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Bicontinuous porosity in ceramics utilizing polymer spinodal phase separation

Charles M. Lofton, Claudia B. Milz, Huiyan Huang[1], Wolfgang M. Sigmund*

Department of Materials Science and Engineering, University of Florida, P.O. Box 116400, 225 Rhines Hall, Gainesville, FL 32611, USA

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Abstract

This paper demonstrates how the combination of inorganic and organic polymers can be used to form bicontinuous porosity in ceramics with pore sizes larger than 5 μm. Spinodal phase separation of pseudo-binary polymer mixtures allows to form larger bicontinuous pore structures than spinodal phase separation of inorganic glasses. Addition of salts allows even more complex compositions of ceramics and glasses to be formed. Here, bioactive glasses are presented that were produced via sol–gel processing of a pseudo-binary mixture of an inorganic and an organic polymer. Due to the addition of an organic polymer to the gelling sol and the spinodal phase separation at a specific equilibrium temperature, both an inorganic polymer ceramic phase and organic polymer-rich phase are formed. The evaporation of the solvent and the burnout of the organic polymer produce a microstructure of interconnected and nearly uniform porosity, which can be controlled by several processing parameters. The dependency of pore size and connectivity is best predicted by polymer phase separation rather than glass melt separation. Results suggest that polymer spinodal phase separation could be useful for the manufacture of a variety of porous ceramics.

Keywords: Sol–gel processing; Porosity; Glass; Polymer; Biomedical applications

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1. Introduction

Numerous ceramic materials are currently used to repair and reconstruct body parts. The surface reactivity of the ceramics in living tissue and the biological response elicited from the tissue varies with ceramic systems. Bioactive glass exhibits a defined surface reaction in vivo,[1] resulting in a calcium phosphate interfacial layer that leads to bonding with both soft and hard tissue.[2] This strong bonding between biological and synthetic systems is useful for the treatment of several medical conditions, including the replacement of the inner ear bones with machined glass pieces and maxillofacial bone reconstruction with powdered glass.

Bioactive glasses that bond to bone, activate bone re-growth, and superficially resorb into the body as non-toxic materials are composed of SiO_2, CaO, Na_2O and P_2O_5. For melt-processed bioactive glasses, low silica content and a high calcia and soda content are required for the glass to have a high surface reactivity in an aqueous medium. Sol–gel-derived bioactive glasses usually do not contain soda and have a much higher silica content, but retain the surface reactivity due to their characteristic large specific surface areas and hydrated silicate surface.[5,6] In glasses from both processing methods, ion exchange and precipitation of hydroxyapatite on the glass surface [3] occurs that allows for cell attachment. This apatite layer not only allows the tissue to bond, but also provides a substrate for deposition of new bone cells.

In order to expand the applications for bioactive glasses in medical devices, the fabrication of load bearing monoliths containing designed porosity is potentially useful. The design of the porosity would need to reflect the impact of surface area, pore size, and uniformity and connectivity of pores to control the device strength, surface reaction rate, dissolution rate, and ability of tissue to grow into the device. A device with a uniform and interconnected porosity in the size range greater than 20 μm would feature two valuable

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* Corresponding author. Tel.: +1-352-846-3343;
fax: +1-352-392-7219.
E-mail address: wsigm@mse.ufl.edu (W.M. Sigmund).

[1] Present address: Department of Biology, University of Louisville, Louisville, KY, USA.

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characteristics: A large specific surface area to allow the gradual and uniform dissolution of the device in the body, and a scaffold-like structure allowing bone cell in-growth, accelerating bond regeneration.

The interconnected porosity could also serve to allow the infiltration of a second, ductile phase in order to increase the rather low strength of bioactive glass devices. Current processing methods for bioactive glasses, however, are not able to provide this type of microstructure. The formation of interconnected pores through foaming or fugitive phase burnout generally requires very high pore volumes that make the material structurally weak. The morphology formed during spinodal phase separation leads to interconnected pores at approximately 50% pore volume.

The interconnected porous microstructure suggested above is formed under certain conditions during spinodal decomposition. Here we present a novel forming process for ceramic materials and glasses based on spinodal phase separation of polymer precursors. This process is novel in respect to using a multicomponent glass with a variety of chemical species as precursors that successfully produces the proper phases of bioactive glasses and the desired porosity. This processing technique will be described using a model developed for the phase separation of two component polymer systems. As will be demonstrated, the condensation of an oxide ceramic from alkoxide precursors can be compared to the polymerization of an organic polymer.

2. Experimental procedure

Pure silica and various bioactive compositions were fabricated using the sol–gel/phase separation technique. The interconnected porosity of the silicate ceramics was possible through controlled spinodal decomposition of a gelling sol containing polyacrylic acid. The bioactive compositions were based on Li's work in the $SiO_2/P_2O_5/CaO$ system where the phosphate content was maintained at 4 mol% and the relative ratios of silica and calcia were varied.[16,17]

First, PAA was dissolved in water and ethanol while stirring the solution for 1 h. Second, TEOS and nitric acid were added into the solvent and stirred for 1 h at 60±2 °C. Triethyl phosphate (TEP) was added and the solution was homogenized for another hour at the same temperature. This delay in the addition of the TEP as necessary due to the greater reactivity of TEP with water compared to TEOS. Calcium nitrate was mixed into the sol for 30 min, followed by casting the sol into a container, which was sealed and allowed to gel and coarsen at a constant temperature for 48 h. To obtain the xerogel, the preliminary silicate gel was washed with deionized water and allowed to dry in a Teflon container covered with deionized water for near-equilibrium drying at 101 ± 2 °C. Under these conditions, the environment above the drying gel remained at nearly saturation humidity, minimizing internal stress due to capillary pressure, and allowing for large monoliths to be fabricated. After 48 h, the specimens were taken out of the dryer and heat treated at a 600 °C for 4 h in order to burnout the PAA and convert the calcium nitrate to calcia, producing an porous oxide monolith. This method and an alternative procedure are sketched in Fig. 4.

The microstructure was analyzed employing both SEM (JEOL 6400) and mercury porosimetry (Autoscan 60). SEM samples were made from fractured monoliths attached to mounts and coated with a Au/Pd conductive coating. From the SEM pictures, the average pore size was calculated and compared to the result from the porosimetry, where in addition the total surface area and porosity could also be evaluated.

3. Results and discussion

When two substances of different composition are mixed together, the stability of the mixture is described using thermodynamics laws:

$$\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}} \qquad (1)$$

with: ΔG_{mix} free energy, ΔH_{mix} enthalpy and ΔS_{mix} entropy of mixing.

If the curve of ΔG_{mix} (χ_1), where χ_1 is the molar fraction of component 1, is concave with no inflection point, then the components will completely mix together into one phase. If the equation above shows two or more inflection points, then miscibility is limited to the composition "outside" the two compositions with a common tangent, the binodal points. Inside the region of those two binodal points, phase separation takes place. There are two mechanisms of phase separation, the nucleation and growth process, and spinodal decomposition, which will take place in the metastable and

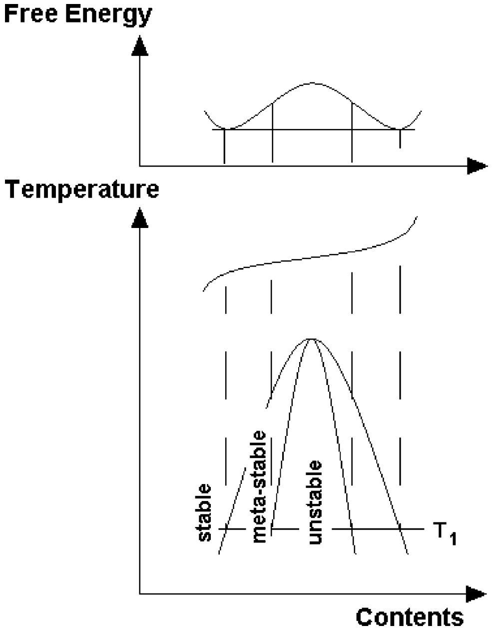

Fig. 1. Glass phase diagram with spinodal phase separation and free energy over composition at $T(1)$.[16]

unstable region as shown in Fig. 1, respectively. There are two spinodal points inside the region defined by the binodal points. At these two thermodynamic limits of metastability, $d^2(\Delta G_{\mathrm{mix}}/N)/d\chi^2 = 0$.

When this term is negative, it describes the area of instability. Spinodal decomposition refers to phase separation inside this region. In this case, the energy barrier is negligible and there are small composition fluctuations present in the system. Diffusion is 'negative,' which means the net flow is in the direction of increasing concentration. This situation leads to two sets of domains which grow in size and compositional difference until the material contains two phases with compositions defined by the spinodal points. If the volumes of the two new phases are approximately equal, then an interconnected, worm-like morphology will form during the coarsening of the domains. In order to maintain the interconnected structure in the desired product, the body can be rapidly cooled to freeze in the morphology at the desired stage of growth.

After the material is frozen in the desired interconnected microstructure, leaching can be used to remove one of the phases, leaving a monolith with continuous, interconnected porosity. This is the method for production of Vycor® by Corning,[4] where the glass is cast, followed by heat treatment to induce phase separation and the subsequent removal of the more soluble phase on cooling of the glass to leave behind a silica-rich skeleton. This method is impractical for a biomedical scaffold application due to limits on the speed of domain coarsening and the size of the phase domains in the glass, limiting the pore size to the range of tens of nanometers.

An alternative application of spinodal decomposition can produce the microstructure with larger pore sizes. Like multi-component, inorganic glasses, melts and solutions of two polymer compositions vary in their stability with respect to mixing. Polymer–polymer blends systems possess the following phase diagram (Fig. 2).[7]

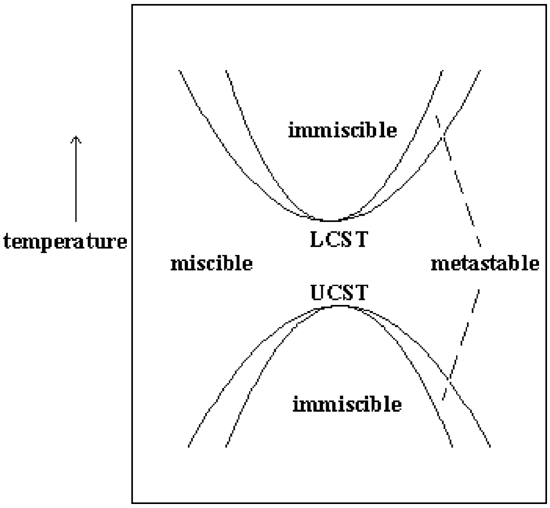

Fig. 2. Phase diagram for polymer–polymer blend systems.[17]

Upper critical stability temperature (UCST) behavior is characterized by phase separation as the temperature is lowered and lower critical stability temperature (LCST) by phase separation as the temperature is raised. Two modes of phase separation are possible, spinodal decomposition and nucleation and growth, depending on the temperature and composition. Usually, when specific interactions (such as hydrogen bonding) are absent, mixing is generally endothermic, i.e. blends display UCST behavior. Here, the Flory-Huggins[8] theory can be used to explain the UCST behavior of polymer blends. It states

$$\Delta G = RT\left\{\left(\frac{\Phi_1}{P_1}\right)\ln\Phi_1 + \left(\frac{\Phi_2}{P_2}\right)\ln\Phi_2 + \chi_{12}\Phi_1\Phi_2\right\} \tag{2}$$

$$\chi = \frac{zw_{12}}{kT} \tag{2a}$$

$$w_{12} = \frac{(\delta_1 - \delta_2)^2}{z} \tag{2b}$$

Where Φ_1 and Φ_2 are the volume fractions of each polymer, P_1 and P_2 are the degree of polymerization of 1 and 2, χ is the interaction parameter, and z is the coordination number of the lattice, δ is the solubility parameter, which depends on the chemical structure. While the first two terms are entropic in origin, the third is enthalpic. For a ternary mixture of a polymer (1)–polymer (2)–solvent, the solvent with substantial compatibility with both polymers acts to dilute the repulsive interaction between the two polymers. Thus, the overall phase relation of the mixture is largely determined by the affinity between 1 and 2 and their molecular weights, and the system can be regarded as a quasi-binary mixture in some cases. Hence the above rule of mixture for the binary polymer system will be applicable for this ternary system following some modification.

The bonding interactions of the two polymer types, such as dipole and hydrogen bonding, favor the de-mixing of the polymers, due to each composition favoring interactions with its own kind. While the entropy of the system favors mixing, the conformational entropy of each polymer chain decreases the interpenetration of chains. This contribution of conformational entropy increases with chain length, reflected in the decrease in entropy of mixing with degree of polymerization. Thus, a stable mixture of two polymers can be made to phase separate simply by increasing the degree of polymerization of one or both of the components.

In the case of sol–gel processing, the addition of an inorganic polymer can lead to phase separation. This effect was investigated by Nakanishi et al.,[9,10] in a system of silica and polyacrylic acid (PAA), including the influences of solvent composition,[11] molecular weight and temperature,[12] catalytic condition,[13] chemical additives,[14] while later works focus on the pore structure control.[15] In this type of system, the silica is first added in the form of tetraethyl orthosilicate (TEOS), which undergoes hydrolysis and condensation reactions, forming silicate clusters in solution. Under conditions of acid catalysis, the kinetics of hydrolysis and condensation will favor the formation of highly branched silica clusters with a high likelihood of bonding to one another. This leads to an increase in the viscosity of the liquid sol, and the formation of a spanning cluster which gels the system at a point where condensation has not yet been completed. This gel retains flexibility on a small length scale where the clusters can rearrange until further condensation reactions lock the microstructure into a rigid position.

The highly branched clusters of silica resemble an inorganic polymer chain in solution, which increases in polymerization by chemically bonding to monomers or other clusters. In the presence of an organic polymer dissolved in solution, the growing silica clusters cause the destabilization of the solution, leading to de-mixing and the formation of two phases; one silica-rich phase plus solvent and one organic polymer-rich phase plus solvent. At the same time, the cluster growth increases the viscosity of the solution with a jump in viscosity at the sol to gel transition. Thus, a properly designed sol–gel system can be homogeneously mixed, followed by the addition of a catalyst that will lead to both phase separation and the freezing in of the microstructure by gelation.

Two critical factors govern the microstructure of the final gel product: The timing of the onset of phase separation relative to gelation and the relative volumes of the silica and polymer-rich phases. If phase separation takes place during gelation and the phase volumes are nearly equal, a gel containing a rigid silica skeleton with an interpenetrating polymer–solvent phase will be formed. If phase separation occurs early, the low viscosity of the sol will lead to nucleation and growth type de-mixing and there will likely be macroscopic phase separation, with the denser silica phase sinking to the bottom of the reaction vessel. If phase separation occurs late, the gel will have become rigid before the domains can coarsen and the microstructure will not reflect the significant formation of separate phases. If the phase volumes are not equal, no interconnect structure will form, instead, the minor phase will form spheres in a matrix of the major phase, such as the formation of spherical polymer–solvent domains in a silica gel matrix, or the formation of spherical silica colloids in a polymer–solvent liquid.

This research involves the spinodal phase separation of an organic rich phase (PAA dissolved in the solvent) and an inorganic phase (SiO_2 plus CaO and P_2O_5 precursors dissolved in the solvent) to obtain the interconnected porous structure. TEOS and PAA are substantially compatible with the water–ethanol solvent, such that phase separation will

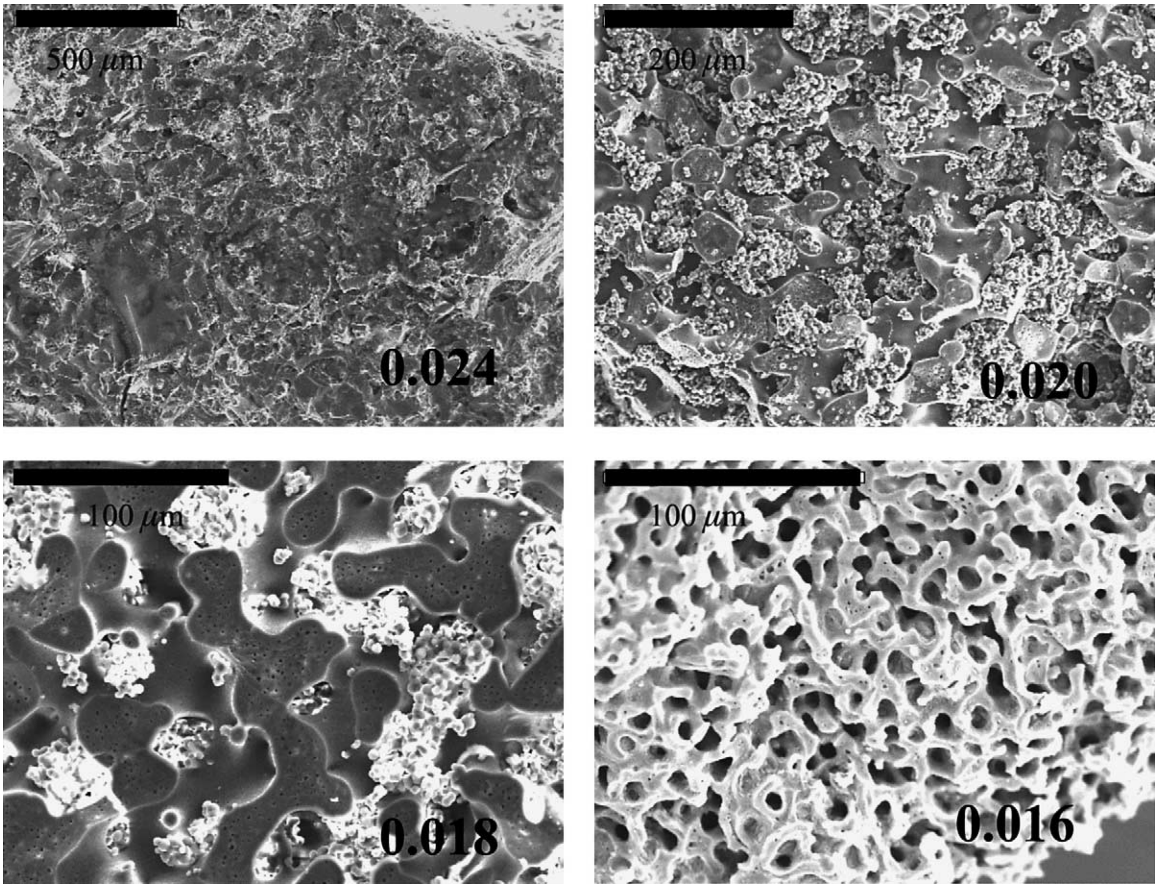

Fig. 3. 77S glass monoliths with decreasing concentrations of PAA and silica (PAA/silica ratio constant, concentration given in weight ratio of PAA to solvent) causing a delay in phase separation until gelation has started to take place.

only take place as the TEOS forms silica clusters. When a catalyst is added to the solution, the rate of hydrolysis and condensation is accelerated, leading to the growth of SiO_2 clusters in the suspension until gelation and the freezing of the structure. The affect of five processing factors on the microstructure of the gels were investigated. The total concentration of PAA and silica was used to determine the relative timing of phase separation and gelation in the bioactive composition 77S. The ratio of silica to polymer was used determine the relative volumes of the two phases, controlling whether an interconnect morphology forms. The concentration of catalyst and the temperature of aging were varied to allow the phase domains to coarsen to different degrees, determining the size of the pores in the dried ceramic body. Finally, expanding the bioactive glass compositions outside of the 77S composition, the affect of modifying additional calcia on the microstructure was investigated.

When the concentration of PAA and silica in the solvent mixture was altered while keeping the relative ratios of PAA and silica constant, as well as other processing factors constant, the effect on the gel microstructure was observed to change as seen in Fig. 3.

In sample A, the sample was made with the highest concentration of PAA and silica, and was taken from the reaction vessel after aging as a small pellet with a large amount of viscous fluid above it. The viscous fluid was found to contain a high concentration of PAA, while the gel was found to be very dense with no evidence of phase separation. Because of the high concentration of polymers in the solvent, phase separation was accelerated relative to the rates of hydrolysis and condensation. Eq. (2) is a description of a binary polymer system, however, a system with two polymers and a mutual solvent can be described by this equation as a pseudo-binary system. The effect of the solvent is to reduce the enthalpic bonding interactions of the polymers by increasing the distance between them. Because the enthalpic factor in the free energy equation drives the system towards de-mixing, dilution of the polymers is expected delay phase separation, while higher concentrations of polymers should accelerate the timing of de-mixing. In the case of A, the phase separation occurred so early in the gelation process that the system was still a low viscosity sol, and phase separation took place on a macroscopic scale, with the denser silica sinking to bottom of the vessel and the PAA solution forming on top. As the polymers are diluted in samples B and C, the samples were found not to be phase separated on a large scale, and gels showed evidence that gelation was taking place during phase separation. The microstructures, however, were not

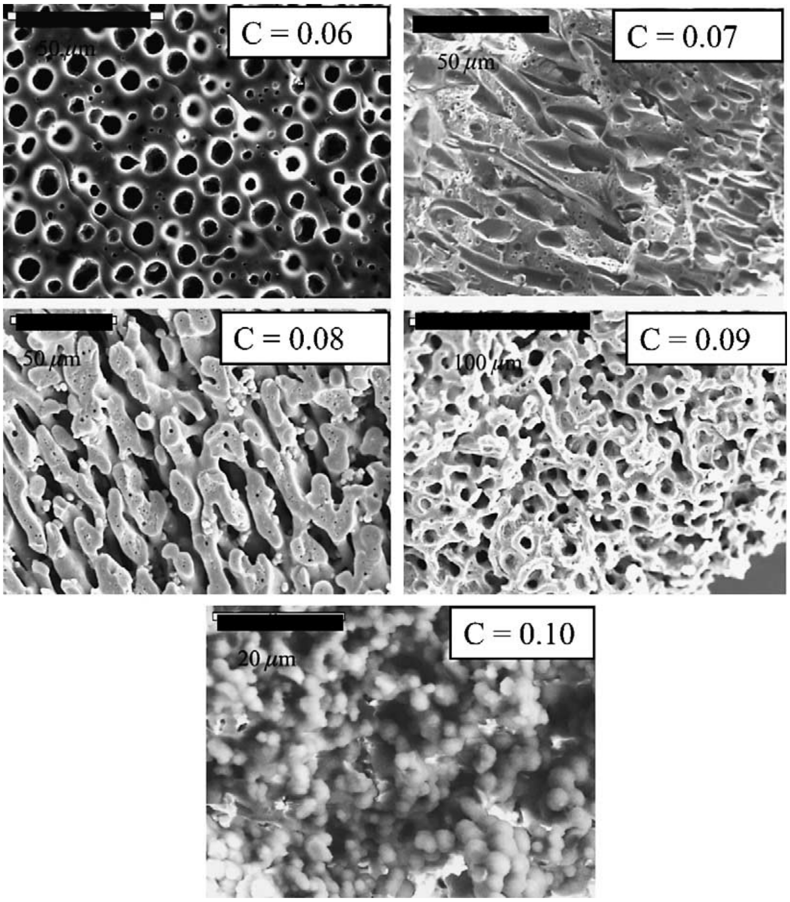

Fig. 4. SEM images of the microstructure of a 77S glass with varying *C* ratios.

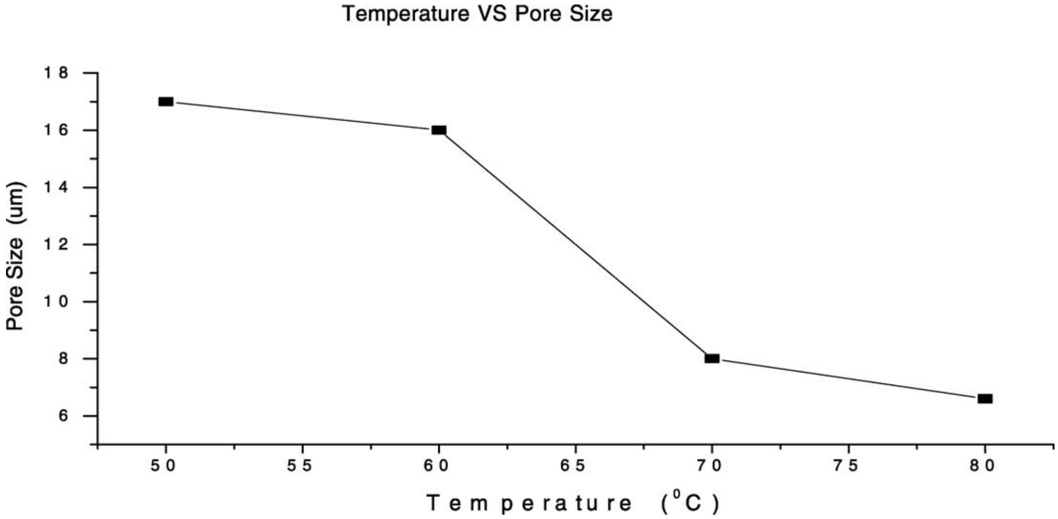

Fig. 5. The relationship of pore size to aging temperature. The increase in temperature reduces the time for domain coursening, reducing the pore size in the final body.

well-developed, and contained large amounts of spherical precipitates in the pore channels created by the PAA-rich phase. These precipitates indicate that phase separation initiated at certain points before gelation, resulting in droplets of the silica-rich phase being trapped in the PAA-rich phase. In sample D, the concentration of polymers was dropped even lower, and the final microstructure showed the desired interconnected form free of precipitates.

The *C* ratio, or the ratio of PAA to silica repeat units, was found to determine the relative phase volumes of the PAA-rich and silica-rich phases. The effect of the *C* ratio on the microstructure of a 77S gel, maintaining other processing factors constant, is shown in Fig. 4.

At $C = 0.06$, the volume of the polymer-rich phase is much less that that of the silica-rich phase, and a microstructure of isolated spherical pores is formed, containing PAA and solvent. As the ratio increase, as in $C = 0.07$ and 0.08, the pores begin to elongate, but have not achieved the interconnected morphology desired. At $C = 0.09$, the ideal microstructure is obtained, indicating that the volumes of the polymer and silica-rich phases are equal. At higher *C* ratios, the silica becomes the minor phase, and forms spherical sil-

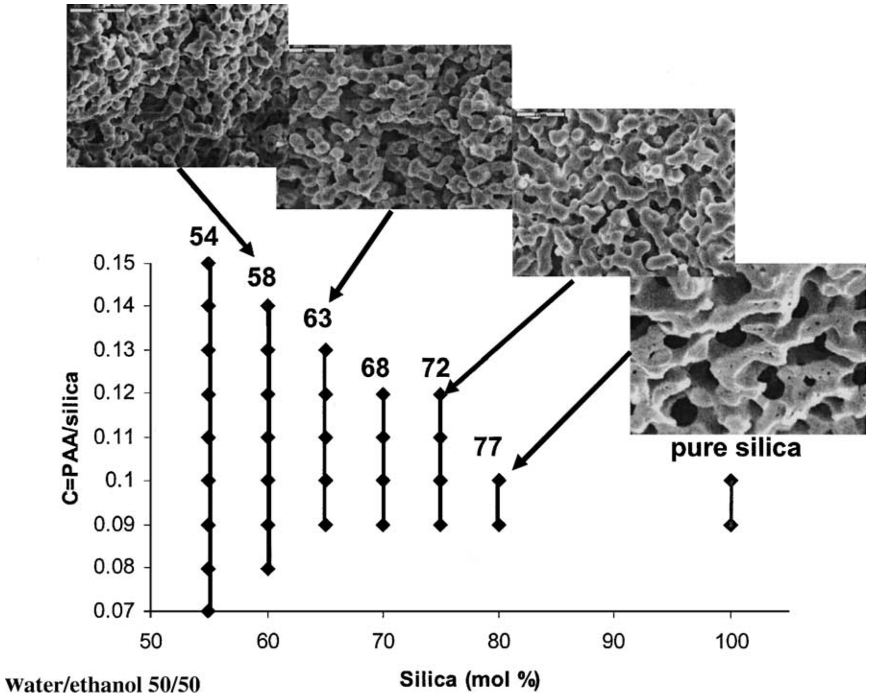

Fig. 6. The range of *C* ratios that produced interconnected morphologies for different silica contents is shown.

ica particles which later agglomerate. It is clear from this that there is only a narrow window of C ratios where the desired morphology can be obtained.

Increases in both temperature and the amount of catalyst accelerate the condensation reactions. Because condensation leads to both gelation and phase separation, the aging temperature and acid concentration were not found to significantly change the microstructure with in a limited range. Instead, they altered the amount of time that the gel network had to coarsen. The size of the phase domains are time-dependent and reflect the amount of time that the silica network has to rearrange to facilitate the segregation of the silica from the PAA before becoming so rigid that it cannot move due to condensation reactions between silica clusters. When the concentration of nitric acid is increased from 1 to 1.5 M for the 77S system, the average pore size decreases from 42 to 26 μm. Likewise, when the gelation temperature is increased, the average pore size is decreased. This is shown in Fig. 5. This design of pore size could only be controlled in a limited range, due to a dramatic slow down in gelation with temperatures below 30 °C, the evaporation of the solvent at high temperatures, and the changes in the condensation mechanism with pH.

When compositions other than 77S were made, the C ratio needed to be altered to maintain the interconnected microstructure. As is seen in Figs. 5 and 6, the general trend is towards a higher C ratio for gels of lower silica content (higher calcia content). This trend is attributed to the volume of the soluble calcium nitrate, which is expected to swell the silica-rich phase. At the low pH region that the gelation is taking place, the silica is positively charged, and the PAA reacts with the ethanol in the solvent to become esterified. This partial esterified PAA is much less soluble in water, and is more soluble in ethanol. The addition of soluble calcium salts is expected to draw a large amount of water with it into the silica-rich phase, increasing the volume of this phase. The increase in the C ratio is needed to increase the PAA concentration to compensate for this effect.

4. Summary and conclusions

A process involving spinodal phase separation has been applied and refined to obtain bone scaffold material with desirable properties. This material consists of porous bioglass, produced via spinodal phase separation of TEOS precursor and PAA in a controlled environment of water and ethanol. The gelation takes place during the phase separation, building an interconnected structure of porous bioglass containing salt deposits which are formed after calcination removes the organic compounds. The application of a pseudo-binary polymer mixture explanation to describe the processing factors that control the gel microstructure was very successful. The total concentration of TEOS and PAA in the solvent determined the timing of phase separation versus gelation. By controlling the ratio of ceramic precursors to polymer, the interconnected microstructure could be achieved. Through control of the aging temperature and the concentration of catalyst, the pore size could be altered in a limited range. The synthesis technique could be modified to accommodate variable amounts of non-network forming ceramic precursors, such as calcium nitrate to form calcia in the calcined body. The versatility of composition and pore size indicate that this processing method could be potentially useful for a variety of ceramic applications besides bioactive scaffolds. Glass bodies can now be fabricated with interconnected pores in the size range of micrometers instead of nanometers. Multicomponent ceramics systems could be crystallized from their sol–gel precursors while retaining a porous microstructure.

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