

Tracing the sol–gel transformation by dynamic torsional vibration method

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Organic/inorganic hybrid materials prepared by the sol–gel approach is an interesting research field in materials science [1]. It is necessary to understand and describe the process of sol–gel transformation because sol–gel reaction plays a key role in the preparation of hybrid materials, and will inevitably affect the final properties of hybrid materials, e.g., the mechanical and optical properties. At the same time, monitoring and discriminating the sol–gel process is still one of the most basic and interesting questions in the field of sol–gel chemistry although numerous studies have been carried out.

The four basic steps of gel formation are nucleation of particles, growth of particles, coagulation to form aggregates and reinforcement of the aggregate structure [2]. Over the past decade, many methods have been made to study this process. Xu *et al.* studied the sol–gel transformation of SiO₂ colloid by light scattering [3]. Vogelsberger and his coworkers applied rheological measurements to study the sol–gel transformation of silica in aqueous solution and the tetraethoxysilane-water-ethanol system [4]. Burgos *et al.* used the Fourier transform infrared (FTIR) spectroscopy to qualitatively study the sol–gel transformation mechanisms of tetraisopropyl orthotitanate (TIPT) derived coatings [5]. Kikteva *et al.* [6] pointed out that by means of the diffusion-controlled fluorescence quenching of Py by Cu²⁺ ions, the sol–gel conversion in the tetraethoxysilane/alcohol/water system can be probed.

This work is an analysis of mechanical properties that aims to describe the whole process of sol–gel transformation of organic/inorganic hybrid materials by the DTVM, which had been developed in our lab and used to investigate the cure behavior of the epoxy resin curing system [7, 8]. The isothermal transformation process with different temperatures was monitored *in situ* by the DTVM, and the non-equilibrium thermodynamic fluctuation theory was used to predict the sol–gel transformation behavior. Good agreement between the experimental results and the theoretical model was generally found.

Hsich's non-equilibrium thermodynamic fluctuation theory [9, 10] clearly describes the changes of physical or mechanical properties of the curing system during cure. Because of the similarity between resin curing system and sol–gel transformation system, in which all the mechanical properties of the system changed, we applied this theory to our study, based on the assumption of taking the sol as a whole invariable system, i.e., ignoring the effect of solvent volatilization in sol. Thus, according to the theory, the physical or mechanical properties of the sol–gel system can be expressed as

$$\frac{G_{\infty} - G(t)}{G_{\infty} - G_0} = \exp \left[- \left(\frac{t}{\tau} \right)^{\beta} \right] \quad (1)$$

where G_0 and G_{∞} are the initial and final physical and mechanical properties (torque, modulus or viscosity, etc.) during the transformation, respectively; $G(t)$ is the property at time t , τ the time parameter (relaxation time) of the transformation system, and β the constant describing the width of the relaxation spectrum. In our experiment the mechanical property is torque.

Methyl methacrylate (MMA), 3-(trimethoxysilyl) propyl methacrylate (MSMA), and tetrahydrofuran (THF, cP) were purified by distillation under vacuum. Azobisisobutyro nitrile (AIBN) was recrystallized from ethanol prior to use, and tetraethoxysilane (TEOS, AR) were used as received.

The preparation of the PMMA/SiO₂ hybrid sol was based on the method reported in the literature [11]. The monomers (methyl methacrylate, MMA, 0.3 mol) and (3-(trimethoxysilyl) propyl methacrylate, MSMA, 0.1 mol), and the initiator, AIBN, were added into a reaction flask and were polymerized at 60 °C under nitrogen flow for 0.5 hr. Then, a homogeneous THF solution of TEOS (0.066 mol), deionized water (0.066 mol) and hydrochloric acid (0.004 mol) were added to the reaction mixture simultaneously with rigorous stirring, and then the PMMA/SiO₂ hybrid sol was obtained.

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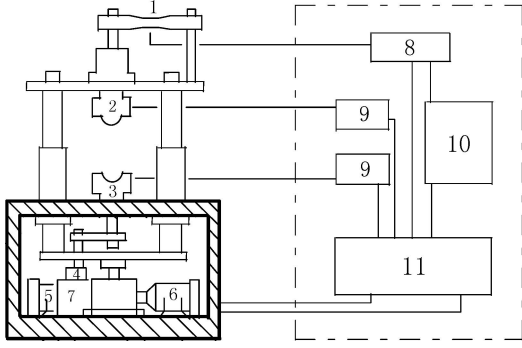


Figure 1 Diagram of the dynamic torsional vibration setup: (1) strain gauge load cell; (2) upper mold; (3) lower mold; (4) eccentric disc; (5) motor for torsional vibration; (6) motor for closing molds; (7) speed change gear; (8) amplifier; (9) temperature controller; (10) recorder; (11) power supporter

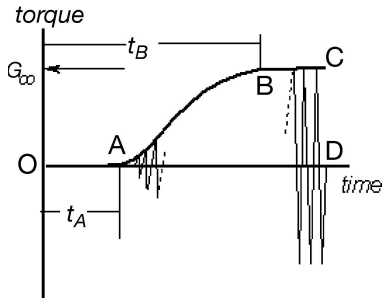


Figure 2 A typical experimental curve obtained by the dynamic torsional vibration method

Dynamic torsional vibration is a non-resonant forced vibration. Fig. 1 shows the schematic diagram of the HLX-I Resin Curemeter, which is a homemade experimental equipment. A detailed description of the setup can be found in Ref. [12].

A typical experimental curve obtained by DTVM is shown in Fig. 2. The abscissa is the time; the ordinate is the torque, which is a relative parameter indicating the degree of transformation.

The PMMA/SiO₂ hybrid sol was rapidly added to the lower mold as soon as it was obtained. At the same time, the two molds were closed, and this time is taken as the starting time of point O. In the range OA of the time, the strain gauge load cell have no signal to input, so the experimental curve is a linear line corresponding to the abscissa.

At point A, the viscosity of the system becomes high enough, i.e., coagulation of particles to form aggregates begin to occur, thus, the torque appears and the strain gauge load cell inputs some signal. Point A is thought as the obvious beginning of transition in sol-gel process, and the time corresponding to OA is defined as the transition time t_A in our system. After point A the torque increases with increasing sol-gel reaction time.

The increasing amplitude of the torque (slope of the curve) reflects the rate of the sol-gel reaction. The increasing trend of the torque tends to steady with increasing sol-gel reaction time. When the equilibrium torque G_∞ is reached (point B), the aggregate structure was formed completely and a steady state of reinforced aggregates was shown in the following BC of the time,

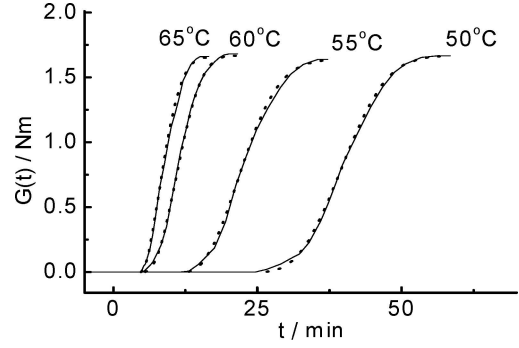


Figure 3 The isothermal transformation curve of PMMA/SiO₂ hybrid sol at various temperatures. (—) Experimental and (---) theoretical

in which it suggested that the gel was formed. Hence, point B is defined as the gel point, and the time corresponding to OB is gel time t_B .

In the end, when the whole sol-gel transformation process is completed, a cup-like experimental curve is obtained. The envelope of the experimental curve corresponds to the change of torque. Since the cup-like experimental curve is symmetric to the time axis, so for convenience we can just take the upper-half of the envelope as the isothermal curve to trace the sol-gel transformation process. A typical experimental curve is shown in Fig. 2.

Fig. 3 shows the isothermal sol-gel transformation curves of the PMMA/SiO₂ hybrid sol system at 50–65 °C with an interval of 5 °C. The transformation curves at different temperatures have similar shape, but obvious differences in their transition time t_A and gel time t_B . In addition, sol-gel reaction rates, that is slope of the curve, also have the tendency to increase.

It is evident from Fig. 3 that t_A and t_B decreased significantly with the enhanced temperature, and the transformation rate is accelerated. This suggested that the process of growth of particles and coagulation to form aggregates in so-gel transformation was promoted significantly at higher temperature. The time t_A and t_B obtained from Fig. 3 and some related data are listed in Table I.

As seen from the isothermal transformation curve in Fig. 3, G_0 is zero, the torque begins to appear only after the transition time t_A . Equation 1 describing the transformation curves after t_A would be

$$\frac{G_\infty - G(t)}{G_\infty} = \exp \left\{ - \left(\frac{t - t_A}{\tau} \right)^\beta \right\} \quad (2)$$

$$G(t) = G_\infty \{ 1 - \exp[-((t - t_A)/\tau)^\beta] \} \quad (3)$$

TABLE I Isothermal transformation data of PMMA/ SiO₂ hybrid sol at different temperatures

T (°C)	G_∞ (Nm)	t_A (min)	t_B (min)	τ (min)	β
50	1.667	27.21	53.66	17.02	2.88
55	1.639	17.40	35.94	11.75	2.33
60	1.681	5.35	19.84	7.10	2.27
65	1.660	4.79	15.56	4.80	1.86

Equation 3 describes the changes in torque of the sol system during transformation, in which t_A and G_∞ can be read directly from the experimental curve.

In order to obtain the relaxation time τ , let $t = t_A + \tau$, thus

$$G(t = t_A + \tau) = G_\infty(1 - e^{-1}) = 0.63G_\infty \quad (4)$$

From a measurement of the time corresponding to $0.63 G_\infty$ in the experimental transformation curve, the relaxation time τ can be obtained from Equation 4:

$$\tau = t - t_A$$

Having determined τ , Equation 3 is reduced to an equation with a single parameter only. A nonlinear regression is used to fit the Equation 3 to all experimental curves. The values of β at various temperatures of PMMA/SiO₂ hybrid sol system can be determined using the line of best fit. With β value, the torque $G(t)$ for any time, i.e., the theoretically predicted value, can be calculated according to the Equation 3 provided that the transition time t_A and the relaxation time τ are already known. The theoretical sol-gel transformation curves are also plotted in Fig. 3 as dot line. The theoretical predictions show good agreement with the experimental curves at various temperatures.

The sol-gel transformation in the preparation of organic/inorganic hybrid materials was first described by the DTVM. The non-equilibrium thermodynamic fluctuation theory originally describing the cure of resin was applied to predict the sol-gel transformation pro-

cess. The theoretical results are good in agreement with experimental data. The results showed that DTVM is applicable to trace the sol-gel transformation process, much useful information can be obtained from the transformation curve, and further study in this field is now in progress.

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