



CHAPTER IV

RHEOLOGY AND HEAT TREATMENT OF ZIRCONIA BASED GELS SYNTHESIZED FROM SODIUM GLYCOZIRCONATE PRECURSOR

Abstract

Zirconia based gels were prepared by the sol-gel route using sodium tris(glycozirconate) complex as precursor synthesized directly from the reaction of inexpensive and readily available compounds via the one step method. Rheological technique was used to investigate the sol-gel transition of zirconium based materials at different water/alkoxide ratio and reaction temperature. The gelation time was determined from the evolution of the storage and loss moduli versus time at various frequencies using the Winter-Chambon criterion. The effect of an increase of the hydrolysis ratio and /or temperature was an enhancement of the kinetics of crosslink reactions, thus decreasing the gelation time. The variation of the gelation time versus temperature could be described by Arrhenius law. Furthermore, zirconia powders prepared from the thermal treatment at 500°C were analyzed by X-ray diffraction and the BET technique.

Introduction

Zirconia is very useful in many applications as catalytic supports, composites, pigments, bioceramics, piezoelectric ceramics and as solid electrolyte in fuel cell or oxygen sensor.¹⁻² Studies of the early stages of monomer or particle aggregation are particularly important for understanding the basic mechanism involving in the gelation process. Most of these kinetic studies are performed on silica-based systems. Studies in zirconia-based solutions are rarely done owing to the difficulties in avoiding fast hydrolysis of zirconium alkoxide in the presence of even a small amount of water. This leads to a fast precipitation of zirconium hydroxide and heterogeneous gels. This problem may be avoided by adding the chelating agents, which allows a controlled crosslinking process.³ However, the modifications are rather complicated and expensive. The use of new metal alkoxides is an alternative way for the sol-gel process. Sodium tris(glycozirconate) is a glycolate derivative of zirconium prepared directly from the reaction of inexpensive and readily available compounds via the one step process. Its presence of ethylene glycolate ligands is hydrolytically stable, thus giving more controllable chemistry and minimizing special handling requirement. It is therefore a candidate for using as precursor in ceramic processing. We herein study the viscoelastic properties and FTIR on sol-gel process of sodium tris(glycozirconate) under different conditions. Additionally, some preliminary thermal studies of a resulting zirconia gel are also observed.

Experimental Section

Preparation and Heat Treatment of Zirconia Gels. Sodium tris(glycozirconate), used as the zirconia source in the sol-gel process, was prepared according to the procedure reported earlier.⁴ The sol-gel process was carried out by adding water to sodium tris(glycozirconate). A study on the influence of the following parameters (the hydrolysis ratio $h = \text{H}_2\text{O}/\text{alkoxide}$ molar ratio and the temperature T) was performed. The range for the parameters was as follows: $h = 6-24$ and $T = 20^\circ-36^\circ\text{C}$. These parameters were chosen to allow a suitable control of the reaction kinetics.

The resulting gels were soaked, washed with deionized water to eliminate sodium and recovered by filtration before drying. Zirconia powders were obtained

by heat treatment of the dried gels in a furnace at 500°C for 7 hr. These materials were checked for the absence of residual sodium using EDX analysis.

Measurements

Sol-gel process

Rheological measurements. The studies of sol-gel transition and dynamic viscoelastic properties were carried out on a rheometer (Model ARES) with a cone-plate geometry (diameter 25 mm, angle 0.04°) covered by the humidity chamber to avoid a drying out during measurements. The gap set was about 0.051 mm. The temperature was controlled by means of a thermostated-circulating bath. The linear viscoelastic range of each sample was first determined by a strain sweep. The multi-wave experiments were conducted within the linear viscoelastic regime of the sample (strain $\gamma = 3\%$) in the 0.2-6.4 rad s⁻¹ frequency range. A narrow frequency range was employed because their properties change remarkably with time. Additionally, no crossover at the certain point designated as the gel point was observed on the plot of $\tan \delta$ versus time at higher frequencies. Although the time requested for G' and G'' to be equal is identified as the gel point by some authors,⁵⁻⁶ a more accurate definition of the gel point has been given by Winter and co-workers as the point where $\tan \delta$ is independent of frequency. According to this criterion, the gel point is determined as the instant in time when the moduli scale is in an identical fashion with frequency, corresponding to parallel lines in a frequency spectrum:

$$G'(\omega) \sim G''(\omega) \sim \omega^n \quad (1)$$

The relaxation exponent, n , can have values in the range $0 < n < 1$ indicating a strongly elastic gel ($n=0$) or a more viscous gel ($n=1$).⁷ In addition, at the gel point, the loss tangent $\tan \delta$ becomes independent of frequency:

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

Thus, the gel point can be conveniently determined by the evolution of $\tan \delta$ with time at different frequencies. Such the different plots coincide at a single point, at which $\tan \delta$ is independent of frequency. The time at which this occurs is the gelation time.⁷

FTIR spectroscopic characterizations. The hydrolysis and condensation of sodium tris(glycozirconate) precursor were followed as a function of the reaction time by FTIR spectroscopy. The FTIR experiments were performed using a Nicolet NEXUS 670 spectrophotometer using a DTGS-KBr with 16 scans at a resolution of 4 cm^{-1} .

Characterization of heated gels. Zirconia powders obtained by heating the gel at 500°C were analyzed using X-ray diffraction and BET techniques. The phase development in the samples thermally treated at various temperatures was obtained at room temperature using X-ray powder diffractometer. XRD spectra were recorded on D/MAX 2000 series using $\text{CuK}\alpha$ radiation as an X-ray source and operating at 40 kV, 30 mA with Ni filter. BET surface area and pore size distribution were measured by using nitrogen at 77 K in Autosorb-1 gas sorption system. All measurements were performed after outgassing the sample at 170°C under vacuum.

Results

Sol-gel process

Rheological measurements. The variation of the storage (G') and loss (G'') moduli and complex dynamic viscosity (η^*) as a function of the time ($h = 12$ and $T = 25^\circ\text{C}$) at 0.2 rad s^{-1} was depicted in Fig. 1. Initially, G'' is larger than G' , which is a characteristic of liquids. As the sample undergoes the reaction, the moduli increased with time. However, G' grows more rapidly than G'' . The increase in G' indicates a development of the network structure with a highly elastic behavior. The viscosity also increased as the gelation grew. Fig. 2 displays the time evolution of $\tan \delta$ at various frequencies during the sol-gel process ($h = 12$ and $T = 25^\circ\text{C}$). All the $\tan \delta$ curves converge at a single point, which corresponds to the gel point in accordance

with the Winter-Chambon criterion. The gel time t_{gel} for this system is approximately 6048 ± 235 s. Before the gel point, $\tan \delta$ decreased with increasing frequency, which is typical for a viscoelastic liquid. After the gel point, $\tan \delta$ increased with frequency, as the characteristic of a viscoelastic solid. Apparently, the sample had changed from a viscoelastic liquid to a viscoelastic solid. According to previous section, values of n near the gelation critical point can be determined from power law character. The slopes of these lines gave n , the viscoelastic exponent in eq.1, for the frequency dependence of the moduli. Both n' and n'' values decreased and then converged to 0.06 at 6048 s. These values of n component corroborate well with the values obtained from Fig. 2 and eq.2. At the gel point, $\tan \delta$ is equal to 0.1, which is coincident with an exponent of $n = 0.06$.

The influence of the hydrolysis ratio. The viscoelastic properties at the gel point were demonstrated in Table 1. The increase of h reduced the times required for gelation. Also, G' outweighed G'' for all systems, showing that the elastic component appreciably predominated over the viscous one at the gel point. Furthermore, G' and η^* decreased while n increased with increase of h . It could be noted that when the h is greater, gel formation evolving quickly through the reaction of hydrolysis and condensation contains low interconnected networks. Consequently, the network is looser with lower value of G' . On the contrary, a system with a lower h grew slowly resulting in a denser network with higher G' . Correspondingly, a higher value of n is related to a lower elastic system indicating that intermolecular crosslinks are weaker.

The influence of the temperature. The results of measurements performed for different temperatures between 20° and 36°C ($h = 12$) were reported in Table 2. At higher temperatures gelation occurs faster, resulting in a shorter time to gel. The dynamic moduli at the gel point decreased with increasing temperature. The trend of these results is analogous to that of other studies.^{7, 8} Additionally, the temperature dependence of η^* was also similar to that of the moduli. In contrast, the n values obtained for all systems increased with temperature. These observations indicate that

the network formation proceeded faster with increasing temperature, whereas the gel texture is rather loose.

There is some discussion in the literature regarding apparent activation energy for the gelation reaction calculated from the gel time at different temperatures.⁸ Fig.3 exhibits a t_{gel} versus $1/T$ curve in semilogarithmic scale, which can be fitted by the apparent Arrhenius law

$$\ln(t_{gel}) = A + E_a/RT \quad (3)$$

where A is a constant, R is the ideal gas constant, and T is temperature. The activation energy E_a of the gelation can be calculated from the slope of a plot of $\log t_{gel}$ against $1/T$. The values of E_a were estimated to be approximately the same in each case, about $87 \pm 0.6 \text{ kJ mol}^{-1}$. This implies that E_a of the gelation does not depend on hydrolysis ratio.

FT-IR analysis. The FTIR spectra of the gel as a function of time were compared to elucidate the study of the hydrolyzed sodium tris(glycozirconate). As the reaction proceeded, a decrease in the intensity of the Zr-O-C vibration of sodium tris(glycozirconate) at 1090 cm^{-1} was observed. The width and intensity of some peaks present at $900\text{-}500 \text{ cm}^{-1}$ regions increased. This result corresponded to the formation of Zr-O-Zr bonds according to the condensation reaction. Fig.4 depicts the FTIR spectra of hydrolyzed systems at different hydrolysis ratio. The intensity of Zr-O-Zr was maximized at $h=24$ with decreasing the intensity at lower hydrolysis ratio. The decrease in intensity of Zr-O-C band is accompanied with the increase of Zr-O-Zr band as hydrolysis ratio increases. This implies that the gelation can be accelerated with increasing hydrolysis ratio leading to the reduction of the gel time. It is obvious that the hydrolysis ratio is the important factor affecting the gel time. Furthermore, it was found that these FTIR observations are consistent with the rheological results.

Characterization of heated gel. Some preliminary studies of heated gel were performed to observe the effect of temperature on the properties of obtained zirconia. XRD patterns of thermally treated gel at different temperatures ranging between 400° and 1000°C showed amorphous phases at 400°C, see Fig. 5. After a heat treatment of 500°C, crystallization occurred. The peak intensity increased with temperature, indicating an improvement in crystallinity of zirconia. Heat treatment to 1000°C brought about the tetragonal to monoclinic transformation. The sample treated at 500°C shows the monomodal pore size distribution in the mesopore range. Also, the resulting powder shows the nitrogen adsorption/desorption isotherms of type IV (IUPAC classification) which exhibit hysteresis loops mostly of type H2.⁹ Further investigations on the heat treatment of zirconia gel obtained various reaction conditions are in progress and will be reported later.

Discussion

Sol-gel process. From the results of the multiple waveform rheology, the gelation point can be detected by the Winter criterion, as mentioned previously: (a) frequency independent loss tangent; (b) the equality of slopes in the frequency spectrum. The Winter criterion thus seems to work remarkably well for our system. The validity of the data obtained using the multi-wave technique was verified by comparing with continuous time sweeps conducted at the same temperature. The exponent (n) observed in our system was so low (0.06 ± 0.001). Most studies based on thermoplastic elastomers have found $n > 0.5$. Values of n below 0.2 have been reported in some cases.^{8,10} However, trends in n found can be analyzed to understand why the value obtained in this work is very low. Winter has shown that if $n > 0.5$, the gel point occurs before the crossing-point of G' and G'' . On the contrary, if $n < 0.5$ the crossing-point preceded the gel point. This is agreement with the results for our system. It is thus difficult to precise exactly the nature of the gel with the n value. However, the value of n is related to the elasticity of the material. Some authors mentioned that a low n value implies that the material is a mostly elastic body with the limit of $G'' = 0$ at $n = 0$ and vice versa. This is reasonable in our case because the system develops a predominantly elastic character as gelation

proceeds. These gels show the property of being fluid before the gel point allowing their easy fabrication into special products, and reach a high viscosity after the gelation time. Concerning the h dependence of the gelation time, it was found a strong decrease of the gelation time with h showing that the crosslinking process was accelerated. The gel formation needs to cross an energetic barrier corresponding to the apparent activation energy. E_a .

The FTIR spectroscopy for a direct examination of the sol-gel process was used. It also gave information about the crosslinking reaction in sol-gel process. The bands located at 1090 cm^{-1} can inform about the hydrolysis of sodium tris(glycozirconate). This band decrease continuously with increase of reaction time. The polymerization process was followed by the band located at $900\text{-}500\text{ cm}^{-1}$ associating to Zr-O-Zr stretching. This band increases with the reaction time. The decrease in intensity of Zr-O-C band in tris(sodium glycozirconate) was accompanied with the increase of new band of Zr-O-Zr bond leading to the formation of network structure.

Heated gels. DTA showed an exothermic peak around 500°C which corresponded to the crystallization of the material, but the temperature program of the DTA scan was a continuous ramp with no hold, unlike the calcination procedure. Although no exact temperature can be pointed to as the crystallization temperature, it could be noted that the crystallization into the tetragonal phase occurred in the temperature range $400^\circ\text{-}500^\circ\text{C}$. Further heat treatment converted the tetragonal to monoclinic phase, meaning that the sol-gel preparation was able to stabilize zirconia into either an amorphous, or tetragonal, or monoclinic material, simply by varying the heat treatment.

Conclusions

Sodium tris(glycozirconate) can be used as metal alkoxide precursor for preparing high surface zirconia powders by sol-gel process. The multiple-waveform rheological technique and FTIR were found to be effective for studying the gelation of sodium tris(glycozirconate). Hydrolysis ratio and temperature affected

dramatically the gel time. An increase of these parameters leads to the decrease of gel time. However, the strength of the gel network formed more quickly is lower than that obtained gradually. The value of n for our systems was found to be fairly low indicating high elastic gel. The E_a of the gelation reaction determined directly from gelation time measurement at different temperatures was about 87 kJ mol^{-1} . Heat treatment of the resulting zirconia gels at 500°C produces a homogeneous mesopore zirconia with high surface area.

Acknowledgments

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Figure Captions

Figure 1. Time evolution of the storage (G') and loss (G'') moduli and complex viscosity (η^*) for $h = 12$ at 25°C .

Figure 2. Variation of $\tan \delta$ as a function of time for $h = 12$ at 25°C .

Figure 3. Semilogarithmic curve of gelation time versus $1/T$ where the temperature is expressed in Kelvin.

Figure 4. FTIR spectra of zirconia gel at 25°C and various hydrolysis ratio of (a) $h = 6$; (b) $h = 12$; (c) $h = 24$.

Figure 5. XRD patterns of zirconia gel heated up to various temperatures of (a) 400°C ; (b) 500°C ; (c) 700°C ; (d) 800°C ; (e) 1000°C .

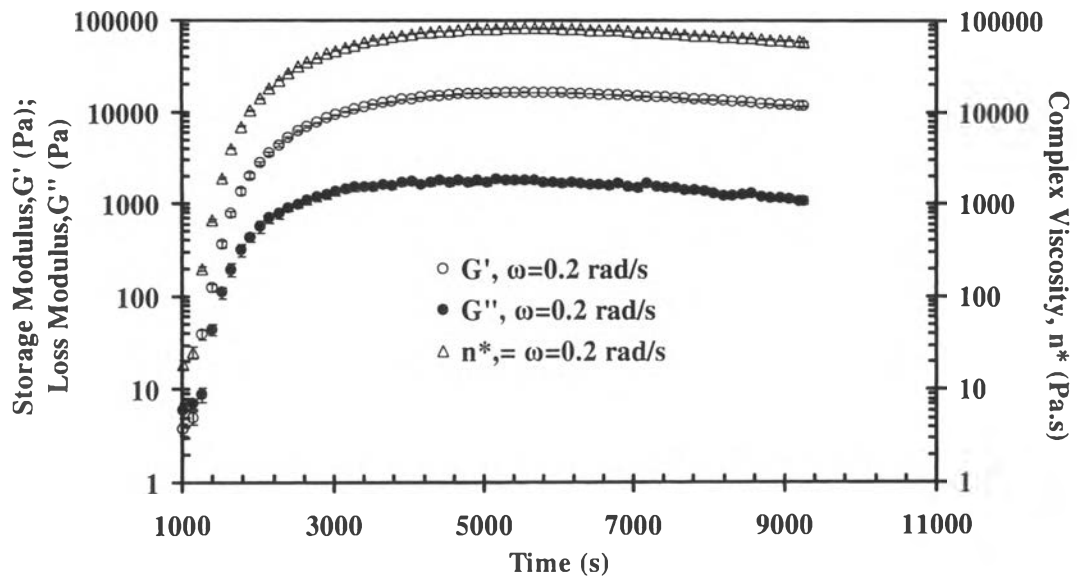


Figure 1. (Ksapabutr et al.)

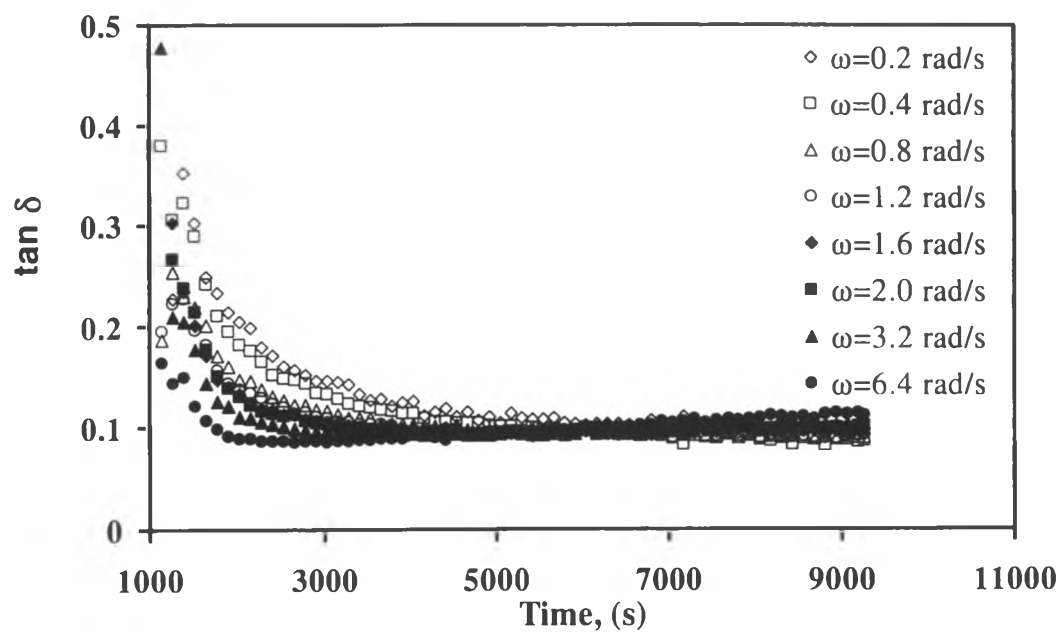


Figure 2. (Ksapabutr et al.)

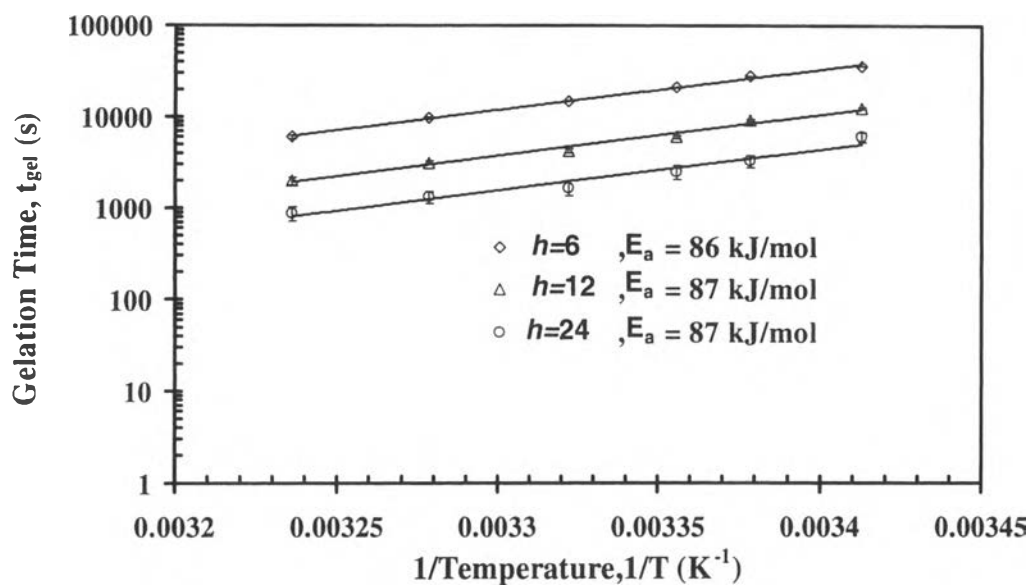


Figure 3. (Ksapabutr et al.)

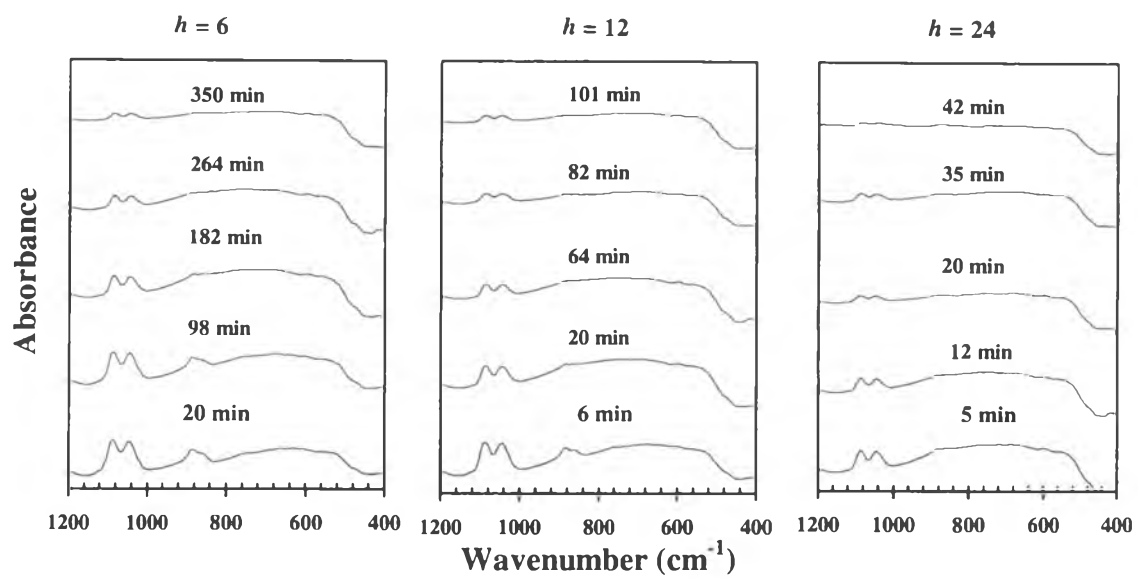


Figure 4. (Ksapabutr et al.)

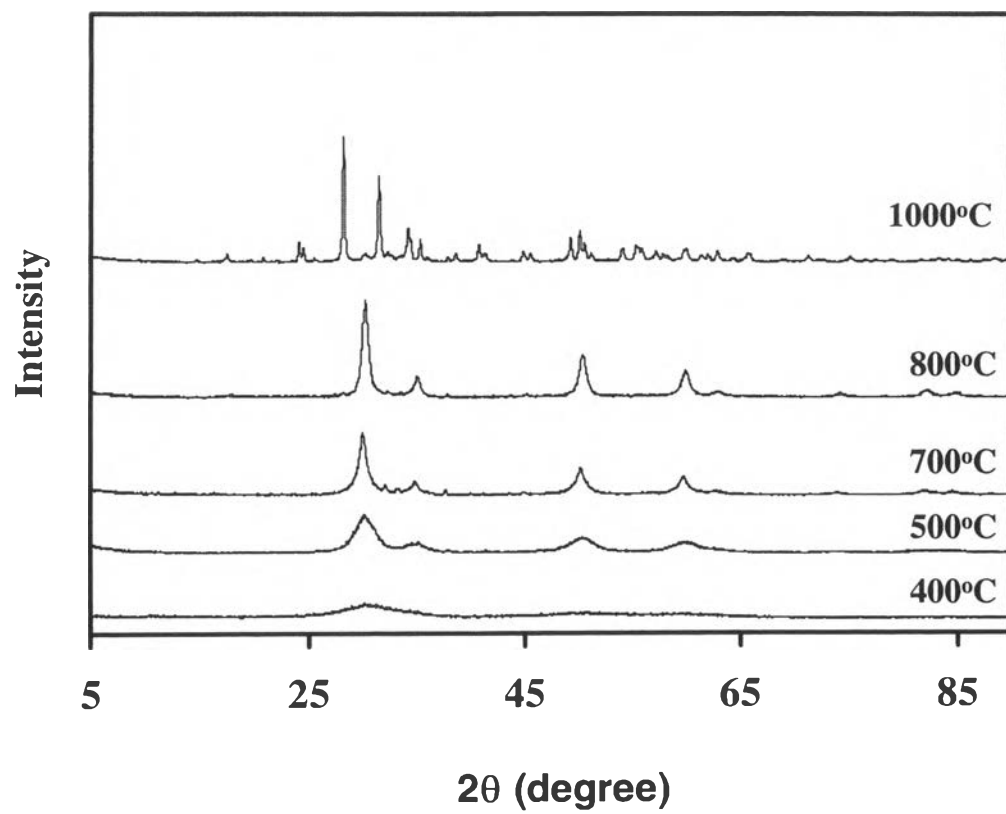


Figure 5. (Ksapabutr et al.)

Table Captions

Table 1. Hydrolysis ratio effect on the gelation time and viscoelastic properties at 25°C

Table 2. Temperature effect on the gelation time and viscoelastic properties for $h = 12$.

h	t_{gel} (s)	G'	G''	η^*	G'/G''	n
6	21000±236	23042.2±421	1516.6±75	115460.3±2125.1	15.2±0.47	0.04±0.001
12	6048±235	16041.0±635.3	1634.5±86	80620.5±2302.2	9.8±0.13	0.06±0.001
24	2500±421	9945.4±331	1734.8±87	50477.8±1705.1	5.7±±0.1	0.11±0.002

Table 1. (Ksapabutr et al.)

$h=12$	t_{gel} (s)	G'	G''	η^*	G'/G''	n
20°C	12570±325	23381.3±542.0	1521.1±101	117153.6±2737.1	15.4±0.67	0.04±0.002
23°C	9142±254	19796.0±452.1	1623.0±93	99312.1±2290.4	12.2±0.42	0.05±0.002
25°C	6048±235	16041.0±635.3	1634.5±86	80620.3±3202.2	9.8±0.13	0.06±0.001
28°C	4245±186	13123.3±526.5	1678.7±79	66151.2±2658.8	7.8±0.05	0.08±0.001
32°C	3159±165	9562.6±354.4	1714.3±95	48575.2±1826.0	5.6±0.1	0.11±0.002
36°C	1999±201	7821.3±203.1	1745.4±107	40068.4±1107.1	4.5±0.16	0.14±0.005

Table 2. (Ksapabutr et al.)