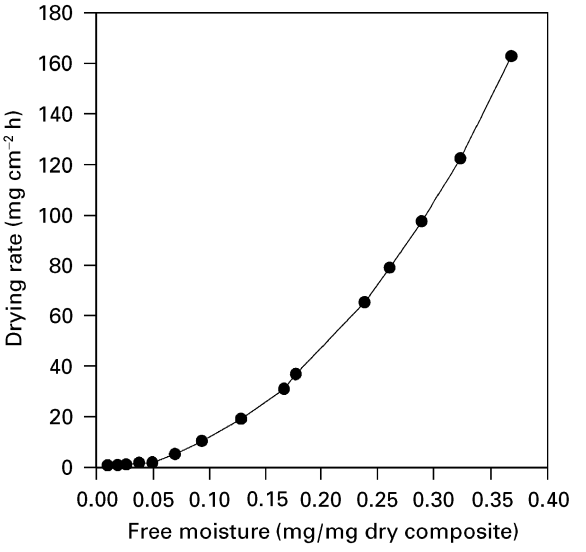


*Figure 8* Drying rate curve for the composite obtained from precursor microemulsion ($r'$ ratio 0.25) and a composition: 60 wt % TEOS, 20 wt % AA and MMA (3:1) and 20 wt % water using 15 wt % (total sample weight) CTAB. EGDMA used is 8 wt % of the combined weight of MMA and AA in the sample.

[1, 13, 15, 21–24]. It is known that an acid promotes the rate of hydrolysis reaction more than the polycondensation reaction and that a base promotes the polycondensation reaction more than the hydrolysis reaction. The polycondensation reaction creates additional bridging bonds and increases the viscosity. This may explain our observation of shorter gelation times for the base catalysed systems. Our earlier studies, [12] also revealed that nitrogen purging of the precursors with low $r$ and $r'$ ratios did not have a significant effect on the gel times. Nitrogen purging of the precursor is essential since oxygen inhibits the free radical polymerization of the organic monomers [5].

The drying rate curve for the composite obtained from the pH 7.0 precursor microemulsion is shown in Fig. 6. The results for an $r$ ratio of 0.25 and an $r'$ ratio of 0.25 are shown in Figs 7 and 8 respectively. These results indicate that the composites formed from the neutral precursor show only one exponentially decreasing slope indicating that the composite possess a closed cell (non-porous) structure and that of the composites formed with a $r$ ratio of 0.25 and a $r'$ ratio of 0.25 showed two distinctive drying rate slopes in the falling rate period zone indicating that the structures are open-cell (porous). The transition of closed-cell (non-porous) structure to open-cell structure (porous) was similar for both acid and base cases.

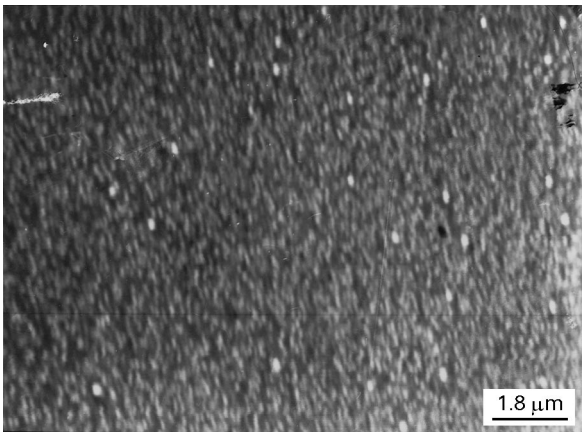


*Figure 9* SEM micrograph of the polymer composite formed with the neutral precursor composition: 60 wt % TEOS, 20 wt % AA and MMA (3:1) and 20 wt % water using 15 wt % (total sample weight) CTAB.

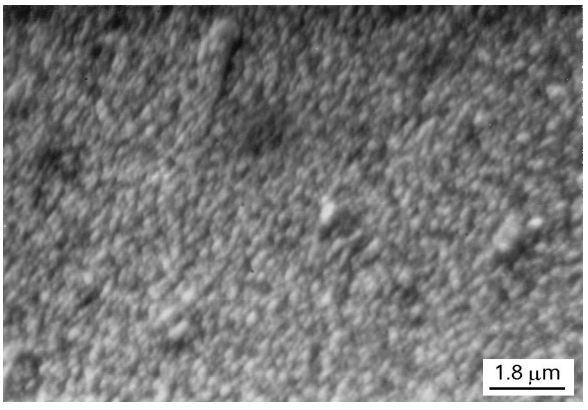


*Figure 10* SEM micrograph of the polymer composite formed with the precursor ($r = 0.01$) and a composition: 60 wt % TEOS, 20 wt % AA and MMA (3:1) and 20 wt % water using 15 wt % (total sample weight) CTAB.

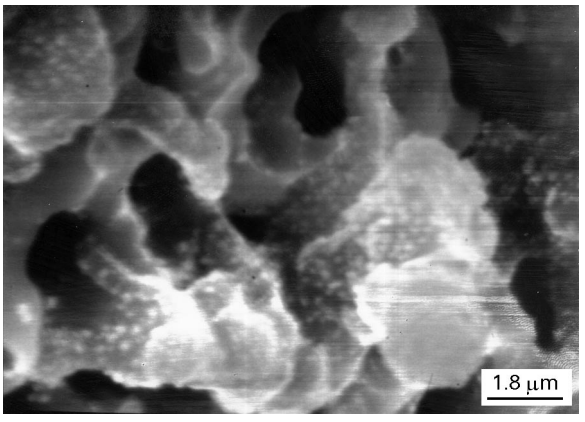


*Figure 11* SEM micrograph of the polymer composite formed with the precursor ($r = 0.1$) and a composition: 60 wt % TEOS, 20 wt % AA and MMA (3:1) and 20 wt % water using 15 wt % (total sample weight) CTAB.

An SEM micrograph of the composite formed from the neutral precursor with the composition of 20 wt % AA/MMA (3:1), 60 wt % TEOS, 20 wt % water and 15 wt % CTAB is shown in Fig. 9. The micrograph indicates a closed-cell structure. The micrographs of composites with $r$ ratios of 0.01, 0.1 and 0.25

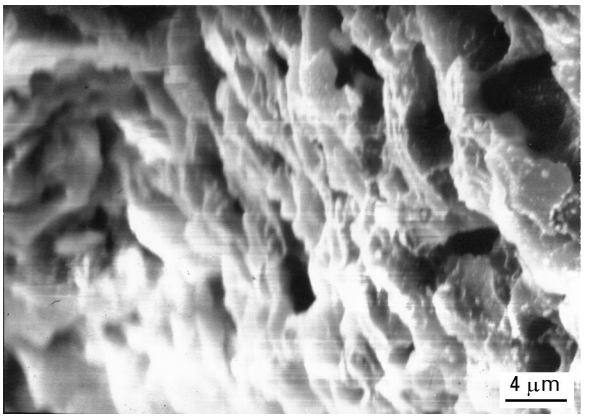


*Figure 12* SEM micrograph of the polymer composite formed with the precursor ($r = 0.25$) and a composition: 60 wt % TEOS, 20 wt % AA and MMA (3:1) and 20 wt % water using 15 wt % (total sample weight) CTAB.

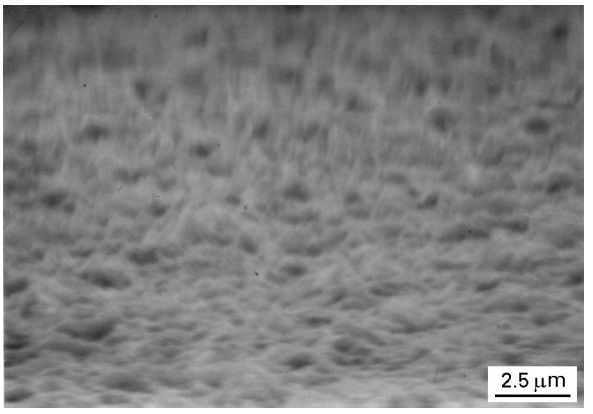


*Figure 13* SEM micrograph of the polymer composite formed with the precursor ($r' = 0.01$) and a composition: 60 wt % TEOS, 20 wt % AA and MMA (3:1) and 20 wt % water using 15 wt % (total sample weight) CTAB.

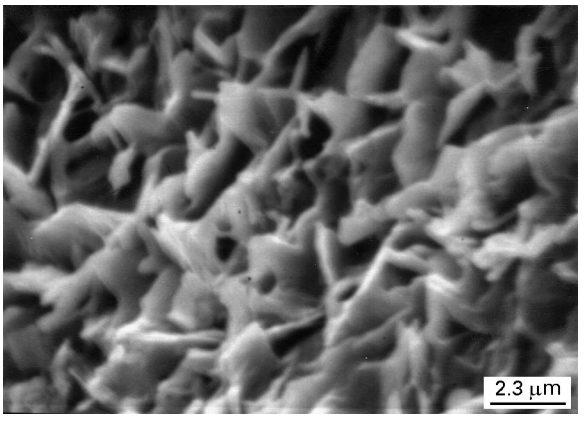


*Figure 14* SEM micrograph of the polymer composite formed with the precursor ($r' = 0.15$) and a composition: 60 wt % TEOS, 20 wt % AA and MMA (3:1) and 20 wt % water using 15 wt % (total sample weight) CTAB.

(Figs 10–12) and $r'$ ratios of 0.01, 0.1 and 0.25 (Figs 13–15) indicate open-cell pore structures and an increase in the pore size as the $r$ or $r'$ ratio increases. The micrographs are consistent with the pore continuity results obtained using drying rate curves.

A difference in the pore morphology is observed between the acid and base catalysed systems. For base catalysed systems a progression is observed from irregular particle shapes to roughly spherical particles

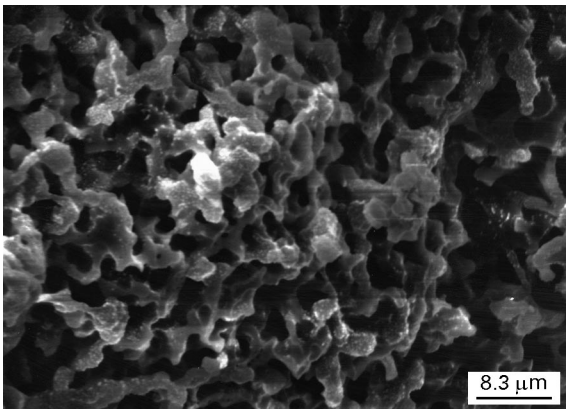


*Figure 15* SEM micrograph of the polymer composite formed with the precursor ($r' = 0.25$) and a composition: 60 wt % TEOS, 20 wt % AA and MMA (3:1) and 20 wt % water using 15 wt % (total sample weight) CTAB.

as the $r'$ increases between 0.01–0.25. The behaviour for base catalysed composites at a high $r'$ ratio (0.25) can be attributed to the hydrolysis reaction that occurs due to the nucleophilic substitution mechanism, which leads to material of a particulate nature [1, 26, 27]. When a base is used as a catalyst, colloidal particles are formed in the early stages of TEOS hydrolysis and these aggregate to form a network structure as the reaction progresses. At low base concentrations (low $r'$ ratios) small irregularly-shaped particles and branched strand like materials will be produced which tend to aggregate to form strands of irregular shapes (Fig. 14). The connectivity between the spherical particles observed at high $r'$ ratios (0.25) can also be attributed to the agglomeration/flocculation effect of the surfactant CTAB through which the silica particles are held together by the micelles of the cationic surfactant [17]. These micelles occupy the silica surface only at the points of contact between the particles which is shown in Figs 14 and 15. Iler [17] in his work on the flocculation effect of CTAB, mentioned that 5 wt % of CTAB is sufficient to produce aggregation of silica particles. In the present study 15 wt % CTAB was used to stabilize the microemulsion. This could lead to the aggregation of silica particles. We also observed that the particle size is bigger for base catalysed composites than for acid catalysed composites. Similar results have been reported by Debsikdar [22].

In contrast to the spherical particles observed in the base catalysed systems, the acid catalysed systems produced linear structures. This tendency of acid catalysed sols to develop linear structures with very little branching has been described in the small angle X-ray scattering (SAXS) studies performed by Hench and West [15].

## 4. Conclusions

Our earlier studies, [12] showed that the thermal stability of these composites is higher than that of the copolymers obtained from the precursor microemulsion without TEOS. The present study has shown that acid or base catalysis of the inorganic reactions has a significant influence on the morphology of the final inorganic/organic polymer composites.

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