TA Instruments – Application Note

Isothermal Analysis of Materials Fabrication via the Sol-Gel Process

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Introduction

A sol-gel is an integrated chemical network formed by chemical solution deposition, also known as the sol-gel process. The sol-gel process is commonly used to fabricate the nanoscale materials that are used in optics and electronics. Recently, medical research has adopted the sol-gel process for fabricating materials for use in tissue engineering, large molecule drug delivery and genetic engineering. Successful fabrication of materials via the sol-gel process is often determined by imaging techniques such as x-ray, neutron, or light scattering, as well as various microscopy techniques; however, implementing use of real-time thermodynamic analyses could compliment structural analyses and allow for complete determination of the mechanism by which a particular sol-gel forms. Isothermal calorimetry is a straightforward and direct thermodynamic method that provides the real-time measurement of the heat released, or absorbed, when a chemical reaction occurs. To demonstrate the use of isothermal calorimetry in the process of sol-gel fabrication, we used the TA Instruments TAM III Calorimeter to monitor the reaction heat flow profile and reaction duration of a model sol-gel system.

Materials and Methods

Sol-gel experiments performed in the TAM III equipped with a 4mL multicalorimeter at 25°C consisted of 2.5 mL 98% tetraethyl orthosilicate (TEOS) (Acros Organics) and 0.5 mL formic acid (Fischer Scientific) at varying percentages (8%, 4%, 2%, 1%, 0) in separate 4 mL Hastelloy screw-cap ampoules with o-ring seal. A single negative-control reaction was also prepared that consisted of 2.5 mL TEOS and 0.5 mL deionized water. Each reaction equilibrated in the calorimeter for 15 minutes prior to data collection. The data were collected and analyzed using TAM Assistant Software.

Results

To illustrate how thermodynamic techniques can be used to reveal the fine details of the sol-gel process, we monitored the real-time heat flow from the acid catalyzed polymerization of tetraethyl orthosilicate (TEOS) at various concentration of catalyst (formic acid). Increasing concentrations of formic acid in the presence of TEOS elicited a proportionate increase in reaction heat flow, time to heat flow peak maximum and reaction end-point (Figure 1). 8% formic acid yields an immediate reaction with a maximum heat flow of approximately 25 mW in approximately 2 hours, and the total reaction reaches completion after 3 days, 4% formic acid yields a maximum heat flow of approximately 13 mW in just less than 4 hrs. For 4% formic acid-TEOS reaction, the time to reaction completion is equivalent to the sample of 8% formic acid-TEOS; however, the 4% formic reaction shows increased resolution of the initial reaction period from zero to 1 day. TEOS reactions with both 2% and 1% formic acid display a much slower initiation period (1 day and 2 days, respectively). This is followed by a putative autocatalytic event that peaks at approximately 11mW in approximately 1 ¼ days (2% formic acid) and 7 mW in approximately 2 ¼ days (1% formic acid). The control experiment with TEOS and no formic acid shows a constant zero heat flow signal indicating no reaction. Thus, proof that the reactions present in the other samples are the result of the acid catalyzed sol-gel reaction. Integration of the peaks corresponding to each of the reactions in TAM Assistant Software yielded average heat value of 263.6 ± 1.9 Joules, indicating each sample ran to completion. Integrating the area under each reaction over the duration of the measurement was performed by using the linear integration function of TAM Assistant software.

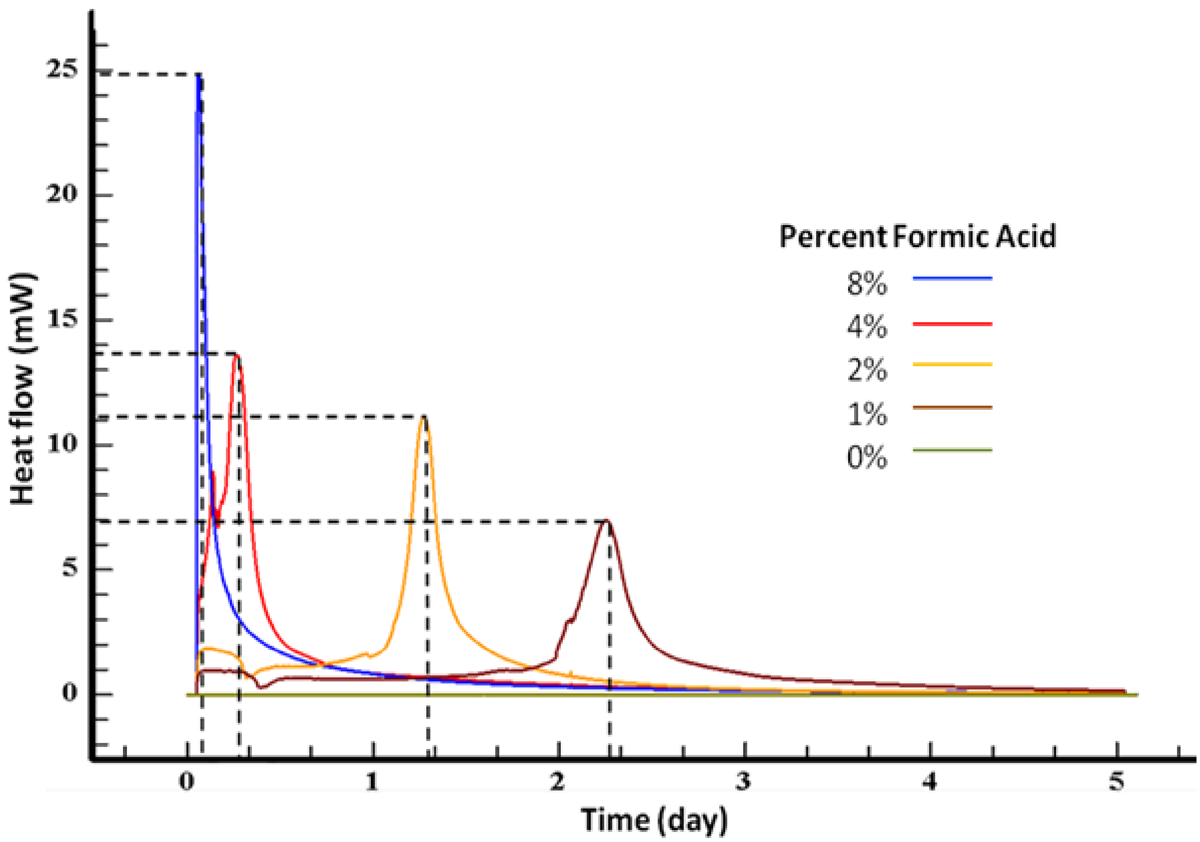

Figure 1. Real-time analysis of TEOS polymerization at various concentrations (0, 1%, 2%, 4%, and 8%) of the formic acid catalyst with the TAM III Calorimeter. Peak heat flow (mW) for each sample indicates the maximum reaction heat produced at a particular time (days).

Conclusion

The TAM III Calorimeter is an analytical tool capable of continuous and real-time analysis of the reaction heat flow, such as the sol-gel process. The TAM Assistant Software is capable of allowing for simple analyses such as determination of total heat and total reaction time, as well as complex analyses such as reaction kinetics. Furthermore, the ability of the TAM to perform measurements at temperature ranges as high as 150°C allows researchers to determine the temperature dependence of a reaction of interest in order to optimize the reaction process.