IMPROVING ADHESIVE BONDING OF COMPOSITES THROUGH SURFACE CHARACTERIZATION

Variables that affect contact angle measurements on peel ply surfaces

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ABSTRACT

This research was motivated by the need for quality assurance methods to insure proper surface preparation of composites for adhesive bonding. Water break tests have been specified to insure proper surface preparation, but recent research has shown them to be inadequate for composite surfaces. Contact angle measurements are more sensitive and have potential as a quality assurance method. The purpose of this research is to examine which measurement variables affect contact angle measurements, and thus surface energies, on composite surfaces prepared with peel-plies. The composites panels were produced from carbon fiber-epoxy prepreg and polyester peel ply. After the composite panels are cured, the peel ply is removed and contact angle measurements are taken on sessile drops of several fluids. The contact angle measurements are shown to be dependent on the orientation of the peel ply and drop contact time. The effects of the variables on the contact angle measurements are analyzed using surface energies and wettability envelopes..

1. INTRODUCTION

The purpose of this research is to investigate which variables affect contact angle measurements, and thus surface energies, on peel ply prepared composite surfaces. Surface energy can be defined as a "measure of its attractive force on other materials due to unsatisfied chemical bonds, hydrogen bonding, and van der Waals forces at its surface," and is expressed in units of free energy per unit area [1]. Thus, surface energy can be used as a way to characterize a substrate. This is of particular importance in the aerospace industry where joining composites by adhesive bonding rather than mechanical fasteners is desired. Adhesive bonding will reduce weight, thus increasing efficiency, and will eliminate stress concentrations introduced by mechanical fasteners. This paper will discuss two variables that have been tested and shown to affect contact angle measurements and thus surface energy. These include time to measure contact angle and peel ply orientation. If contact angle measurements are to be used as a quality assurance method for surface preparation, it is important that the effect of measurement variables is well understood.

1.1 Time to Measure Contact Angle

After a sessile drop is placed onto a surface, the drop will stop spreading and reach equilibrium at some time. How long this time is and how it affects contact angle measurements for a variety of fluids is one of the focuses of this research. Wang, et al. showed that contact angle measurements for water on polymer surfaces are time dependent, showing specifically that contact angles decreased with increasing time [1,2]. The reasoning for this was attributed to the reconstruction of the surface when the water drops were applied to the polymer substrate [2]. The

"starting" contact angle was affected by the hydrophobic component of the polymer, while the equilibrium contact angle was contributed by the hydrophilic component of the surface of the polymer[3]. Varennes and Schreiber also showed time dependence of contact angle measurements on various polymers including PMMA, P(S-4VP), and P(S-MAA) [2]. They did not, however, show significant variations in contact angle measurements for PS with time [2]. This research motivates us to test our system (carbon fiber/epoxy) to see if time can significantly change contact angle and thus surface energies and wettability envelopes.

1.2 Peel Ply Orientation

Peel plies leave an imprint of the fabric on the surface of the composite upon removal. A SEM image of the imprint left by a polyester peel ply is shown in Figure 1. This imprint is not only affected by the individual pics of polyester, but also by the curvature of the fabric defined by the yarn warp and weft as they cross over and under each other. The surface texture left by removal of the peel ply affects the measured surface energy as compared to a smooth surface. This is supported by well-known experiments conducted by Busscher [4], Mori [5], and Oliver [6]. During the mid-1900s, Wenzel conducted the first quantitative theoretical analysis of the effects of roughness on contact angle measurements[6]. Though the theory seemed suitable at first, as it was supported by two studies, the theory was later seen to be lacking validity, due to the fact the studies never directly measured the roughness factor, and that it seemed to be valid only for special cases "under certain geometrical restrictions" [6]. Thus, more experimentation was inspired. Future studies by Oliver showed that factors aside from surface roughening, such as surface chemistry and changes made to the morphology of surface layer, have an affect on the wetting hysteresis[6]. However, surface roughening still does account for a large portion of this hysteresis. For example, Oliver demonstrated that for extremely oriented roughness, such as

parallel channels as observed to be a result of peel ply removal (see Figure 1), the liquid drops

formed on the surface are non-circular in shape [6]. This phenomenon will be discussed further in

the "Results and Discussion" section as it clearly pertains to the results observed during this
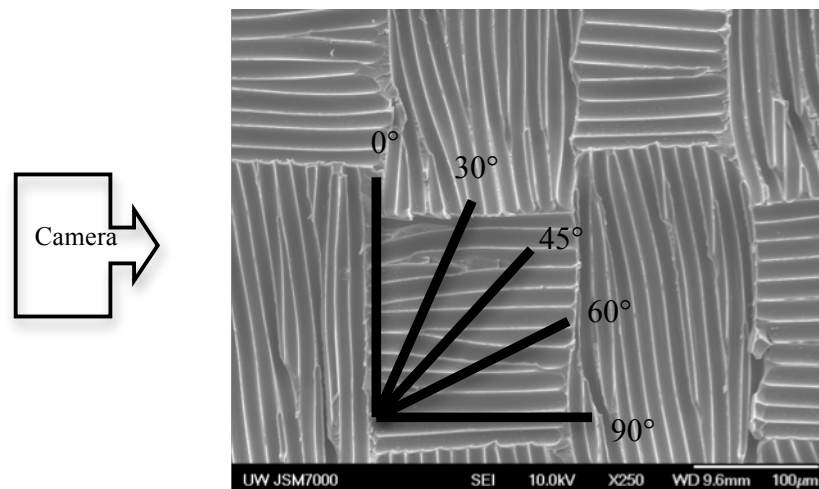
research.

Figure 1: SEM Picture of peel ply surface with 0, 30, 45, 60 and 90 degree orientations relative

to the video geoneometer superimposed.

2. EXPERIMENTATION

Time to measure contact angle and peel ply orientation have been examined using contact angle

measurements obtained by use of a VCA Optima video goniometer. These variables were tested

on 4-ply panels of carbon fiber prepreg composite surface prepared with a polyester peel ply. These panels were prepared by laying up 4-plys of unidirectional carbon fiber-epoxy prepreg at 0/90/90/0 degrees, vacuum bagging the panel and curing it in an autoclave. The cure cycle for the autoclave is as follows:

- Heat to 57.2°C (135°F) at a rate of 1.1°C/min (2°F/min), increase pressure to 0.6MPa (89psi) at a rate of 0.1MPa/min (20psi/min), soak for 0 min

- Heat to 176.7°C (350°F) at a rate of 5.6°C/min (10°F/min), maintain pressure of 0.6MPa (89psi), soak at 176.7°C and 0.6MPa for 120 min

- Cool to 10°C (50°F) at a rate of 5.6°C/min (10°F/min), maintain pressure of 0.6MPa (89psi), soak for 0 min

- Decrease pressure to 0Mpa (0psi) at a rate of 0.1MPa/min (20psi/min), while maintaining a temperature of 10°C (50°F), soak 0 min

After the panels were cured, they were removed from the autoclave and cut into 1 in by ½ in test strips using a diamond saw. The fluids used for contact angle measurement were de-ionized water (DI water), dimethylsufoxide (DMSO), formamide (form.), glycerol (gly.), and ethylene glycol (E.G.). Immediately before testing, the peel ply was removed and the test strip was placed on the goniometer stage. The stage was always confirmed to be level. Drops of 1 μL volume were dispensed from the syringe and then placed on the test strip by raising the stage and "catching" the drops. The image of the side view of the drop was frozen at a predetermined time and the contact angles were obtained. These were determined by measuring the angle these drops made with the substrate using the goniometer software, as shown in Figure 2. A total of 20 measurements (i.e. 10 drops) were recorded for each value reported. Averages and standard deviations for these measurements were calculated. These averages were used to calculate the

polar and dispersive components of the surface energy of the composite. To calculate the surface

energies, equation (1) was used.

$$\frac{\gamma_{lv}(\cos\theta + 1)}{2\sqrt{\gamma_{lv}^{p}}} = \sqrt{\gamma_{sv}^{d}}\left(\sqrt{\frac{\gamma_{lv}^{d}}{\gamma_{lv}^{p}}}\right) + \sqrt{\gamma_{sv}^{p}}$$

(1)

where the variables are defined below as follows:

- γ_{lv} is the total surface energy between the liquid and the vapor,

- γ^{p}_{lv} is the polar component of the surface energy between the liquid and vapor,

- γ^{d}_{lv} is the dispersive component of the surface energy between the liquid and the vapor,

- γ^{p}_{sv} is the polar component of the surface energy between the solid and the vapor, and

- γ^{d}_{sv} is the dispersive component of the surface energy between the solid and vapor.

From equation (1), equations (2) and (3) are calculated and plotted for each fluid, with (2) as the

y-coordinate and (3) as the x-coordinate.

$$\frac{\gamma_{lv}(\cos\theta + 1)}{2\sqrt{\gamma_{lv}^{p}}}$$

(2)

$$\sqrt{\frac{\gamma_{lv}^{d}}{\gamma_{lv}^{p}}}$$

(3)

A best-fit line was plotted for these points, generating a Kaelble plot [7,8] which shows the

relationship between the contact angle measurements obtained with each fluid. The polar

component of the surface energy was calculated to be the y-intercept of this plot squared. The

dispersive component of the surface energy was the slope of this plot squared. From these

components of the surface energy, wettability plots were created. These were generated by

inputting the polar and dispersive components of the surface energy of the composite into the

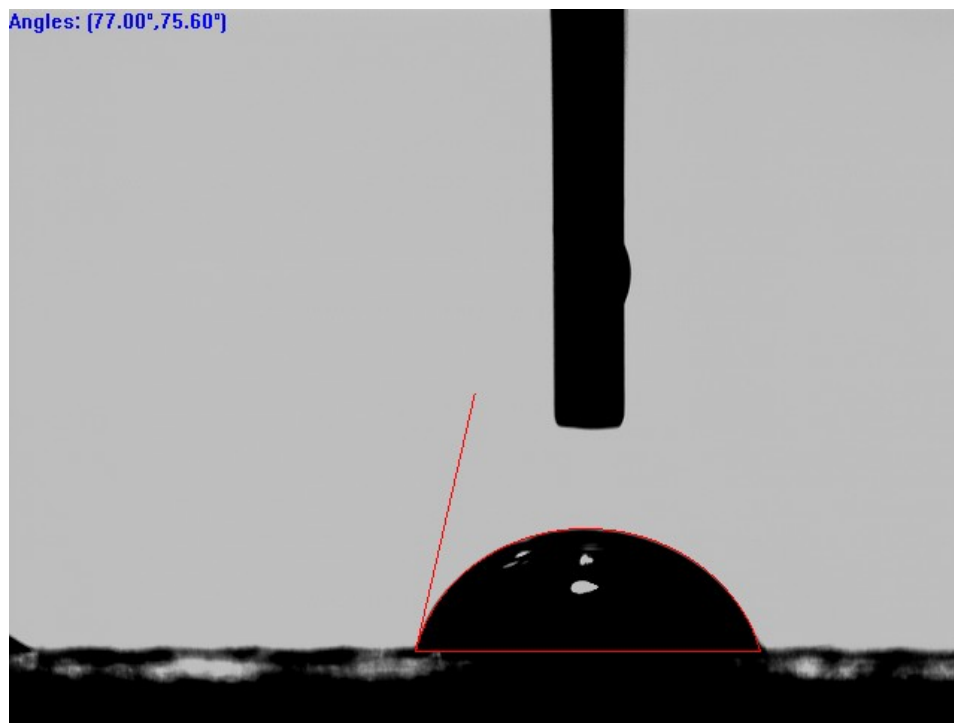computer program BKCWet v 1.1 originally written by Mark Tuttle and later edited by Brian

Clark [9].

Figure 2: Side view of a drop as seen from the goniometer camera, showing contact angle

measurements in the upper left corner of the image, as calculated using the goniometer software

2.1 Time to Measure Contact Angle

For this portion of our research, the time to measure the contact angle was a variable. The time to measure the contact angle can be defined as the time from the placement of the drop onto the substrate to the time the image on the video goniometer is frozen to measure the angle. The times examined were 0, 5, 10, 30, and 60 seconds. Four fluids were used to make these contact angle measurements. These were DI water, DMSO, formamide, and glycerol. These contact angle measurements were made at 0 degrees with the respect to the peel ply pattern, as shown in Figure 1.

2.2 Peel Ply Orientation

The variable tested here was the orientation of the peel ply imprint with respect to the goniometer camera, as depicted in Figure 2. The angles tested were 0, 30, 45, 60, and 90 degrees. These angles are defined below in Figure 1 and were tested by rotating the substrate through the angles with respect to the camera. The fluids used for contact angle measurement were DI water, ethylene glycol, formamide, and glycerol. After the drop was applied to the surface, the image of the side view of the drop was frozen after 5 seconds and the contact angle measured.

3. RESULTS AND DISCUSSION

3.1 Time to Measure Contact Angle

Figure 3 graphically displays the average contact angle at each of the times analyzed for each of the fluids used. Table 1 presents this same information in tabular form along with a standard deviation calculated for each average. The average contact angle for DI H_2O decreased from 85 to 77 degrees over the measured times   DMSO average contact angle measurements decreased

from 30 to 20 degrees. The contact angles for formamide and glycerol did not vary significantly

over the measured times. DI water and DMSO show a trend that as the time to measure the

contact angle increase, the contact angle decreases. This relationship is not observed for
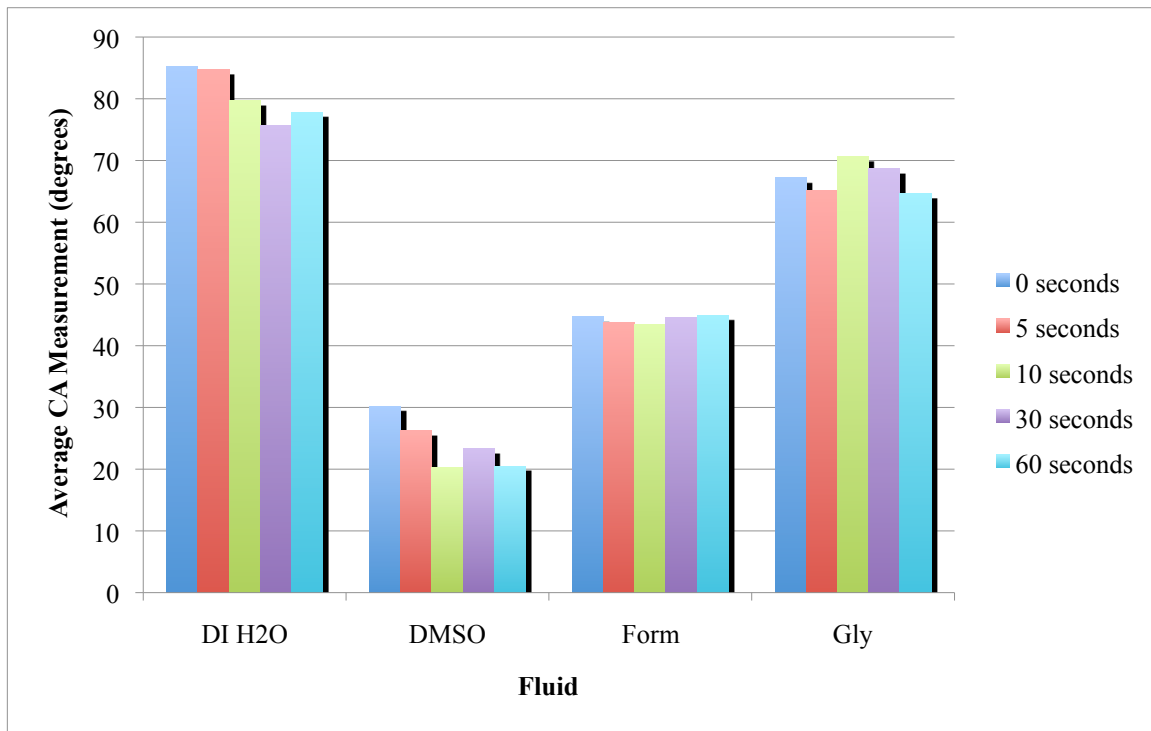
formamide or glycerol.

Figure 3: Average contact angle measurement for each fluid at 0, 5, 10, 30, and 60 seconds

Table 1: Average contact angle measurements and standard deviations for each fluid at 0, 5, 10, 30, and 60 seconds

Fluid	Time (seconds)	Average CA (degrees)	STD Dev (degrees)
DI H2O	0	85.2	2.4
	5	84.8	2.7
	10	79.7	5.7
	30	75.7	4.8
	60	77.8	3.5
DMSO	0	30.2	4
	5	26.2	3.8
	10	20.3	3.2
	30	23.3	3.5
	60	20.5	3
Formamide	0	44.7	4.2
	5	43.7	2.7
	10	43.5	4
	30	44.6	3.8
	60	44.9	6.6
Glycerol	0	67.2	4.8
	5	65.1	6.3
	10	70.7	2.6
	30	68.7	4.6
	60	64.7	2.6

Figure 4 displays the polar and dispersive components of the surface energies calculated from the measured contact angles as discussed in the "Experimentation" section. The figure also shows the total surface energy. As shown, the polar component is much lower than the dispersive component of the surface energy of the composite. Also, it can be observed that the polar components of the surface energy increase with increasing time to measure the contact angle. The dispersive component does not show this same trend.
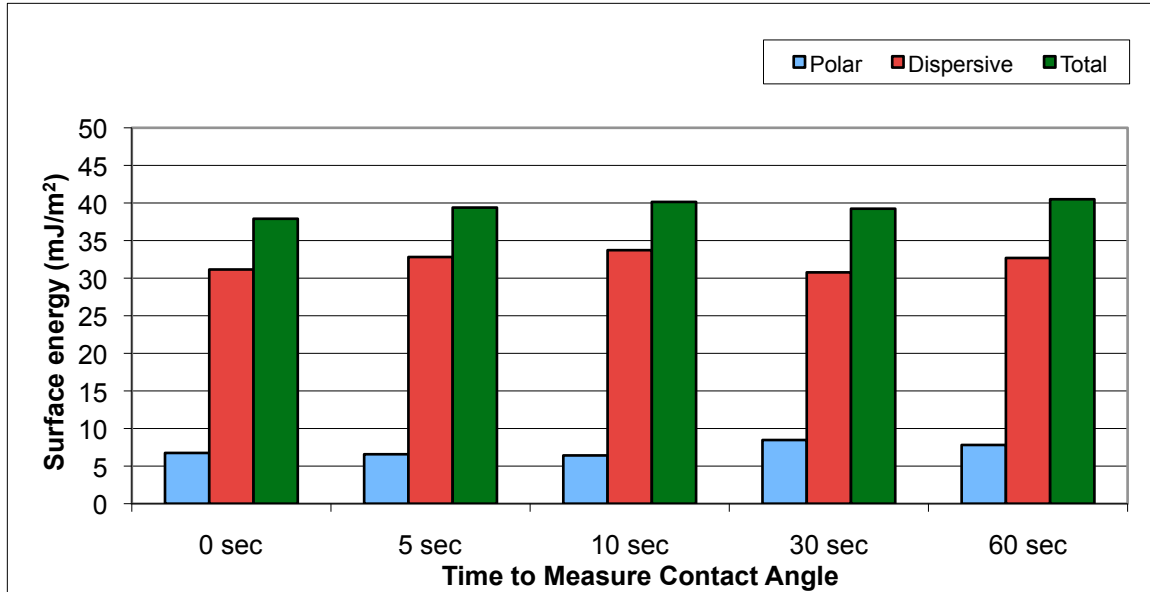
Figure 4: Surface Energies for Times to Measure Contact Angle

Figure 5 shows the wettability envelopes generated from the contact angle measurements taken at different times. These plots show that as the time to measure the contact angle increases, the wettability envelopes increase. This is due to the trend observed for DI water and DMSO of decreasing contact angle with increasing time.
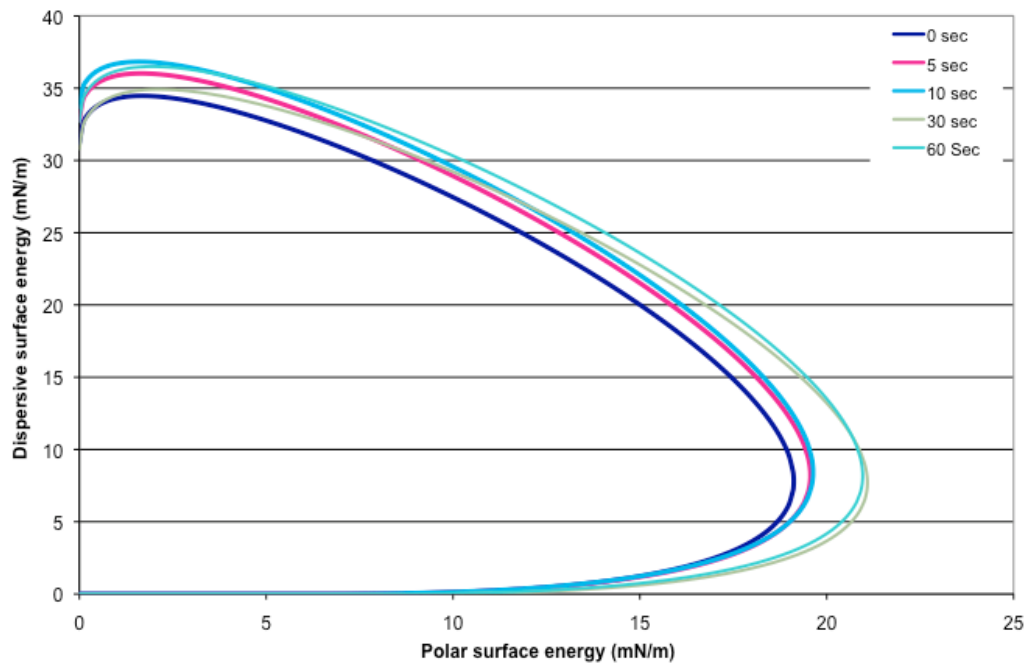
Figure 5: Wettability Envelopes for each Time to Measure Contact Angle

The time to measure contact angles has an effect on the measured surface energy possibly because of viscosity effects or interactions between the fluid and the substrate such as adsorption of the fluid onto the surface. After performing contact angle measurements on release film, an inert and smooth surface, viscosity effects were ruled out because the trend of decreasing contact angle with increasing time was not observed. This is supported by Table 2, which shows that the contact angles for DI water and DMSO did not vary significantly with time. DI water is highly polar and DMSO highly dispersive with respect to formamide and glycerol. This large difference between the polar and dispersive components of the surface energy may be the cause for contact angles for DI water and DMSO showing time dependence.

Table 2: Average contact angle measurements and standard deviations for DI water and DMSO at 0, 5, 10, 30, and 60 seconds

Fluid	Time (seconds)	Average CA (degrees)	STD Dev (degrees)
DI H2O	0	110.5	1.6
	5	110.5	1.8
	10	109.6	1.3
	30	108.0	1.9
	60	107.2	1.1
DMSO	0	71.4	1.3
	5	71.2	1.4
	10	71.3	1.9
	30	71.5	1.1
	60	72.3	1.3

3.2 Peel Ply Orientation

Figure 6 displays the average contact angle measured at each peel ply orientation. The figure shows that the contact angles measured at 30 and 60 degrees were close in value. It can also be observed that the contact angle measurements for 0 and 90 degrees gave larger contact angles than all other angles measured. The average contact angle measured at 45 degrees for each fluid is similar to those measured at 30 and 60 degrees. However, the average contact angle measurement differed enough as to generate a wettability envelope different from those of 30 and 60 degrees.
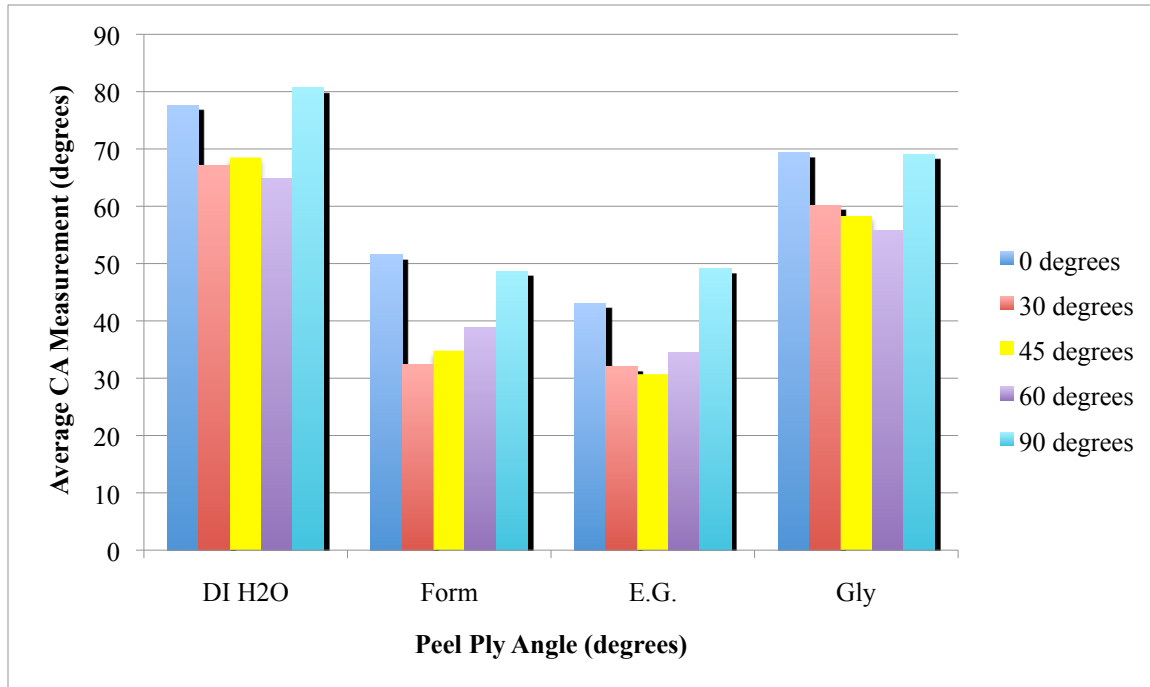
Figure 6: Average contact angle measurement for each fluid at 0, 30, 45, 60, and 90 degree orientations

Table 3 displays the same information as Figure 6 in tabular form, in addition to the standard deviation for each average. It shows that the average contact angle measurements for DI water range from 65 to 81 degrees. Ethylene glycol produced contact angles ranging from 31 to 49 degrees. Formamide produced contact angle measurements that range from 32 to 52 degrees. Finally, contact angle measurements for glycerol range from 56 to 69 degrees

Table 3: Average contact angle measurements and standard deviations for each fluid at 0, 30, 45, 60, and 90 degree orientations

Fluid	Peel Ply Orientation (degrees)	Average CA (degrees)	STD Dev (degrees)
DI H2O	0	77.6	6.6
	30	67.2	3.7
	45	68.5	3.7

	60	64.9	4.8
	90	80.7	4.4
Ethylene Glycol	0	43.1	5.3
	30	32	5.6
	45	30.7	4.2
	60	34.4	3.6
	90	49.2	5
Formamide	0	51.6	5.4
	30	32.4	2.3
	45	34.8	2.7
	60	38.8	2.6
	90	48.7	3.5
Glycerol	0	69.4	3.6
	30	60.2	5.3
	45	58.3	3.7
	60	55.8	3.9
	90	69.1	6.2

Figure 7 displays the polar and dispersive components of the surface energy, as well as the total surface energy of the composite. It is observed that the polar component is much smaller than the dispersive component for 0 and 90 degrees. For 30 and 60 degrees, the polar component is larger than the dispersive component, though close in value. Lastly, the polar component of the surface energy for 45 degrees is smaller than the dispersive component, but does not show as much difference in value as 0 and 90 degrees.
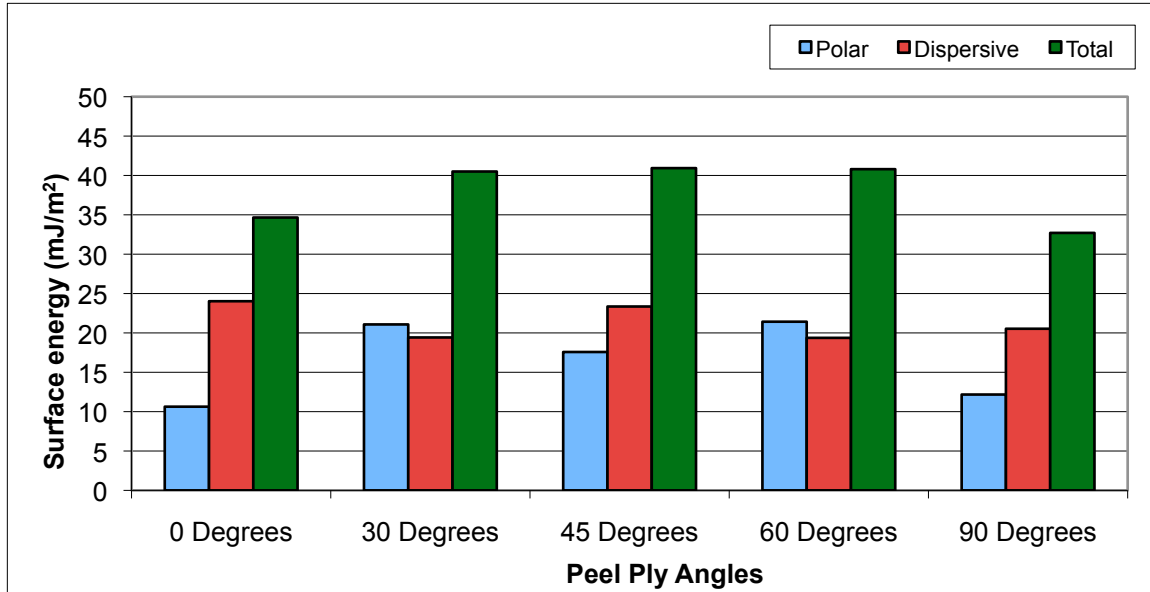
Figure 7: Surface Energies for Peel Ply Angles

Figure 8 shows the wettability envelopes generated from the contact angle measurements taken at differing peel ply orientations. This shows that contact angles measured at 30 and 60 degrees produce similar wettability envelopes. It also shows that contact angles measured at 0 and 90 degrees generate smaller wettability envelopes due to the higher average of contact angle measurement. Lastly, contact angles measured at 45 degree orientation produce a wettability envelope similar in size of the envelopes created by contact angles measured at 30 and 60 degrees though different supporting that contact angle measurements are sensitive to the orientation of the peel ply imprint at which they are measured with respect to the goniometer camera.
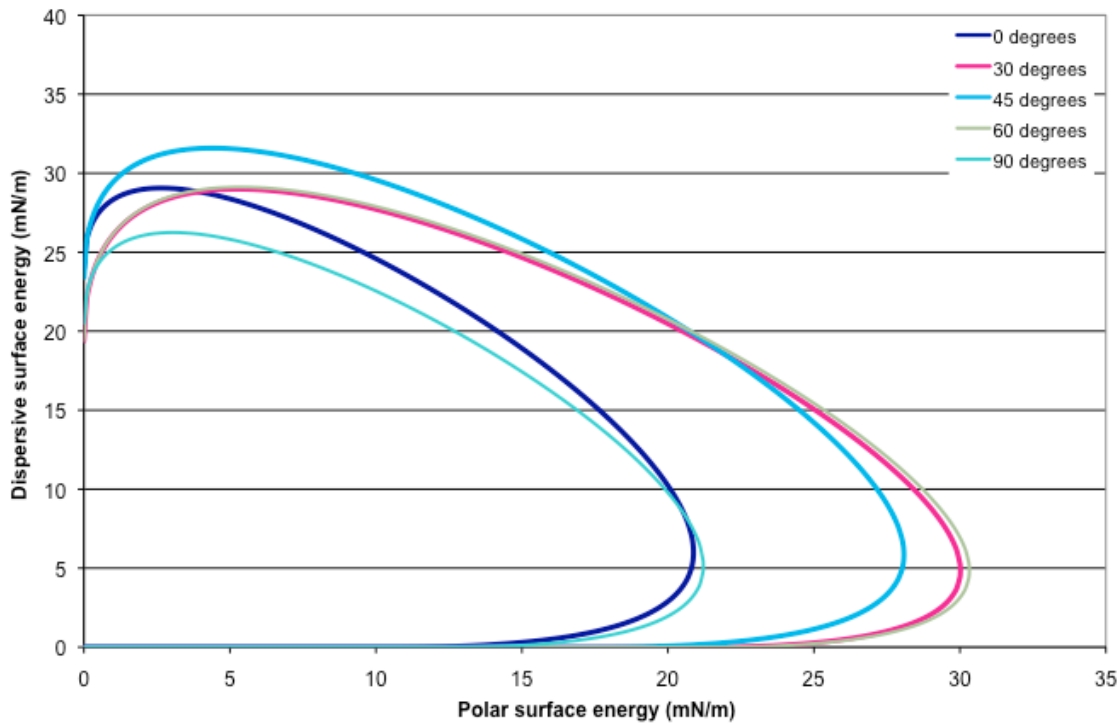
Figure 8: Wettability Envelopes at each Peel Ply Angle

The differences observed in contact angles due to peel ply orientation are supported by top down pictures of the sessile drops. Top down pictures of formamide, DI water, ethylene glycol, and glycerol are shown in Figure 9. The white circles in the figure are merely a reflection and can be ignored. The checkered pattern is the imprint left by the peel ply after removal. As can be seen in these pictures, the drops are not circular as expected. Ethylene glycol produced the most oblong shaped drop of all the fluids used, though all drops show the phenomenon of non-circularity. As discussed briefly in the introduction, Oliver found that "spreading was very smooth along the grooves whereas across the grooves pronounced stick-jump movements resulted" [6]. This is observed here, especially in the close-up picture of the DI water drop in Figure 9. It seems that the fluid spreads through the peel ply channels freely and then resists

movement when the fluid reaches a peel ply imprint with perpendicular peel ply channels. Thus, the drops are not perfectly rectangular, but rather an amorphous shape.
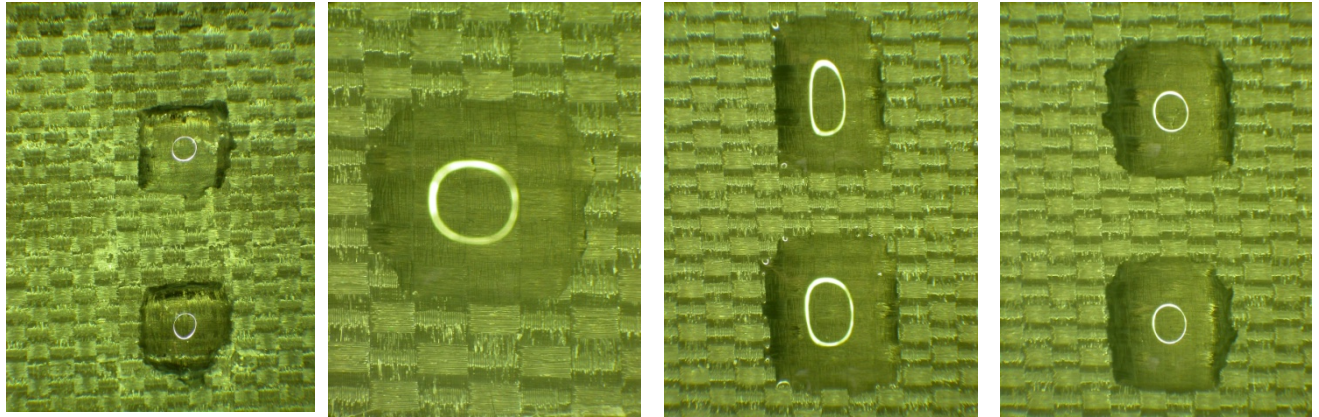

Figure 9: Top down pictures from right to left of formamide, DI water, ethylene glycol, and glycerol drops

Non-circular drops can explain why the contact angle measurements at different peel ply orientations differ. By examination of Figure 9 and the measured contact angles for 0, 45 and 90 degrees, Figure 10 is generated. Figure 10 shows an exaggerated image of the side view of two drops with one placed directly in front of the other. The drop seen from a 45 degree orientation is observed to have a lower contact angle the drop observed from a 0 or 90 degree orientation.
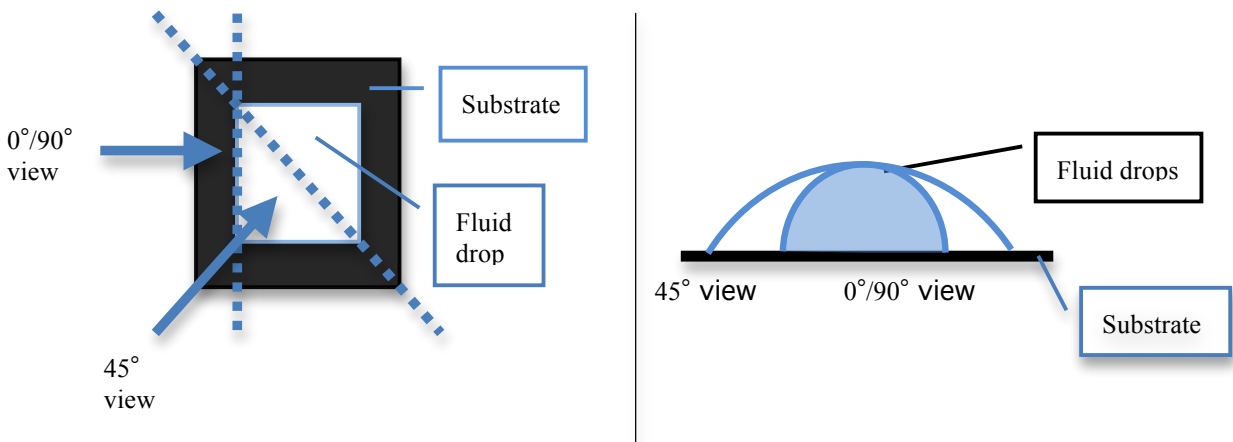
Figure 10: Top view (left) and side view (right) sketches of a drop observed at a 45 degree orientation and a drop observed at a 0 or 90 degree orientation

This phenomenon of non-circular drops may be due to the surface texture left in the resin by the peel ply. As shown in Figure 2 and 11, the peel ply leaves channels. The fluid should more easily flow down these channels than across them. This idea is displayed in Figure 12.
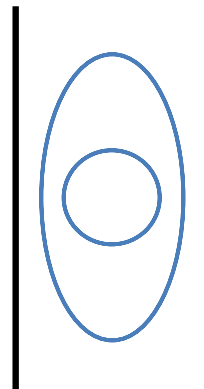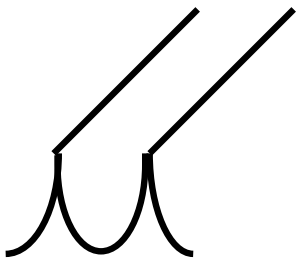
Figure 11: Schematic of resin channel

Figure 12: Top down image of resin channel

4. CONCLUSIONS

4.1 Time to Measure Contact Angle

We discovered that the contact angle and thus surface energies and wettability envelopes are dependent on the time from applying the drop onto the substrate to the time the image is frozen and the contact angle measurement made. Contact angle measurements using DI water and DMSO decrease with increasing time, resulting in an increase in size of the wettability envelope. Formamide and glycerol did not show this relationship. The contact angles measured using these fluids stayed relatively uniform with differing time. However, due to the DI water and DMSO, it is observed that contact angle is dependent on time. Thus, 0 seconds showed the smallest wettability envelope while 30 and 60 seconds showed the largest. Viscosity effects were omitted as a reason for time dependence and further research is needed to confirm or disconfirm the hypothesis of adsorption.

4.2 Peel Ply Orientation

We found the orientation of the peel ply produces differing contact angle measurements and thus differing wettability envelopes. The contact angles measured at 0 and 90 degrees gave the smallest wettability envelopes and show correlation to each other. Similarly, 30 and 60 degrees give almost entirely overlapping wettability envelopes. The wettability envelope for 45 degrees is similar in size to those for 30 and 60 degrees but show significant difference. This variation in

contact angle measurements may be due to the lack of spherical symmetry of the drops. For example, formamide produced square-shaped drops.

4.3 Concluding Remarks

Using contact angle measurements as a way to measure surface energies is proving to be sensitive to many variables. The orientation of the peel ply texture on the composite surface and time to measure contact angle have been demonstrated to affect surface energy calculated from contact angles. This leads us to further our analysis to discover what other variables affect contact angle measurement and thus surface energy. Some future work includes analysis of environment, such as temperature, humidity, and cleanliness, as well as differences among lots of prepreg and differing operators making contact angle measurements. If this is to be a method for determining bondability of composites with adhesives, a standard must be set, as to ensure repeatability and uniformity.

5. ACKNOWLEDGMENTS

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