

Rheological Analysis of the Gelation Behavior of Tetraethylorthosilane/Vinyltriethoxysilane Hybrid Solutions

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(Received 2 July 2001 • accepted 13 September 2001)

Abstract—The gelation behavior of tetraethylorthosilane (TEOS) sol in the presence of a silane coupling agent vinyltriethoxysilane (VTES) was investigated experimentally. Specifically, the gel time and gel structure were analyzed by the rheological multiwave test of Fourier transform mechanical spectroscopy (FTMS) for the mixtures of TEOS/VTES with various molar ratios at different temperatures. Gelation was accomplished through the sol-gel reactions of the silicon alkoxide TEOS in aqueous acidic solution. The results showed that, at elevated temperatures, the gel point was scattered and obscured by the noise in low frequencies owing to the enhanced thermal agitations. In this case, the statistical method was used to find the exact gel time. The activation energy of gelation and the gel exponent ranged from 25 to 30 kJ/mol and from 0.581 to 0.771, respectively, depending on the TEOS/VTES composition. The fractal dimension was estimated from the gel exponent and indicated the gel structure and that the TEOS/VTES solutions formed a relatively open and coarse gel structure.

Key words: Gelation Time, Sol-gel Chemistry, Multiwave Test, Fourier Transform Mechanical Spectroscopy, Gel Exponent

INTRODUCTION

Traditionally, synthesis of the coating materials and their processes has been undertaken by empirical trial and error methods due to the complexity of the flow and gelation behavior. However, these trial and error methods inevitably lead to high process and operation costs [Brinker and Scherer, 1992; Hench and West, 1990; Khan et al., 1989; Lee et al., 1999; Eu et al., 2000]. Clearly, a more systematic method is required, especially for the determination of a gelation point. Several studies have been carried out to measure the gel point [Power and Rodd, 1998; Orcel and Hench, 1998]. A simple measurement method by steady shear extrapolation has been used to determine the gel point of a polymeric gel by defining the gel point as the time at which its steady shear viscosity begins to diverge [Flory, 1953; Winter and Chambon, 1986; Oh et al., 1999b]. However, the detection of the gel point by steady shear test seems to be ambiguous and very difficult since it is based on an extrapolation as the shear viscosity diverges to infinity, as pointed out by Winter [1987]. This method has the following major disadvantages. First, the infinite viscosity can never be measured because of equipment limitations, and thus the gel time must be obtained by extrapolation. Second, shear flow may destroy or delay the network formation especially at high shear rates. Finally, the gelation may be confused with vitrification or phase separation as both the processes lead to an infinite viscosity [Halley and Mackay, 1996; Oh et al., 1999a].

Meanwhile, the crossover point of the storage and loss moduli $G'(\omega)$ and $G''(\omega)$ curves as a function of the frequency ω is a good estimate of the gel point of a gel transition material [Tung and Dynes, 1982]. However, it is only an estimate, because as the gel network

structure forms stress relaxation also occurs. Thus, unless measurements on the gelling system are made fast enough, the exact gel point will be obscured by changes due to the stress relaxation. As noted by Winter [1987], the crossover point is only valid for stoichiometrically balanced systems or those with excess hardener. According to Winter and Chambon [1986, 1987], a storage and loss moduli can be expressed as:

$$G' = \frac{G''}{\tan(n\pi/2)} = \frac{\pi S \omega^n}{2\Gamma(n)\sin(n\pi/2)} \quad (1)$$

in which S is the material strength constant related to the molecular flexibility, and n is the relaxation exponent (or gel exponent). For stoichiometrically balanced systems, n is 1/2. However, for stoichiometrically imbalanced gel systems of which n is greater than 1/2, the gel point occurs prior to the moduli crossover and detection is more difficult. Generally,

$$\tan\delta = \tan(n\pi/2) = G''/G' \quad (2)$$

is measured as a function of time for a given strain at a fixed frequency. This allows a convenient way to describe the kinetics of the gelation process but is obviously insufficient to characterize the viscoelastic behavior at every step of gelation process, particularly in the vicinity of the gel point. One of the main limitations of this technique is related to the experimental time that is needed for the viscoelastic characterization of the gelling system over a reasonable range of frequencies, particularly at low frequencies. Therefore, a more reliable method is needed in order to provide a description of the viscoelastic behavior in the frequency range of interest within measurement time scales much shorter than the time required for appreciable change in the structure of the system. One possible way is the use of Fourier transform mechanical spectroscopy (FTMS) developed by Holly et al. [1988]. In and Prudhomme [1993] conducted experiments using FTMS to characterize the gela-

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tion of zirconium alkoxide based ceramic precursors. In this method, a multiwave oscillatory strain is applied and the resulting stress is measured. The gel point is determined by taking several simultaneous multiwave frequency sweeps to measure $\tan\delta$ in the time scale of gelation. Analysis of the resulting stress wave form determined by FTMS of the multiply superimposed frequencies allows a means to describe the frequency dependence of the dynamic moduli, $G'(\omega)$, $G''(\omega)$, and $\tan\delta$. The multiwave test has an advantage that a response can be measured instantaneously as a function of the frequency, and thus the response is not influenced by the timescale of test as in the ordinary dynamic frequency sweeps. Because $\tan\delta$ is independent of the frequency at the gel point, the curves pass through a single point and unambiguously define the instant at which the gel forms. A simultaneous multiwave frequency sweep test is advantageous for testing a gel transition material that requires speedy testing because its structure may change during the test.

In the present work, the gel point of a hybrid coating solution of TEOS [(C₂H₅O)₄Si] and VTES [(C₂H₅O)₃Si(CH=CH₂)] was determined by the dynamic multiwave test of FTMS for various molar ratios at different temperatures up to 65 °C. Gelation proceeded by the sol-gel reactions in acidic aqueous solution. The gel point was uniquely determined by the multiwave test at room temperature. However, at relatively high temperatures, the gel point was scattered by low frequency data noise. In this case, the multiwave method in conjunction with a statistical treatment was used to predict the gel point unambiguously. In addition, glassy behavior was observed at high frequencies of up to 64 rad/s. The glassy behavior was strong compared to pure polymeric gels due to the rigidity of the silica network.

EXPERIMENTAL

The coating solution was prepared by mixing TEOS (Aldrich, 98%) and VTES (Shin Etsu Silicone, 96%) in ethanol (GR grade,

Merck) at a given molar ratio. The mixture was agitated with a magnetic stirrer for 3 minutes to ensure a homogenized state. Then, 0.08 mol of hydrochloric acid (HCl, Junsei) to each mol of alkoxide was added to the mixture to induce the sol-gel reaction. The hydrochloric acid was added into deionized water to control the molarity of acidic water. The molar ratios of ethanol and water to TEOS/VTES mixture were maintained at 1 and 2, respectively. After mixing for 30 minutes, the solution was kept in an incubator at various temperatures to investigate the temperature effect on the gelation time. For convenience, the gelling solutions of the binary mixture of TEOS/VTES were labeled with a prefix 'TV' next to which the number represented the composition of the constituent substances. For example, for the sample labeled as TV37, the molar ratio of TEOS to VTES is 3 : 7. If necessary, the temperature was specified as TV55C65 for which the gelation proceeded in the equimolar solution at 65 °C. Otherwise, the gelation occurred at room temperature.

The rheological behavior and the gel point of TEOS/VTES solutions were measured with ARES rheometer (Rheometrics) with no modification. The ARES rheometer is of rotational mode that is useful at relatively low strains. To measure the gel point, the dynamic multiwave test was carried out. In this method, an oscillatory small strain $\gamma(t)$ was imposed to the sample:

$$\gamma(t) = \sum_{i=1}^m \gamma_i \sin \omega_i(t) \quad (3)$$

in which m is the number of the superimposed harmonics, and γ_i and ω_i denote the amplitude and the frequency of the i -th harmonic, respectively. The frequencies of the harmonics were $\omega_n = 2^{(n-1)}\omega_1$ ($n=1, 2, 3, \dots, m$) with the fundamental frequency $\omega_1 = 1$ rad/s. In Fig. 1, typical small amplitude oscillatory strains imposed to the sample were plotted as a function of time for case F2 of $m=6$ with $\gamma_i=2\%$, and case F3 of $m=7$ with $\gamma_i=1\%$. Also included for comparison is the strain for case F1 of $\omega_1=1, 5, 10, 25$ rad/s with $\gamma_i=5\%$. As noted from Fig. 1, the maximum strain scaled by γ_i , i.e.,

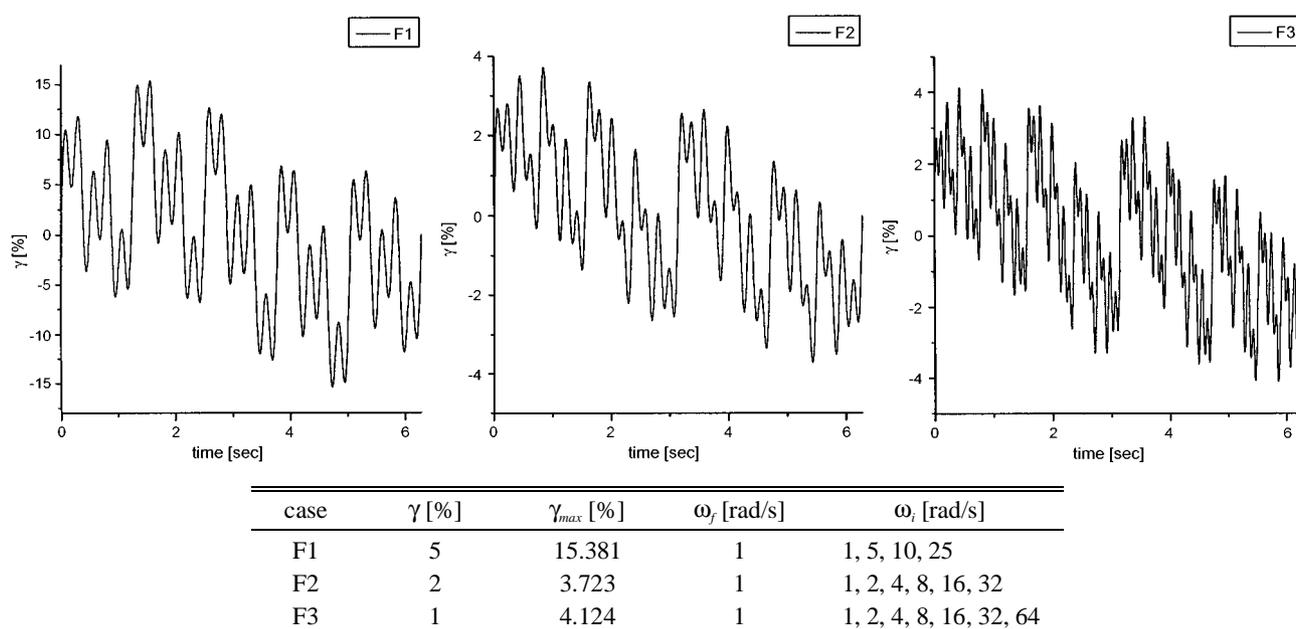


Fig. 1. Imposed small amplitude oscillatory strain as a function of time for three types of tests conducted in this study.

γ_{max}/γ_i was about 3.08 for case F1. Meanwhile, $\gamma_{max}/\gamma_i=1.85$ and 4.12 for cases F2 and F3, respectively. The shear stress response $\tau(t)$ was measured and decoupled by FTMS, which leads to the separate responses of individual frequencies.

$$\tau(t) = \sum_{i=1}^m (A_i \sin \omega_i t + B_i \cos \omega_i t). \tag{4}$$

Then, the loss tangent of a frequency ω_i is given by

$$\tan \delta(\omega_i) = \frac{B_i}{A_i}. \tag{5}$$

In addition, the gelation time and phase behavior were determined by visual observation. The gelation time was determined by a simple visual observation while the test tube was gently inverted upside down. The time when the sample stopped flowing was determined as the gelation point.

RESULTS AND DISCUSSION

In the present study, the sample was tested in the linear viscoelastic response regime. In Fig. 2, the complex viscosity was plotted as a function of the strain at different reaction times. As shown in Fig. 2, the linearity was preserved in the entire strain regime before the gel point. However, after the gel point, the linearity was not valid when the strain exceeded 100%. To ensure the linearity, all experiments were carried out below $\gamma=10\%$. Also noted was that initially the complex viscosity was increased gradually with time due to the continuous growth of polysilicate species. This is analogous to a particle suspension of which the suspension viscosity increases smoothly with the particle loading in the dilute or semi-dilute regime. As the condensation reactions proceeded, the polysilicate species grew in size and the particle-particle interactions became pronounced. As time approached the gel point, the complex viscosity increased rapidly and the nonlinear feature was observed at high strains.

As mentioned earlier, the exact gelation time can be determined from the multiwave method in which the decoupled loss tangent for each constituent harmonic is plotted as a function of time. The

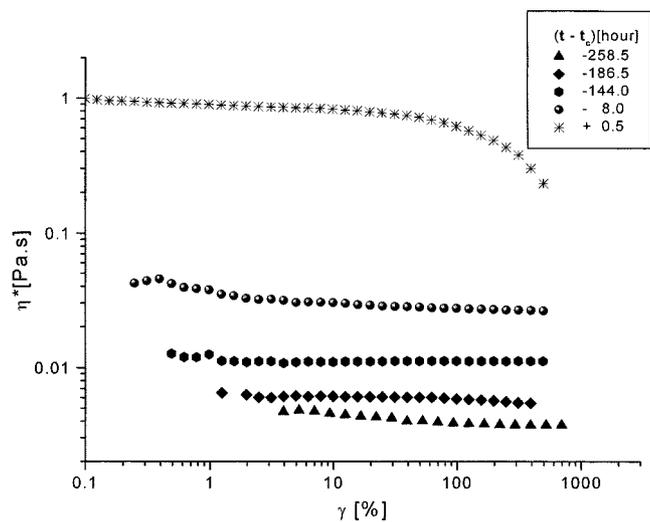


Fig. 2. Complex viscosity of sample TV37C25 as a function of the strain at $\omega=10$ rad/s for various reaction times.

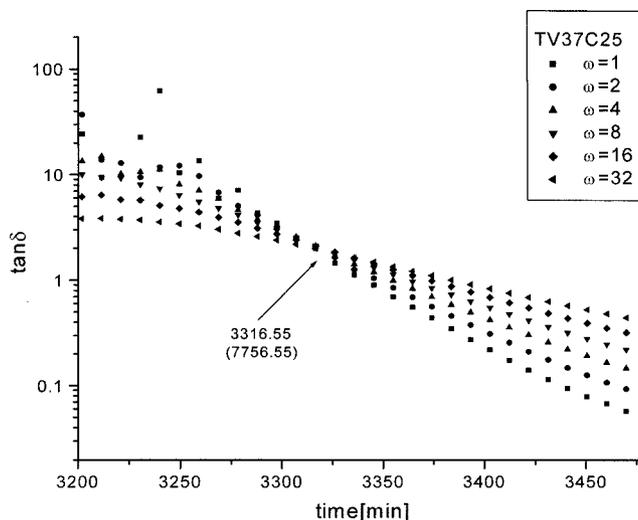


Fig. 3. Loss tangent of sample TV37C25 as a function of time obtained from the multiwave test.

result was reproduced in Fig. 3 for sample TV37C25. If the proposed method works out, the loss tangents for all frequencies are identical at the gel point, which is solely a material property. Indeed, the loss tangent $\tan \delta$ vs. time curves for various frequencies determine uniquely the gel point since the loss tangent is independent of the frequency at the gel point. In Fig. 3, the measured gelation time was 3,316 min. However, the real gelation time was 7,756 min because the sample was aged for 4,440 min before the rheological test.

A number of prior studies have suggested that the gel point occurs at the crossover point of the loss and storage moduli [Tung et al., 1982]. To confirm their suggestion, the loss and storage moduli of sample TV37C25 were plotted as a function of time for two different frequencies $\omega=1$ and 32 rad/s in Fig. 4. As expected, the loss and storage moduli increased with time. Moreover, the storage modulus grew more rapidly and crossed over the loss modulus as the

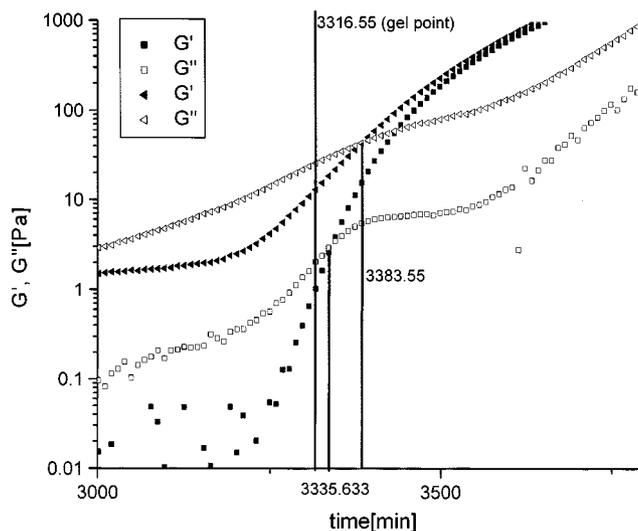


Fig. 4. Storage and shear moduli of sample TV37C25 as a function of time. Rectangles for $\omega=1$ rad/s and triangles for $\omega=32$ rad/s.

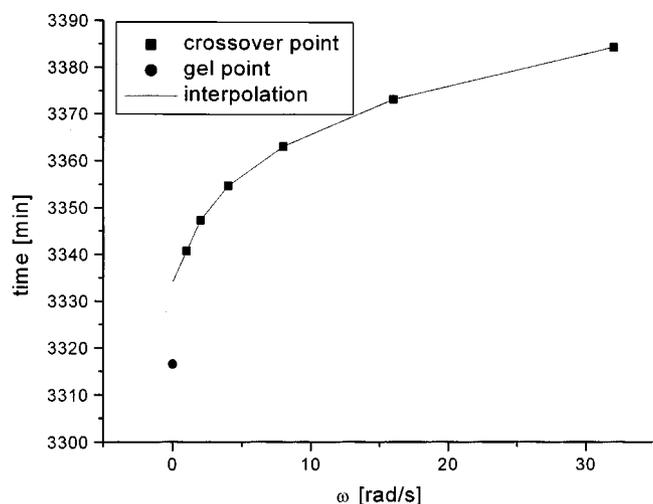


Fig. 5. Crossover point of the storage and loss moduli as a function of the frequency for sample TV37C25.

gelation started at a certain time. It can be easily seen, however, that the crossover point was dependent upon the frequency and occurred earlier at lower frequencies [Argen and Rosenholm, 1998]. Specifically, the crossover points were 3,336 min and 3,384 min for $\omega=1$ and 32, respectively. Although close to the gel point, the crossover point is not identical with the real gelation time. This is because the gelation point is strictly a material property and cannot depend on the frequency of the small amplitude dynamic rheological test. It is noteworthy that at the gel point, the loss tangent is greater than unity. This indicates that the crossover point of G' and G'' occurs prior to the real gel point. The increase in the loss and storage moduli beyond the gel point observed in Fig. 4 implies that the gel structure is solidified as suggested by Hodgson and Amis [1991]. Since the crossover point approaches the real gel point as the frequency decreases, the gel point can be predicted from the gel point in the limit of $\omega \rightarrow 0$. To do this, the crossover point of sample TV37C25 was plotted as a function of the frequency in Fig. 5. As noted, the crossover point approached asymptotically the gel point estimated from the multiwave method. Therefore, the extrapolation of the crossover point in the limit of $\omega \rightarrow 0$ provided successfully the gel point.

The gel point has been considered as a point at which the viscosity begins to increase abruptly. In Fig. 6, the complex viscosity of TV37C25 was plotted as a function of time for various frequencies. As expected, the determination of the gel point from the complex viscosity was ambiguous. It can be noted from Fig. 6 that the complex viscosity began to increase rapidly near the gel point, but the starting point of the rapid increase was not unique and depended upon the frequency. However, as the frequency became lower, the gel point predicted from the complex viscosity was closer to the real value from the loss modulus. Thus, the complex viscosity exhibited a trend consistent with the crossover point of the storage and loss moduli.

Rude et al. [1996] proposed a modified multiwave method to determine gel point unambiguously by treating the scattered data statistically. The statistical method is needed because the multiwave test is intrinsically a superposition of discrete experimental data. In the statistical method, the gel point can be determined without error by taking a time at which $\log(s/\langle \tan \delta \rangle)$ is minimum. Here, $\langle \tan \delta \rangle$

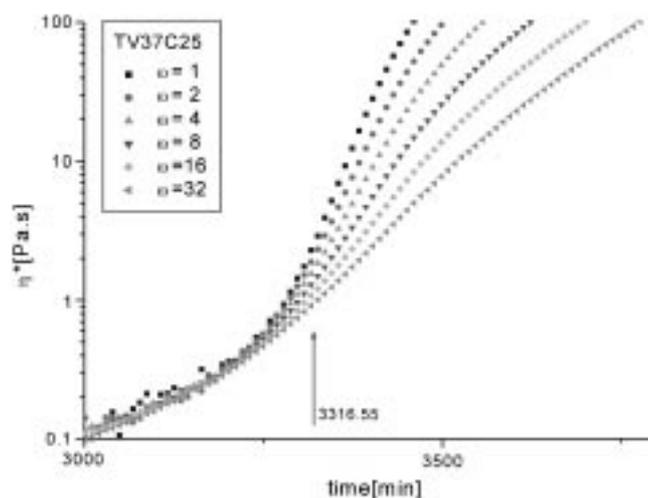


Fig. 6. Complex viscosity of sample TV37C25 as a function of time for various frequencies.

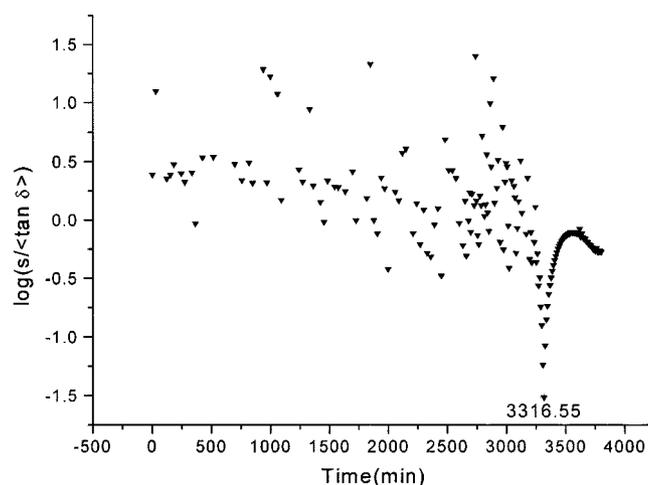


Fig. 7. Statistical variable $\log(s/\langle \tan \delta \rangle)$ of sample TV37C25 as a function of time. $\omega_n = 2^{(n-1)}$ rad/s ($n=1, 2, \dots, 6$).

and s denote the mean value and standard deviation of $\tan \delta$ respectively. This is physically reasonable because the loss tangent is a material quantity and should be unique independently of the frequency. Therefore, it is expected that, although the raw data are scattered, the standard deviation of the loss tangent should be minimum at the gel point. Indeed, as noted from Fig. 7 in which $\log(s/\langle \tan \delta \rangle)$ of sample TV37C25 was plotted as a function of time, the minimum point of the statistical variable was well coincident with the gel point.

To investigate the temperature effect on the gelation of TEOS/VTES hybrid solutions, the multiwave method was applied for the samples prepared at 35 °C and 45 °C, i.e., samples TV37C35 and TV37C45, respectively. As previously observed, the gel point by the simple multiwave test could be uniquely determined at 25 °C. In Figs. 8a and 8b, the loss tangents of samples TV37C35 and TV37C45 were plotted as a function of time. The gelation was facilitated as the reaction temperature was elevated because of the difference in the hydrolysis and condensation rates of sol-gel reaction. As noted, the gel point was scattered and obscure at elevated tem-

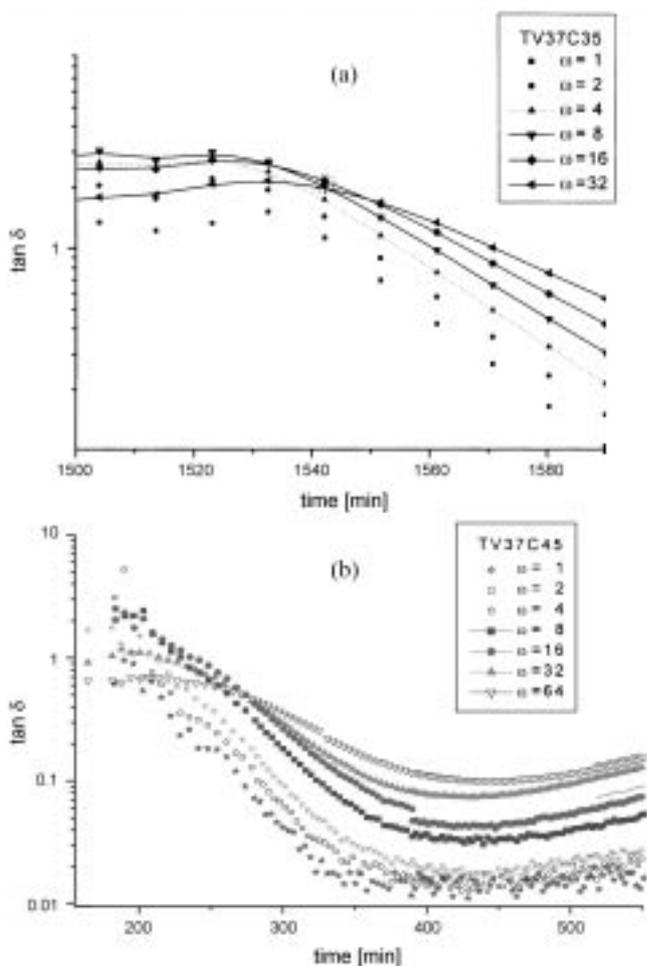


Fig. 8. Loss tangent of sample TV37 as a function of time at two different temperatures. (a) at 35 °C, (b) at 45 °C

peratures, by the noise in the low frequencies, which was due to the problem in treating discrete data. The low frequency noise was induced by the enhanced thermal fluctuations. Nevertheless, the gel points could be obtained approximately from Figs. 8a and 8b and the resulting gel points of TV37C35 and TV37C45 were around 1,540 min and 220 min, respectively. Therefore, at elevated temperatures, it is essential to use the statistical method. By plotting the statistical variable $\log(s/\langle \tan \delta \rangle)$ as a function of time, the gel points were found uniquely as 1,533 min and 216 min at 35 °C and 45 °C, respectively. It is noteworthy that the loss tangent is reduced continually after the gel structure is formed, i.e., the rate of increase of the storage modulus is faster than that of the loss modulus. This implies that the networking of the gel structure occurs continually beyond the gel point.

The gel point t_{gel} is related to the activity energy by the following equation [Raghavan, 1997]:

$$\text{Int}_{gel} = E/RT + \text{constant} \quad (6)$$

in which t_{gel} is the gelation time and E is the overall activity energy, which includes the activation energy in the hydrolysis, condensation, and diffusion process. In our preceding study, the gelation time was measured as a function of the composition of VTES/TEOS at

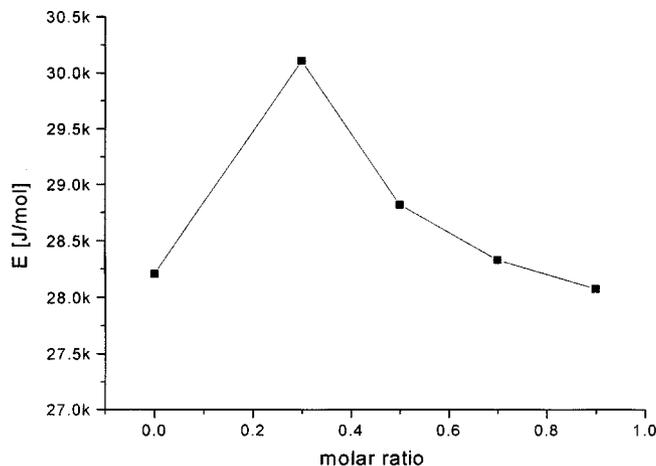


Fig. 9. Activation energy as a function of the molar ratio of VTES.

various temperatures [Kim et al., 2001]. Although the raw data was not reproduced here, the linear relationship (6) between Int_{gel} and E was valid in the present system. Therefore, Eq. (6) provides a good estimation of the activation energy. In Fig. 9, the activity energy was illustrated as a function of the VTES content. The activity energy ranged from 25 to 30 kJ/mol for the entire range of the VTES content. When the molar ratio of TEOS/VTES was 7 : 3 (i.e., for sample TV73), the activity energy was largest. The maximum activation energy of sample TV73 implied the minimum gelation time or the formation of the most dense gel structure for sample TV73 [Kim et al., 2001]. Indeed, as we shall see shortly, the fractal dimension of sample TV73 is largest, which is indicative of the formation of the most dense gel structure.

A number of researches have been conducted to relate the gel exponent n to the gel structure [Agren and Rosenholm, 1998; Chambon and Winter, 1987; Durand et al., 1987; Mours and Winter, 1996; Muthkumar, 1989; Raghavan et al., 1996]. The gel exponent is simply calculated from the gel point by (2) as $n = 2\delta/\pi$ since we have found the loss modulus $\tan \delta$ from the multiwave method. In Table 1, the gel exponent predicted from the multiwave method is listed for various molar ratios of TEOS/VTES. As shown in Table 1, the gel exponent ranged from 0.561 to 0.771 and displayed a local minimum when the molar ratio of TEOS/VTES was around 7 : 3. The gel exponent predicted from the multiwave method was very close to 0.67 of the percolation theory [Stauffer, 1985]. According to the percolation theory, the fractal dimension d_f and the gel exponent are related by

$$n = \frac{d}{d_f + 2} \quad (7)$$

Table 1. Predicted gel exponents and fractal dimensions

Sample	n	D_f [Eq. (7)]	D_f [Eq. (8)]
TEOS	0.581	3.16	1.90
TV73	0.561	3.34	1.92
TV55	0.654	2.59	1.80
TV37	0.733	2.09	1.69
VTES	0.771	1.89	1.64

in which d is the physical dimension of the gel structure, i.e., $d=3$ for a 3-D structure. Meanwhile, Muthkumar [1989] developed the relationship between the fractal dimension and the gel exponent as

$$n = \frac{d(d+2-2d_f)}{2(d+2-d_f)} \quad (8)$$

by considering the excluded volume effects in the course of cross-linking. For a rigid spherical aggregation with no void fraction the fractal dimension would be $d_f=3$. However, for the real gels, the fractal dimension should be less than 3. In Table 1, the fractal dimensions calculated from (7) and (8) were included. Since $d_f < 3$ the fractal dimension predicted from (8) reflects the gel structure more realistically than the percolation theory. The predicted fractal dimension from (8) is in the range of 1.64-1.92, which is relatively small. Consequently, this small value of d_f is indicative of the formation of a relatively open and coarse gel structure. This is because the cluster-cluster growth mechanism is prevalent in acid condition. It is also worth pointing out that the fractal dimension becomes largest when the molar ratio of TEOS/VTES is 7 : 3. As we discussed previously, at this particular composition, the activation energy is maximum or the gel exponent is minimum. Therefore, the gel structure of TV73 is most densely formed.

SUMMARY

The gelation point and gel structure of the hybrid solutions of TEOS/VTES were considered by examining the dynamic rheological behavior. The multiwave small strain oscillations determined the gel point unambiguously at room temperature. However, at elevated temperatures, the low frequency noise caused by thermal fluctuations led to the scattered gel point and a statistical approach was needed. As expected, the multiwave method in conjunction with the statistical treatment showed that the gel point was reduced significantly with temperature. The gel exponent and activation energy were calculated from the multiwave rheological data for various molar ratios of TEOS/VTES. The result showed that the activation energy exhibited its maximum when the molar ratio was around 7 : 3. At this composition, the solution formed the most dense gel structure. This was consistent with the fractal dimension that was related to the gel exponent predicted from the multiwave method. The fractal dimension showed that the gels formed in TEOS/VTES solutions had relatively open and coarse structure. The general feature of the gelation behavior examined by the rheological responses was in qualitative agreement with the visual observations, although the gel point in the multiwave method was a little shorter than that of the visual observation. This was due to the inevitable evaporation during the multiwave test.

ACKNOWLEDGMENT

This work has been supported partially by a grant from the Korea Science and Engineering Foundation. The authors appreciate also a partial support from the Brain Korea 21 Project.

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