Kinetic Analysis of a Crosslinked Polysiloxane

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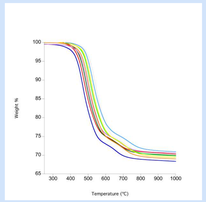
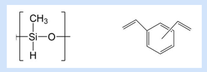
Introduction

- Silicon oxycarbide (SiCO), also known as black glass, is derived from organopolysiloxanes that are crosslinked or by sol gel techniques
- SiCO materials have applications in lithium anode materials, temperature and pressure sensors, fibers and aerogels
- Isoconversional, model fitting, and decomposition analyses are used to determine the kinetic triad (activation energy, reaction model, and pre-exponential factor) to better understand the processes occurring during the heating of a material





PMHS DVB

Motivation

- Learn about the synthesis of PMHS crosslinked with DVB
- Understand the processes and use as a model system for further methodology development that can be applied to other systems

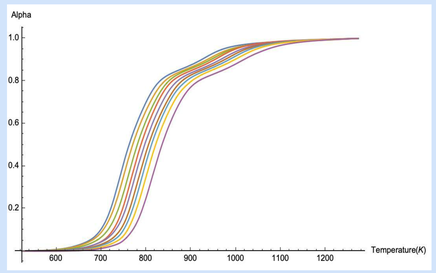
Method

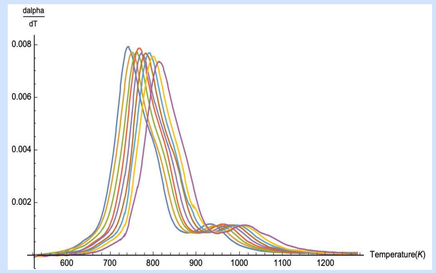
- 5 ppm Pt catalyst (relative to polymethylhydrosiloxane (PMHS)
- 100% divinylbenzene (DVB) by mass (relative to PMHS)
- stirred for 10 minutes
- added PMHS dropwise while stirring
- stirred for an additional 10-15 minutes
- retained overnight at room temperature
- heat treated in N_2 at 120ºC for 12 hours
- ball milled

Sample Size: 5-6 mg in 90 μL alumina crucible
TGA Analysis: 30 min purge under N_2 > Ramp > 1000ºC
Heating rates: 2,3,5,7,10,15,20,30 and 50 ºC/min

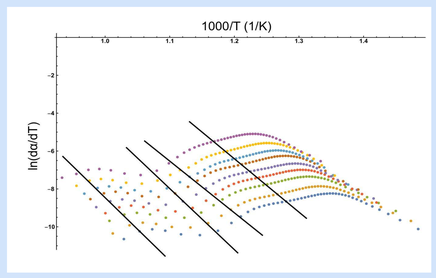
Friedman Isoconversional Kinetic Analysis

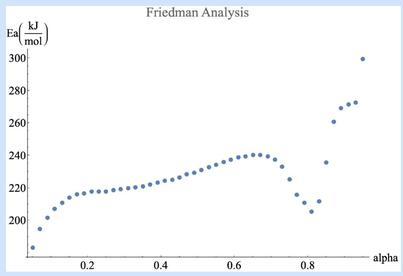
$$\frac{d\alpha}{dT} = \varphi(T,\alpha) = k(T)\cdot f(\alpha) = \frac{A}{\beta}\cdot e^{-E_a/RT}\cdot f(\alpha)$$





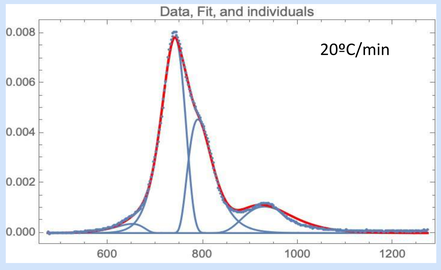
$$\ln\left(\frac{d\alpha}{dT}\right)_{\alpha,\beta} = \ln[A_\alpha f(\alpha)] - \frac{E_\alpha}{RT_{\alpha,\beta}}$$

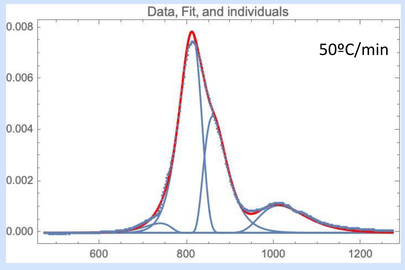


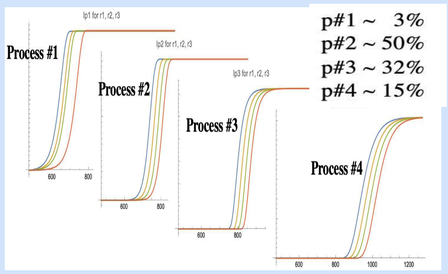


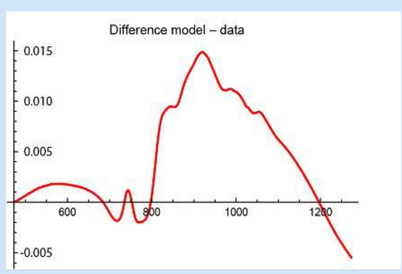
Decomposition of Complex Processes

$$\frac{d\alpha}{dT} = y(T) = a_0\cdot\exp\left[-\ln(2)\cdot\left[\frac{\ln\left(1+2a_3\frac{T-a_1}{a_2}\right)}{a_3}\right]^2\right]$$

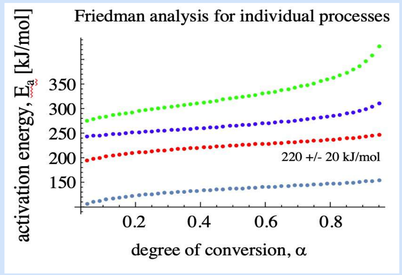






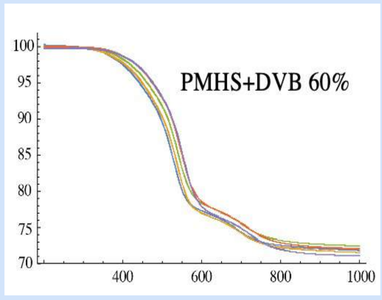


Results of Kinetic Analysis



Asymmetry parameter, a_3		
process #1	–0.45	*~D3*
process #2	–0.30	**F1**
process #3	0.48	*~F4*
process #4	0.39	*~F3*

Future Work



- Change mass ratio of PMHS to DVB
- Change meso-porosity of system
- Develop analytical tools further

Summary

- Thermo-kinetic study of a model system (PMHS + DVB)
- Multi-process analysis using peak fitting
- Activation energies of individual processes
- PMHS+DVB is dominated by an F1 process with an E_a = 220 +/- 20 kj/mol

References

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