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Particle network re-structuring in highly-concentrated ceramic suspensions*

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In this study, the restructuring behavior of particle networks in highly-concentrated zirconia-wax suspensions as model suspensions is investigated in terms of temperature and solids concentration. The restructuring kinetics is analytically determined such that it can be formulated by a linear correlation between the relative viscosity (η_r) of the suspensions and the logarithmic time (t) of isothermal annealing. Upon restructuring, a gelling point t_{gel}, defined as the time period of which the discrete particle networks in the pre-sheared suspensions are observed to start to form a continuous structure. Above t_{gel}, a sharp increase in suspension viscosity is commonly observed. The t_{gel} varies as a function of both temperature and solids concentration, The temperature effect provides valuable information for a better understanding of the restructuring behavior from an energy viewpoint. The influence of solids concentration, i.e., the t_{gel} decreased linearly with increasing solid concentration, suggests a stronger interparticle attraction that further accelerates flocculation. © *2000 Kluwer Academic Publishers*

1. Introduction

Colloidal processing has been recognized as an attractive technique for the fabrication of ceramic components with reliable and improved properties. However,, in the case of ceramic fabrication, the solids concentration in colloidal suspensions is usually high and the particles employed are relatively small in size, typically in a sub-micrometer scale. Under suitable conditions, these fine particles can collide and bind together to form a particle cluster over a wide variety of size distribution.

In a direct observation through the use of an optical microscope, Onoda [1] has shown that under weakly attractive conditions, colloidal particles can join together to form clusters of different sizes and a particle with fewer bonds seems to be more attractive than that with more bonds. Shih *et al*. [2] further proposed a reversible-growth model to predict the structure of particle clusters with different interparticle attractive energies. All these observations either from experiment or by computer simulation [3, 4] appear to suggest the fact that interparticle attraction plays a crucial role in particle network restructuring. For practical applications such as in ceramic processing, such restructuring would deteriorate the packing efficiency and finally give rise to microstructural inhomogeneities in both green and sintered compacts, resulting in poorer final properties. Therefore, the understanding of particle network restructuring in colloidal suspensions is relatively important both technologically and scientifically.

Relevant studies on the restructuring behavior in concentrated suspensions particularly for ceramic processing are not extensive. A recent experimental investigation was reported by Song *et al*. [5], who employed a ceramic suspension typically used for ceramic injection molding applications. They particularly stressed the importance of flocculation on structural integrity of the moulded artifacts during thermal treatment. They took the time of collision between two closely approached particles as the time of flocculation and calculated by means of a kinetic model based on either London attraction or Brownian movement. Although the basic assumption in their calculation is too ideal to be practically useful in real suspension systems, the suggestions based on their experimental observations for suspension preparation are important and encouraging.

The suspensions they employed are good examples for flocculation studies simply because a prolonged heat treatment (typically of a few days) is essentially required for removal of organic vehicles in ceramic injection-moulded artifacts, i.e., at the thermal debinding stage. Such a prolonged time duration allows a detailed investigation of the restructuring behavior under a variety of processing variable such as temperature and solids concentration. In fact, a better understanding of these processing variable on flocculation is critical not only for suspension preparation but also in providing an alternative strategy for binder removal [6].

It is generally recognized that the viscosity of flocculated suspensions can be reduced by breaking apart the connected particle network structure into smaller flow fragments. The viscosity behaviour of the suspension can thus be used as one of the parameters for the

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assessment of suspension microstructure. This has been further elucidated in a previous study [7] where the microstructural evolution (i.e., breakup mechanism) of a zirconia-wax suspension under different conditions of shear is quantitatively evaluated via a novel approach, by freezing the microstructure of the suspension after each shearing. The shear-induced change in suspension microstructure can further be characterized in terms of two important parameters, i.e., the relative viscosity (η_r) and the maximum packing density, ϕ_m, of the suspensions. Both η_r and ϕ_m are interrelated according to the previously-proposed viscosity model [8] which has he form:

$$\eta_\mathrm{r} = [a(\phi_\mathrm{m} - \phi)]^{-2} \tag{1}$$

where ϕ is the solids concentration and a is a suspension-dependent constant. Therefore, by analogy, it should be reasonable to use one of these parameters to evaluate the restructuring kinetics of the suspensions. In the current investigation, the viscosity term is selected simply because it offers a direct and easy way of measurement from experiments. More importantly, it offers a link between the restructuring kinetics and the structural parameter, ϕ_m, faciliating a further analysis on the microstructural evolution of a given suspension. This study, to our knowledge, may be the first practice on growth kinetics of particles networks in such a highly-concentrated suspension.

2. Resturcturing kinetics models

Kinetics of particle network restructuring in colloidal suspensions is essentially a study on the growth of particle cluster or simply on the kinetics of flocculation in colloidal suspension. The dynamic behaviour of particle clustering in suspensions as well as the resulting fractal structure of the growing cluster has received considerable interest [1–5, 9]. However, in view of the literature, many efforts have focused on dilute rather than concentrated systems [10] and the growth behaviour in dilute suspensions is frequently described by either a reaction-limited kinetics:

$$R = R_0 \exp(Ct) \tag{2}$$

where t is time, R is the characteristic cluster size, and C depends on experimental conditions, or a diffusion-limited kinetics:

$$R \approx t^{1/d} \tag{3}$$

where d is fractal dimension.

One common feature in these equations is relating the cluster size R as a principal physical parameter to the time (t). However, this may become practically difficult for concentrated colloidal suspensions, primarily because the so-called R can hardly be clearly identified with accuracy in these suspensions. This may be one of the primary reasons why the researchers like Song *et al*. [5] used the time of impact (t) between spherical particles of diameter d_0 separated by a distance x as a representation for flocculation kinetics.

Song and Evans [5] proposed a kinetic model based on London attractions for a highly-concentrated ceramic suspensions, which has a form of,

$$\alpha\frac{\mathrm{d}^2x}{\mathrm{d}t^2} + \beta\frac{\mathrm{d}x}{\mathrm{d}t} + \frac{\gamma}{x^2} = 0 \tag{4}$$

where

$$\alpha = \frac{\pi d_0^3 \rho}{6} \tag{5a}$$

$$\beta = 3\pi d_0 \eta_0 \tag{5b}$$

and

$$\gamma = \frac{A d_0}{24} \tag{5c}$$

The first term on the left-hand side of Equation 4 is a result of a net force between two approaching particles of density r, the second term represents the Stoke's law which indicates a resistive force on the particle moving with a velocity $\mathrm{d}x/\mathrm{d}t$ in a matrix fluid of viscosity η_0, and the third term is due to London attractions with an effective Hamaker constant (A).

However, their model in complex and can hardly be solved analytically. Most critically, Equation 4 essentially originated from a two-particle system that, as they indicated, can not give a precise description in a real, concentrated suspension system, i.e., a many-particle system. Therefore, for better description of the restructuring behaviour in a highly-concentrated suspension system, a new model to formulate the restructuring behaviour is required and this is the work intended to be achieved in this study. Furthermore, it is also expected that the new model has a simple form and most importantly, can be related to the viscosity model described in equation 1. The latter requirement is essentially an important consideration which allows microstructure evolution in suspensions during restructuring to be evaluated in a quantitative manner. With these considerations, a model is proposed which has a conventional differential form as that observed for most chemical reactions:

$$\frac{\mathrm{d}\eta_\mathrm{r}}{\mathrm{d}t} = kt^m \tag{6}$$

where η_r is the relative viscosity of any given suspension, k is ate constant and m is an exponent value which is determined experimentally. Here we formulate the restructuring kinetics as a function of the relative viscosity not only due to the η_r being an easily measurable property for colloidal suspensions but also representing a physically significant parameter in relation to the microstructure of suspension. The differential form of Equation 6 has to be determined via a correlation between η_r and t for a given suspension.

3. Experimental proccedures

Highly-concentrated suspensions containing 58–62 vol% of zirconia powder (Tosoh-3YS, Japan, having a mean diameter = 250 nm) and low-molecular-weight wax (Echo Chemicals, Inc. Taiwan, having a melting point = 55°C and an average molecular weight = 500) were prepared via a ball-milling route for 24 h in a toluene medium with high-purity zirconia balls as grinding media. Prior to mixing, the powder particles were coated with a monolayer of 12-hydroxystearic acid (Tokyo Chemicals Inc., Japan) having a specific adsorption of 1.6 mg/m^2. This dispersant has been realized to provide slightly attractive potential between particles [11] and a certain degree of flocculation in the model suspensions is expected.

The mixture were stir-dried and ground into small granules using a mortar and pestle. The zirconia-wax mixtures of about 3.5 gm were compression-moulded into a cylindrical specimen with dimensions of 10 mm × 10 mm under a pressure of 20 MPa at 55°C. This may ensure no residual pores inside the specimens. For the restructuring study, the specimens were first sheared under a constant shear force of 0.736 MPa and consolidated into identical geometry via an identical compression-moulded procedure. The re-consolidated specimens were annealed at temperatures from 85°C to 115°C with a time frame of few minutes up to 2400 min. The annealed specimens were then characterized using a capillary rheometer (Shimadzu, CFT-500, Japan) for viscosity measurement under a constant shear force of 0.367 MPa and the test temperature was kept at 85°C throughout the measurement. An average of five specimens of identical composition was used for each measurement. The error of the measurement is evaluated to be approximately 3%. A thermal gravimetric analysis (Netszch, model 401, German) was used to evaluate any loss of organic wax during the annealing especially at temperature of 115°C and the results showed no loss in wax content during the time period of thermal annealing, indicating no change in solids content.

4. Results and discussion

4.1. Temperature effect

The temperature effect on the restructuring behaviour for the suspensions with 60 vol% solid concentration is illustrated in a semi-logarithmic plot of Fig. 1 where the error bars represent the standard deviation of the measurements. The temperature ranges from 85°C to 115°C with 10°C intervals. The viscosity of the wax medium (η_0) at 85°C is about 0.027 Pa.s (determined via a cone-and-plate viscometer), a value used to compute the relative viscosity ($\eta_r = \eta_s/\eta_0$) of the suspensions. The semi-logarithmic correlation between the relative viscosity (η_r) and the time of annealing (t) for the model suspensions is determined by the solid lines based on a least-squares best-fitting approach. The restructuring kinetics equation is thus evidenced from this correlation, which can be expressed in a form of,

$$\eta_r = S\,\mathrm{bg}(t) + C \tag{7}$$

where S is the slope of the straight line and C, a constant depending on processing conditions. In comparison to Equation 6, it is clear that the exponent term, m, should take a value of -1 and the rate constant k has a value identical to value of the slope S, described in Equation 7.

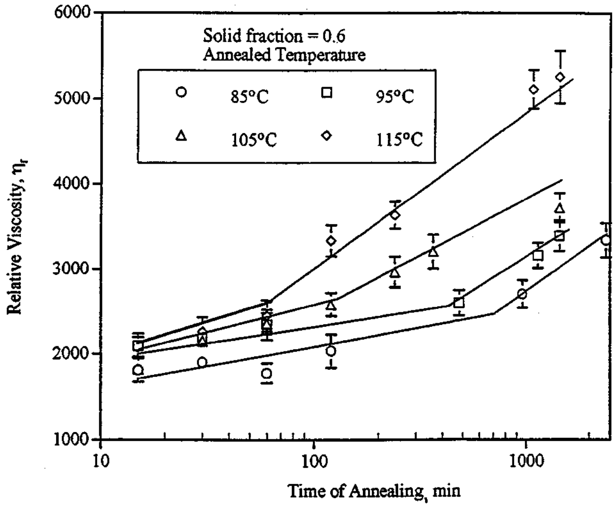

Figure 1 The relative viscosity of the model suspension with solid volume fraction = 0.60 as a linear function of log t, the time of thermal annealing at different temperatures.

Increase of the annealing time causes an increase in suspension viscosity. This is due primarily to the restructuring behaviour of the broken particle networks, a mechanism that is similar but operating in a reverse manner to that of network breakup mechanism [7, 12, 13]. The higher the annealed temperature results in a higher value of relative viscosity under identical time period of annealing. A more interesting finding is that a deflection point is commonly observed along the solid lines depicted in Fig. 1 at each temperature, for each composition as will be discussed in later section. The viscosity increases considerably when the time is increased over the corresponding deflection point. From the viewpoint of microstructure evolution, such a sharp increase in suspension viscosity at t_{gel} is suggested to be a result of the formation of connected particle networks. In other words, the deflection point can be defined as the gelling point at which the discrete networks start to interconnect with each other to form a continuous structure. Therefore, the time at the deflection point can be viewed as a gelling time, t_{gel}. A further increase in viscosity above t_{gel} suggests an increased degree of connectivity between the particle networks. Accordingly, such network connection would energetically proceed until an equilibrium point is reached where no or negligible change in viscosity can be expected. This, from an energy viewpoint, suggests a transition of network structure from a high-energy configuration (unstable structure) to a low-energy configuration (stable structure) as the thermal annealing proceeds, which will later be confirmed by an Arrhenius relation. A differential form of Equation 7 with respect to t gives,

$$\frac{d\eta_r}{dt} = \frac{S}{t} \tag{8}$$

which further reveals that the rate change in viscosity is reduced as the time of annealing proceeds until the

TABLE I The calculated t_{gel} and corresponding value of the relative viscosity (η_r) for the 60% suspensions at different temperatures. An average η_r is also tabulated

Temperature (°C)	t_{gel} (min)	η_r at t_{gel}
85	524	2285
95	432	2519
105	158	2700
115	41	2345
		Average = 2462 ± 108

value of t is sufficiently large where no appreciable change in $d\eta_r/dt$ will be observed.

Since the restructuring behaviour can be formulated according to Equation 7 over the time frame up to the entire range of the annealing period under investigation, the t_{gel} can be calculated by the value intercepted by these lines each corresponding to the time regimes below and above the t_{gel}. The resulting values of t_{gel} are determined and given in Table I, together with the relative viscosity at corresponding t_{gel}. It is interesting to note that the obtained η_r at t_{gel} has a roughly similar value of, on the average, 2462 ± 108 (where ± represents the standard deviation) for the given suspension. This average η_r at t_{gel} is likely to be independent of the annealing temperature, suggesting the resemblance of the resulting microstructure in the "annealed" suspensions.

The increased viscosity with annealed temperature indicates thermally-activated acceleration of network restructuring kinetics. Therefore, the network restructuring behaviour can be described in an energy sense and this is illustrated by an Arrhenius plot, as shown in Fig. 2, with the rate constant, i.e., the value of S in Equation 7, in terms of annealed temperature for the regimes below and above t_{gel}. Below t_{gel}, the restructuring energy ($E = 44$ kJ/mol) is higher than that above t_{gel} ($E = 13.4$ kJ/mol), which is in agreement with previous argument on microstructure restructuring, i.e., from high-energy configuration to low-energy configuration. By analogy, this energy concept may be used inversely to account for a breakup mechanism under shearing: part of the energy imposed by the shear force can be absorbed by bond breaking between two connected network structures. Since it is widely recognized that the interparticle attractions dominate the restructuring behaviour, some correlations between the interparticle attractive potential and the restructuring energy should exist and this will be discussed in a separated article.

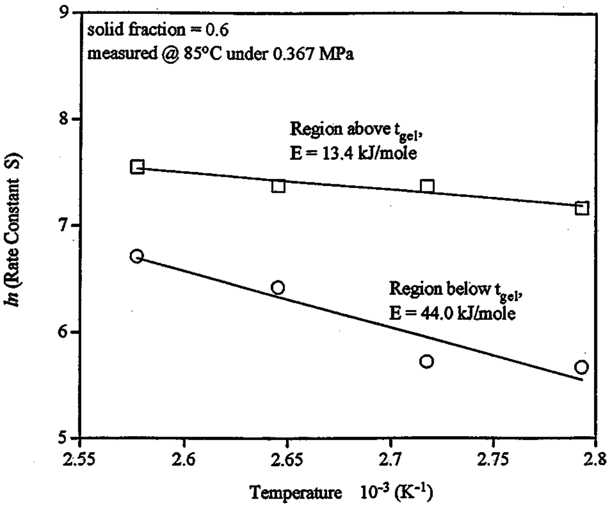

Figure 2 An Arrhenius relation for the model suspension of solid fraction = 0.60 at time regimes below and above the t_{gel}.

4.2. Solid concentration effect

The influence of solid concentration on the restructuring behaviour of the model suspensions is shown in Fig. 3 where the temperature of annealing was kept at 115°C. Similar correlation between η_r and $\log t$ is clearly shown for all ranges of solid concentration, 58%–62%, under investigation. The t_{gel} is clearly present and is given in Table II. The higher solid concentration leads to a lower value of t_{gel}, suggesting a faster rate of restructuring to form a connected network structure. This is reasonable because a greater solid concentration suggests a shorter distance between particles. According to the London attraction, the attraction force (F_{att}) between two particles separated by a surface-to-surface distance λ can be expressed by,

$$F_{att} = \frac{Ad_0}{24\lambda^2} \tag{9}$$

Equation 9 is identical to the third term on the left-hand side of Equation 4. Obviously, a lower value of

TABLE II The value of t_{gel} (min) of the model suspensions of different solids concentration (ϕ), together with the corresponding value of the relative viscosity (η_r) at t_{gel}

ϕ	t_{gel}	η_r at t_{gel}
0.58	75.2	810
0.60	40.7	2345
0.61	19.4	3445
0.62	12.3	8635

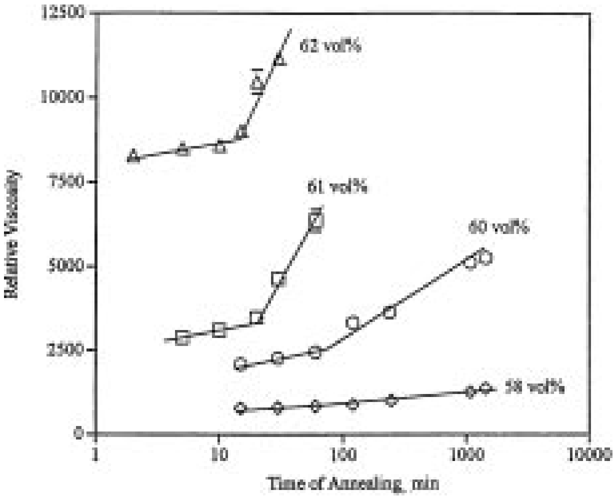

Figure 3 The relative viscosity of the model suspension as a linear function of log t, the time of thermal annealing at different solids concentration.

λ indicates a greater attractive force between the particles, suggesting a greater attractive potential for network restructuring [2]. If we defined the t_{gel} as a physically significant parameter representing the ability for restructuring, then it is possible to correlate t_{gel} as a function of the inverse square of interparticle distance, $1/\lambda^2$, a representation of F_{att} in identical system. Before this correlation can be performed, the interparticle distance λ should be accurately determined. Unfortunately, the determination of λ is complicated by the polydispersity as well as the geometry of the powder particles. In a recent paper by Agarwala *et al.* [13] who used an equation by modifying a computation model deduced from stereological technology [14] to calculate the surface-to-surface distance (l) of two identical spheres of radius r in a given suspension, which has a form related to the solid fraction (ϕ) by,

$$\lambda = \frac{4}{3} r \frac{1-\phi}{\phi} \tag{10}$$

However, this equation may be too optimistic to give a true representation of interparticle distance primarily because it averages the fraction of the entire matrix medium, i.e., the term $(1-\phi)$, over the fraction of all individual particles in a given suspension without considering the realistic particle packing configuration. That is, the particles are closely in contact when $\phi \rightarrow \phi_{\text{m}}$ and the value λ should approach 0 rather than some finite value based on Equation 10. In other words, the effective space for particles to move in a suspension is $(\phi_{\text{m}} - \phi)$ as previously defined [15, 16] rather than $(1-\phi)$. The value λ calculated from Equation 10 should certainly be an overestimated value. Therefore, by taking the concept of particle packing into account, Equation 10 can be re-written in terms of $(\phi_{\text{m}} - \phi)$, which gives,

$$\lambda = \frac{4}{3} r \frac{\phi_{\text{m}} - \phi}{\phi} \tag{11}$$

The ϕ_{m}, according to the previous study [8], has to be determined, particularly when the suspensions were pre-sheared before the kinetics investigation. By applying the viscosity model described in Equation 1, the fm can be determined by correlating the value of $1 - \eta_{\text{r}}^{-1/2}$ with respect to the solid concentration ϕ and the result is depicted in Fig. 4 where the "as-fabricated" defines the suspensions initially prepared without any pre-sheared treatment. The obtained fm under constant shear force of 0.367 MPa has a value of 0.6309 for the "as-fabricated" suspensions and increases to a value of 0.6424 after pre-sheared at 0.736 MPa. Obviously, the pre-sheared treatment modified the suspensions with an improvement of particle packing efficiency. This is consistent with the experimental results observed in a previous study [7].

The interparticle distance in the model suspensions can thus be calculated by using the values of $r = 125$ nm, $\phi_{\text{m}} = 0.6424$, and $\phi = 0.58$–0.62 for the pre-sheared suspensions through Equation 11. The calculated $1/\lambda^2$ is then plotted against tgel, as shown in Fig. 5.

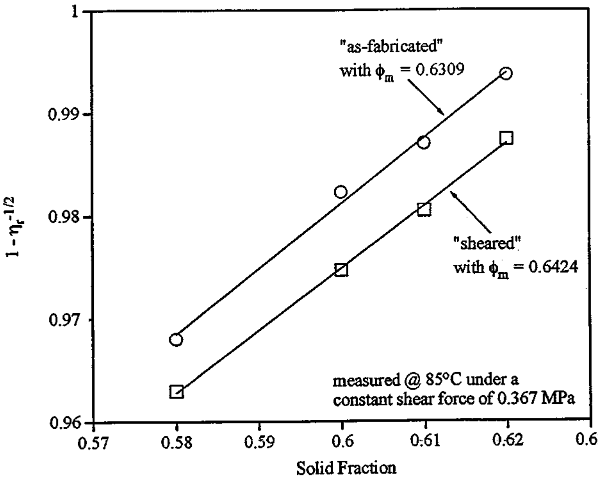

Figure 4 The linear $1 - \eta_{\text{r}}^{-1/2} - \phi$ correlation for the model suspensions before and after a pre-sheared treatment, showing different particle packing efficiency denoted by ϕ_{m}.

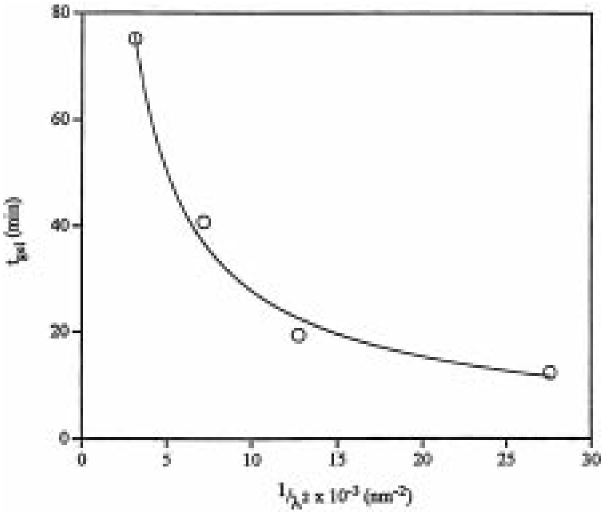

Figure 5 The gelling point, tgel, as an exponentially decreasing function of interparticle attractive force, representing by $1/\lambda^2$.

Interestingly, this curve can be well-fitted (with a correlation coefficient of 0.981) by a power law dependence as depicted by the solid curve. This strongly suggests that the restructuring ability of the flocculated suspensions can be decreased exponentially as the London attractive force decreased due to an increased separation between particles, e.g., by reduction of solid concentration.

For practical applications, especially those in fine ceramic fabrications, this restructuring behaviour could finally deteriorate ceramic properties to some significant extent, for instance, by introduction of defects such as voids and cracks. Therefore, it would be a critical issue if the restructuring behaviour can be inhibited by either creating repulsive potential between particles or reducing interparticle attraction to a negligibly small level. For the model suspensions, the latter approach is likely to be a plausible alternative. Since an interparticle attractive potential prevails in the model suspensions [11], according to Fig. 3, the potential can be reduced by a lower solid concentration and a decreased restructuring kinetics is expected. Therefore, the solid

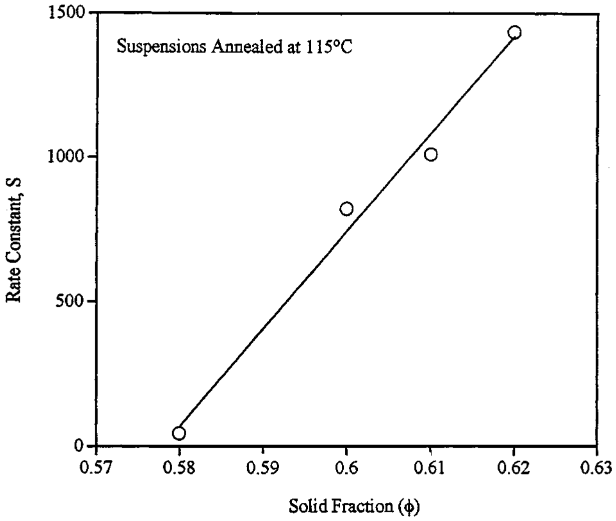

Figure 6 The rate constant for the restructuring kinetics as a linear function of solid concentration.

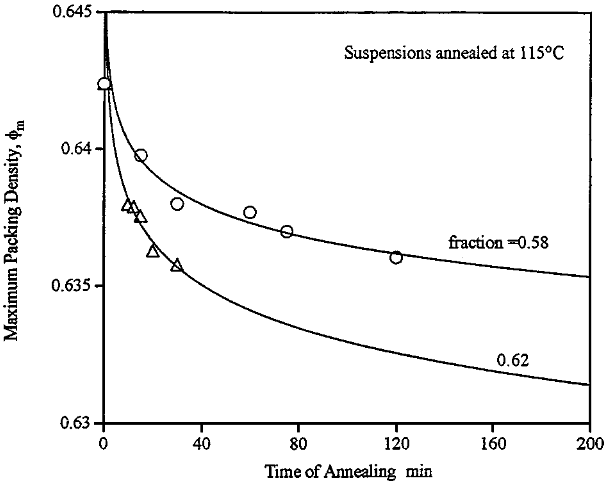

Figure 7 The maximum packing density shows as a function of the time of thermal annealing, representing a microstructure evolution map for the model suspensions. Increase in the annealing time causes a reduction in ϕ_m, indicating a reduction in particle packing efficiency.

concentration with a negligible restructuring kinetics can be obtained by plotting the solid concentration (f) in terms of the corresponding rate constant (S) over the regions below t_{gel}. Fig. 6 shows the resulting relation at an annealed temperature of 115°C. The correlation is nearly linear and by extrapolation of the line to $S \rightarrow 0$ yields $\phi = 0.578$ which is the maximum solid fraction that can be achieved with a negligible restructuring kinetics for current suspensions. This concentration suggests a microstructurally stable suspension that can be prepared from this model system and is believed to be suitable for ceramic fabrication.

4.3. Microstructure evolution during restructuring

During network restructuring, the particle packing efficiency would be reduced and this can be evaluated by examining the resulting maximum packing density, ϕ_m, as mentioned by Wildemuth *et al.* [17] and Liu [7]. By combining Equations 1 and 7, the ϕ_m on the restructuring can be calculated by means of Equation 12 with the measured η_r at different time periods of annealing,

$$\phi_m = \phi + \frac{1}{a}\left(\frac{1}{\eta_r}\right)^{1/2} \qquad (12)$$

where the value of a in Equation 12 is set to 0.6, approximately the slopes of the parallel lines in Fig. 4. By inserting the obtained ϕ_m at corresponding annealing time t, the map of microstructure evolution during restructuring can be constructed, as depicted in Fig. 7 (for clarity, solid fractions of 0.58 and 0.62 are selectively shown). It is clear that the particle packing efficiency is significantly reduced (a decreased ϕ_m) during the earlier period of annealing. This becomes particularly pronounced when the solid concentration is high. More importantly, it is conceivable, from the microstructure evolution map, that, if restructuring phenomenon is unavoidable in a given colloidal suspension, the reduction in solid concentration may be one critical strategy of maintaining a desired particle packing efficiency for subsequent processing. In fact, a proper temperature control offers an alternative strategy (e.g., Fig. 1) for a better microstructure manipulation in concentrated suspensions as those currently prepared.

5. Conclusion

The network restructuring behaviour of the model suspensions in the system of zirconia-wax mixture is investigated. A restructuring kinetic model is proposed which is capable of describing the restructuring behaviour of the model suspensions over a variety of temperatures and solids concentration. This proposed restructuring model allows the resulting particle packing efficiency to be predicted and this leads to a successful mapping for microstructure evolution during particle network restructuring.

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