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Form Approved  
OMB No. 0704-0188

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<b>1. REPORT DATE (DD-MM-YYYY)</b> 17 March 2016		<b>2. REPORT TYPE</b> Briefing Charts		<b>3. DATES COVERED (From - To)</b> 24 February 2016 – 17 March 2016	
<b>4. TITLE AND SUBTITLE</b> Insights into surface structure and performance of fluorinated silicates from cohesive energy studies				<b>5a. CONTRACT NUMBER</b>	
				<b>5b. GRANT NUMBER</b>	
				<b>5c. PROGRAM ELEMENT NUMBER</b>	
<b>6. AUTHOR(S)</b> Andrew J. Guenther; Timothy S. Haddad; Michael D. Ford; Jeffrey R. Alston; Kevin R. Lamison; Shawn P. J. Kirby; Raymond Campos; Josephus Dossen; Joseph M. Mabry				<b>5d. PROJECT NUMBER</b>	
				<b>5e. TASK NUMBER</b>	
				<b>5f. WORK UNIT NUMBER</b> Q16J	
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> Air Force Research Laboratory (AFMC) AFRL/RQRP 10 E. Saturn Blvd. Edwards AFB, CA 93524-7680				<b>8. PERFORMING ORGANIZATION REPORT NO.</b>	
<b>9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b> Air Force Research Laboratory (AFMC) AFRL/RQR 5 Pollux Drive Edwards AFB, CA 93524-7048				<b>10. SPONSOR/MONITOR'S ACRONYM(S)</b>	
				<b>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</b> AFRL-RQ-ED-VG-2016-056	
<b>12. DISTRIBUTION / AVAILABILITY STATEMENT</b> Approved for Public Release; Distribution Unlimited.					
<b>13. SUPPLEMENTARY NOTES</b> For presentation at American Chemical Society 251st National Meeting; San Diego, CA (17 March 2016) PA Case Number: #16153; Clearance Date: 3/18/2016					
<b>14. ABSTRACT</b> Viewgraph/Briefing Charts					
<b>15. SUBJECT TERMS</b> N/A					
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b>  SAR	<b>18. NUMBER OF PAGES</b>  17	<b>19a. NAME OF RESPONSIBLE PERSON</b> A Guenther
<b>a. REPORT</b> Unclassified	<b>b. ABSTRACT</b> Unclassified	<b>c. THIS PAGE</b> Unclassified			<b>19b. TELEPHONE NO</b> (include area code) N/A

Standard Form  
298 (Rev. 8-98)  
Prescribed by ANSI  
Std. Z39.18

# Insights into surface structure and performance of fluorinated silicates from cohesive energy studies



17 March 2016

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# Outline



- **Background: Complexity of Fluorosilicate Interactions**
- **Performance comparisons of Fluorosilicate Compounds**
- **Surface Migration Studies of F-decyl-M2**



**Acknowledgements: Air Force Office of Scientific Research, Air Force Research Laboratory, CSU STARS Program**



# Why is Surface Science Essential for Propulsion?



- Propulsion efficiency relies on achieving fast, controlled motion of fluids with minimal interference from solids



**Required: surfaces with well-controlled fluid interaction that can survive extreme environments → Si/O, F**



# Fluorosilicates Can Interact in Complex Ways

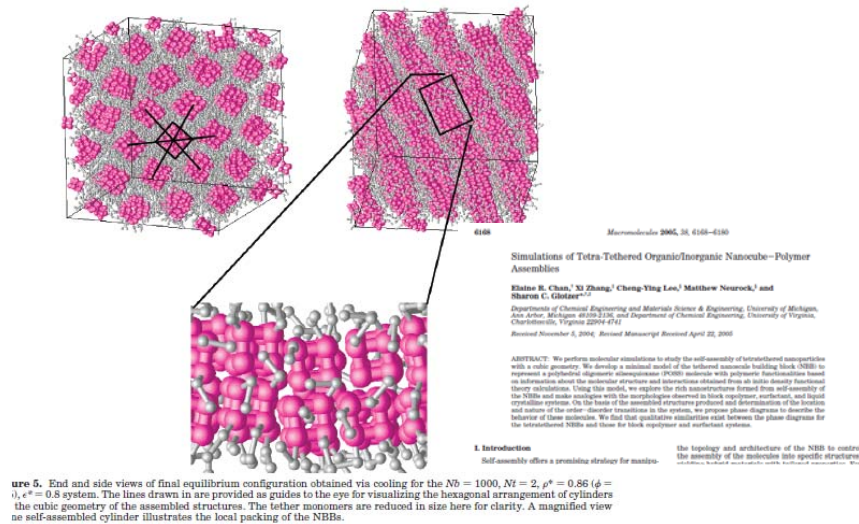
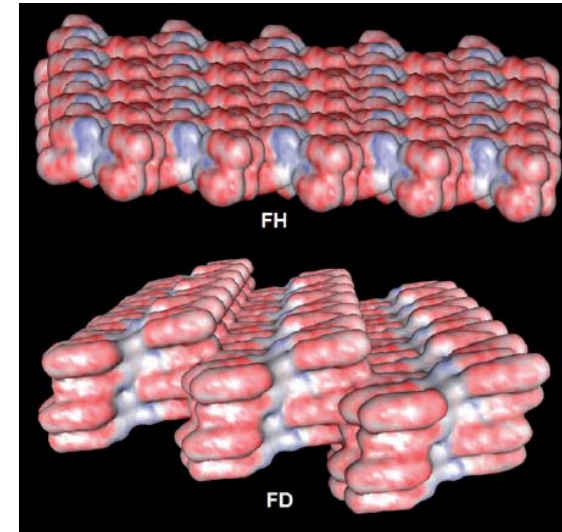


Figure 5. End and side views of final equilibrium configuration obtained via cooling for the  $Nb = 1000$ ,  $Nt = 2$ ,  $\rho^* = 0.86$  ( $\rho = 0.8$ ),  $\epsilon^* = 0.8$  system. The lines drawn in are provided as guides to the eye for visualizing the hexagonal arrangement of cylinders the cubic geometry of the assembled structures. The tether monomers are reduced in size here for clarity. A magnified view of a self-assembled cylinder illustrates the local packing of the NBs.



Chan, E. *et al. Macromolecules* **2005**, 38, 6168-6180.

Mabry, J.. *et al. Angew. Chem. Int. Ed.* **2008** 47, 4137-4140.

- Translational Migration
- Phase Separation / Surface Concentration
- Self-Assembly
- Orientational Ordering (Intra-molecular and Inter-molecular)
- Peripheral Group Ordering (e.g. Intra-molecular Helices, Intermolecular Crystals)
- Molecular Ordering (e.g. Si – F Intra- and Inter-molecular Interaction, Cage-Cage Interactions)
- Dynamic Covalent Chemistry



# Comparison of Surface Energy Parameters for Fluorosilicates



Table 3. Computed Values of the Dispersion ( $\gamma_{sv}^d$ ), Acidic ( $\gamma_{sv}^+$ ), and Basic ( $\gamma_{sv}^-$ ) Components of Solid-Surface Energy (mN/m) for Various Fluoroalkylated Silicon-Containing Moieties

	alkanes (Zisman analysis)	all liquids <sup>b</sup> (eq 1 with $\varphi_{sl} = 1$ )	diiodomethane, dimethyl sulfoxide and water (eq 5)				
	$\gamma_c$	$\gamma_{sv}$	$\gamma_{sv}$	dispersion ( $\gamma_{sv}^d$ )	polar ( $\gamma_{sv}^p$ )	acidic ( $\gamma_{sv}^+$ )	basic ( $\gamma_{sv}^-$ )
fluorodecyl T <sub>8</sub>	5.5	9.3	8.8	8.7	0.1	0.04	0.1
fluorooctyl T <sub>8</sub>	7.4	10.6	10.9	10.6	0.3	0.2	0.1
fluorohexyl T <sub>8</sub>	8.5	11.6	47.4	11.4	36.0	20.8	15.6
fluoropropyl T <sub>8</sub>	19.7	18.7	38.4	19.1	19.3	11.8	7.9
hexafluoro- <i>i</i> -butyl T <sub>8</sub>	17.7	19.1	26.9	26.8	0.1	0.002	0.8
fluorodecyl T <sub>8</sub>	5.5	9.3	8.8	8.7	0.1	0.04	0.1
fluorodecyl Q <sub>4</sub>	14.5	14.3	14.9	14.5	0.8	0.0	0.2
fluorodecyl M <sub>2</sub>	19.6	26.8	39.7	30.9	8.8	2.0	9.7

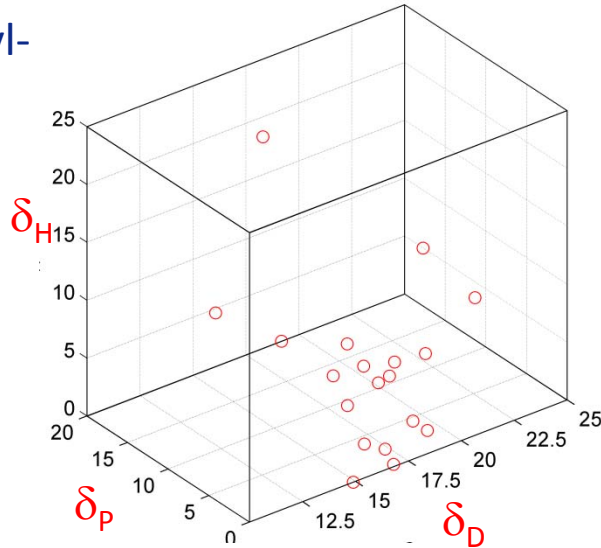
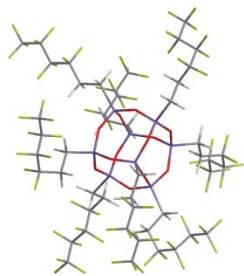
- Typical Surface Energies:  $-\text{CF}_3 = 6 \text{ mN/m}$ ;  $-\text{CF}_2- = 18 \text{ mJ/m}$ ;  $-\text{Si}(\text{CH}_3)_2\text{O}- = 20 \text{ mJ/m}$ ;  $-\text{CH}_2- = 27 \text{ mJ/m}$  – depends on number density of groups
- F-decyl-T8 is typical of  $-\text{CF}_3$ , suggesting at least a highly oriented structure
- F-decyl-M2, despite having a similar make-up of group, is much higher, presumably due to random orientation (F-decyl-M2 in bulk is a liquid under ambient conditions)
- The values reported are also potentially affected by surface reorganization and solubility of the compounds in the probe liquids (F-decyl-T8 is highly insoluble, F-decyl-M2 is soluble in many liquids).



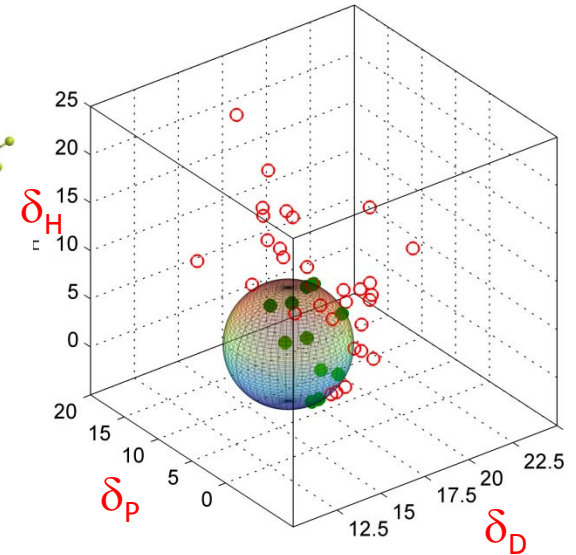
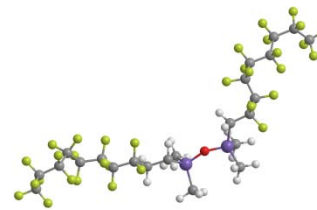
# Cohesive Energy Characteristics of Fluorosilicates



Octa-fluorohexyl-POSS



Fluorodecyl-M2



- Green dots indicate solubility > 100 mg/mL, red dots indicate solubility < 100 mg/mL
- Even the shorter-chain F-hexyl-T8 is highly insoluble compared to the F-decyl-M2

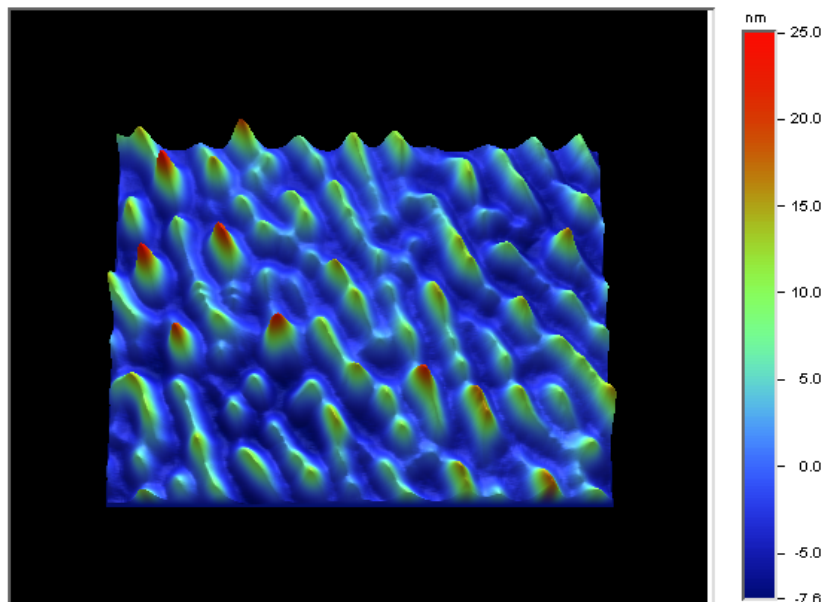
POSS / Silicate Type	$\delta_D$	$\delta_P$	$\delta_H$	$R_0$	#Exceptions / #Good
Fluorodecyl-M2	15.0	4.3	4.0	6	0/11



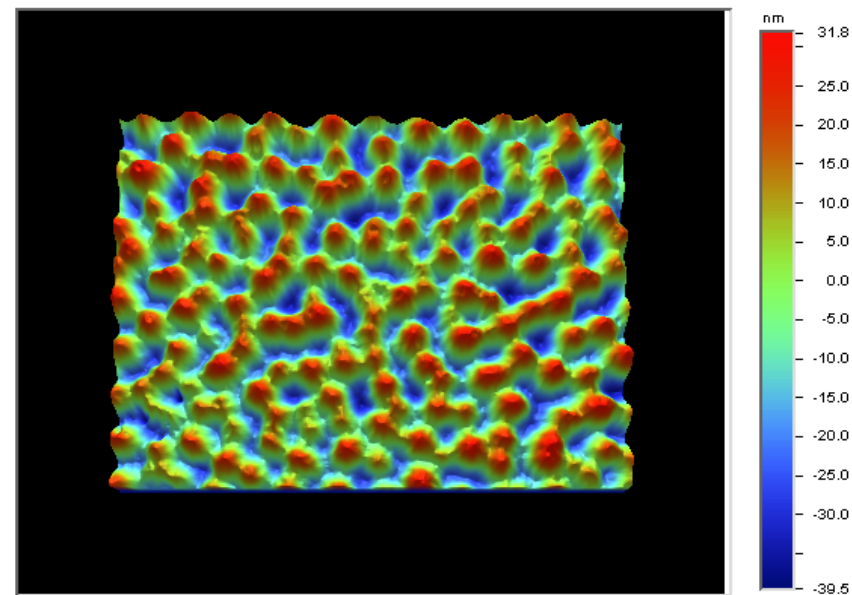
# Insolubility of F-decyl-T8 Drives Surface Migration / Crystallization



Domain Formation \from 20 Wt % Blend in PMMA, 10 mg/mL in AK225, Spin Coated @ 1500 rpm for 30 sec



As-coated,  $R_a = 4$  nm

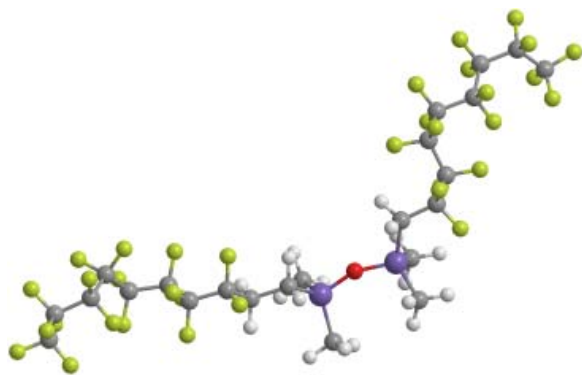


Annealed 110 °C, 270 min.,  $R_a = 11$  nm

F-decyl-T8 migrates to the surface and phase separates from matrices such as PMMA. Concentrated F-decyl-T8 at the surface crystallizes; the crystals create a surface texture. Surface energy, inhomogeneity, and texture each affect wetting properties..



# F-Decyl-M2: Multiple Configurations Possible



Hairpin: Lowest Surface Energy w/ Gradient



Random: "Entropy Wins" – True in Bulk



Extended: Minimum Intra-molecular Strain; Easier to Crystallize

The relatively high solubility of F-decyl-M2 enables potential competition among multiple driving forces during film formation when mixed with PMMA, cast, dried, and subsequently annealed.



# Materials & Methods



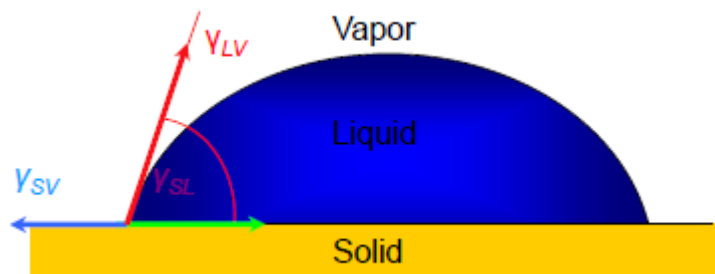
Matrix:  $3 \times 10^4$  MW PMMA.

F-decyl-M2: synthesized at AFRL

Film Deposition: Achieved by dissolving both PMMA and F-decyl-M2 in dichloro-pentafluoropropane (AK225), 10 mg/mL total solids; 20-50 wt% F-decyl-M2, prepared via pin casting @ 1500 rpm for 30 sec  
Thermal annealing of films at temperatures of 80-110 C for 30 – 270 mins as an optional step

Analytical tools: direct observation (OM/SEM), surface deformation (interferometry), dynamic contact angle measurements

1. As-cast and equilibrium morphology
2. Dynamics of aggregate formation and growth
3. Aggregate morphology and its relationship to processing

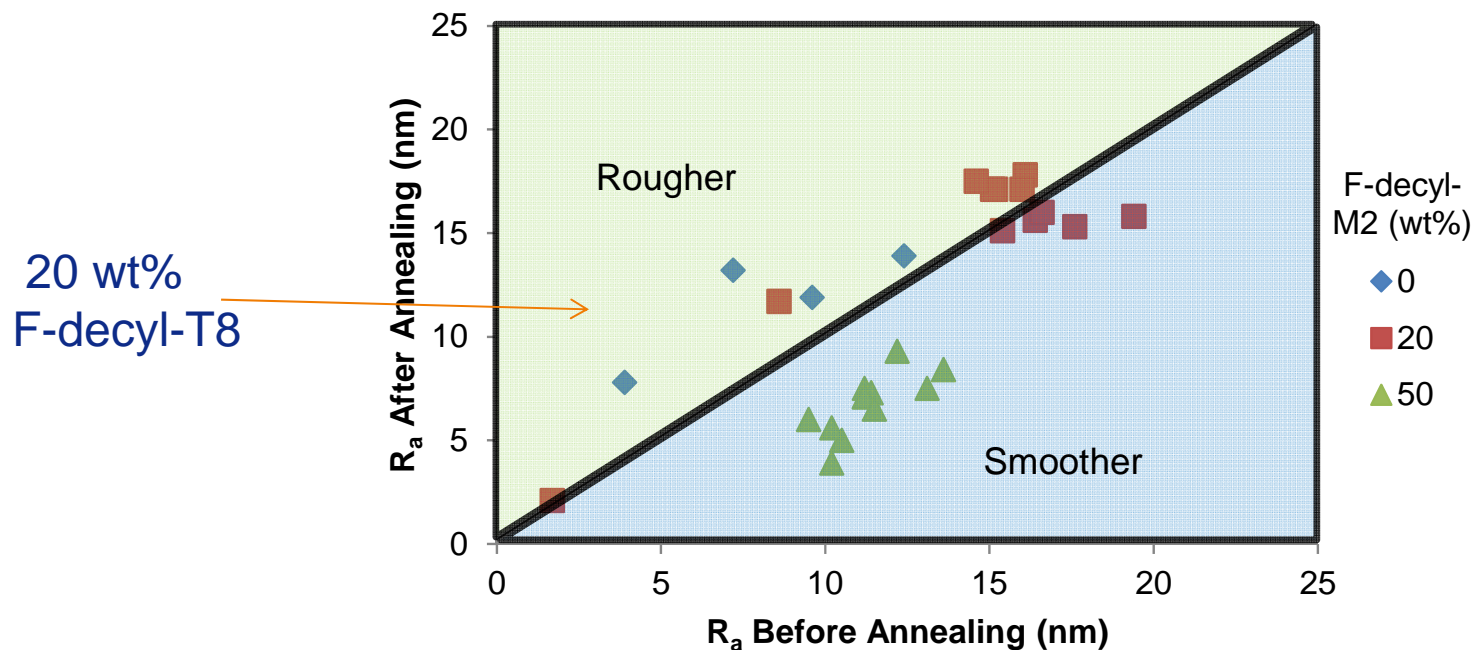




# F-decyl-M2 Acts as a Surface Plasticizer



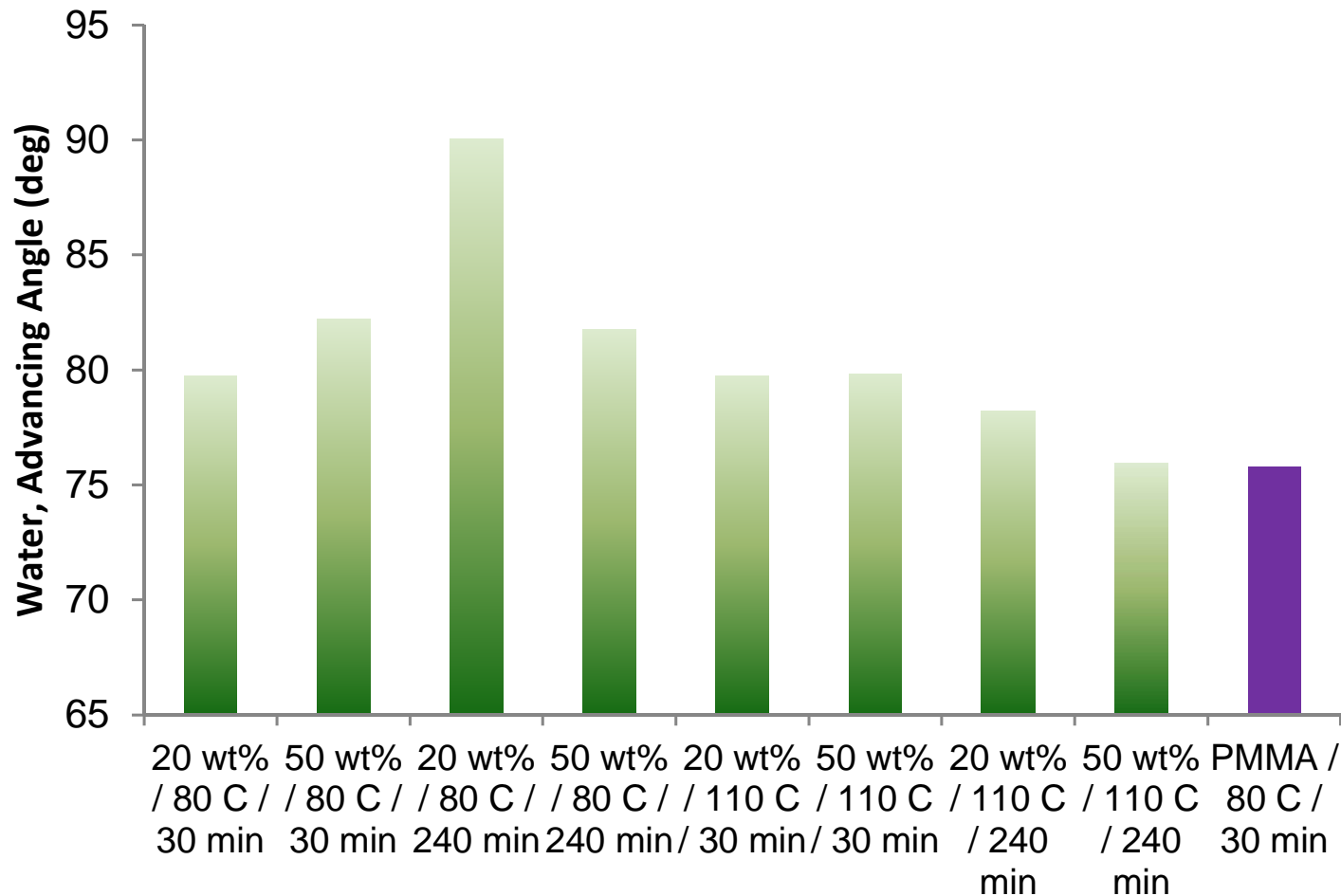
## Comparison of Average Roughness Before and After Annealing (All Annealing Conditions)



Spin casting produces “wrinkled” textures of ~10 nm average roughness; annealing slightly increases roughness in pure PMMA, but smooths it in mixtures rich in F-decyl-M2.



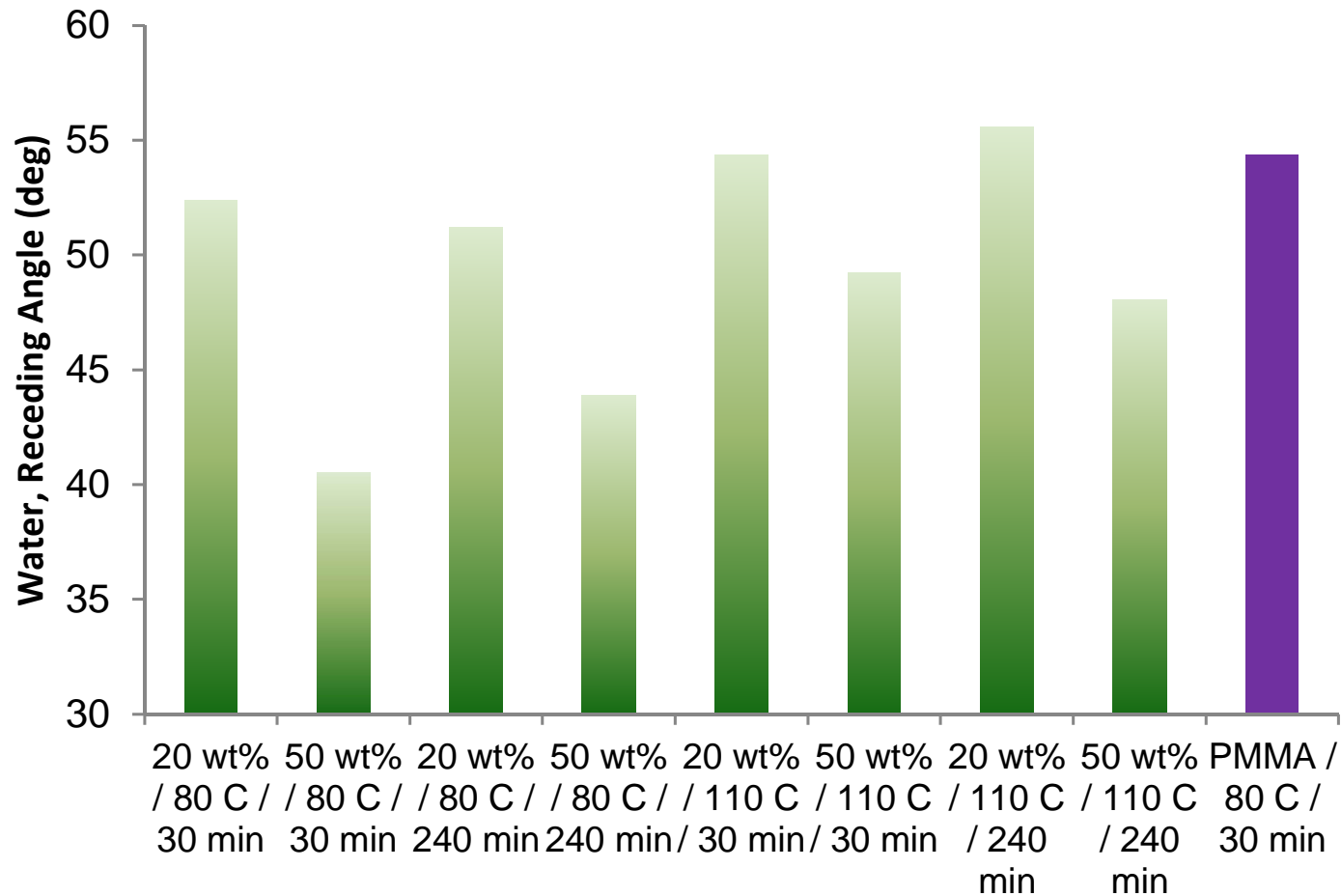
# F-decyl-M2 / PMMA: Water Advancing Angles



F-decyl-M2 surfaces tend to have slightly higher advancing contact angles compared to PMMA, in line with the slightly lower surface energy of F-decyl-M2



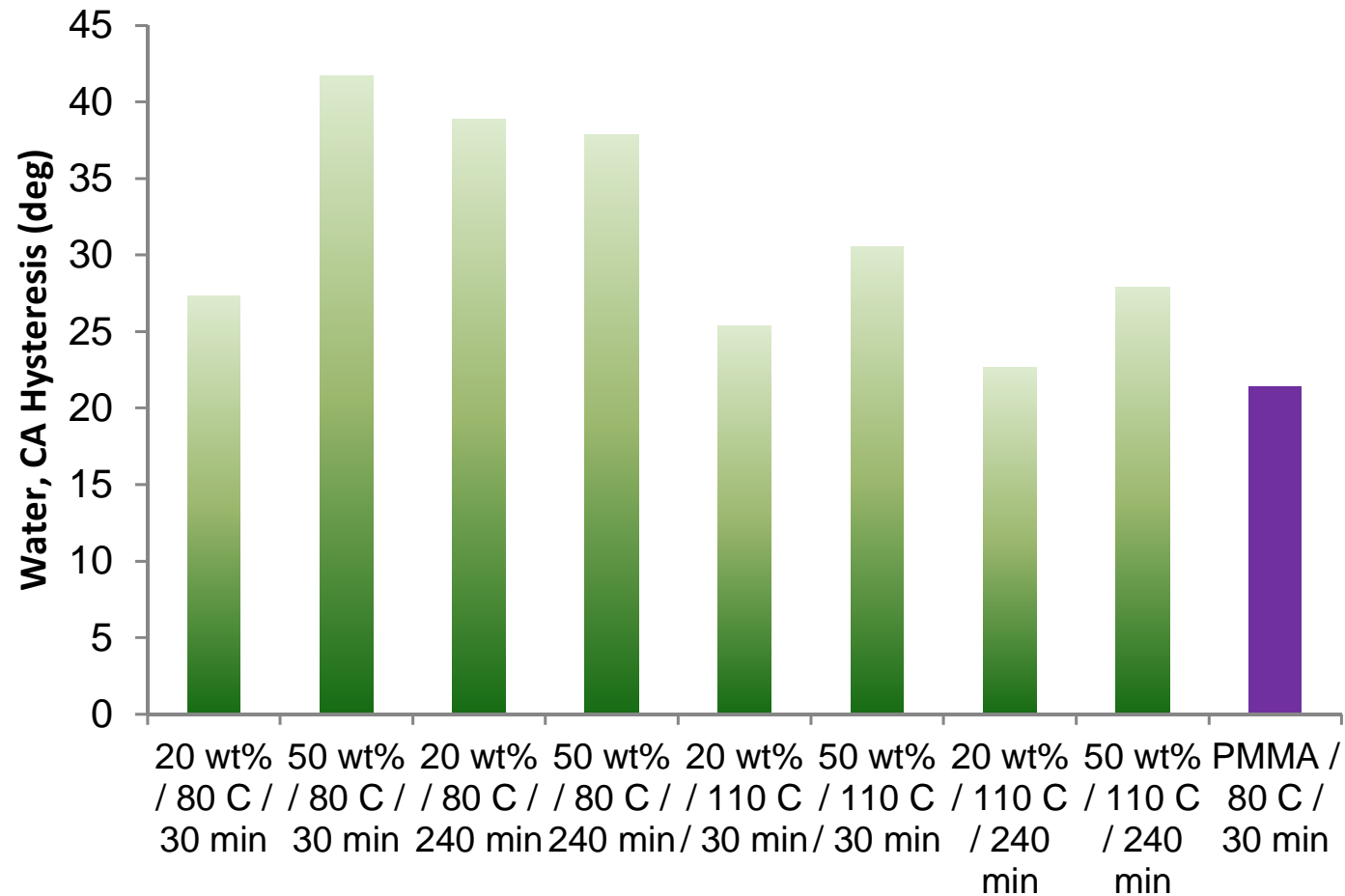
# F-decyl-M2 / PMMA: Water Receding Angles



Definite trend toward lower receding angles at higher F-decyl-M2 loading; more extensive annealing tends to mitigate this effect



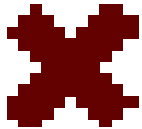
# F-decyl-M2 / PMMA: Water CA Hysteresis



In general, lower F-decyl-M2 loading, and annealing above the matrix glass transition temperature, tends to result in lower hysteresis



# Factors Responsible for CA Hysteresis in F-Decyl-M2 / PMMA



- **Roughness:** Samples tend to be wavy with ~50 nm amplitude and ~50 micron wavelength, therefore the Wenzel ratio is insignificantly different from unity. Thus, roughness should not contribute appreciably to hysteresis.



- **Heterogeneity:** Should result in both increased advancing angle coupled with decreased receding angle, does not seem to agree with data. Surface textures do not show evidence of significant heterogeneity development, though some may be present. Also does not explain hysteresis in pure PMMA. Nonetheless, needs to be checked via XPS / EDAX.



- **Rearrangement:** Should result in little change in advancing angles with large change in receding angle. Expected to be more significant with higher F-decyl-M2 loading, and the most “molecularly random” (least annealed) samples. Consistent with data.



# Summary



- Spin coated films of F-decyl-M2 / PMMA are smooth enough to avoid too much interference with contact angle measurements from roughness, but are rough enough to probe relaxation effects on annealing
- F-decyl-M2 does appear to migrate to the surface, though the extent needs quantification
- The primary role of F-decyl-M2 appears to be as a plasticizer, meaning that no ordering is likely to take place; concentration of F-decyl-M2 at the air interface likely facilitates the random configurations typical of bulk material
- The plasticizing effect of F-decyl-M2 may facilitate rearrangement of the surface upon contact with water (likely bringing polar groups in PMMA to the surface); annealing may suppress this effect by allowing PMMA “trapped” near the surface during drying to move into the bulk.

