Improving Adhesive Bonding of Composites Through Surface Characterization Using Inverse Gas Chromatography (IGC) Methods

Rita Taitano Johnson

Brian Flinn

University of Washington

Participants

Federal Aviation Administration
    David Westland, Curtis Davies
Center of Excellence in Advance Materials in Transport Aircraft Structures

The Boeing Company
    Kay Blohowiak, John Osborne, Ryan Wilson, Gail Hahn

University of Washington Material Science Engr
    Dr. Brian Flinn

Outline

- Motivation & Key Issues
- Introduction
  - Measuring Surface Energy
  - Objective
  - Contact Angle Methodology
  - IGC Methodology
- Experimentation
- Results
  - Contact Angle Measurements
  - IGC Measurements
- Conclusions/Discussions
- Future Work

A Center of Excellence
AMTAS
Advanced Materials in Transport Aircraft Structures

Motivation and Key Issues

- Most important step for bonding is surface preparation
- Inspect the surface prior to bonding to ensure proper surface preparation for high bond qualities
- Common surface energy measurement methods useful, but doesn't provide all answers
- Investigating new method to be able to discern between:
  - High and low energy site profiles/distributions
  - Different surface preparation techniques
  - 2hour and 6hour cure dwells

A Center of Excellence
AMTAS
Advanced Materials in Transport Aircraft Structures

Measuring Surface Energy

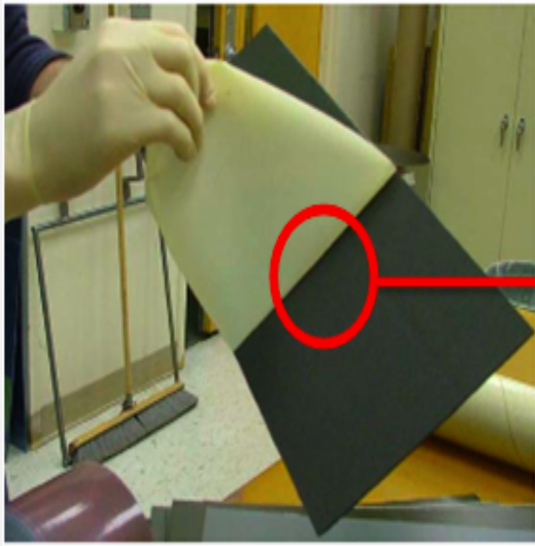
– Contact angle measurements is a preferred method

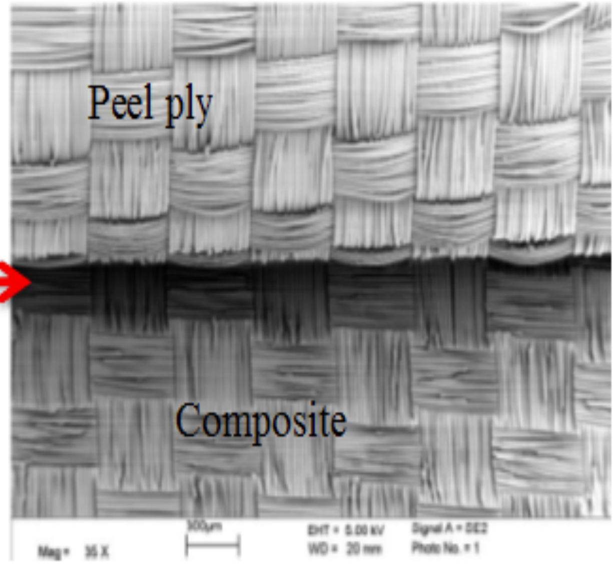
Contact Angle	Inverse Gas Chromatography
Flat, smooth samples	powders, nano particles, films, semi-solids
Homogenous data	Heterogeneous data
Ambient test conditions	Varying test conditions
Quick Test Time: complete in minutes to hours	Long Test Time: complete in hours to days
Inexpensive, portable	Expensive, non-portable

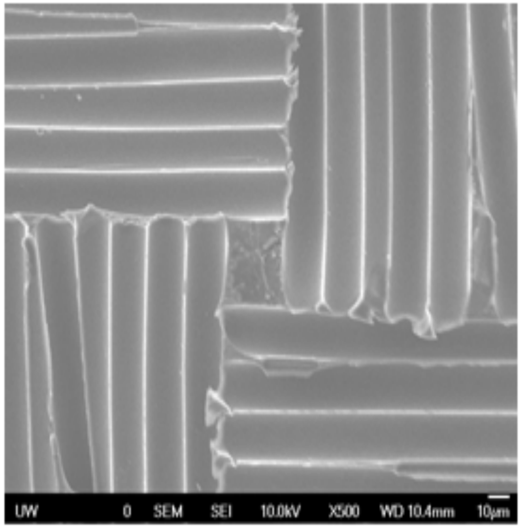
Objective:

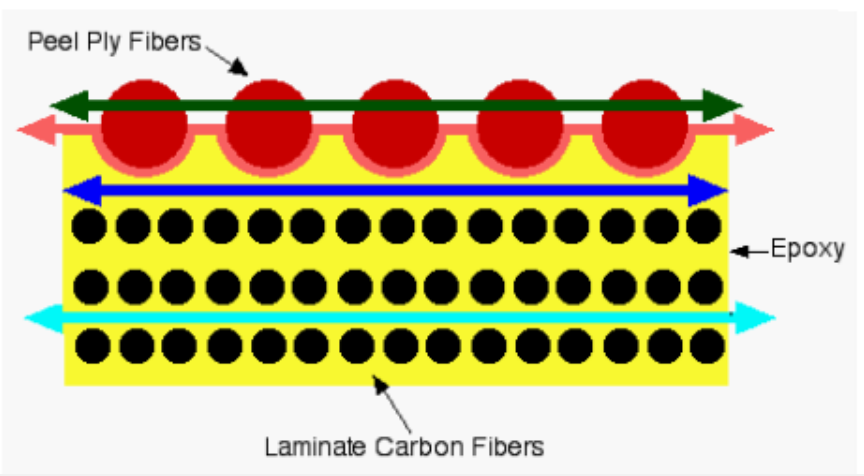
Investigate Inverse Gas Chromatography as a reliable, repeatable method to characterize various surface preparation methods with high fidelity

Peel Ply Surface Preparation



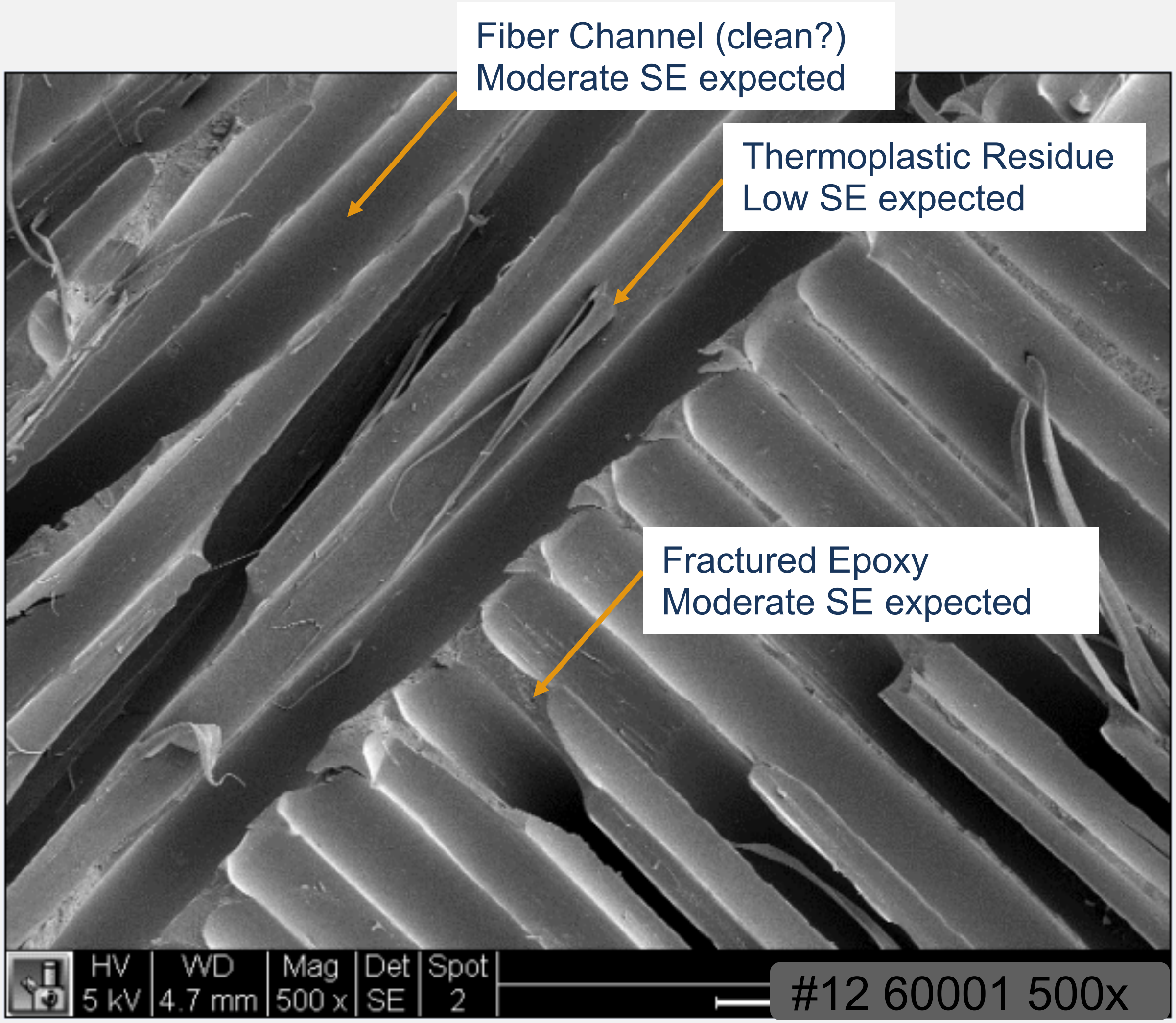






A Center of Excellence
AMTAS
Advanced Materials in Transport Aircraft Structures

Peel Ply Surface Preparation

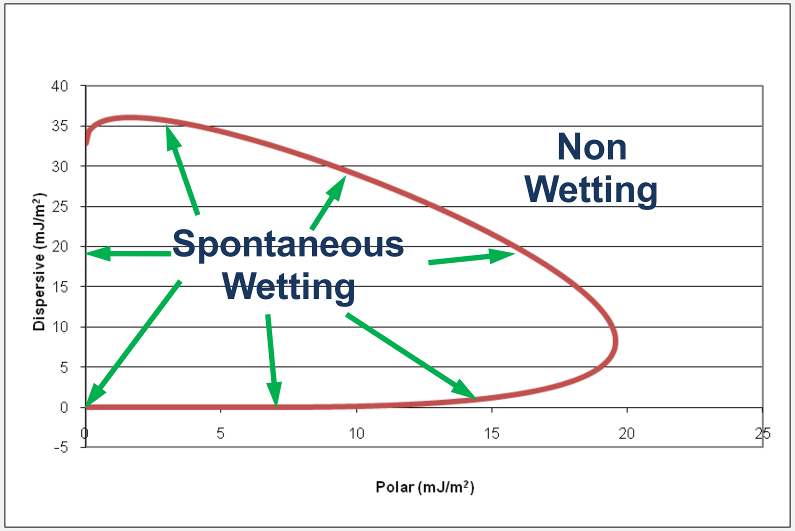


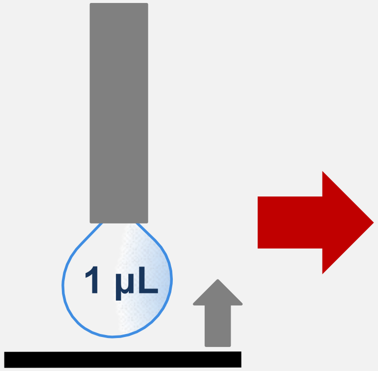
➢ Heterogeneous surface created by peel ply removal

A Center of Excellence AMTAS Advanced Materials in Transport Aircraft Structures

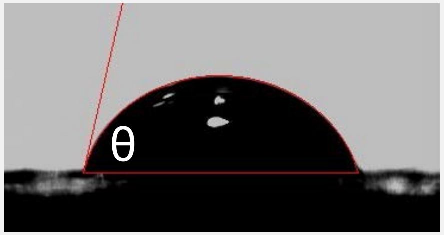
Contact Angle Methodology

- Adhesive must wet substrate for bonding– controlled by surface energy
- Surface energy calculated from Owens-Wendt model $(\gamma_{tot} = \gamma^p + \gamma^d)$
  - Four fluids: deionized water (DI H_2O), diiodomethane (DIM), ethylene glycol (EG), and glycerol (GLY)
- Wettability envelopes: 2D representation of surface energy





Drop application: dispense drop, raise surface



Side-view of drop as viewed from goniometer camera

IGC Methodology

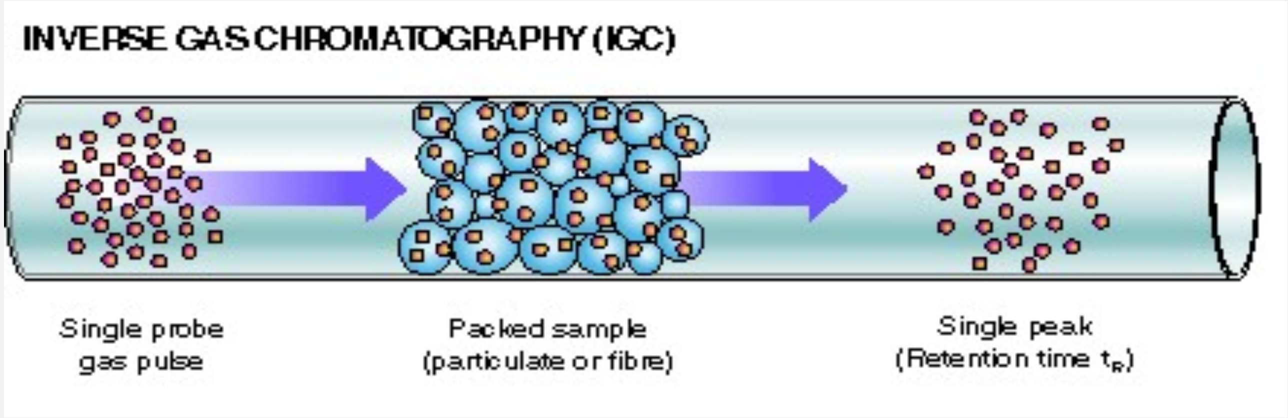
- Technique to characterize physicochemical properties of materials
- A carrier gas transports probe molecules over a surface
- Ideal for powders, fibers, nano particles, granules, films, semi-solids
- Displays heterogeneity of the surface

iGC Film Shell

iGC equipment

A Center of Excellence AMTAS Advanced Materials in Transport Aircraft Structures

IGC Methodology



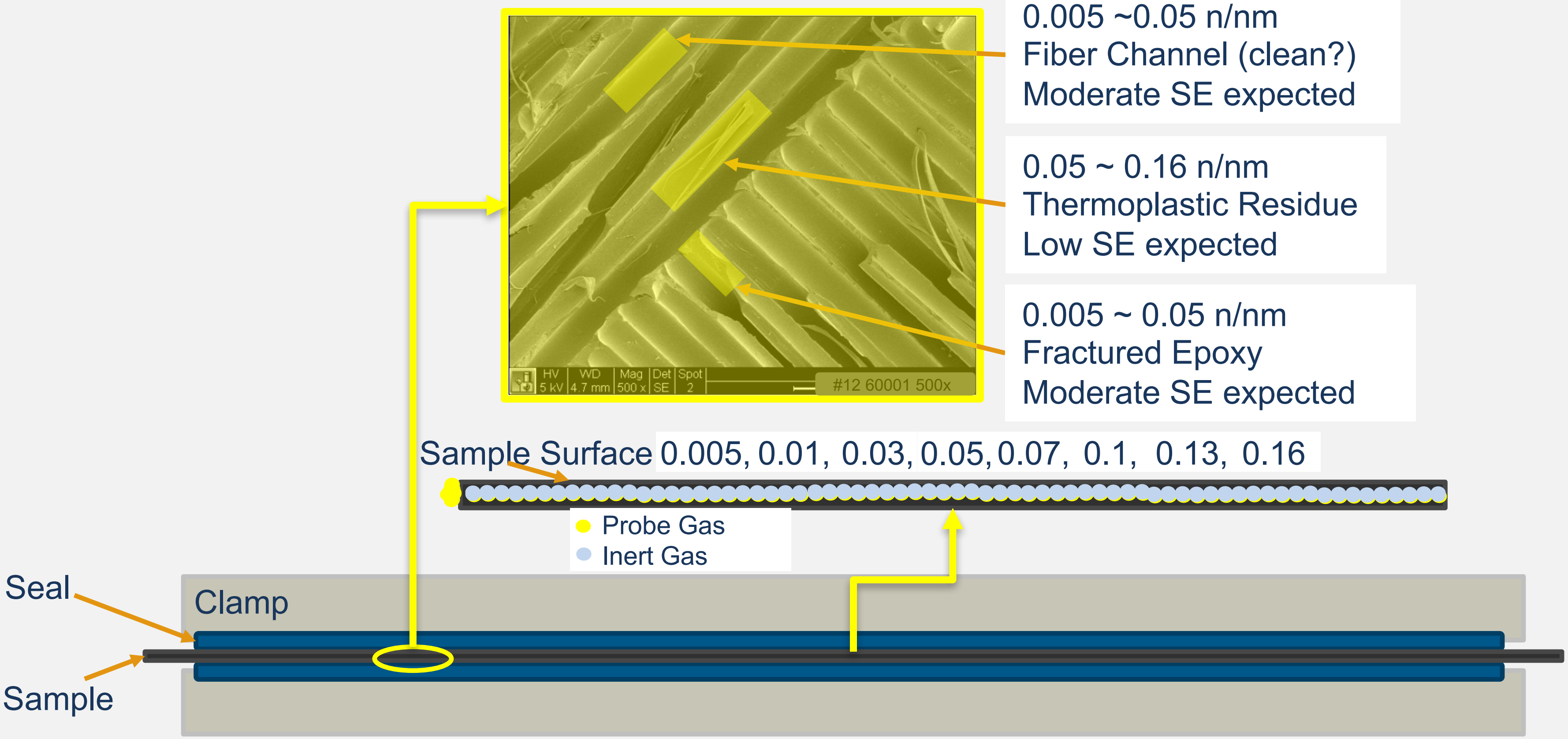
- Sample is loaded into column/clamp
- Single probe gas is injected at specific concentrations → fractional surface coverage
- Time for probe to travel across surface gives retention time → thermodynamic properties

Retention time → retention volume → surface energy →Thermodynamic work adhesion and cohesion

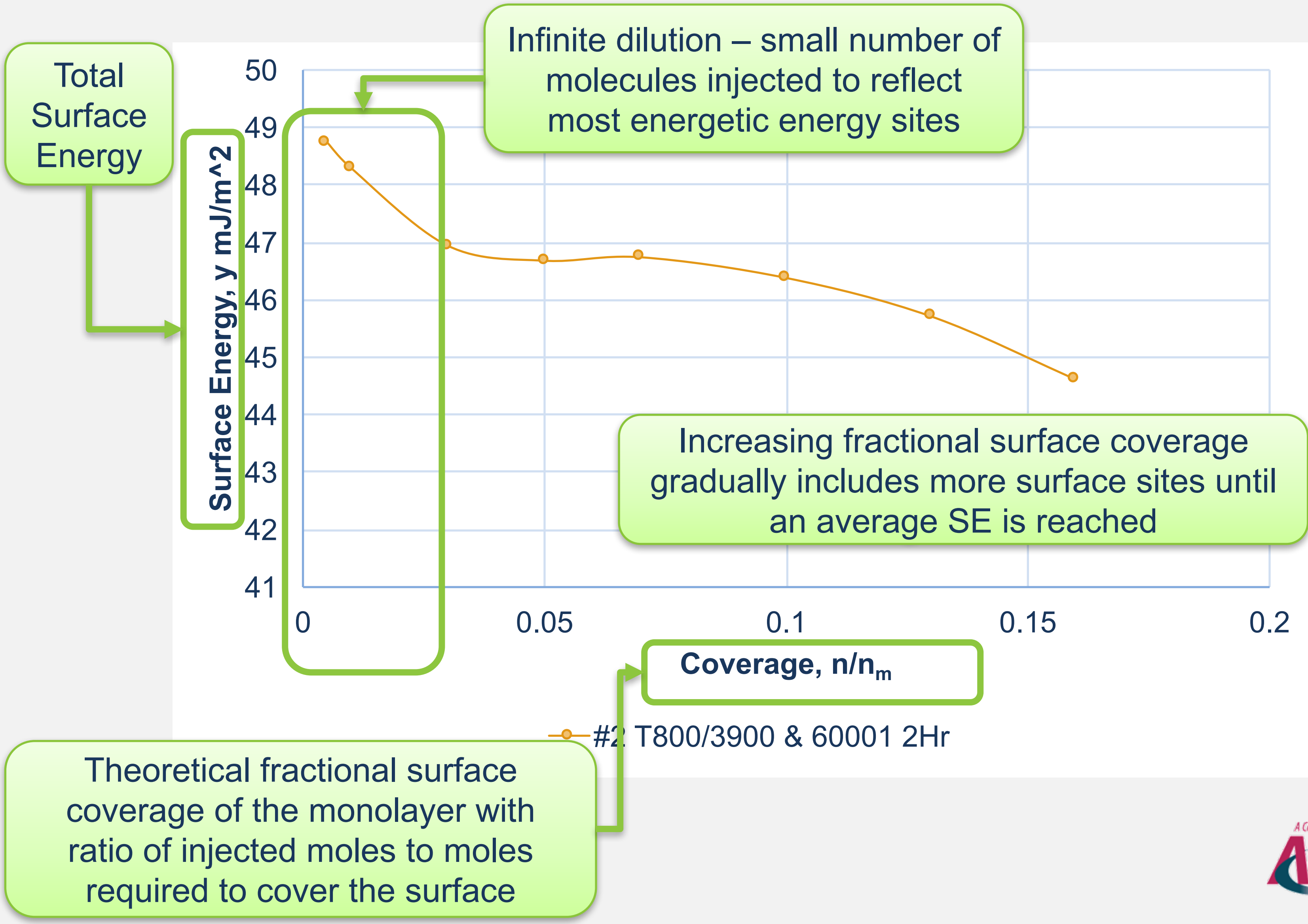
A Center of Excellence AMTAS Advanced Materials in Transport Aircraft Structures

IGC Methodology

Probe Gases	Undecane, Decane, Nonane, Heptane, Dichloromethane, Ethyl Acetate, Acetonitrile, Acetone
Targeted Fractional Surface Coverage	0.005, 0.01, 0.03, 0.05, 0.07, 0.1, 0.13, 0.16 n/nm



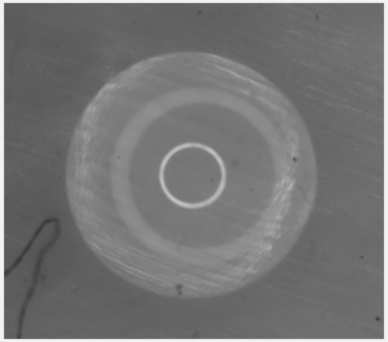
IGC Surface Energy Profiles



IGC vs. Contact Angle

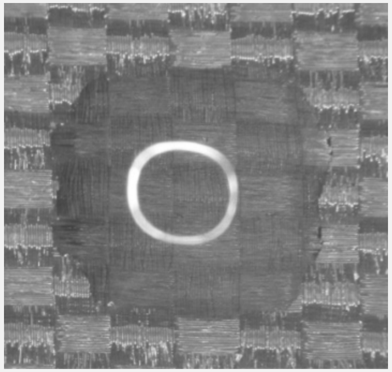
Contact Angle (CA)

- Small drops (1 ml) of 3-5 known liquids placed on surface
- Surface energy calculated over small area (order of mm2)
- Can be affected by surface texture (non-circular drops)
- Quick, inexpensive, can be portable



Inverse Gas Chromatography (IGC)

- 8-10 Known gases flow over surface
- Larger area sampled (2”X8”)
- More information obtained (higher fidelity data)
- Distribution of surface energy
- Greater sensitivity to subtle changes
- Expensive equipment, skilled operator



A Center of Excellence
AMTAS
Advanced Materials in Transport Aircraft Structures

Experimentation

Test Specimens:

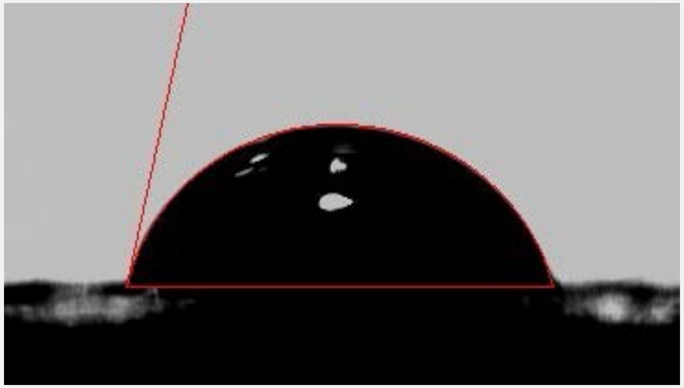
Variable	Description
Prepregs	Toray's 3900/T800 6K
	Cytec Solvay's Cycom 970/T300 3K HyE 970/PWC
Peel Plies Surface Preparation	Precision Fabrics Group's Polyester Peel Ply 60001
	Precision Fabrics Group's Nylon Peel Ply 52006
	Precision Fabrics Group's Super Release Blue (SRB) Peel Ply
	DIATEX 1500EV6 Polyester Peel Ply
	Henkel EA9895 0.033psf Wet Peel Ply (WPP)
	Cytec Solvay MXB-7668
	Fluorinated Ethylene Propylene (FEP) Release ply
Cure Holds	2hr cure hold, 176 °C (350 °F), 85 psi
	6hr cure hold, 176 °C (350 °F), 85 psi

Panel ID#	Adherend (Fabric, Prepreg)	Peel Ply	Cure Dwell
1	3900/T800	60001 Polyester	2hr
2	3900/T800	DIATEX 1500EV6 Polyester	2hr
4	3900/T800	52006 Nylon	2hr
5	3900/T800	SRB	2hr
6	3900/T800	60001 Polyester	6hr
7	3900/T800	DIATEX 1500EV6 Polyester	6hr
11	3900/T800	FEP*	2hr
12	970/T300	60001 Polyester	2hr
13	970/T300	DIATEX 1500EV6 Polyester	2hr
14	970/T300	EA9895 Wet PP	2hr
15	970/T300	MXB-7668	2hr
16	970/T300	60001 Polyester	6hr
17	970/T300	DIATEX 1500EV6 Polyester	6hr
19	970/T300	MXB-7668	6hr
22	970/T300	FEP*	2hr

Experimentation

Contact Angle:

- Probe Liquids: DI Water, Ethylene Glycol, Diiodomethane
- Average taken from 20 angle measurements from 1 μL drops of each liquid
- Peel ply orientation: 0/90 degree



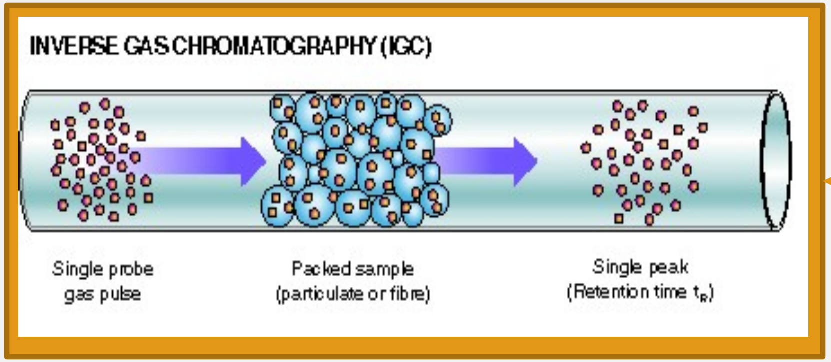
A Center of Excellence AMTAS Advanced Materials in Transport Aircraft Structures

Experimentation

IGC Test Method:

- Test area 2”x8” within the shell clamp
- Probe Molecules: undecane, decane, nonane, octane, heptane, dichloromethane, ethyl acetate, acetonitrile, acetone
- Target Fractional Coverages (n/nm):

  0.005, 0.01, 0.03, 0.05, 0.07, 0.01, 0.13, and 0.16



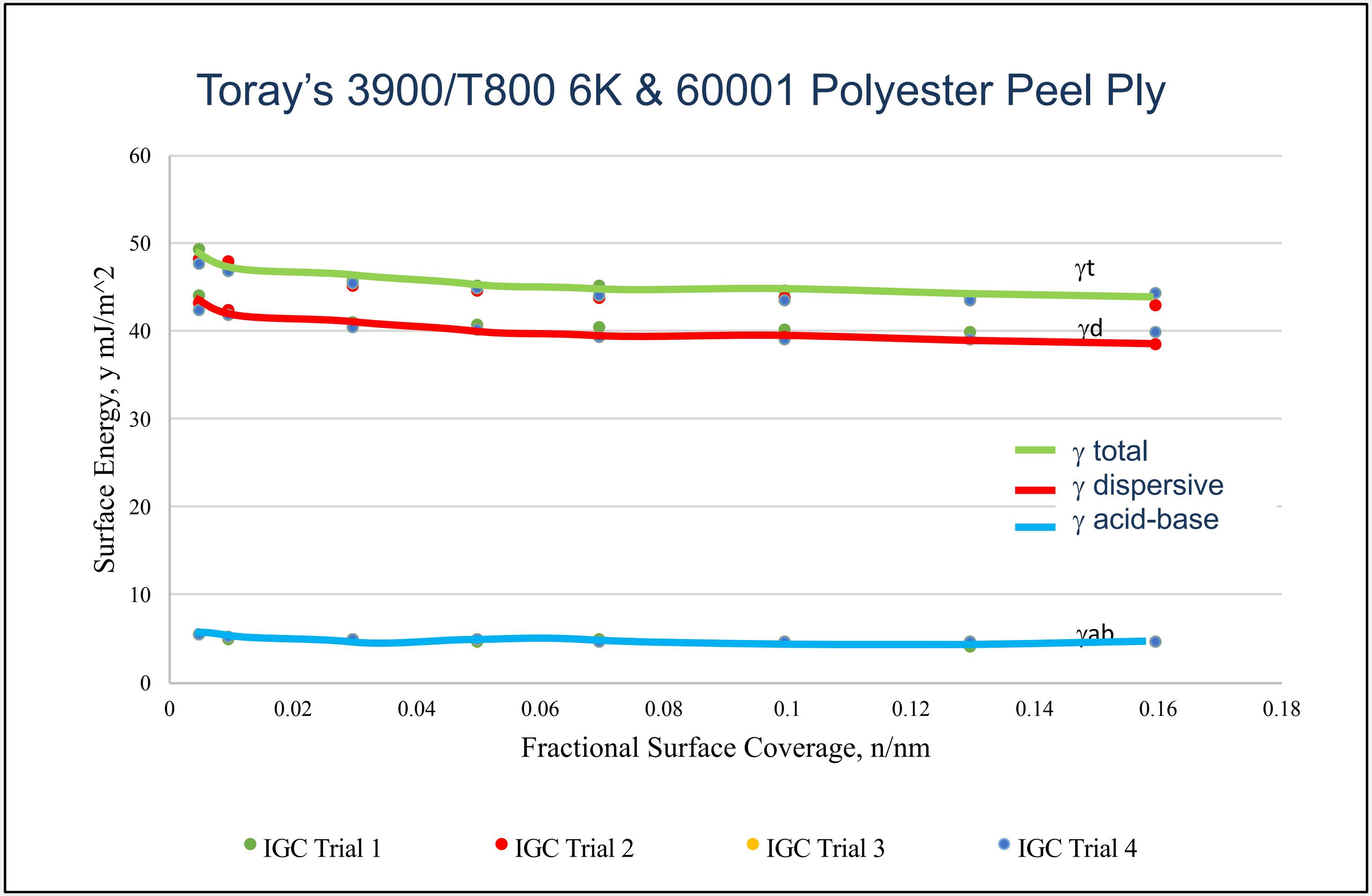
iGC Film Shell

iGC equipment

A Center of Excellence AMTAS Advanced Materials in Transport Aircraft Structures

IGC Repeatability

IGC Repeatability



Statistical T-testing confirms data sets are identical

- Confirms IGC method repeatable

A Center of Excellence AMTAS Advanced Materials in Transport Aircraft Structures

IGC and Contact Angle Comparison

Contact Angle Results

Contact angles converted into IGC comparable surface energy components using three known contact angle measurements A, B, C, with known LW, acidic and basic components can be used to calculate SE of the solid (Fowkes' Theory)

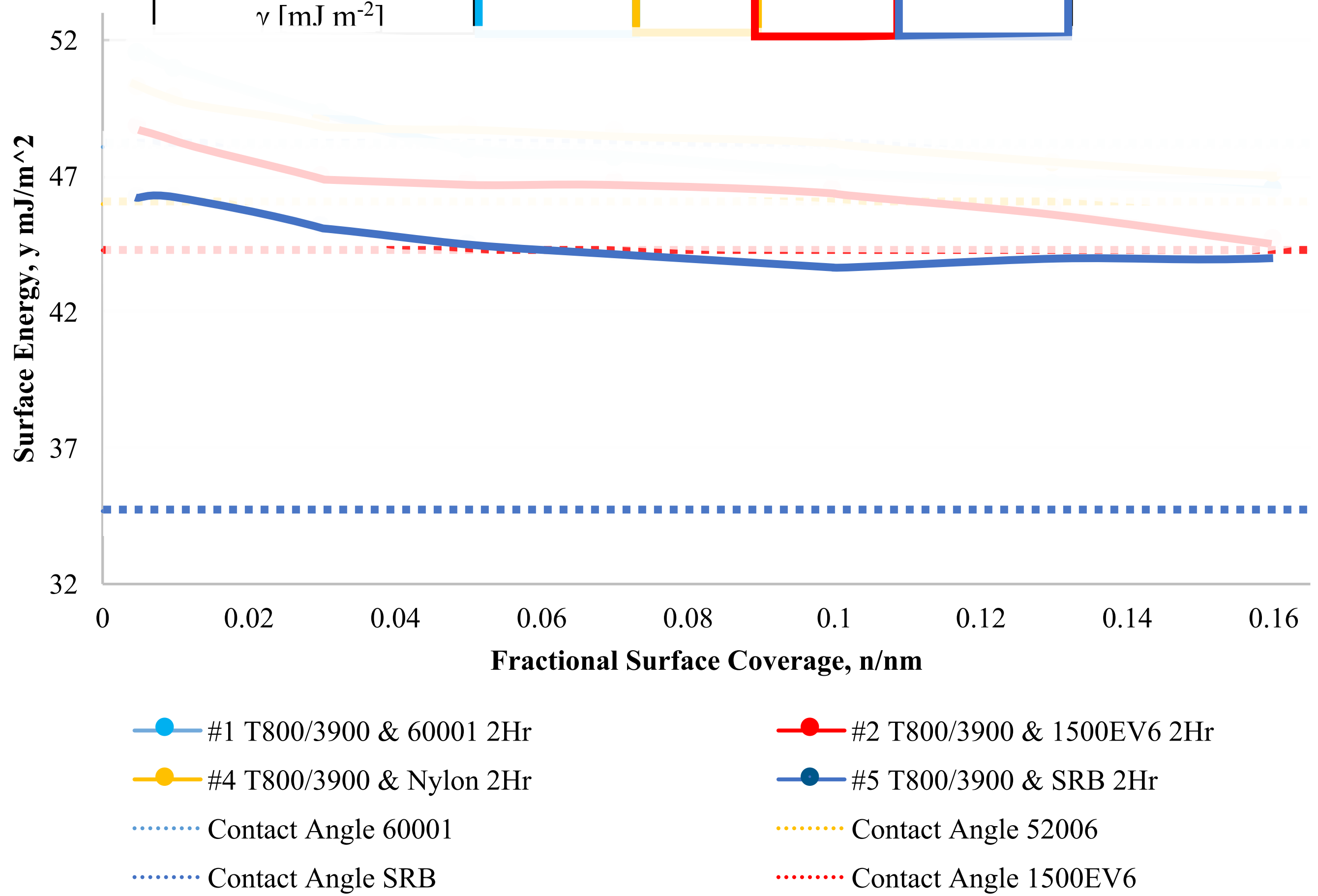
	60001 Polyester	52006 Nylon	Diatex Poly 1500EV6	Super Release Blue (SRB
γ^B , γ_{1-} [mJ m-2]	4.56	23.01	37.22	0.10
γ^A , γ_{1+} [mJ m-2]	0.02	0.07	0.01	0.04
γ^{LW} , $\gamma_L{}^d$ [mJ m-2]	47.42	43.37	42.94	34.55
γ^{AB} [mJ m-2]	0.61	2.6	1.3	0.1
γ total [mJ m-2]	48.03	45.97	44.27	34.68

A Center of Excellence AMTAS Advanced Materials in Transport Aircraft Structures

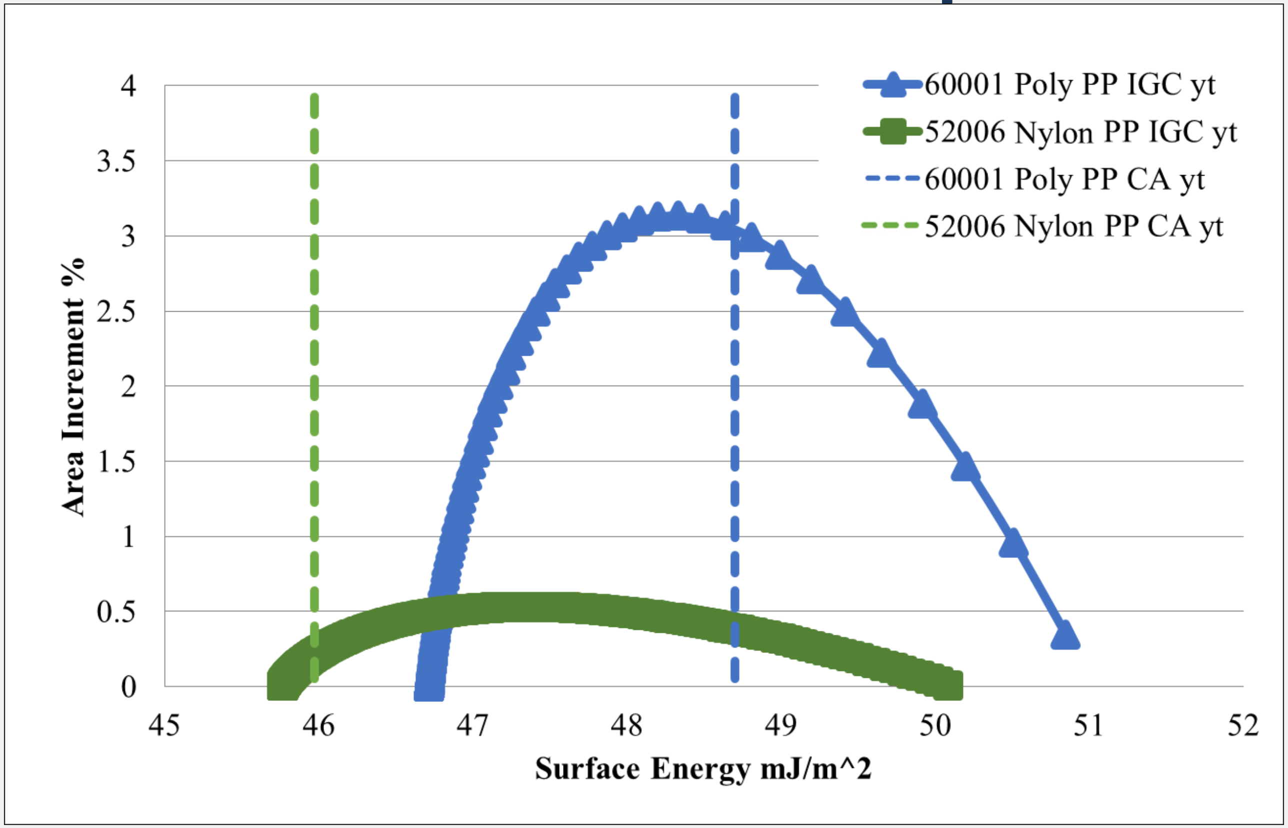
IGC and CA Comparison

	60001 Polyester	52006 Nylon	Diatex Poly 1500EV6	Super Release Blue (SRB
IGC highest energy site γ [mJ m^{-2}]	51.39	50.21	48.78	46.11
IGC Average SE γ [mJ m^{-2}]	46.63	47.04	44.61	43.61
CA SE Measurement γ [mJ m^{-2}]	48.03	45.97	44.27	34.68

- Heterogeneity of SE
- Suggests contact angle is not panel's average surface energy



IGC and CA Comparison

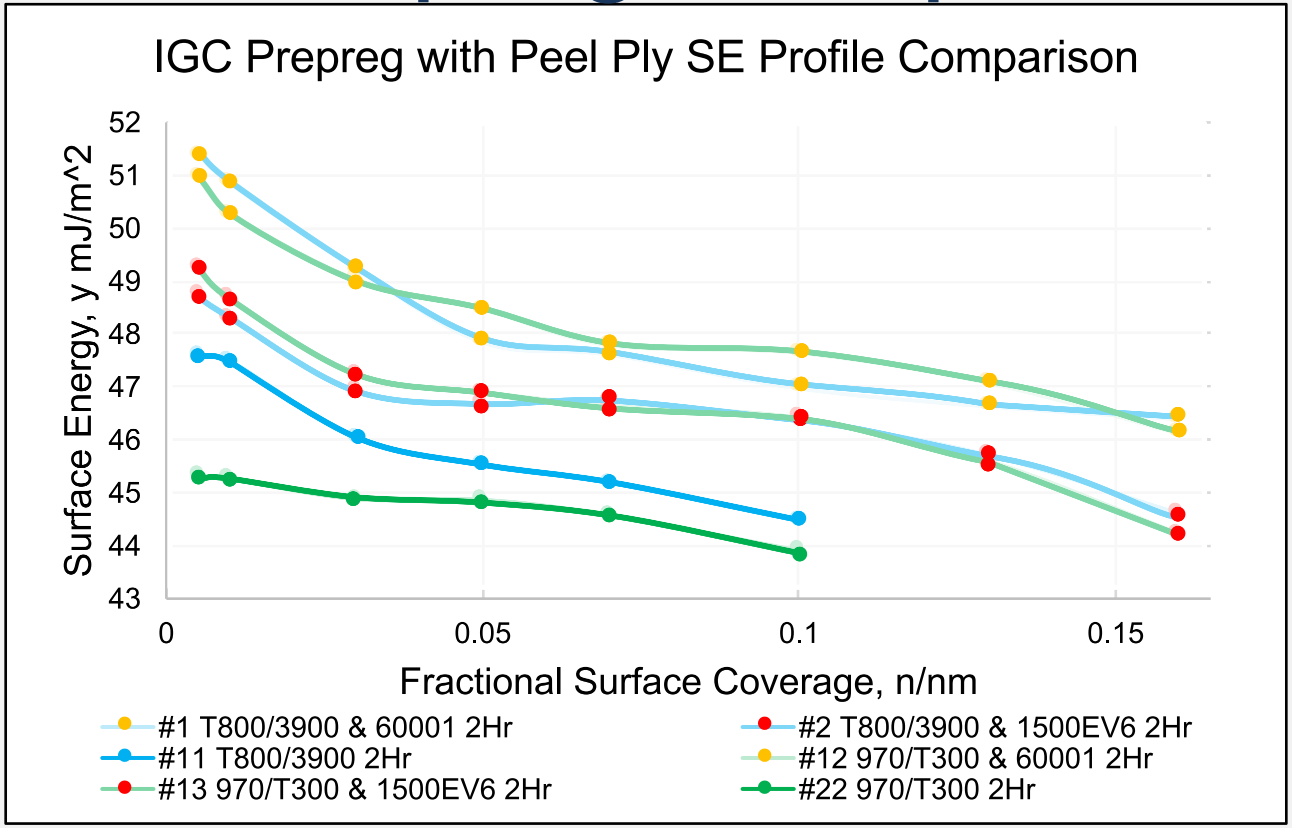


1. Nylon and Polyester have significantly different distributions according to IGC

2. Contact angle is controlled by complex wetting phenomena

3. Contact angle correlation to the IGC data is different for each peel ply type

IGC Prepreg Comparison



1. Peel ply surface preparation methods result in surface energies that remain consistent with the original prepreg material trends and are statistically unique

Conclusions/Discussion

IGC Repeatability:

- IGC statically replicated data over several tests of a given peel ply
    - Trials were statistically identical
- Highest energy sites are represented by fractional surface coverages under 0.05 n/nm
- Small variability likely from panel fabrication and actual versus target fractional surface coverage areas

Conclusions/Discussion

IGC Compared to Contact Angle Surface Energy Values:

- Contact angle measurements allow only a homogeneous representation
- Different interactions between fluids (contact angle) and gases (IGC) with textured surfaces
- IGC is able to show the heterogeneous nature of the surface
- Distribution of the surface energy measurements show the contact angles are within IGC measured ranges
- Distributions indicate the degree to which the panels are heterogeneous
- Suggests contact angles do not necessarily represent the average surface energy

Future Work

Continued research is recommended to study the applications of IGC:

- Understand the advance models of wetting versus gas interactions
- Characterize additional surface preparation methods with IGC
- Relate surface preparation to bond quality types
- Additional statistical data and material coupon testing for a more complete representation of the bonding surface
  - X-ray photoelectron spectroscopy (XPS)
  - Scanning electron microscopy (SEM)
  - Double cantilever beam (DCB)

Although IGC is able to provide more information on surface energies related to various surface preparations techniques, other components contributing to the quality of the bonding surface need to be investigated.

Questions?

References

1. Satterwhite, J., J. Aubin, and B.D. Flinn. "Partial Laminate Curing for use in Peel Ply- Prepared Adhesive Bonding." SAMPE 2009 – Baltimore, MD May 18 – 21, 2009.

2. Burnett, Dan. "Surface Characterization of Nanomaterials by Inverse Gas Chromatography - Surface Measurement Systems." Surface Measurement Systems. Surface Measurement Systems, 7 Oct. 2015. Web. 17 Apr. 2016.

3. Van Oss, C.J., et al., Interfacial Lifshitz-van der Waal and polar interactions in macroscopic systems. Chemical Reviews., 1988. 88 p. 927-941

4. Fowkes, F.M., Acid-base interactions in polymer adhesion, in Physicochemical Aspects of Polymer Surfaces, K.L. Mittal, Editor. 1981, Plenum Press: New York. P 583-603

5. Cognard, Philippe. Adhesives and Sealants: General Knowledge, Application Techniques, New Curing Techniques. Amsterdam: Elsevier, 2006. N. pag. Print.

6. Lee, Lieng-Huang. Fundamentals of Adhesion. New York: Plenum, 1991. Print.

7. Tracey, Ashley C., and Brian D. Flinn. IMPROVING ADHESIVE BONDING OF COMPOSITES THROUGH SURFACE CHARACTERIZATION - Variables That Affect Contact Angle Measurements on Peel Ply Surfaces. Thesis. U. Washington - Seattle, 2014. Seattle: JAMS, 2014. Print.

Backup Slides

IGC Repeatability

	IGC Trial 1 & 2 γt Comparision		IGC Trial 2 & 3 γt Comparision		IGC Trial 3 & 4 γt Comparision	
	Trial 1 *yt*	Trial 2 *yt*	Trial 2 *yt*	Trial 3 *yt*	Trial 3 *yt*	Trial 4 *yt*
Mean	45.62	44.78	44.78	44.78	44.78	44.58
Variance	3.39	4.03	4.03	2.35	2.35	1.86
Observations	7	8	8	8	8	8
Pooled Variance	3.7353		3.1900		2.1062	
Hypothesized Mean Difference	0		0		0	
df	13		14		14	
t Stat	0.8421		-0.0042		0.2705	
P(T<=t) one-tail	0.2075		0.4984		0.3954	
t Critical one-tail	1.7709		1.7613		1.7613	
P(T<=t) two-tail	0.4150		0.9967		0.7908	
t Critical two-tail	2.1604		2.1448		2.1448	
	Equal		**Equal**		**Equal**	

Good Repeatability

Contact Angle Methodology

Contact angles converted into IGC comparable surface energy components using three known contact angle measurements A, B, C, with known LW, acidic and basic components can be used to calculate SE of the solid (Fowkes' Theory)

$$W_{12A} = \gamma_{1A}(1 + \cos\theta_A) = 2\left(\gamma_{1A}^{LW}\gamma_2^{LW}\right)^{1/2} + 2\left(\gamma_{1A}^{+}\gamma_2^{-}\right)^{1/2} + 2\left(\gamma_{1A}^{-}\gamma_2^{+}\right)^{1/2}$$

$$W_{12B} = \gamma_{1B}(1 + \cos\theta_B) = 2\left(\gamma_{1B}^{LW}\gamma_2^{LW}\right)^{1/2} + 2\left(\gamma_{1B}^{+}\gamma_2^{-}\right)^{1/2} + 2\left(\gamma_{1B}^{-}\gamma_2^{+}\right)^{1/2}$$

$$W_{12C} = \gamma_{1C}(1 + \cos\theta_C) = 2\left(\gamma_{1C}^{LW}\gamma_2^{LW}\right)^{1/2} + 2\left(\gamma_{1C}^{+}\gamma_2^{-}\right)^{1/2} + 2\left(\gamma_{1C}^{-}\gamma_2^{+}\right)^{1/2}$$

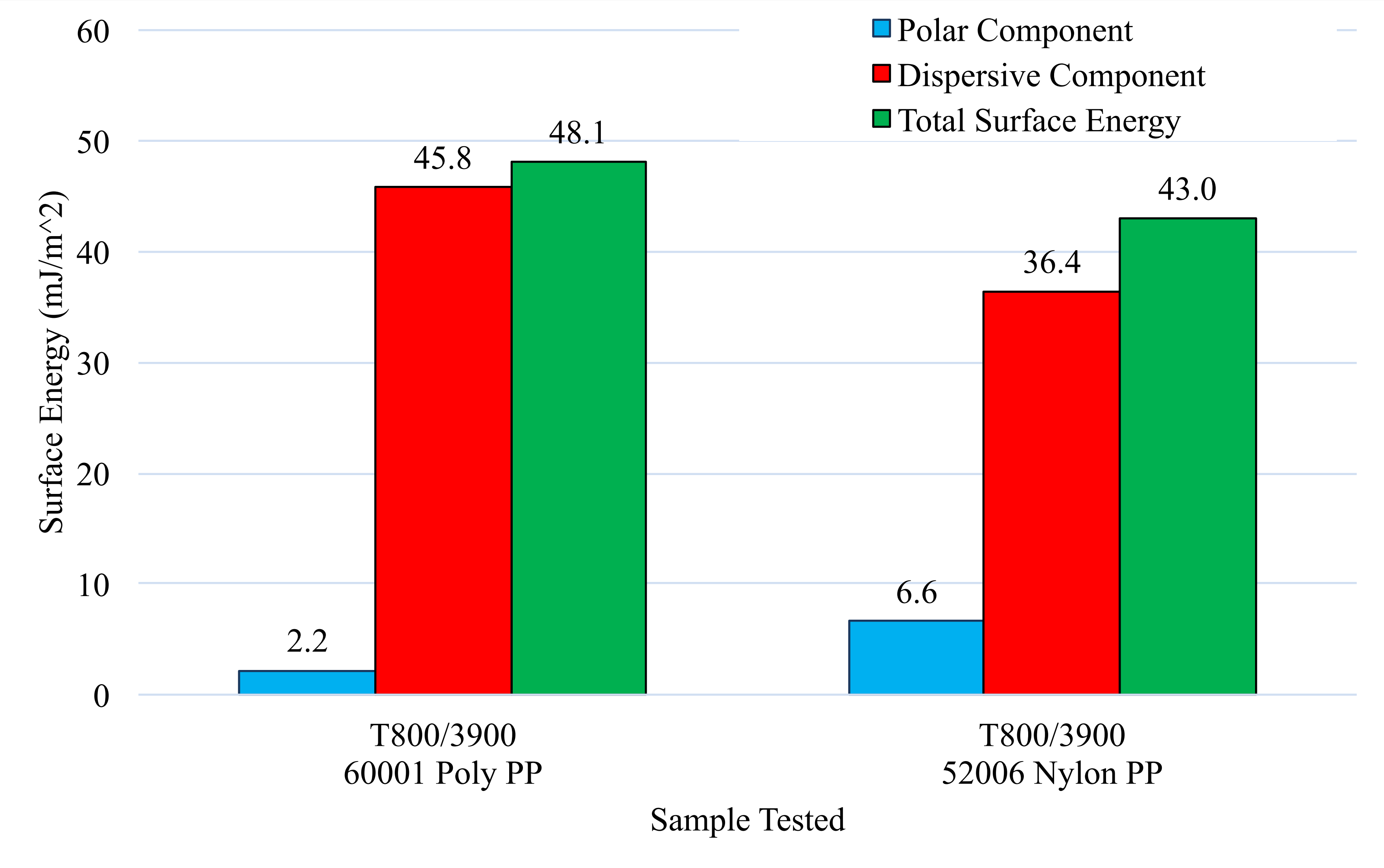
$$a = \begin{matrix} (\gamma_2^{LW})^{1/2} \\ (\gamma_2^{-})^{1/2} \\ (\gamma_2^{+})^{1/2} \end{matrix}$$

$$\alpha = \begin{matrix} \frac{(\gamma_{1A}^{LW})^{1/2}}{\gamma_{1A}} & \frac{(\gamma_{1A}^{+})^{1/2}}{\gamma_{1A}} & \frac{(\gamma_{1A}^{-})^{1/2}}{\gamma_{1A}} \\ \frac{(\gamma_{1B}^{LW})^{1/2}}{\gamma_{1B}} & \frac{(\gamma_{1B}^{+})^{1/2}}{\gamma_{1B}} & \frac{(\gamma_{1B}^{-})^{1/2}}{\gamma_{1B}} \\ \frac{(\gamma_{1C}^{LW})^{1/2}}{\gamma_{1C}} & \frac{(\gamma_{1C}^{+})^{1/2}}{\gamma_{1C}} & \frac{(\gamma_{1C}^{-})^{1/2}}{\gamma_{1C}} \end{matrix}$$

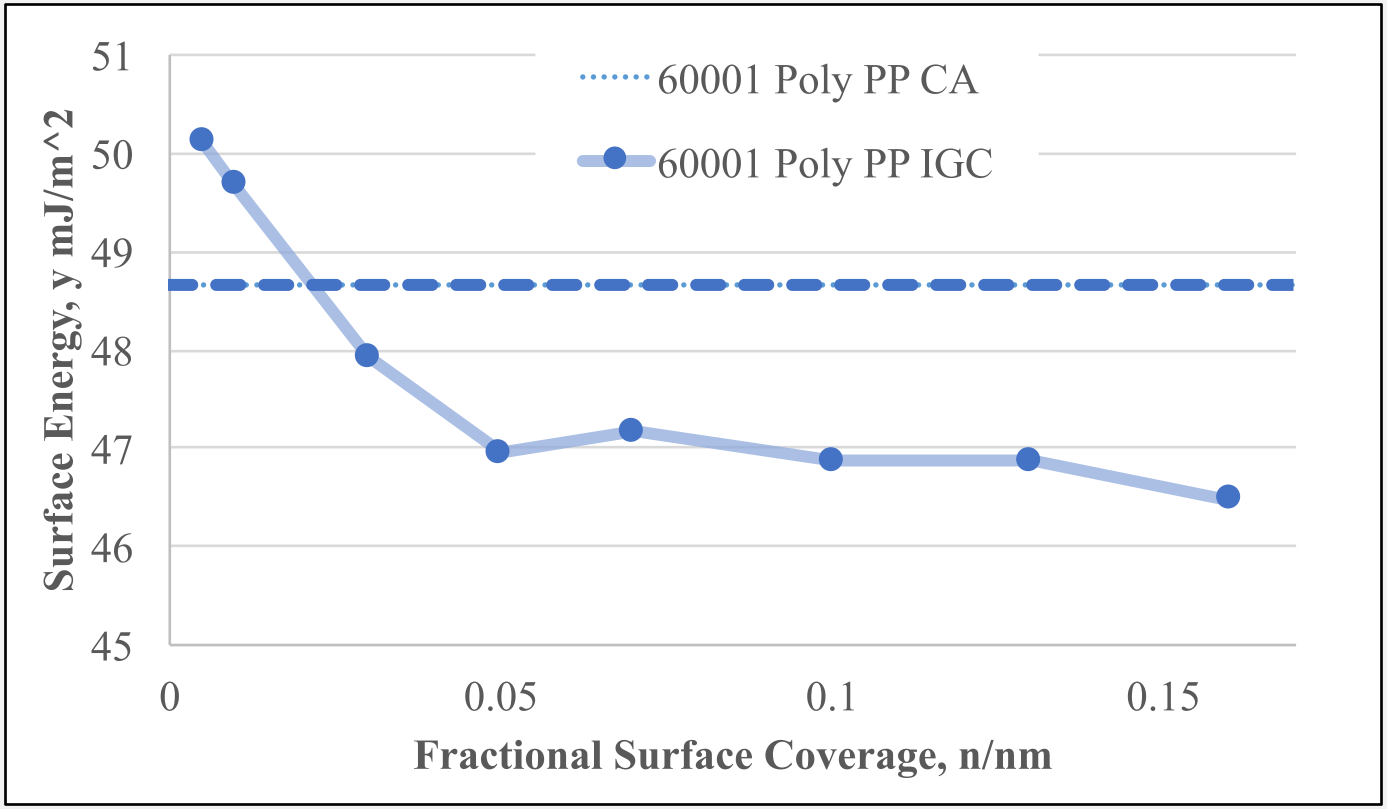
$$\beta = \begin{matrix} \frac{(1+\cos\theta_A)}{2} \\ \frac{(1+\cos\theta_B)}{2} \\ \frac{(1+\cos\theta_C)}{2} \end{matrix}$$

$$a = \alpha^{-1}\beta$$

Contact Angle Results



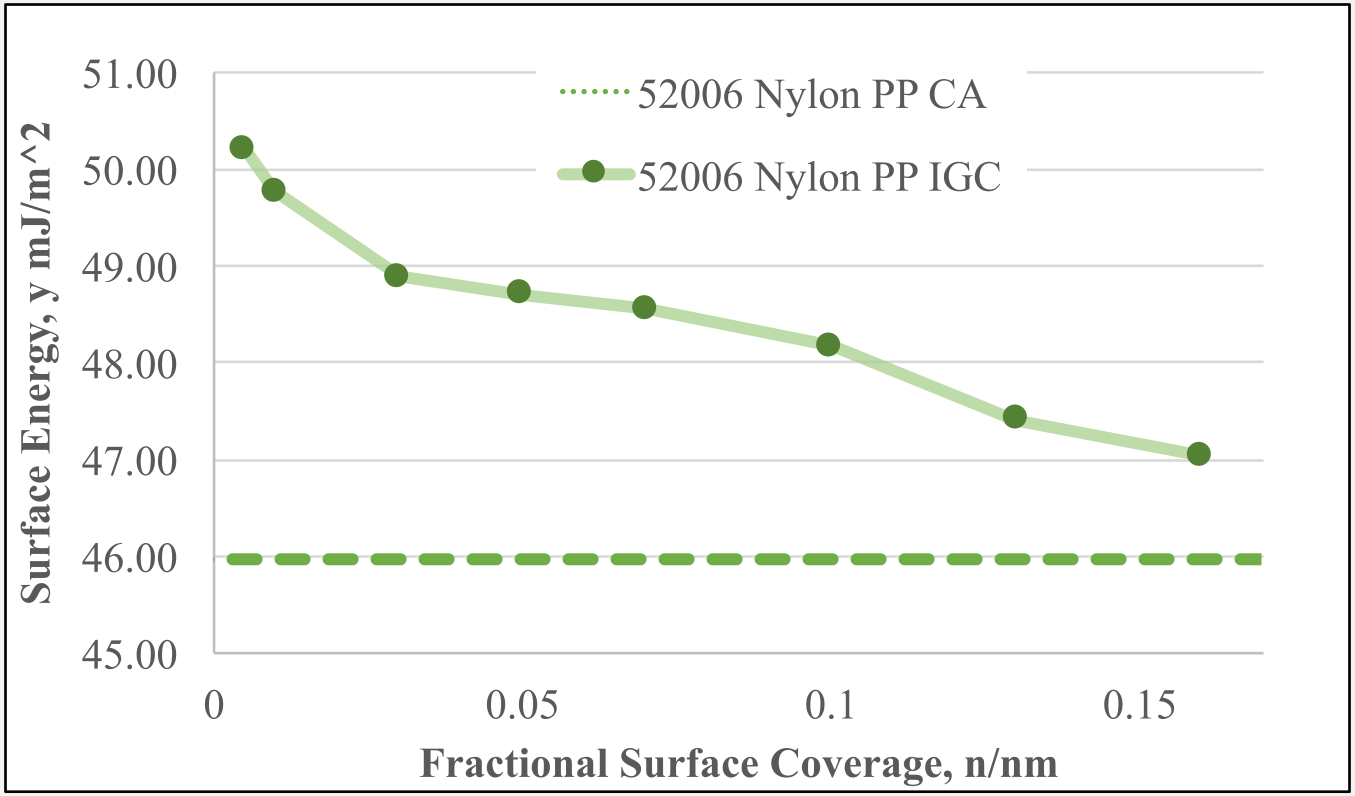
IGC and CA Comparison



1. Contact angle represents homogeneous approximation of the higher surface energy sites
2. IGC with lower fractional coverage shows the highest surface energy sites, and an estimated average at higher fractional surface coverages

A Center of Excellence AMTAS Advanced Materials in Transport Aircraft Structures

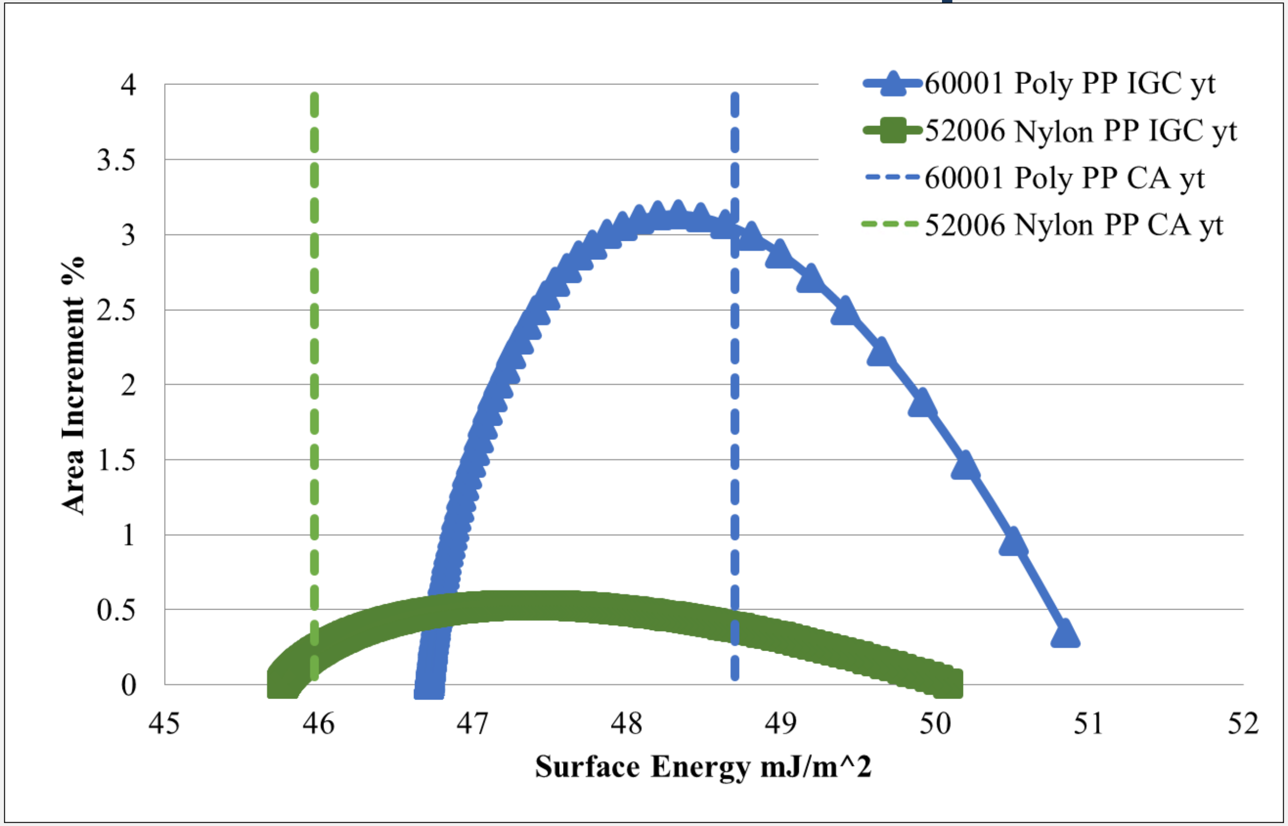
IGC and CA Comparison



1. Contact angle is homogeneous approximation of the lowest surface energy sites
2. IGC with lower fractional coverage shows the highest surface energy sites, and an estimated average at higher fractional surface coverages

A Center of Excellence AMTAS Advanced Materials in Transport Aircraft Structures

IGC and CA Comparison



1. Nylon and Polyester have significantly different distributions according to IGC
2. Contact angle is controlled by complex wetting phenomena
3. Contact angle correlation to the IGC data is different for each peel ply type