

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) Dec 2014		2. REPORT TYPE Briefing Charts		3. DATES COVERED (From - To) Dec 2014- Dec 2014	
4. TITLE AND SUBTITLE Water Uptake Vs. Density and Conversion in Silicon Containing Cyanate Esters				5a. CONTRACT NUMBER In-House	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Michael D. Ford, Andrew J. Guenther, Jacob J. Zavala, Joseph M. Mabry				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER Q0BG	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RQRP 10 E. Saturn Blvd. Edwards AFB CA 93524-7680				8. PERFORMING ORGANIZATION REPORT NO.	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RQR 5 Pollux Drive Edwards AFB CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-RQ-ED-VG-2014-330	
12. DISTRIBUTION / AVAILABILITY STATEMENT Distribution A: Approved for Public Release; Distribution Unlimited.					
13. SUPPLEMENTARY NOTES Briefing Charts presented at Silicon-Containing Polymers and Composites, San Diego, CA, 15 December, 2014. PA#14581					
14. ABSTRACT A study was conducted which explored the density, percent water uptake by weight, and coefficient of thermal expansion as a function of conversion as measured by DSC in bis(4-cyanatophenyl)-dimethylsilane (SiMCy). The density of SiMCy was found to decrease with increasing conversion due to the formation of more free volume as the cyanurate networks cure, and this decline in density was found to be similar in magnitude to that of other cyanate ester resins which have been previously studied. The water uptake followed similar trends as compared to other cyanate esters in that it was similarly dependent on conversion, but did not correlate with the development of free volume except at high conversions (80%-100%). However, SiMCy did show a much lower percent water uptake as compared to other cyanate ester resins such as Bisphenol-E dicyanate (LECy). This data taken together would suggest that water has a much lower affinity for the cyanurate oxygens in SiMCy than in other cyanate esters.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 19	19a. NAME OF RESPONSIBLE PERSON Joseph Mabry
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NO (include area code) 661-275-5857



Water Uptake Vs. Density and Conversion in Silicon Containing Cyanate Esters

17 December 2014

Michael D Ford,^{1*} Jacob J Zavala,¹ Dr. Andrew J Guenthner,² Dr. Joseph M Mabry²

¹ERC Incorporated, Air Force Research Laboratory, Edwards AFB, CA 93524

²Aerospace Systems Directorate, Air Force Research Laboratory, Edwards AFB, 93524

Ph: 661/275-5093; e-mail: michael.ford.40.ctr@us.af.mil



Outline



- Background
- Density as a Function of Conversion
 - Uncatalyzed and catalyzed LECy
 - Uncatalyzed and catalyzed SiMCy
 - Catalyzed BADCy
- Water Uptake as a Function of Conversion
 - Uncatalyzed SiMCy and LECy



Acknowledgements: Air Force Office of Scientific Research, Air Force Research Laboratory – Program Support; PWG team members (AFRL/RQRP)

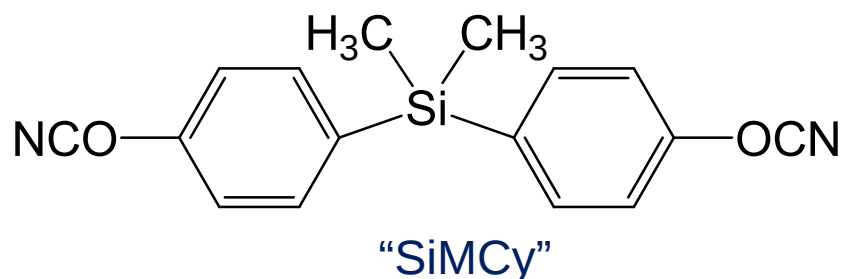
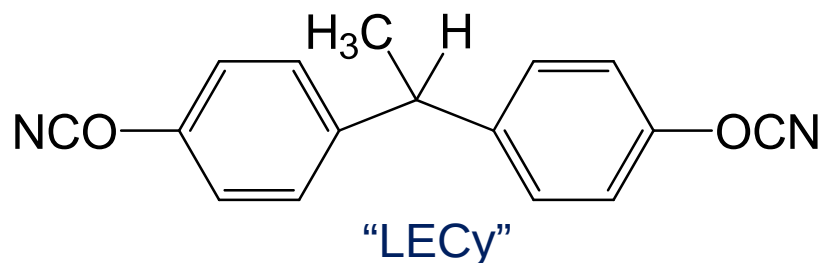
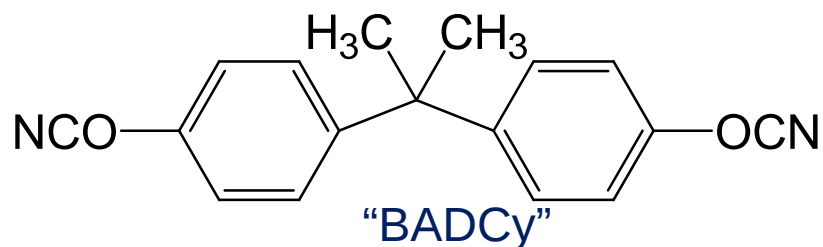


Background

- New methods of density measurement allow for 3x improvement in precision of density determination (typical error ~ 0.001 g/cc) with greatly reduced effort
- New methods of conversion measurement allow for a similar 3x improvement in precision (typical error now 0.01 – 0.02 or better across a broad range of conversion)
- Improved methods allow for quantitative investigation of issues that previously could only be addressed through qualitative studies
- Qualitatively, it is known that cyanate ester networks decrease in density as conversion increases, and that moisture uptake increases as conversion increases at conversions greater than 0.8
- It is speculated that the lower densities allow for greater free volume, which can accommodate more water in micro-voids within the network
- Quantitative studies can help to confirm or refute this model, as well as test applicability to different types of cyanate ester networks (flexible vs. rigid backbones), along with differences between catalyzed and uncatalyzed networks.



Materials and Methods



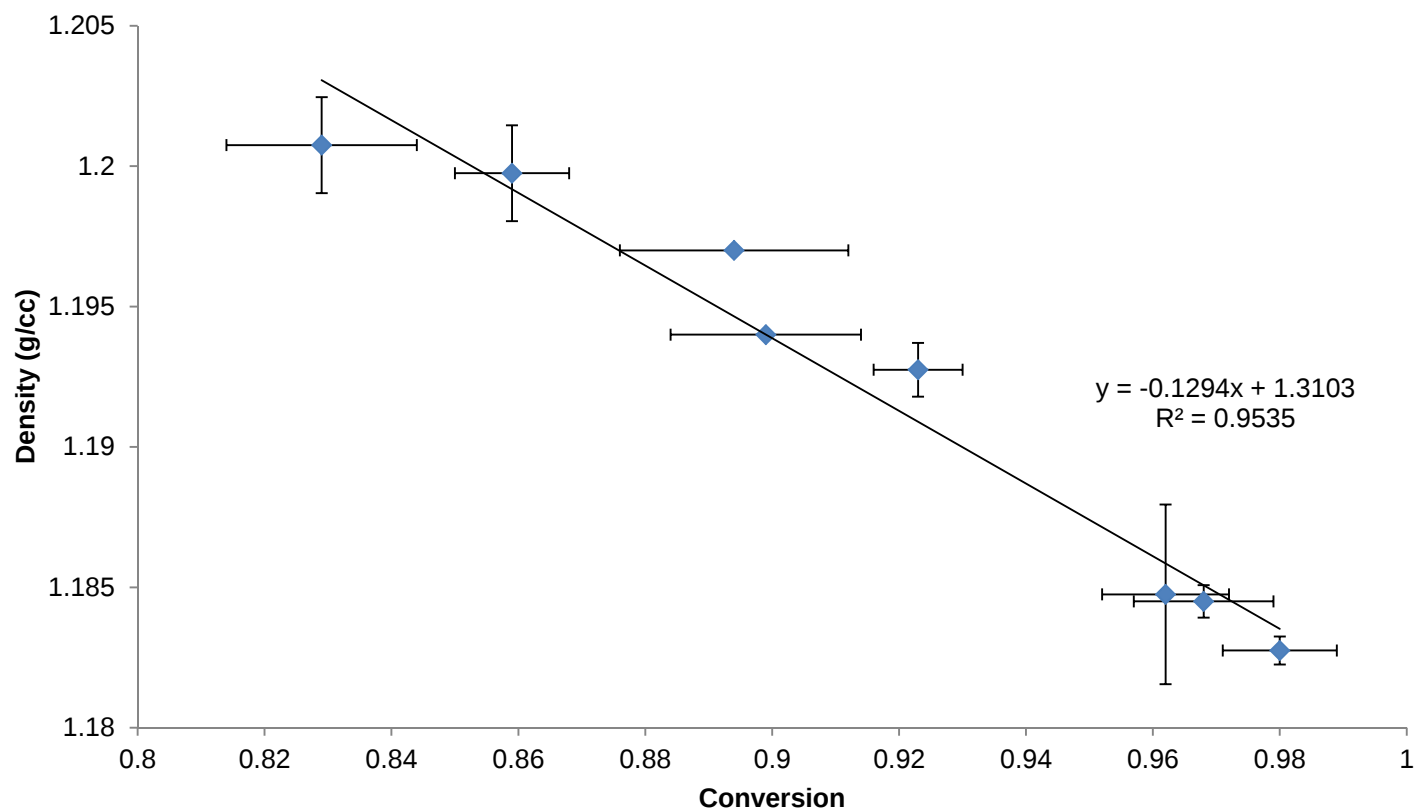
Name	MW (g/mol)
BADCy	278.3
LECy	264.3
SiMCy	294.4

- LECy is slightly smaller and more flexible than BADCy due to the missing methyl group
- SiMCy is slightly larger than BADCy due to the longer Si-C bonds, but also more flexible

- Density determination method: measure specific gravity by immersion in ethanol and air (Mettler-Toledo balance with specific gravity kit added).
- Conversions and Tg values were measured by DSC using a heating rate of 10 °C / min, with two scans to 350 °C for “as cured” and “fully cured” values, respectively.



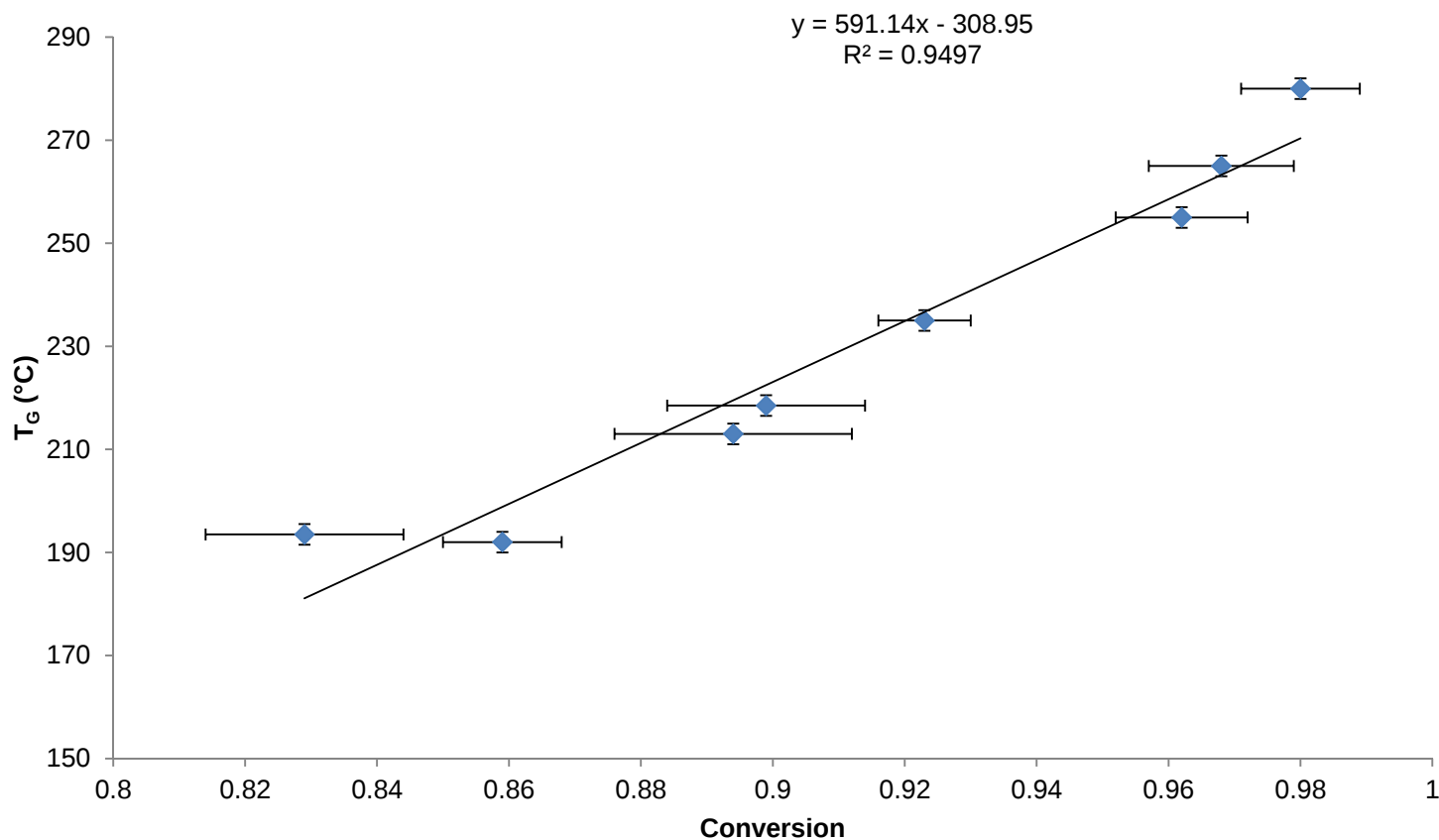
Catalyzed BADCy Data



- Catalyzed BADCy, Density vs. Conversion



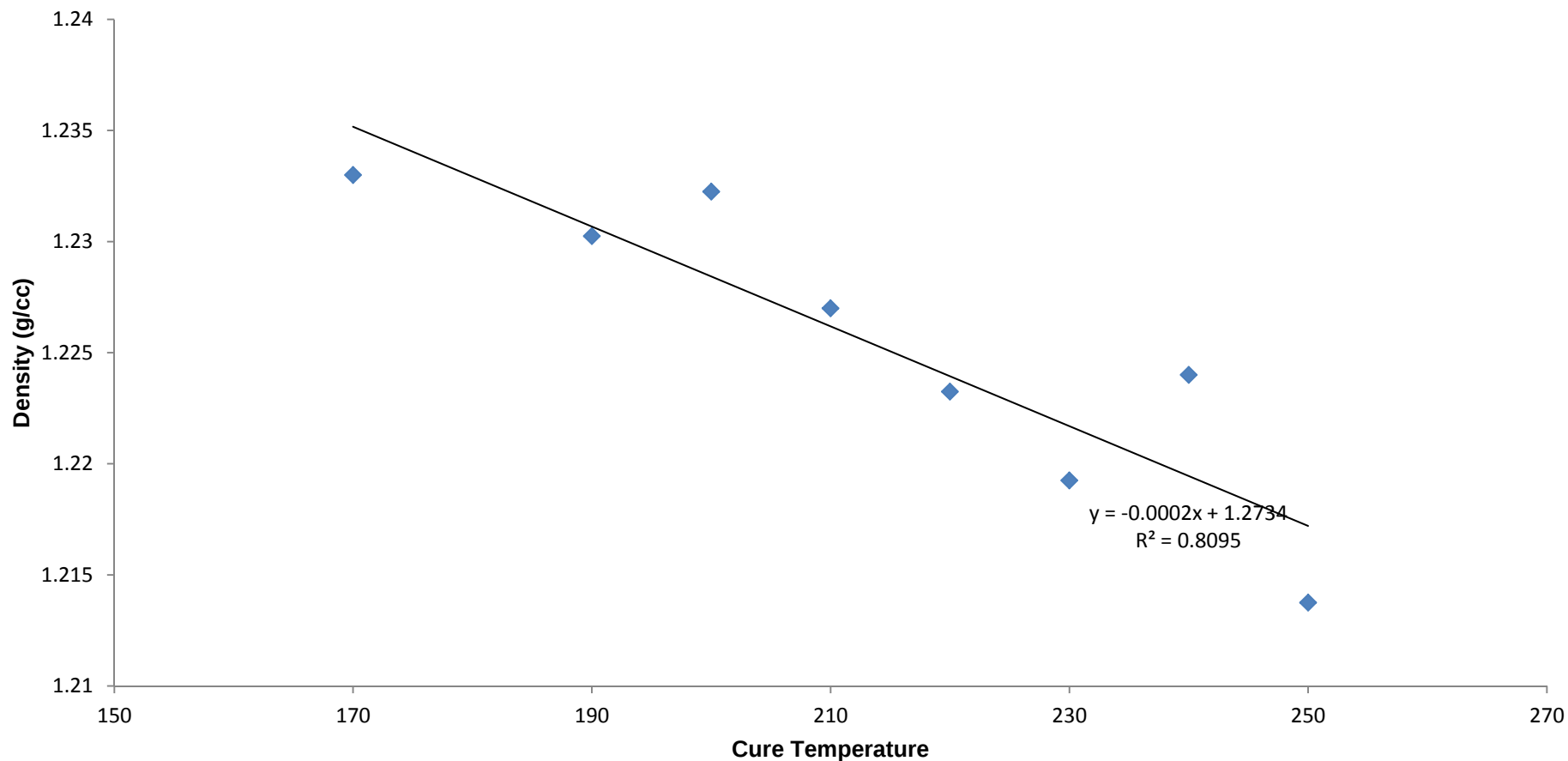
Catalyzed BADCy Data



- Catalyzed BADCy, T_g vs. Conversion; follows diBenedetto equation



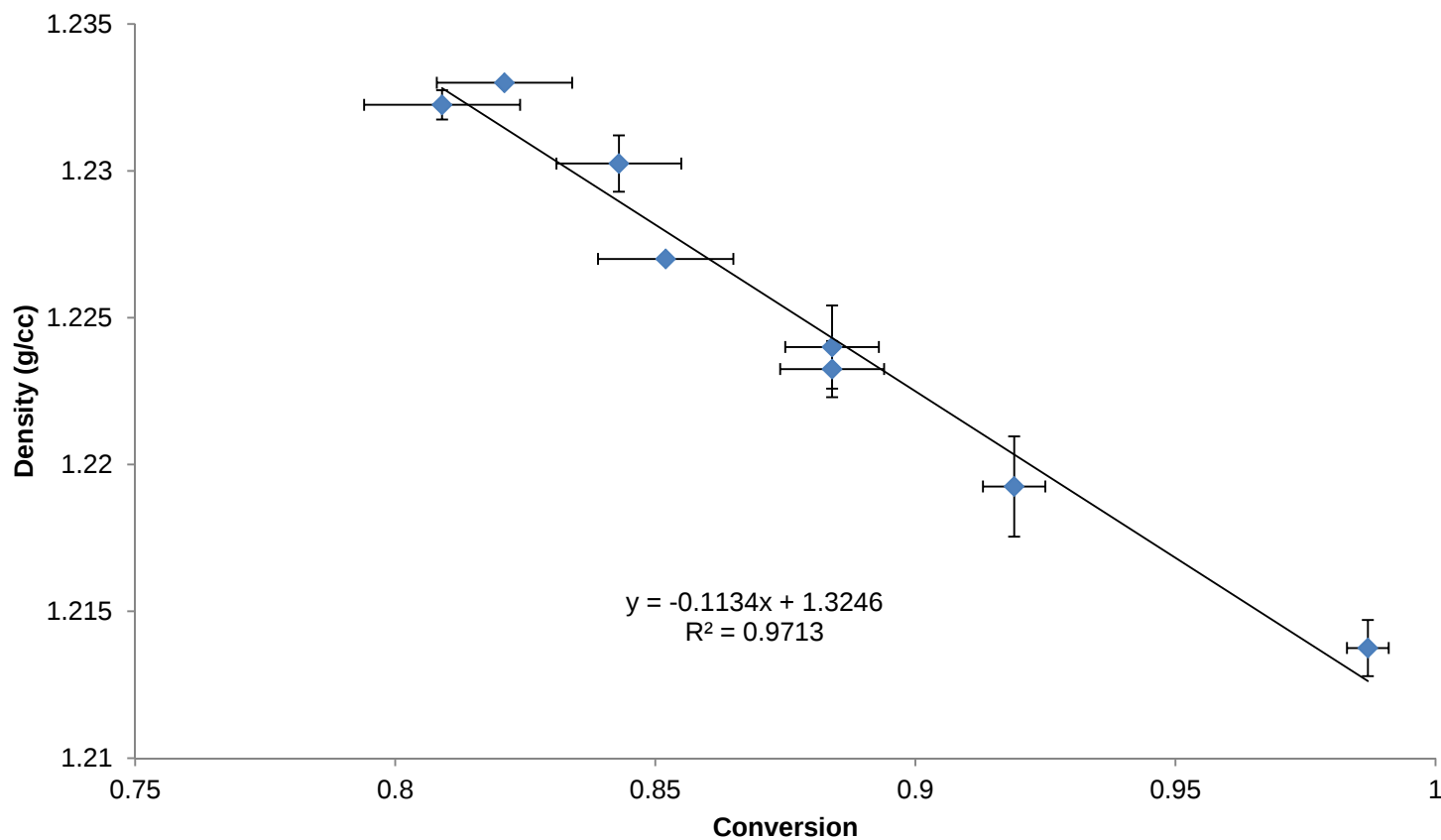
Uncatalyzed LECy Data



- Uncatalyzed LECy, Density vs. Cure Temperature



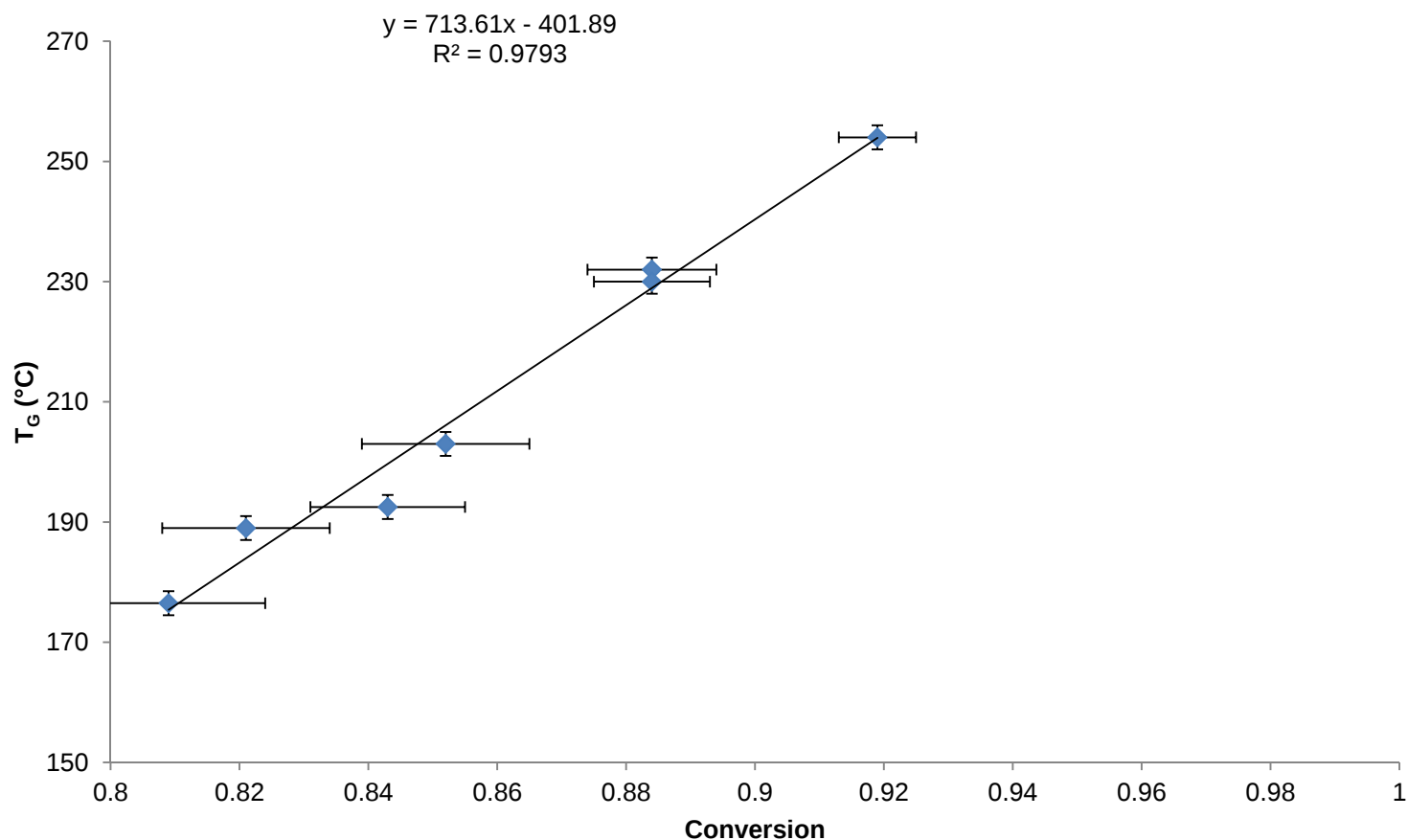
Uncatalyzed LECy Data



- Uncatalyzed LECy, Density vs. Conversion



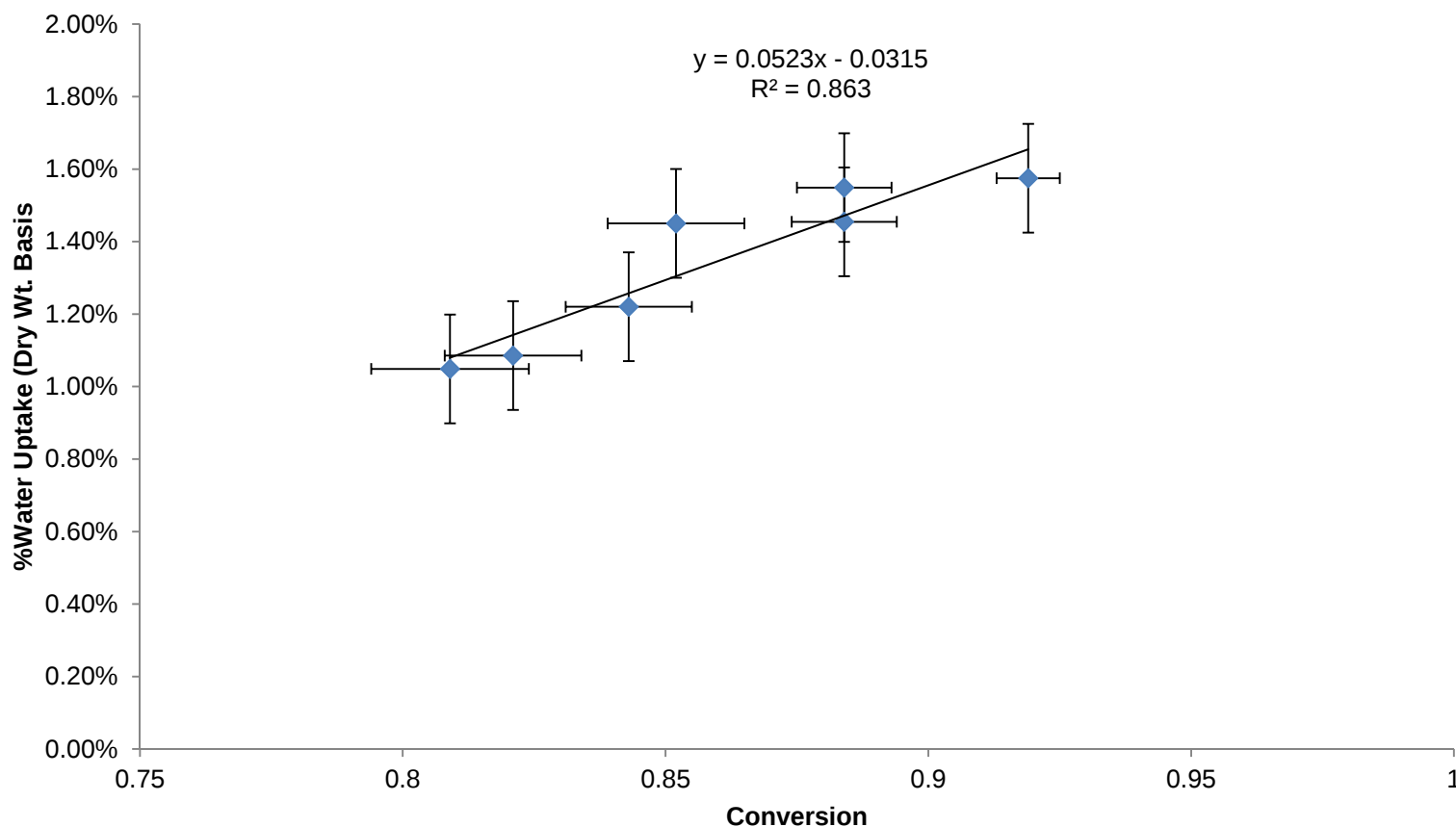
Uncatalyzed LECy Data



- Uncatalyzed LECy, T_g vs. Conversion; follows diBenedetto equation



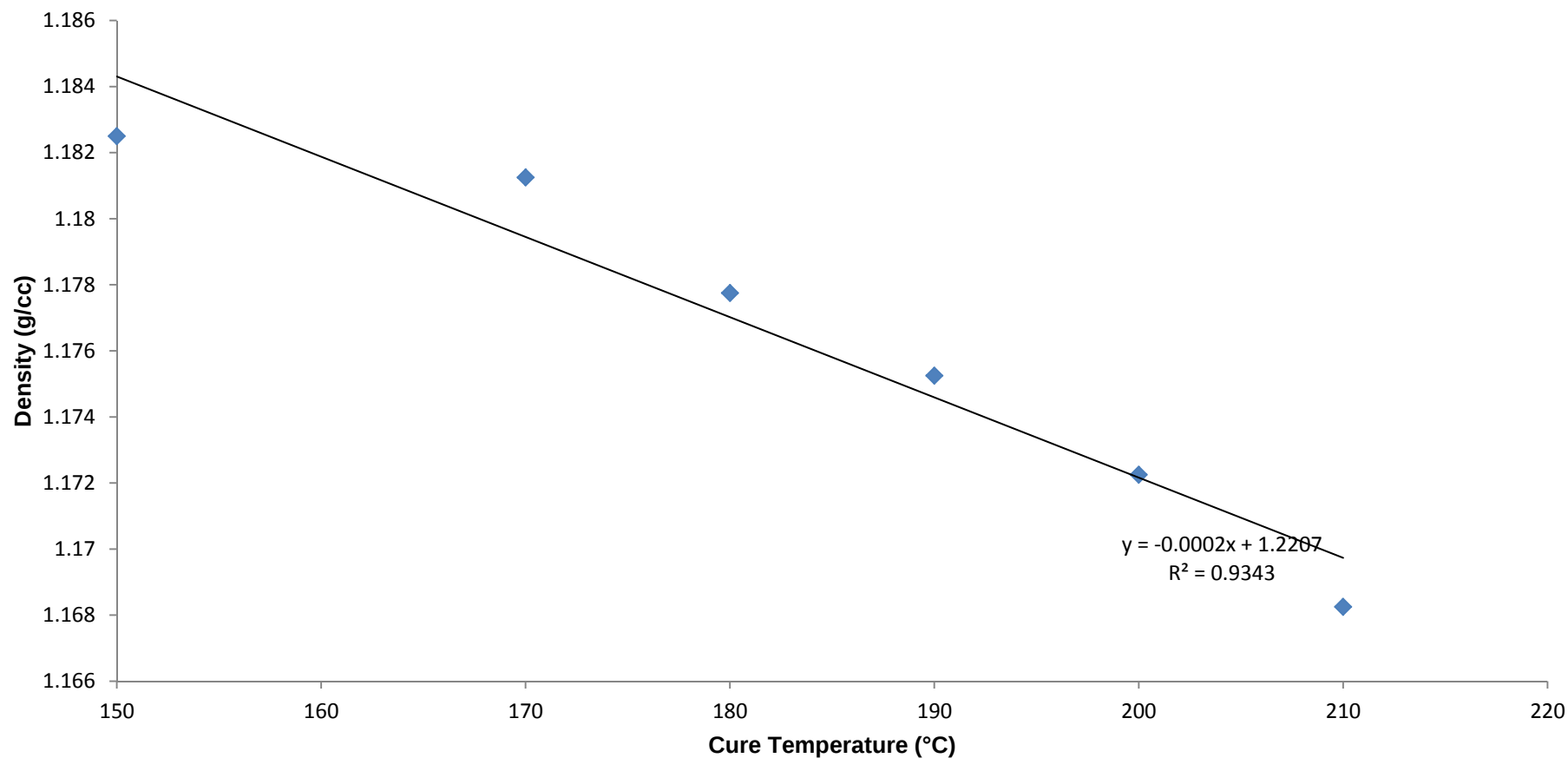
Uncatalyzed LECy Data



- Uncatalyzed LECy, %Water Uptake vs. Conversion



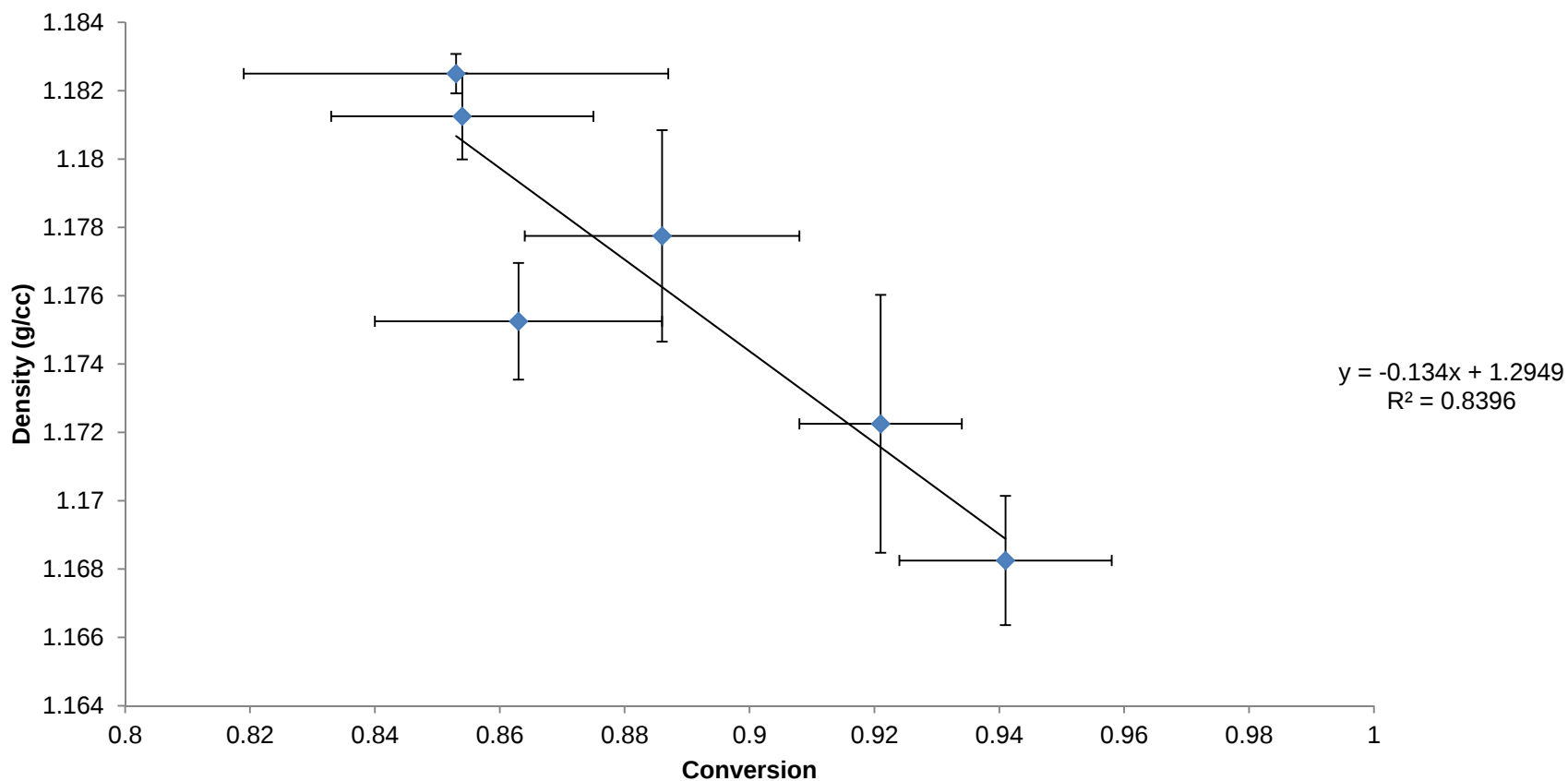
Catalyzed SiMCy Data



- Catalyzed SiMCy, Density vs. Cure Temperature



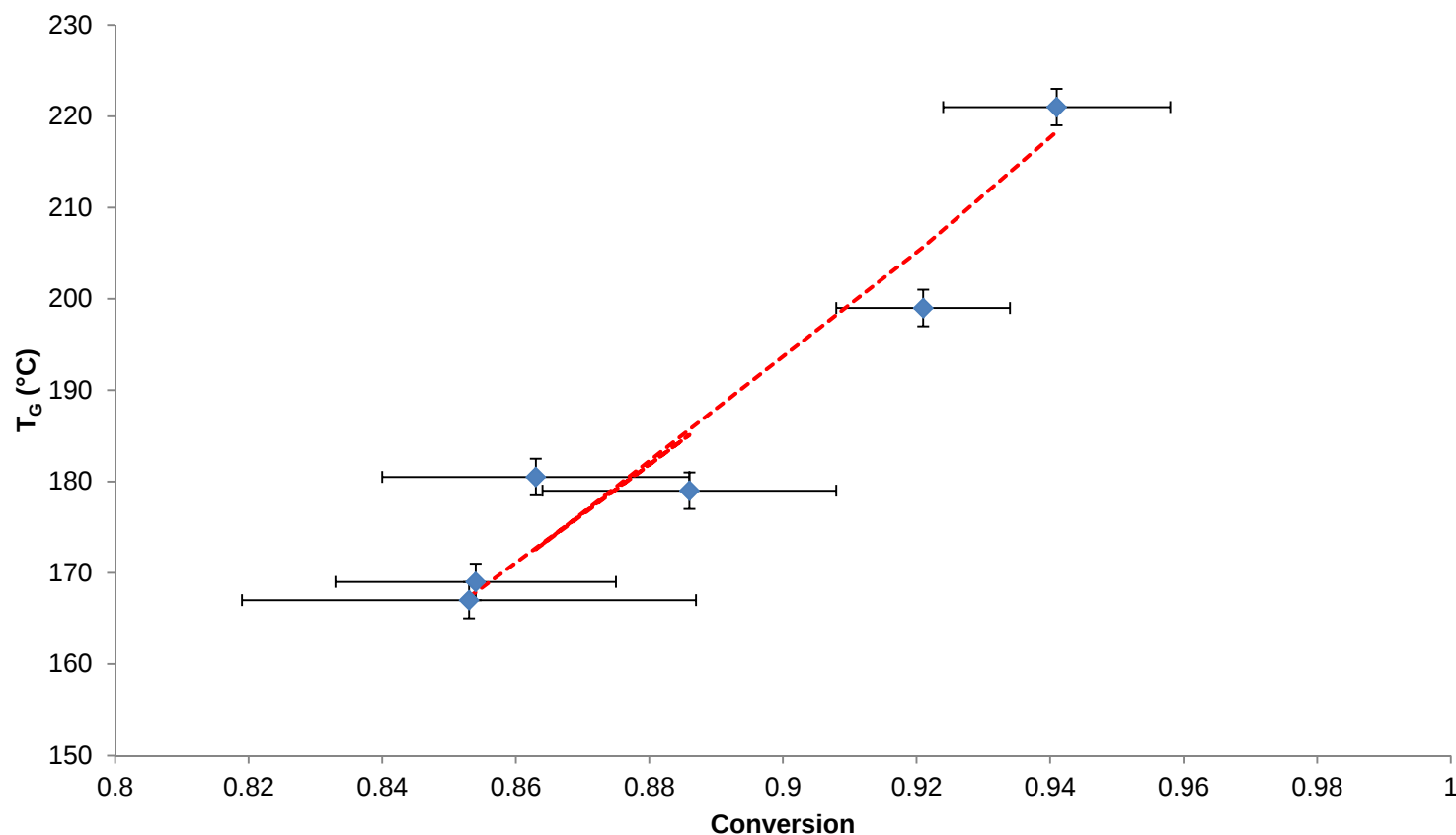
Catalyzed SiMCy Data



- Catalyzed SiMCy, Density vs. Conversion



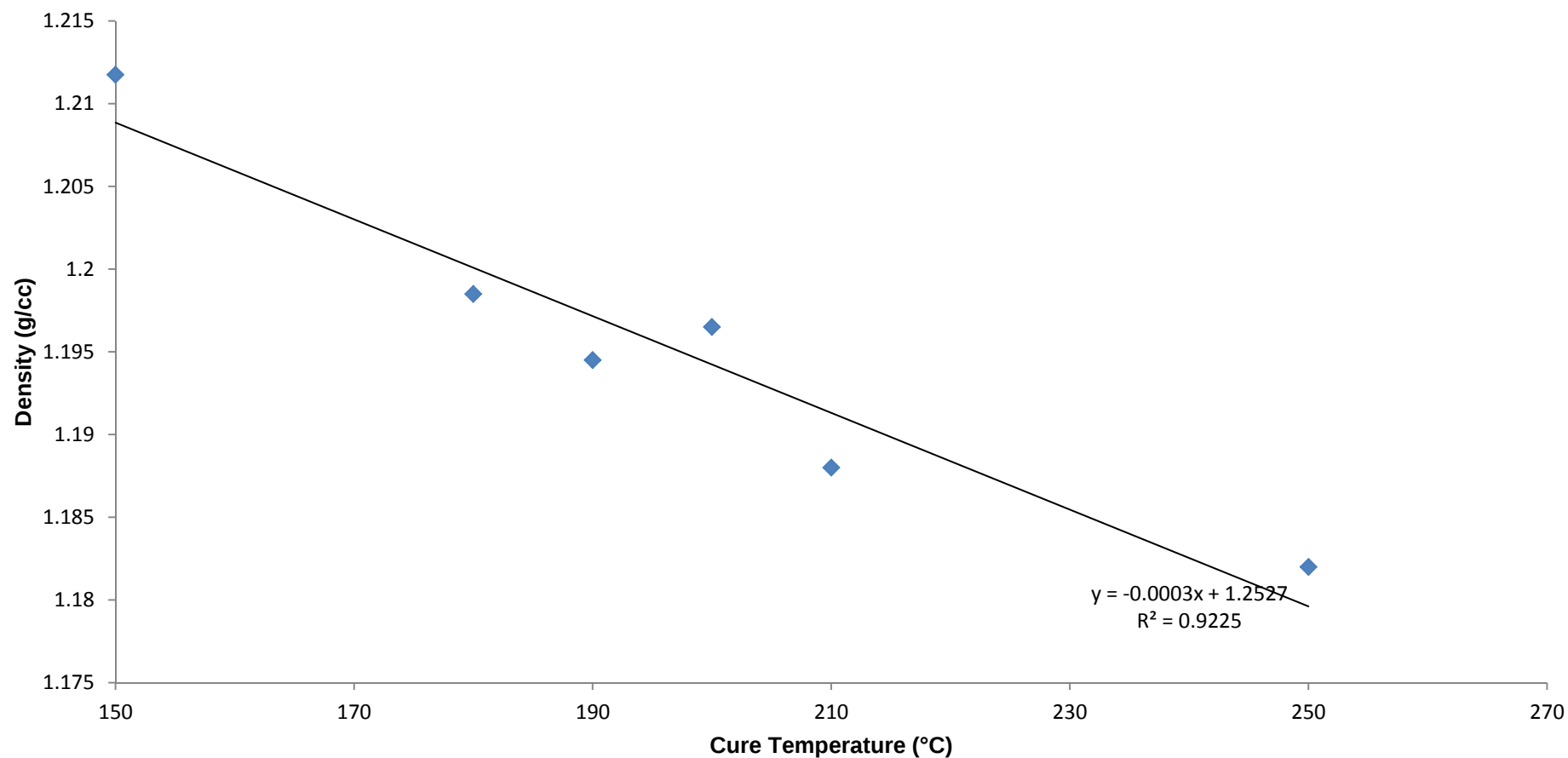
Catalyzed SiMCy Data



- Catalyzed SiMCy, T_g vs. Conversion, with fitted diBenedetto equation shown



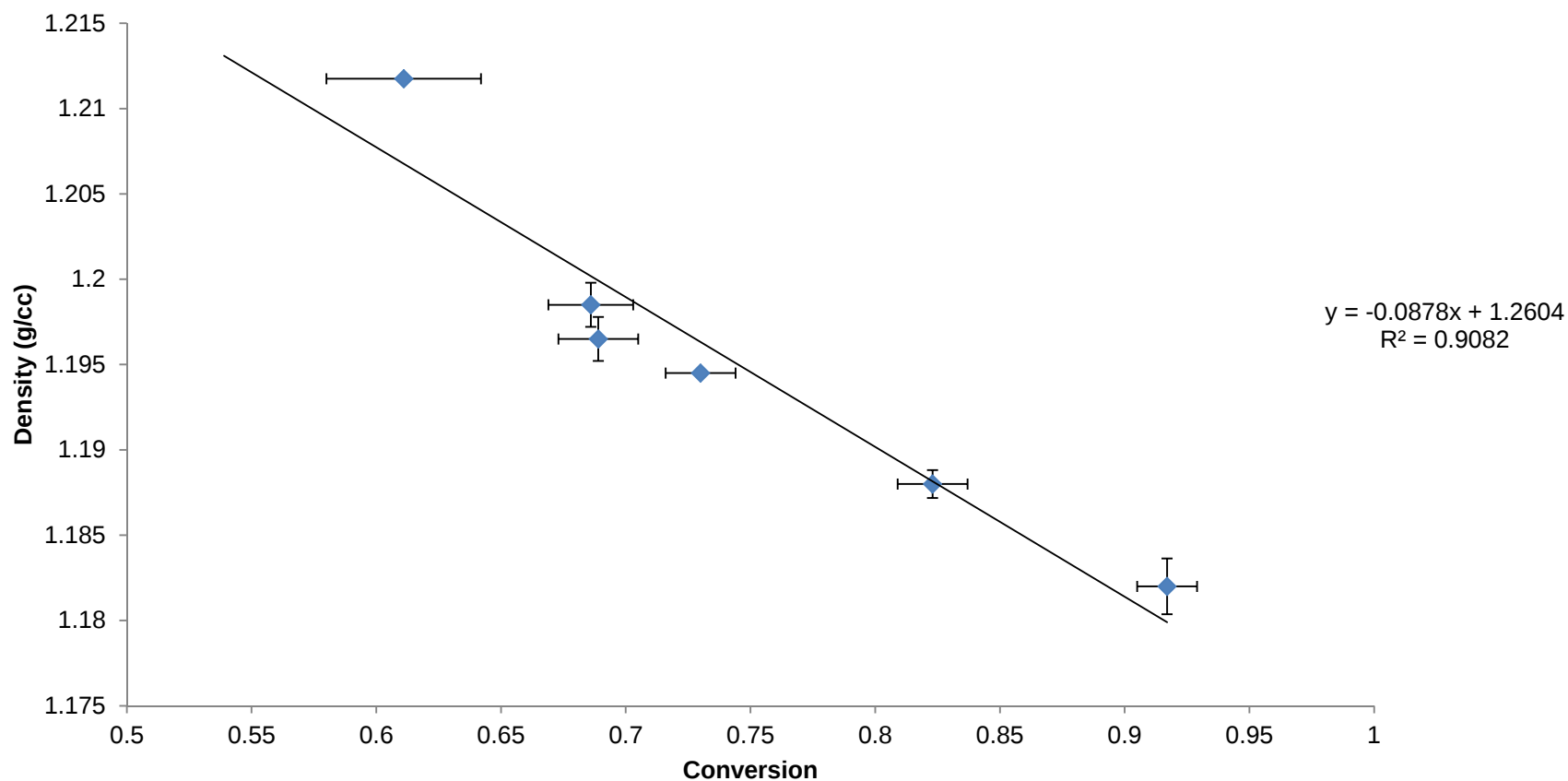
Uncatalyzed SiMCy Data



- Uncatalyzed SiMCy, Density vs. Cure Temperature



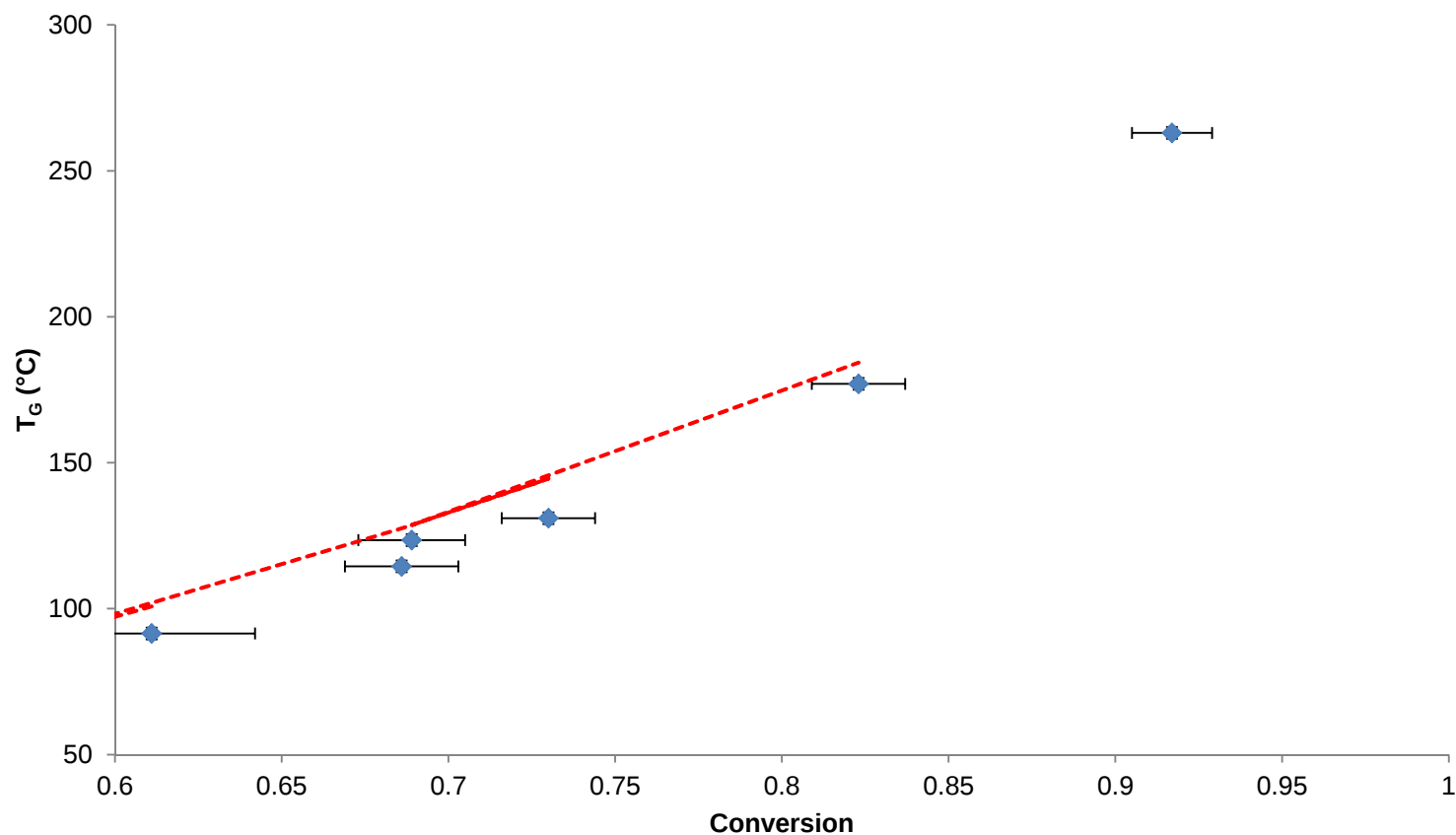
Uncatalyzed SiMCy Data



- Uncatalyzed SiMCy, Density vs. Conversion



Uncatalyzed SiMCy Data

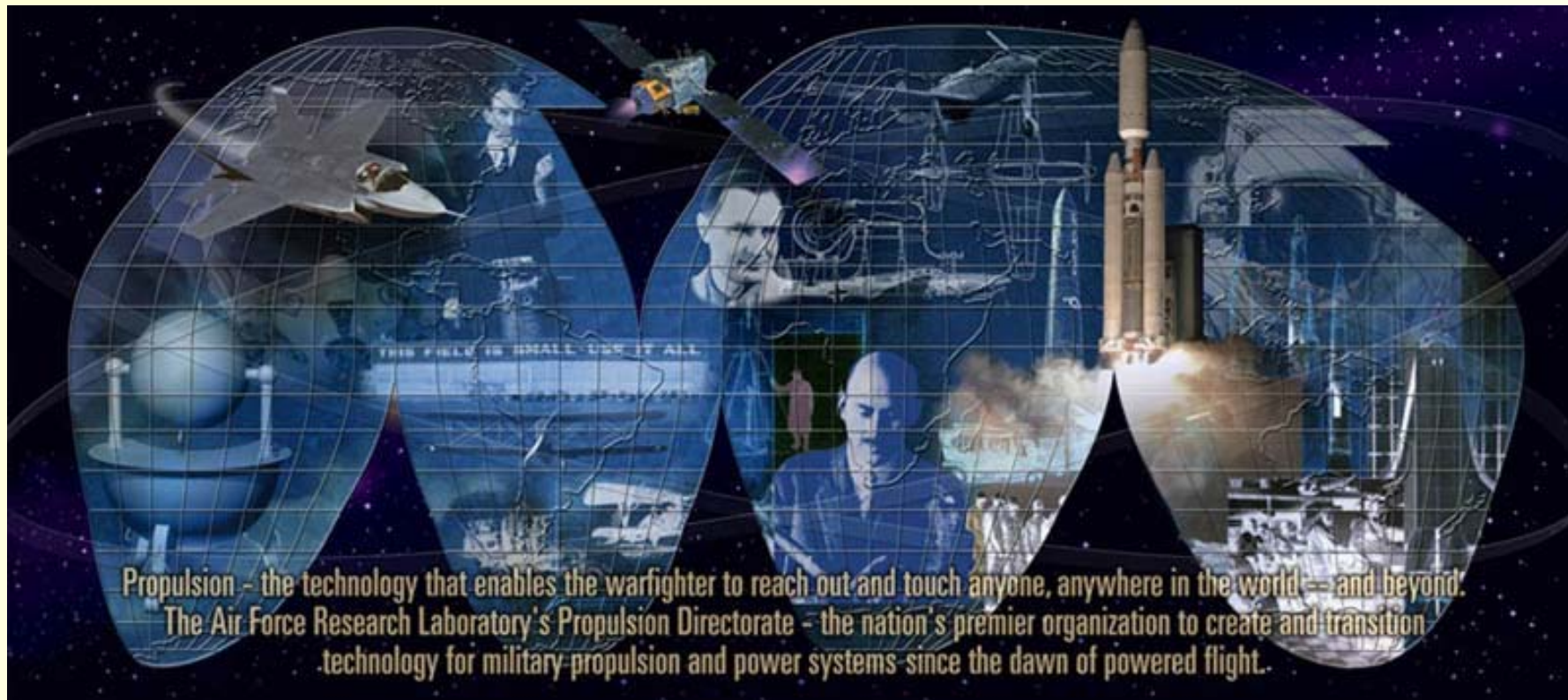


- Uncatalyzed SiMCy, T_g vs. Conversion, with DiBenedetto Equation Fit Shown



Summary

- As expected, higher cure temperatures lead to higher conversions due to vitrification effects
- Density vs. conversion data show a remarkably linear dependence across a broad range of conversions. At a given conversion, the trend $BADCy > LECy > SiMCy$, and the negative effect of catalyst inclusion on density, are all confirmed.
- T_g vs. conversion data follow the diBenedetto equation as expected, with the plasticizing effect of catalyst inclusion clearly distinguishable.
- Water uptake vs. conversion shows clear non-linear behavior and is not directly related to density. Water uptake may be influenced by both the loss in density and the formation of hydrophilic side products at higher cure temperatures.
- The water uptake for SiMCy is lower than for BADCy at all conversions studied, despite higher free volume in SiMCy, and similar increases in free volume with conversion. SiMCy appears to have an intrinsically lower affinity for water uptake.



AFRL

THE AIR FORCE RESEARCH LABORATORY
LEAD | DISCOVER | DEVELOP | DELIVER



DISTRIBUTION A: Approved for public release. Distribution is unlimited..