

## CHAPTER IX

### VISCOELASTIC PROPERTIES OF CERIA GELS

#### **Abstract**

The viscoelastic behaviors of different ceria gelling systems prepared through sol-gel transition were investigated by the rheological measurement. The gelation time was observed by the frequency independence of  $\tan\delta$ , and increased with increasing acid:alkoxide molar ratio. At the gel point, both storage and loss moduli ( $G' \propto \omega^n$ ,  $G'' \propto \omega^n$ ) exhibited a power law dependence of applied frequency with  $n' = n'' = n$ . The viscoelastic exponents and gel strength parameter were dependent on the composition of system. The increase in HCl:alkoxide molar ratio increased the  $n$  value while decreased the S parameter.

**Keywords:** Cerium glycolate, Cerium dioxide, Complex viscosity, Rheology and Sol-gel process.

## INTRODUCTION

The most significant oxide of rare earth elements in industrial catalysis as structural and electronic promoters in order to improve the activity, selectivity and thermal stability of catalysts is certainly CeO<sub>2</sub>. Specifically, CeO<sub>2</sub> has potential uses for the removal of soot from diesel engine exhaust, for the removal of organics from wastewaters (catalytic wet oxidation), and as a promoter of catalysts in environmental clean-up, fuel cell technologies, and well-established industrial processes such as FCC, TWCs, and ethylbenzene dehydrogenation, where CeO<sub>2</sub> is a key component in catalyst formulation[1-4].

To improve the catalytic properties, the increasing of specific surface area with homogeneous distribution of particle is required. For the last two decades, the sol-gel processing has become one of the successful techniques for preparing metallic oxide materials [5]. Sol-gel processing of metal alkoxides offers various possibilities for obtaining tailor made materials [6]. Two of the important sol-gel parameters are the hydrolysis ratio, defined as the number of moles of water per mole of precursor used, and the amount and type of catalyst used [7].

Although much of the work done to characterize the sol-to-gel transition has used spectroscopic techniques, most of these techniques do not provide information about molecular weights. On the other hand, rheological measurements are sensitive to the structural and textural evolution of gels and are complementary to spectroscopic experiments. Knowledge of the evolution in rheological properties during sol-gel processing is a useful guide to the manufacturer when formulating dispersion to optimize the physical properties required in the final product [8]. Thus, in this work, the objective is to study the rheological properties of cerium glycolate complex synthesized directly from inexpensive and widely available cerium hydroxide and ethylene glycol via the Oxide One Pot Synthesis (OOPS) method. The influence of the acid concentration used in acid-catalyzed hydrolysis is investigated.

## EXPERIMENTAL

### Materials

Cerium (IV) hydroxide ( $\text{Ce}(\text{OH})_4$ ) containing 87.4%  $\text{CeO}_2$  as determined by TGA were purchased from Aldrich Chemical Co. Inc. (USA) and used as received. Ethylene glycol (EG) was purchased from Farmitalia Carlo Erba (Barcelona) and purified by fractional distillation under nitrogen at atmospheric pressure,  $200^\circ\text{C}$  before use. Sodium hydroxide was purchased from Merck Company Co., Ltd. (Germany) and used as received. Triethylenetetramine (TETA) was purchased from Facai Polytech. Co., Ltd. (Bangkok, Thailand) and distilled under vacuum (0.1 mm/Hg) at  $130^\circ\text{C}$  prior to use. Methanol and acetonitrile were purchased from Lab-Scan Company Co.Ltd. and purified by standard techniques. Hydrochloric acid solution (HCl) were diluted with deionized water at various concentrations

### **Instruments**

Fourier transform infrared spectra (FT-IR) were recorded on a VECOR3.0 BRUKER spectrometer with a spectral resolution of  $4\text{ cm}^{-1}$  using transparent KBr pellets containing 0.001 g of sample mixed with 0.06 g of KBr. Thermal gravimetric analysis (TGA) was carried out using a Perkin Elmer thermal analysis system with a heating rate of  $10^\circ\text{C}/\text{min}$  over  $30^\circ\text{--}800^\circ\text{C}$  temperature range. The mass spectrum was obtained on a Fison Instrument (VG Autospec-ultima 707E) with VG data system, using the positive fast atomic bombardment mode ( $\text{FAB}^+\text{-MS}$ ) with glycerol as the matrix, cesium gun as initiator, and cesium iodide (CsI) as a standard for peak calibration.

### **Methodology**

#### ***Preparation of Cerium Glycolate***

Preparation of cerium glycolate complex was duplicated from previous work. A mixture of 5 mmol (1.04 g) cerium hydroxide ( $\text{Ce}(\text{OH})_4$ ), 18 mL of ethylene glycol(EG) and 5 mmol (0.73 g) triethylenetetramine (TETA) with sodium hydroxide (NaOH) at about 12 mole percent equivalent to cerium hydroxide were mixed, magnetically stirred, and heated to the boiling point of ethylene glycol for 18 hours under nitrogen to distill off ethylene glycol with removal of water liberated from the reaction. The reaction mixture was cooled overnight under nitrogen. The product was filtered and washed with acetonitrile (3x15 mL), followed by drying under vacuum. The precursor obtained was identified using TGA and FTIR.

FTIR: 2939 and 2873  $\text{cm}^{-1}$  ( $\nu$  C-H), 1080  $\text{cm}^{-1}$  ( $\nu$  Ce-o-C), and 550  $\text{cm}^{-1}$  ( $\nu$  Ce-o).  $^1\text{H}$  NMR spectra of product recorded in deuterated DMSO : 3.4 ppm assigned to chelated glycolate ligands. TGA : one transition at 400 C and the percentage ceramic yield is 65.9.

### ***Rheological study of cerium glycolate***

The rheometric measurements were conducted using an ARES rheometer with parallel plate geometry, 25 mm in diameter. The storage ( $G'$ ) and loss ( $G''$ ) moduli were determined using oscillatory shear at frequencies in the range 0.2-6.4 rad/s. The strain amplitude was small enough to ensure that all experiments were conducted within the linear viscoelastic region, where  $G'$  and  $G''$  are independent of the strain amplitude. cerium glycolate 0.026 g was hydrolyzed in different HCl:alkoxide molar ratios of 0.8, 0.9, 1.0 or 1.1 and at constant water at 50 molar. The hydrolysis temperature was selected to be 30°C. The mixtures were stirred until homogeneous before being transferred to the rheometer.

## **RESULTS AND DISCUSSION**

From the rheological study of different ceria gelling system, the effects of different HCl:alkoxide molar ratio 0.8, 0.9, 1.0, and 1.1. on the rheological properties of systems have been investigated. The gelation time ( $t_g$ ) can be determine by employing the well established criterion of gelation, proposed by Winter and co-workers [9]

$$\text{Tan}\delta = G''/G' = \tan(n\pi/2) \text{ or } \delta = n\pi/2 \quad (1)$$

at a frequency-independent value of  $\text{tan}\delta$  obtained from a multifrequency plot of  $\text{tan}\delta$  versus gelation time (figure1). The result indicate that  $t_g$  value increases as a function of amount of acid because the larger amount of acid not only hydrolyze but strongly inhibit the condensation process, thus the network cannot form so easily cause the hydrolysis rate become larger than condensation rate. From the comparison with an alternative method to determine the gel point by plotting the viscoelastic exponent  $n'$  and  $n''$

$$G'(\omega) \propto G''(\omega) \propto \omega^n \quad (2)$$

the gel point is observed at a crossover where  $n = n' = n''$  [10]. Figure 2 shows an example at HCl:alkoxide molar ratio 0.9. The crossover of  $n'$  and  $n''$  is at 868 s which is equal to the gelation time from the plot of  $\tan\delta$ .

The different stages of the critical moments near the gelation were observed by the plot between  $G', G''$  (Pa) with  $\omega$  (rad/s) at pregel stage, gel point, and postgel stage as figure 3. For all investigation the  $G'$  ( $\omega$ ) are greater than  $G''$  ( $\omega$ ) because of the colloidal system which the solidlike behavior become predominant since the initial stage. As is well known both  $G'$  and  $G''$  could exhibit a power-law dependence on applied frequency, at gel point ( $t_g$ ) and  $G'$  and  $G''$  were parallel [11-15].

The effect of HCl:alkoxide molar ratio on the gel strength,  $S$ , is shown in figure 4. The gel strength increase slightly from 0.8 to 1.0 molar ratio and then decrease dramatically at 1.1 molar ratio. The investigation can suggest that the  $S$  parameter increase with the increasing of the cross-link and entanglement [11]. The viscoelastic exponent increase as the increasing of acid ratio roughly located in the range 0.1-0.2 (table 1). The result suggests that the viscoelastic exponent depends on the acid concentrations and at higher crosslink density will probably reduce the value of  $n$ . The different viscoelastic exponents reflect different structures at the sol-gel transition point [13]. The connection between the fractal dimensions and the viscoelastic exponents as equation described by Muthukumar [16]

$$n = d(d+2-2d_f)/2(d+2-d_f) \quad (3)$$

which  $n$  = viscoelastic exponent,  $d$  = space dimension, and  $d_f$  = fractal dimension show that the value of  $n$  depends also on the fractal dimension, i.e. also on cluster structure. The estimation of fractal dimensions are calculated because the scaling exponents do not have a direct physical meaning. The connection between the viscoelastic exponents and fractal dimensions is justified because the value for viscoelastic exponent comes from the spanning cluster under stress that is dependent on the polymer structure [16]. The value of fractal dimension as table 1 decrease with the decreasing of  $n$  value and the increasing of acid ratio indicated that the incipient gel with high values of the relaxation exponent have low fractal dimensions are open structure and gel with lower  $n$  values have higher fractal dimensions are tight structure [13,17]. The effect of the frequency of oscillation on the complex viscosity

( $\eta^*$ ) of 0.9 molar ratio is given in figure 5. At pregel stage, the complex viscosity is lowest which at gel point and postgel stage the  $\eta^*$  are increased and have similar values. The complex viscosity decreased as increasing the frequency (rad/s) and the general pattern of behavior of  $\eta^*$  is similar at all conditions.

## CONCLUSIONS

From the rheological study of different ceria gelling system HCl:alkoxide molar ratio 0.8,0.9,1.0, and 1.1, the viscoelastic properties were investigated. As evaluated by Winter et al., the gelation time increases as increasing of HCl:alkoxide molar ratio. The gel strength increases as a function of acid ratio and the fractal dimension determined from the frequency scaling exponent of the modulus at the gel point indicates a tight structure at low acid ratio.

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Table 9.1 The summary of the result of viscoelastic exponent ( $n$ ), fractal dimension ( $d_f$ ), and gelation time at different HCl:alkoxide molar ratio

<b>Acid:alkoxide (molar ratio)</b>	<b><math>n</math></b>	<b><math>d_f</math></b>	<b>Gelation time (s)</b>
0.8	0.1389	2.3786	868
0.9	0.1411	2.3766	931
1.0	0.1560	2.3628	1182
1.1	0.2431	2.2795	5206



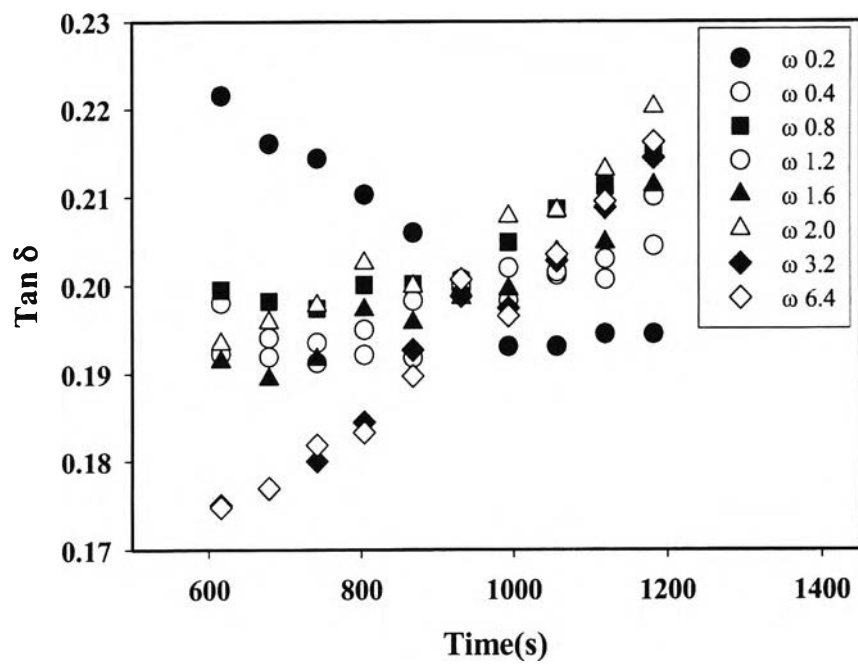


Figure 9.1 The plots of  $\tan \delta$  with time(s) at HCl:alkoxide molar ratio 0.9.

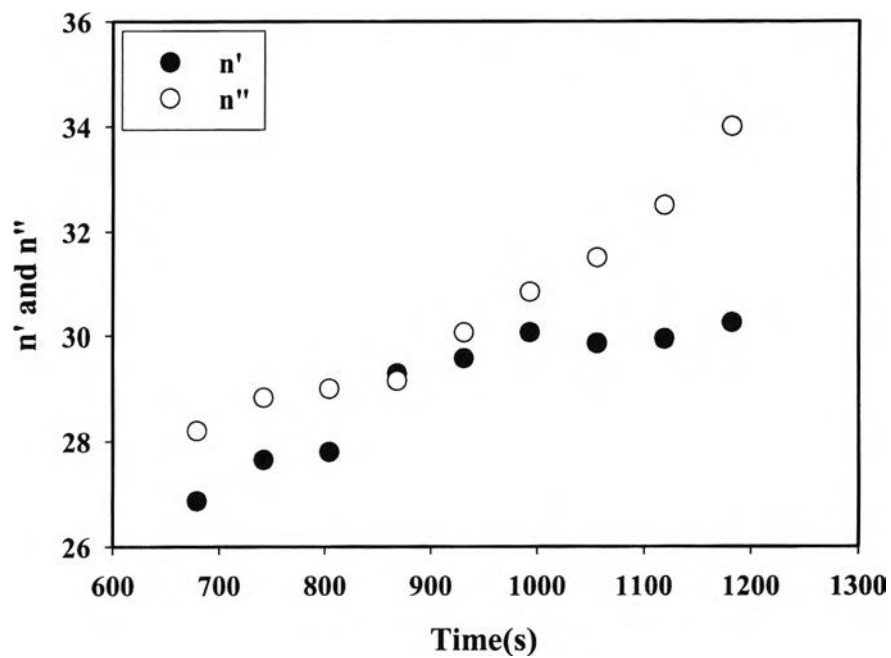


Figure 9.2 The plot of the apparent exponents, the storage moduli ( $n'$ ) and the loss moduli ( $n''$ ) during the course of gelation for the HCl:alkoxide molar ratio 0.9.

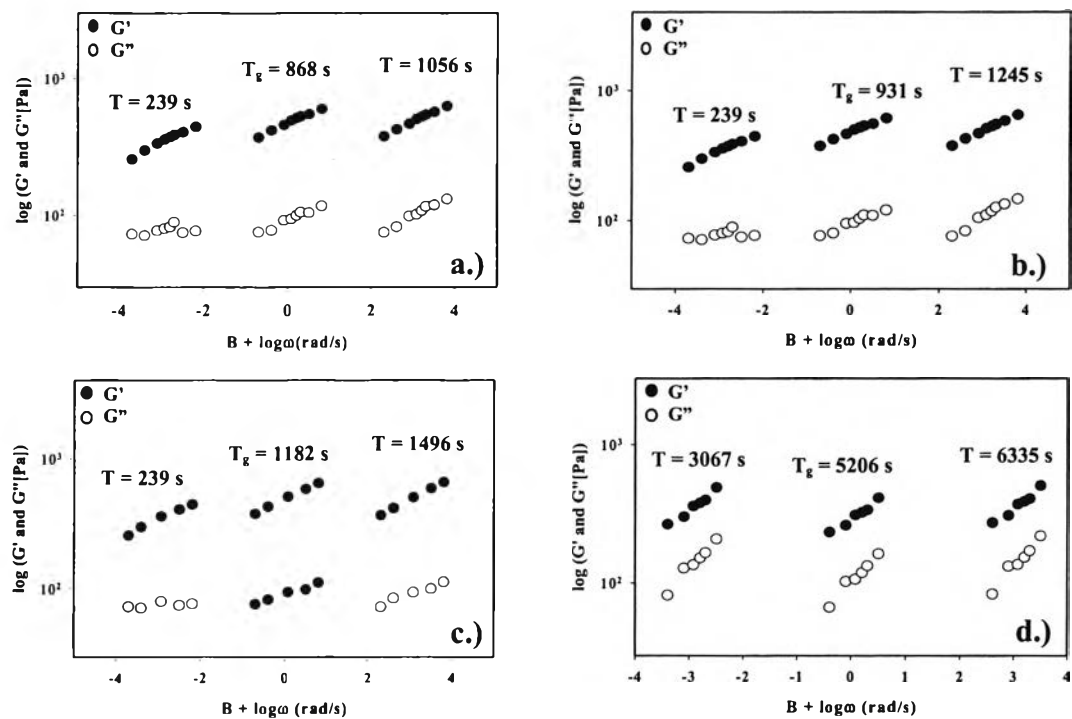


Figure 9.3 The frequency dependence curves of ( $\bullet$ )  $G'$  ( $\omega$ ) and ( $\circ$ )  $G''$  ( $\omega$ ) at pregel stage ( $B = -3$ ), gel point, and ( $B = 0$ ), and postgel stage ( $B = 3$ ): a.) 0.8, b.) 0.9, c.) 1.0, and d.) 1.1 molar ratio.

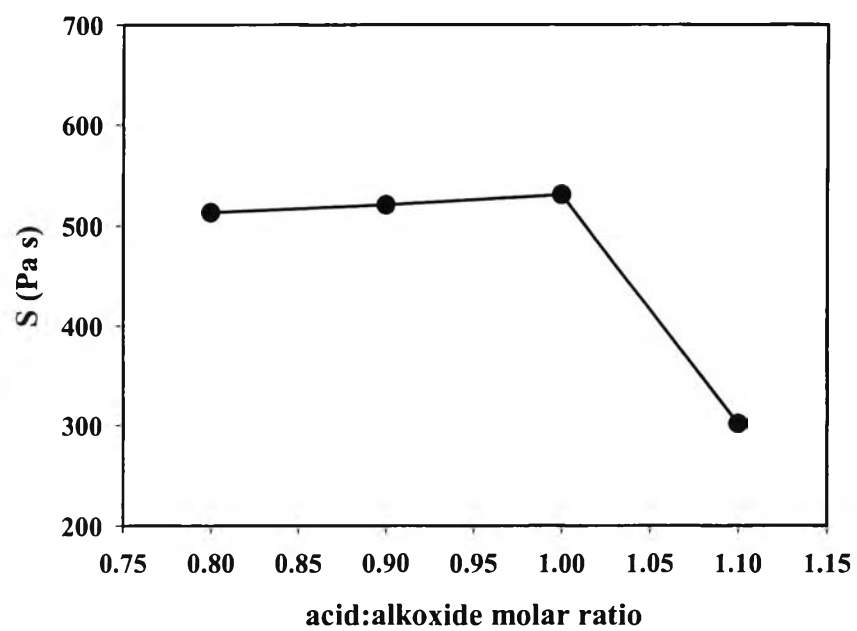


Figure 9.4 The plot of gel strength parameter  $S$  at the gel point as a function of HCl:alkoxide molar ratio.

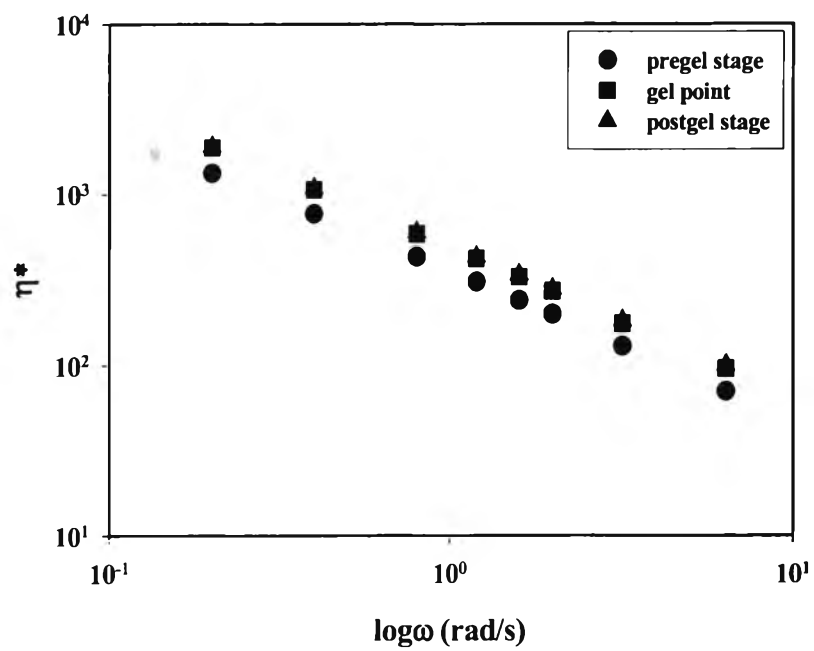


Figure 9.5 The plot of complex viscosity ( $\eta^*$ ) with  $\omega$  (rad/s) at pregel stage, gel point, and postgel stage of 0.9 molar ratio.