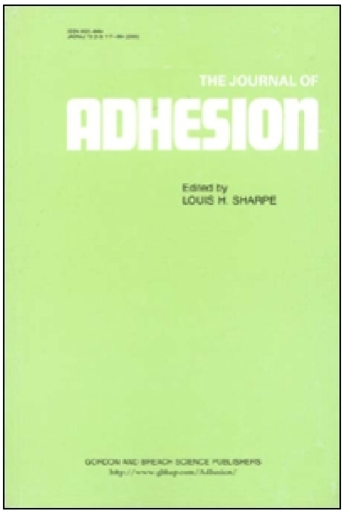

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Surface Energy and Adhesion in Composite-Composite Adhesive Bonds

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Surface Energy and Adhesion in Composite–Composite Adhesive Bonds

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In the absence of weak boundary layers, surface energy can be an excellent indicator of the suitability of a fiber-reinforced composite surface for adhesive bonding. Mechanical surface treatments such as grit blasting are effective and commonly used to prepare composite surfaces, but the roughness introduced by these treatments makes quantification of the surface energy by contact angle methods difficult. This paper shows that the diameter *of a small drop of a low-viscosity fluid chosen to have surface tension characteristics very similar to the adhesive can be used as an effective predictor of adhesive bond fracture energy. This technique could form the basis of a sensitive quality assurance tool for manufacturing.*

Keywords: Adhesive bonding; Composite materials; Quality assurance; Surface energy

INTRODUCTION

Composite materials are attractive for aerospace structural applications because of their high strength-to-weight ratios. The performance and affordability of utilizing composite materials can be improved by the implementation of unitized and bonded structures. Although excellent bonds are obtainable using currently available surface-preparation techniques and rigorous, experience-based process control, the relationship between surface-preparation parameters and adhesive bond performance is still not well understood. This is particularly true for bonds that use room-temperature curing paste adhesives. These

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show a greater sensitivity than hot-bonding processes to surface preparation but can also provide the greatest economic benefit.

The types of surface pretreatments used to prepare composite materials for adhesive bonding can be *mechanical* (hand sanding, grit blasting, peel ply removal) or *chemical* (plasma treatment, corona treatment, UV or UV/ozone exposure). All of these methods have been shown to improve adhesive bond performance by varying degrees. The mechanical pretreatments are undoubtedly most commonly used, and although each is capable of producing good composite–composite adhesive bonds, the variables associated with these treatments are not well understood. Partly because of this lack of understanding, composite–composite bonding with paste adhesives is not as widely used as high-temperature film adhesives for structural applications in aircraft.

The current work has been motivated by a desire to better understand the parameters associated with a good surface pretreatment for adhesive bonding of composite materials with paste adhesives. In particular, this article discusses the relationship of surface energy, fracture toughness, and failure mode of adhesive bonds between grit-blasted composite laminates.

Grit blasting has been successfully employed for many decades as an integral part of many metal surface pretreatment processes. Adhesive joints prepared from metal adherends roughened in a controlled manner have higher G_{I}c values (for failure near the interface) due to a change in stress state at the interface from pure Mode I to a mixed Mode I/Mode II [1]. As a surface preparation for composites, grit blasting removes contaminants such as mold release agents and roughens the surface. This provides for improved wetting, creates the potential for covalent bond formation with a thermosetting adhesive, and allows for mechanical interlocking between the adhesive and substrate [2–4]. However, damage from overly aggressive abrasive blasting can lead to weakening of surface plies and decreased G_{I}c values for the adhesive joint. Damage may be induced below the surface of the laminate by the blasting process and has been postulated as a source of weakening of the laminate [5].

Given cohesively strong adherends and the absence of a weak boundary layer, the adherend surface energy is probably the single most important factor affecting performance of an adhesive bond and strongly influences the fracture energy of the resulting joint. Fracture energy of an established adhesive joint is a function the thermodynamic work of adhesion, W_{A}, as expressed by the Young–Dupré equation:

$$W_{\mathrm{A}} = \gamma_{\mathrm{lv}}(1 + \cos\theta)$$

This is directly related to the fracture energy, G, of the adhesive joint:

$$G = W_{\mathrm{A}} + \psi,$$

where ψ represents the work dissipated in plastic and viscoelastic deformation during fracture.

W_{A} is generally orders of magnitude smaller than G, and some workers have argued that the work of adhesion affects the fracture energy in a multiplicative way [6]:

$$G = W_{\mathrm{A}} * \phi,$$

where φ is a rate- and temperature-dependent term. This relationship predicts that small changes in the work of adhesion can result in large changes in fracture energy.

Given that the solid surface energy is a critical term in predicting adhesive joint performance, how is it determined? One of the most widely used methods is the multiliquid approach of Kaelble [7,8]. This method is used to determine the polar and dispersive components of the surface energy of a solid surface by measuring the contact angles of several liquids chosen to exhibit a range of polar and dispersive components of surface tension.

Applicability of contact-angle techniques to determine the energy of very rough surfaces is suspect, however, and surface roughness is a very important characteristic of grit-blasted composite surfaces. The most common treatment of roughness is the approach by Wenzel [9,10], which states that the roughness factor, r, which represents the ratio of the actual area to the apparent (or measured) surface area, is given by

$$r = \frac{\cos\theta_{\mathrm{r}}}{\cos\theta_0},$$

where θ_{r} is the contact angle obtained on the actual (rough) surface and θ_0 is the contact angle of the fluid against the same surface in the absence of roughness. This approach predicts that wetting of rough surfaces will be improved for $\theta < 90^\circ$ and lessened for $\theta > 90^\circ$, which holds to be true quite generally, and this treatment appears to be well suited to surfaces that are rough on a scale comparable with droplet dimensions, but when the roughness approaches a microscopic scale this technique may underestimate the true surface area by orders of magnitude [11].

An increase in specific surface area is only one effect of roughness. Roughness on a microscopic scale implies a surface that is fundamentally different from a planar surface in ways that are not simply topographical. The chemical potential for the surface species on a microscopically rough substrate may be higher because of a much smaller radius of curvature and potentially higher strain energy [11]. These issues are not well understood at this point and could have profound effects on attempts to use surface energies calculated using these techniques to predict adhesive bond performance.

Quantifying the work of adhesion by probing the surface energy of a microscopically rough surface using the multifluid contact-angle technique is uncertain at best. A more suitable surface energy parameter is needed to characterize the energetics of surfaces in a production or shop-floor environment. The ideal surface energy probe would, of course, be a drop of the actual adhesive. However, the viscosity of a formulated paste adhesive or film adhesive is such that the slow kinetics of wetting prevents its use as a probe. A low-viscosity, nonreactive fluid with the same surface tension characteristics as the adhesive could serve this function. In the case of epoxy adhesives, in turns out that dimethyl sulfoxide (DMSO) has surface tension characteristics very similar to the adhesive [12] and a much lower viscosity (Table 1). Based on these considerations, DMSO wetting behavior could be expected to mimic the wetting behavior of an epoxy rather well. DMSO has additional characteristics that make it an attractive probe fluid. It is nontoxic, it has a low vapor pressure, and it does not interact chemically with an epoxy surface.

The contact angle made by a liquid with a surface is normally used to quantify wetting behavior through the Young equation:

$$\gamma_{sv} = \gamma_{sl} + \gamma_l \cos(\theta),$$

where γ_{sv} is the substrate surface energy in equilibrium with the vapor pressure, γ_{sl} is the surface energy of solid–liquid interface, γ_l is the surface energy of the liquid, and θ is the angle formed by the surface and the drop tangent. However, contact angles can be inconvenient to obtain, particularly from rough or nonhorizontal surfaces or surfaces of large manufactured articles with complex shapes. In many of these

TABLE 1 Dispersive (γ^d) and Polar (γ^p) Components of Surface Energy and Viscosity for an Amine-Cured Diglycidyl Ether of Bisphenol A Epoxy (DGEBA) and Dimethyl Sulfoxide (DMSO)

Material	γ^d_{lv} (mJ/m^2)	γ^p_{lv} (mJ/m^2)	Viscosity (Pa·S)
DGEBA epoxy	35	4	160 @ 25°C
DMSO	35	7	0.002 @ 20°C

situations, the diameter of a drop of known volume can be used to calculate the contact angle, given that certain conditions are fulfilled.

The contact area between a liquid drop and a solid surface depends upon the contact angle, the shape and volume of the drop, and the surface tension and density of the liquid. For drops that are large enough such that gravitational distortion of the droplet shape is significant, the relationship among these factors is very complex and cannot be expressed analytically. In this case the problem must be solved by numerical methods, and this approach is the basis for surface energy measurements using axisymmetric drop shape analysis (ADSA) [13]. This method provides very precise values of contact angles through digitization of images of sessile drops of known volumes. However, like the multiliquid Kaelble method, this approach would be somewhat unwieldy to adapt for use in a manufacturing environment.

However, the shape of a sessile drop that is small (0.5–5 mm in diameter) is distorted very little by gravity and assumes a profile that is very well approximated by a spherical cap.

In this case the diameter of the drop is only a function of its volume and the contact angle [14–17]:

$$\frac{d^3}{V} = \frac{24 \sin^3 \theta}{\pi(2 - 3\cos\theta + \cos^3\theta)},$$

where d is the droplet diameter, V is the droplet volume, and θ is the contact angle between droplet and surface.

In the limit of small drop volume, measuring the drop diameter allows calculation of the contact angle. To determine the range of volumes for which this relationship holds, the ratio d^3/V needs to be evaluated for several values of V and then extrapolated to $V = 0$. For low contact angles such as are found between clean epoxy surfaces and liquid epoxies (or probe liquids of similar surface tension), this linear range extends over a large range of droplet sizes. A curve for d as a function of V shows that for small contact angles the relationship is linear over large ranges of droplet volume [13]. We have shown in our laboratory that this relationship does an excellent job of providing contact angles for droplets of DMSO that are smaller than about 10 µl.

Using a fluid as a probe of surface energy of a composite material that may be contaminated with low-molecular-weight, potentially soluble molecules such as oils or greases raises the possibility that the fluid could interact with the contaminant in a way that perturbs the measurement. Solvent activity as expressed by the solubility parameter [18,19] is closely related to surface tension, suggesting that a probe fluid closely matched in surface tension to a contaminant would tend to dissolve the contaminant from the surface, in effect cleaning the surface. This property is designed into adhesives intended for bonding of oily steel surfaces [20,21], which, by virtue of the solvating power of the curing agent, are capable of imbibing significant amounts of oil to effect a strong bond to uncleaned surfaces. These are widely used in automobile assembly.

This concept requires consideration of the fact that the surface may be altered by the probe fluid (contaminants may dissolve into the probe fluid), resulting in a perturbed measurement that does not reflect the properties of the surface that will eventually see contact with the adhesive. Similarly, the surface that is probed prior to adhesive bonding may not be the same surface that exists at the interface of the substrate and the cured adhesive, because of absorption of contaminants by the adhesive.

In the work discussed here, surfaces with similar topography but varying surface energy were created by controlled contamination of grit-blasted composite laminates. The wetting behavior of small drops of DMSO applied to these surfaces was shown to be a quantitative predictor of the fracture toughness of adhesive joints prepared from these surfaces. The correlation was excellent and the nature of the fracture behavior *versus* DMSO wetting gave strong clues as to the relationship between surface contamination and adhesive joint performance. The interaction between probe fluids and contaminants was investigated to determine if their use was appropriate for this study. It was found that although small amounts of contaminants were imbibed by the probe fluids, the effect of this on wetting behavior was not detectable.

EXPERIMENTAL

Control of Surface Energy Through Contamination with Silicone

Composite laminate samples were grit blasted with 220 alumina using 35 psi N_2 to a level that thoroughly deglossed the surface but did not remove enough resin to expose or damage the underlying carbon fibers. Microscopic examination showed that coverage was 100%, as no original surface remained. To control surface energy of grit-blasted composites and to determine the effects of contamination on composite–composite adhesive joints, a method was devised to apply a controllable level of silicone mold release to a surface using a robotic spray gun apparatus. Silicone mold release was chosen as the contaminant because of its use in the manufacture and handling of composite laminate materials. A touch-up spray gun (Central Pneumatic, Camarillo, CA, USA) was fixed on a ring stand next to a vertical stage that could be translated through the spray pattern at a variable rate using a DC motor. In this manner the residence time of a sample in the spray was controlled. Two different silicone mold release agents were used, either Frekote 1711-1 or Frekote 44 (Loctite Aerospace, Bay Point, CA, USA). These are sold as solutions of mold release diluted in heptane. Although chemically similar, these mold releases represent fundamentally different types of contamination: Frekote 1711-1 is a low-molecular-weight silicone oil, whereas Frekote 44 is cross-linkable by curing in a 100–150°C oven for 15 min to form a polymerized film. Although no analysis was performed to determine if the films formed by the mold releases were continuous, the low surface tension of these compounds would favor spontaneous spreading on the surface.

Grazing-angle FTIR of polished aluminum witness coupons that were coated at the same time as the composite laminates were used to quantify the amount of mold release that was deposited. The absorbance of the Si-CH_3 peak near $1260\,cm^{-1}$, proportional to film thickness, provided a convenient metric.

Surface Energy Measurements

Surface energies of contaminated surfaces were obtained using a multiple liquid approach. Small drops of five probe fluids (typically distilled water, glycerol, dimethyl formamide, diiodomethane, and DMSO) were placed on the surfaces to be measured. The drop contact angles were obtained either using a slide projector to project the image of the drop onto a piece of paper or with a Ramé–Hart contact-angle goniometer. Measurements of contact angle at a given point were easily repeatable to within ±0.5°. Grit-blasted surfaces show a range of contact-angle values around the perimeter of the drop, due to pinning of the droplet edge at metastable points (topographical effect) or chemical heterogeneity (composition effect). For this reason, reported contact angles are the average of several values obtained around the drop perimeter. Multipoint Kaelble plots [22] were generated from the contact-angle data, and the surface energies of the contaminated surfaces were determined. Correction of contact angles for surface roughness was performed using the Wenzel approach [9]. Although surface roughness was not explicity measured for these samples, a roughness factor of 1.11 that had been determined for identically prepared laminates in an earlier study [5] was used. Although we believe that the precision of surface energy values calculated in this manner for rough surfaces are suspect, they are at least generally correct and sufficient for the present purpose of evaluating the correlation between DMSO drop diameters and fracture toughness.

DMSO Drop Diameter Measurements as a Probe of Surface Energy

To investigate the relationship between DMSO drop diameter and surface energy, 3-µl drops were placed on contaminated composite laminate substrates. A stereomicroscope with a reticle was used to measure drop diameter to 0.2 mm. Two drop diameter measurements, 90° apart, were taken on each drop.

Relationship between Surface Energy and Adhesive Fracture Energy

Adhesive joint performance was evaluated using double cantilever beam (DCB) specimens (ASTM D5528) prepared using Loctite Hysol EA 9394 epoxy (Loctite Hysol, Bay Point, CA, USA). Composite laminates fabricated from 10 plies of either Hexcel 3K-70-PW T300 or T650 fabric in a 350°F (174°C) cure epoxy (MY 720/DDS, Vantico, Inc., Brewster, NY, USA) were grit blasted as discussed previously.

Surface energies and DMSO drop diameters were obtained from the end of the samples that were destined for the 2.5 in. (6.4 cm) precrack region so as to not affect the adhesive bond. Samples were either bonded as blasted or contaminated with various levels of silicone as described previously. Adhesive specimens were vacuum bagged overnight (23°C, 10 in. (25.4 cm) of vacuum) and postcured 2 h (66°C, 1 atm).

Interaction of Probe Fluids and Contaminants

The ability of the probe fluids to solvate the mold releases was investigated first. Approximately 2 mL of the probe fluids were placed in vials with *ca*. 2 mL of Frekote 1711-1. In general, the fluids were immiscible and formed two distinct phases. After sitting overnight, samples of each phase were carefully extracted with a syringe and placed on KBr pellets for transmission Fourier transfer infrared (FTIR) analysis after evaporation of liquid residue.

The ability of DMSO to absorb the low-molecular-weight silicone oil mold release and the curable, nonmigrating silicone from grit-blasted, contaminated composites was investigated. *Circa* 1 ml of DMSO was placed on the sample surfaces and allowed to sit overnight in covered Petri® dishes (an open container of DMSO was included in the Petri dish to prevent evaporation). After 24 h, DMSO on the sample surfaces was transferred *via* pipette to plasma-cleaned aluminum coupons (O_2, 150 W, 15 min). Following evaporation of the DMSO in a vacuum oven (35°C), reflection FTIR spectra of the coupons were analyzed for silicone.

RESULTS AND DISCUSSION

Measurement of Surface Energy of Grit-Blasted Laminates as a Function of Mold Release Contamination

Establishing DMSO drop-diameter measurements as a surface energy probe able to predict adhesive joint performance requires creating adherends with a range of surface energies. This was accomplished by applying controlled amounts of silicone mold release to freshly grit-blasted adherends. To produce a sample with minimum surface energy, one sample was simply saturated with full-strength mold release. Average contact angles of five probe fluids obtained from these surfaces are shown in Figure 1.

As seen in Figure 1, the contact angles for all of the fluids increased significantly with increasing amount of Frekote 44, confirming that the surface energy was decreasing.

The diameters of 3-μl DMSO droplets applied to these same surfaces correlated very well with the calculated surface energies. This relationship is shown in Figure 2. These surfaces were probed twice

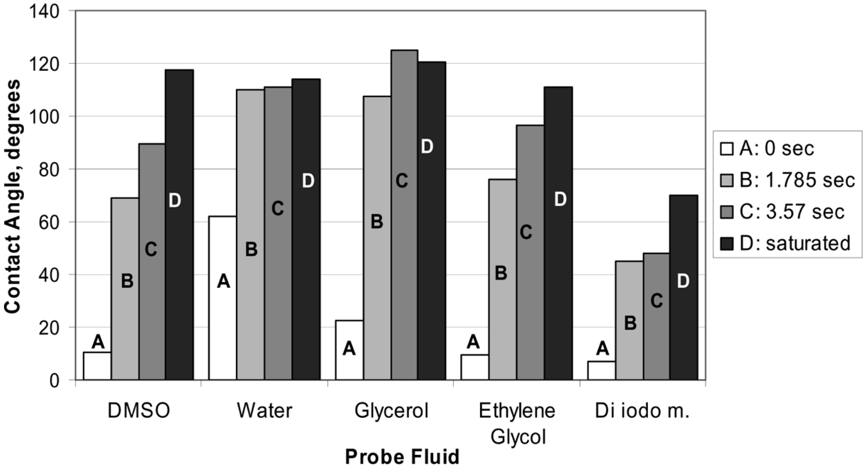

FIGURE 1 Probe fluid contact angles against grit-blasted surfaces as a function of residence time in 5% Frekote 44/heptane spray.

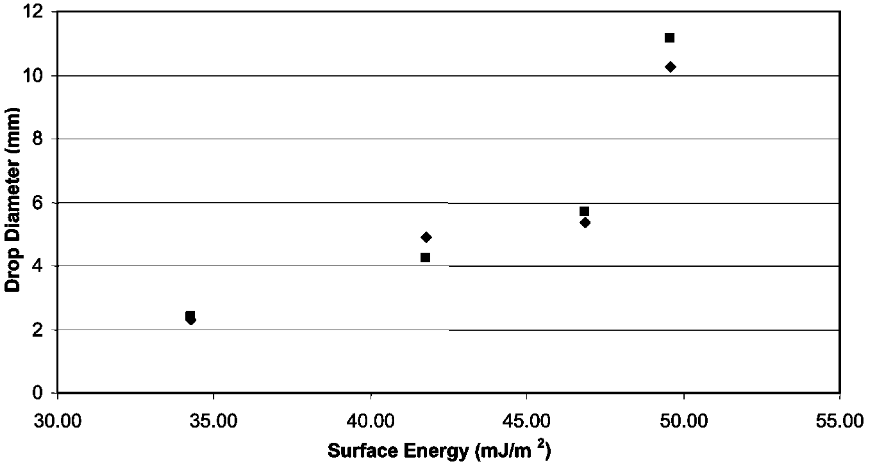

FIGURE 2 Diameters of 3-µl drops of DMSO on surfaces from Figure 1. The two sets of data points represent separate series of droplets placed at different locations on the sample surface.

with two separate series of DMSO droplets, and the results were identical within the precision of the diameter measurement apparatus. These results indicate that DMSO drop-diameter measurements show an excellent ability to detect small changes in surface energy, even on rough surfaces.

DMSO Droplet Size as a Predictor of Adhesive Joint Performance

To investigate the correlation between DMSO drop diameter measurements, surface energy and adhesive joint performance, grit-blasted substrates were recontaminated to various levels, evaluated for surface energies and DMSO drop diameters of 3-µl drops, then bonded into DCB specimens using Loctite EA9394 and tested for $G_{\mathrm{I}}c$. The results from these tests are shown in Table 2. The range of values (2–3 in.-lbs./in.^{2}, or 0.35–0.53 kJ/m^2) is typical for untoughened epoxies adhesives.

As seen in Figure 3, the fracture toughness values correlate very well with the DMSO drop diameter for the range of diameters between about 2 and 4 mm (corresponding to surface energies of 34 to 42 mJ/m^2). Above about 4 mm, the fracture energy plateaus near 2.1 in.-lb./in.^{2} (0.36 J/m^2). The fracture energy increases to about 3 in.-lb./in.^{2} (0.54 J/m^2) for the highest values of surface energy.

TABLE 2 $G_{\mathrm{I}}c$, Failure Mode, and Diameters of 3-μl DMSO Drops from Adherends Contaminated with Silicone Mold Release

Average $G_{\mathrm{I}}c$ (in.-lbs/in^2)	Failure mode	3-μl DMSO drop diameter (mm)
3.29	cohesive	11.2[a]
2.2	mixed	5.5
2.1	mixed	5.4
2.1	mixed	4.5
2	mixed	6.1
1.8	adhesive	3.5
0.89	adhesive	3.1
0.1	adhesive	2.4

[a] The drop diameter for this sample is inaccurate because the DMSO drop spread quickly after its application, making it difficult to obtain a diameter measurement.

The various regions in Figure 3 correspond to different failure modes. Low surface energy (small drop diameter) favors interfacial (or adhesive) failure, whereas high surface energy (large drop diameter) correlates with mixed mode or cohesive failure. Figure 4 shows the data from Figure 3 divided into zones of different failure mode and lends insight into the relationship between adherend surface energy and adhesive joint performance. For adhesive bonds prepared using substrates with DMSO diameters in the range of 2–4 mm, the strength of the adhesive/substrate interface is much less than the

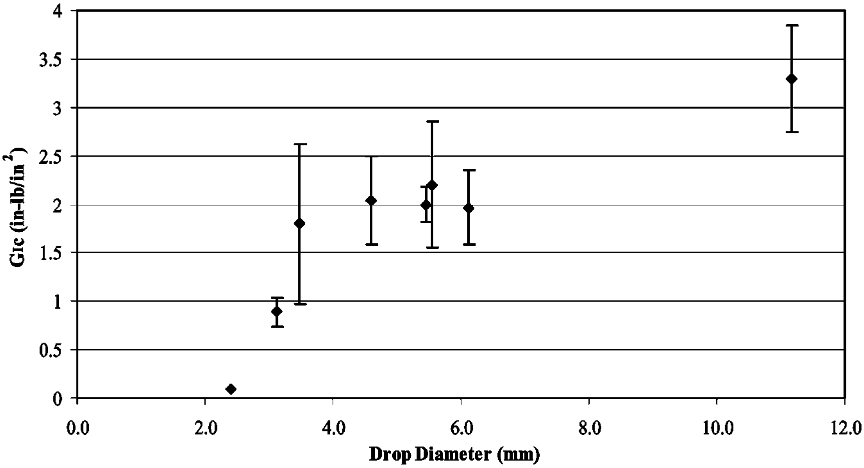

FIGURE 3 $G_{\mathrm{I}}c$ as a function of DMSO drop diameter for grit-blasted substrates contaminated with various levels of silicone mold release.

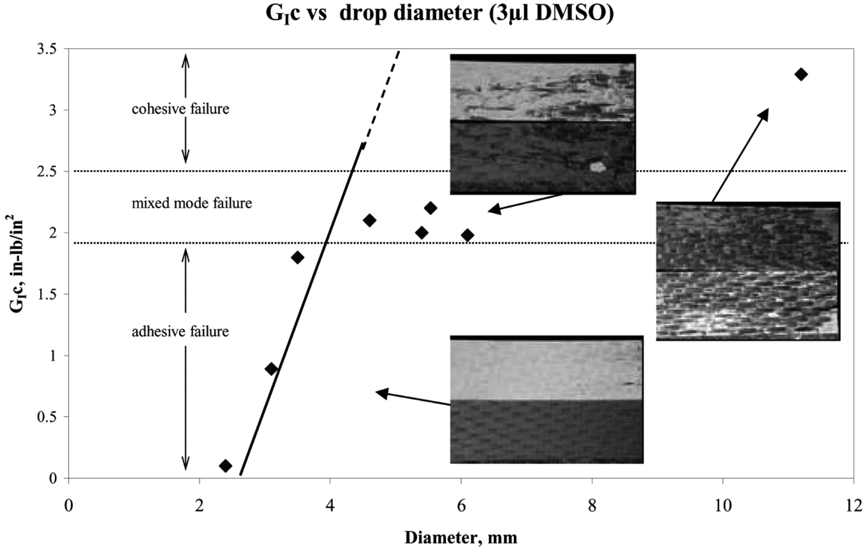

FIGURE 4 Relationship of G_Ic, failure mode, and DMSO drop diameter.

cohesive strength of the laminate. Failure is interfacial, and fracture energy in the region is a strong function of the substrate surface energy. In this range of surface energies, the fracture toughness is governed by the surface energy of the substrate and is therefore proportional to the work of adhesion.

For adhesive bonds prepared from substrates where the DMSO drop diameters were in the range of 4–6 mm, failure is mixed mode. Visual inspection of the fracture surfaces reveals regions where failure is interfacial and regions where substrate resin is torn from the composite surface. Interfacial adhesion in this regime is close to the cohesive strength of the substrate resin, which governs the overall fracture toughness.

When a droplet of DMSO is applied to a freshly grit-blasted surface (no applied contamination), spontaneous spreading occurs. Here the concept of a drop diameter has less significance. DCB specimens prepared from these substrates showed interlaminar failure in the substrate. The interface in these samples has strength close to or above that of the matrix resin, near 3 lbs./in. (0.53 J/m^2).

An explanation for why the fracture energy is constant as a function of amount of contaminant for low levels of silicone is based on work discussed next, which shows that the adhesive is capable of absorbing a certain amount of silicone. If the amount of silicone on the surface is not too great, this absorption can expose the clean laminate surface and allow a strong interface to be established. These levels of contaminant, too low to measurably affect the fracture toughness of the adhesive joint, are nonetheless readily detected by a DMSO drop-diameter measurement.

These data not only show that DMSO droplet diameter can be a predictor of adhesive joint performance but also that exploring the relationship of substrate surface energy, fracture energy, and failure mode in this way is a potentially powerful tool for gaining a greater understanding of the relationships among surface treatment, contamination, and adhesive joint performance for adhesively bonded composites.

Interaction of Probe Fluids with Contaminants

A prerequisite for wetting-behavior-based surface energy measurements is that possible perturbations of the surface by the probe fluids are taken into account. This is particularly important when low-molecular-weight, potentially soluble contaminants may be present. This part of the study investigated the interaction between typical surface-energy probe fluids and silicone mold releases, first by looking at miscibility, then by evaluating the ability of a probe fluid such as DMSO to extract contaminants from the substrate.

Diiodomethane, water, and glycerol showed no tendency toward miscibility with the low-molecular-weight silicone oil solution, whereas DMSO showed definite interaction with this contaminant. Figure 5 is a photograph that compares the behavior of DMSO and water with the silicone oil solution. The water/silicone sample showed no visible interaction. The DMSO/silicone sample did show interaction, however. The location of the interface between the two phases has shifted, as evidenced by a change in the relative volumes of the two phases. There also appears to be a precipitate at the interface. This suggests that the heptane solvent of the silicone may have been miscible in the DMSO. FTIR analysis showed that silicone was also absorbed by the DMSO.

Figure 6 compares the FTIR spectra of evaporated residue obtained from two of the fluids after 24 h in contact with the silicone solution: diiodomethane, which showed no visible interaction, and DMSO, which showed significant miscibility. This figure also includes the FTIR spectrum of the pure silicone (Frekote 1711-1) for comparison.

Although both DMSO and diiodomethane showed small peaks near $1260\,\mathrm{cm}^{-1}$ (indicating the presence of silicone in the probe fluids), DMSO absorbed a much greater amount of silicone than the

FIGURE 5 Left: Frekote 1711-1/DMSO. Right: Frekote 1711-1/water. A precipitate has formed at the interface of DMSO and Frekote. Much of the DMSO/heptane solution has absorbed into the Frekote phase.

diiodomethane. These results show that these surface energy probe fluids have the potential to alter the surface being investigated by absorbing contaminants such as silicones. This tends to lower the surface tension of the probe fluid and increase the surface tension of the substrate, both of which lower the contact angle and result in an overestimation of the surface energy.

To see if interaction between probe fluids and soluble contaminants on a surface could occur, a large drop of DMSO (*ca.* 1 ml) was placed on

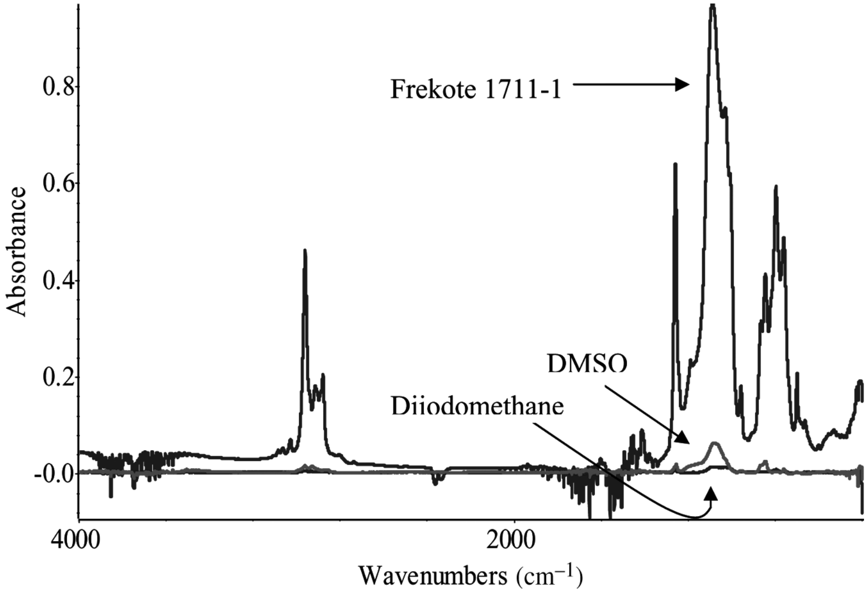

FIGURE 6 Transmission FTIR spectra from probe fluids that were in contact with Frekote 1711-1 overnight. Top: pure Frekote 1711-1; middle: DMSO; bottom: diiodomethane.

composite surfaces that had been contaminated with different levels of either the low-molecular-weight silicone oil (Frekote 1711-1) or a cross-linkable (*i.e.*, "nonmigrating") silicone (Frekote 44) and left for 24 h. Figure 7 shows the FTIR spectra of the evaporated residue from DMSO retrieved from the surfaces contaminated with the low-molecular-weight silicone. The spectrum from the heavily contaminated surface shows a recognizable spectrum of silicone, but the spectrum from the lightly contaminated surface shows no indication of silicone.

As might be expected, less silicone is absorbed from the curable mold release than from the silicone oil mold release. Figure 8 shows similar spectra obtained from the surfaces contaminated with the cross-linkable silicone. The weak, broad absorbance near 1100 cm^{-1} for the extract from the highly contaminated sample indicates a small amount of this silicone was also absorbed by the DMSO. There was no detectable extract from the surfaces that were only lightly contaminated with this release agent.

These experiments showed that DMSO is capable of extracting some silicone-based contaminants from the surface of a grit-blasted laminate.

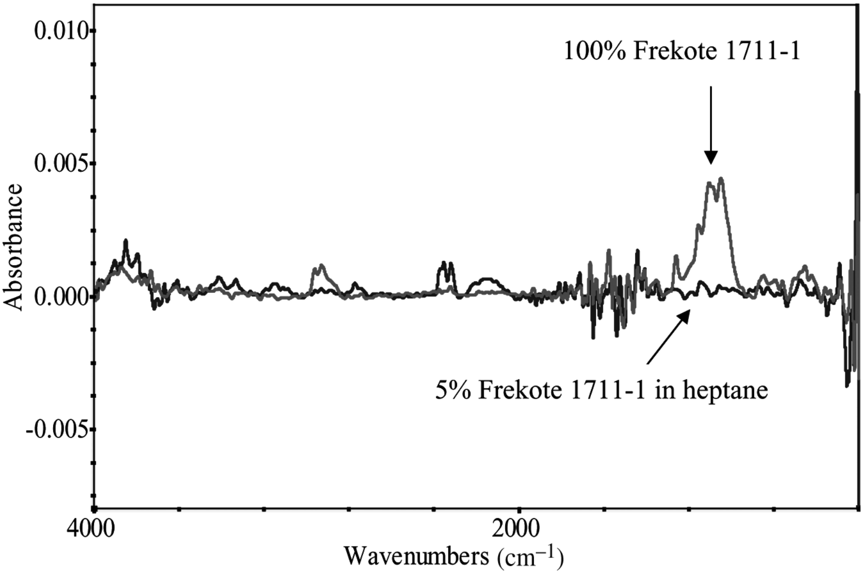

FIGURE 7 Grazing-angle FTIR spectra of residue from DMSO in contact with Frekote 1711-1 silicone oil mold release. Top: from fully saturated sample. Bottom: 1.5-s residence time under dilute solution spray.

DMSO Drop Diameter as a Function of Contact Time

To see if the slight solubility of silicone mold release in DMSO interferes with the utility of using DMSO wetting behavior as a predictor of adhesive bond performance, the diameter of DMSO droplets on contaminated surfaces was monitored as a function of time on samples with a range of contamination. A change in drop diameter over time would indicate significant perturbation of surface tension of the DMSO probe liquid and/or the surface being probed due to absorption of contamination and argue against the robustness of this technique. The results (Figure 9) show a fascinating pattern of interaction between the DMSO and the contaminated surfaces. The zero time diameters correlate very well with the amount of mold release applied: large drop diameters for lightly contaminated surfaces and small drop diameters for highly contaminated surfaces.

However, the very lightly contaminated surfaces are the only ones to show significant change in drop diameter with time. This phenomenon has been discussed in the literature in the context of wetting of contaminated surfaces [20,21,23]. According to this approach, when a wetting liquid is placed on top of a contaminated surface, if the

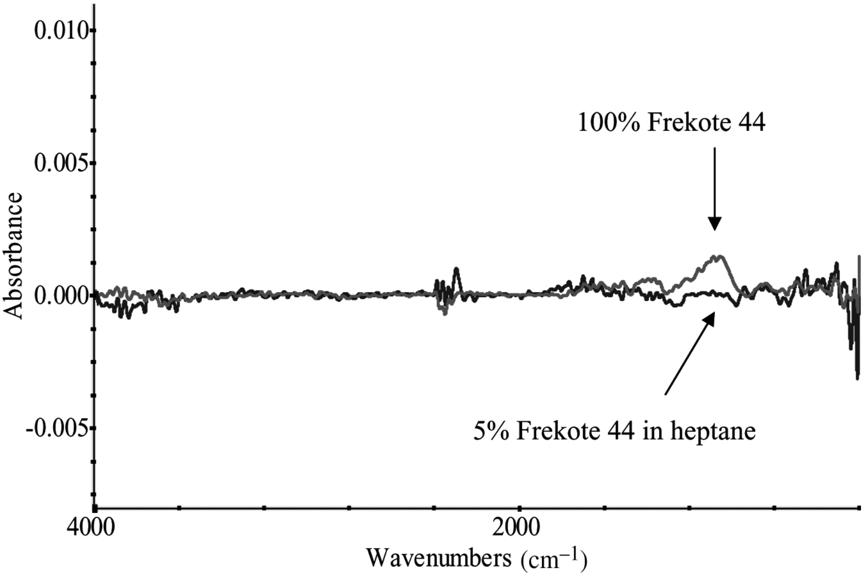

FIGURE 8 Grazing-angle FTIR spectra of residue from DMSO in contact with Frekote 44 nonmigrating mold release. Top: from fully saturated sample. Bottom: 1.5-s residence time under dilute solution spray.

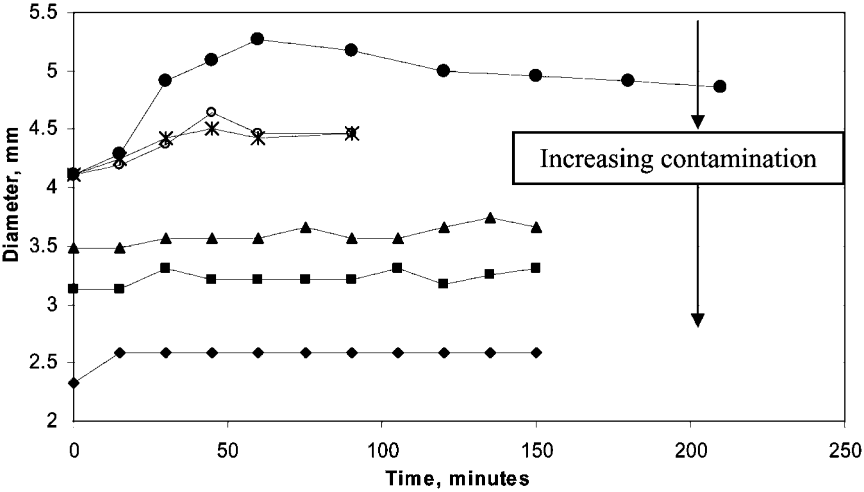

FIGURE 9 Diameters of 3-μl drops of DMSO as a function of time on grit-blasted composite surfaces coated with Frekote 44. Amount of contamination increases from top (1.5-s residence time) to bottom (saturated with mold release).

contaminant is capable of diffusing into the wetting liquid, the interfacial tension will increase with time due to removal of contaminant from the interface, causing the drop to spread. Because of the time constants involved in diffusion and viscosity, the drop has a tendency to overshoot its equilibrium diameter and then shrink back more slowly to this value.

The shapes of the curves for the lightly contaminated surfaces in Figure 9 (the top three traces) follow this predicted profile very well. When the amount of contamination is small, absorption of just a small amount by the DMSO exposes clean laminate. This increases the interfacial tension and the drop spreads as suggested in [20,21,23]. For larger amounts of contamination (bottom two traces in Figure 9), the DMSO still absorbs a small amount of contaminant. However, because there is much more contaminant on the surface, the amount removed is insufficient to expose clean laminate and increase the interfacial tension. In this case increased spreading does not occur.

Given the almost identical surface energy components of DMSO and epoxies, the solubility parameters of these materials will be very similar [18,19]. Prior to curing, an epoxy would be expected to be able to absorb a certain amount of mold release, similar to DMSO. This would in effect clean the underlying laminate, increase the interfacial tension, and produce a strong interface upon curing.

This can explain the relatively high (and constant) value of G_{I}c and the cohesive failure seen in laminates prepared from lightly contaminated substrates, even though these surfaces show a wide range of surface energies. However, when the amount of contaminant is increased beyond the ability of the adhesive to accommodate it through absorption, the adhesive bonds fail interfacially and G_{I}c shows a linear dependence on the surface energy.

CONCLUSIONS

Practical quality assurance tools for joining composite structures using room-temperature curing paste adhesives do not currently exist. Small amounts of contamination (such as silicone mold releases) can wreak havoc on bond performance yet are very difficult to detect on technical surfaces in a manufacturing environment. This work has demonstrated the potential utility of using the wetting behavior of a suitable single liquid as a probe to evaluate the suitability of a grit-blasted laminate surface for adhesive bonding. A suitable liquid probe has surface tension characteristics very similar to that of the adhesive and a sufficiently low viscosity so that equilibrium wetting is achieved in a practical amount of time. In this work, the wetting behavior of small drops of DMSO was shown to correlate very well with adhesive bond performance for grit-blasted composite surfaces that had been contaminated with silicone mold releases to obtain a range of surface energies. Although the silicones were shown to be miscible to some degree in the DMSO probe fluid, this miscibility did not measurably affect the wetting behavior of the probe fluid. Fracture behavior (both fracture toughness and failure mode) were shown to depend upon the level of contamination. The relationship between fracture toughness and failure mode with contamination suggested an adhesive that is capable of imbibing small amounts of contamination to establish a robust interface. Finally, using the diameter of a drop of known volume instead of a contact-angle measurement to quantify wetting of the surface by the probe fluid circumnavigates the technical issues involved with measuring a contact angle on a rough, nonplanar surface of a part or subassembly in a manufacturing process.

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