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The Influence of Manufacturing Process Parameters on Adhesively Bonded Joints: an Evaluation of Surface Preparation, Cure Profile, and Adhesive Out-time

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LIST OF ACRONYMS AND SYMBOLS

AFP	automated fiber placement
AOT	adhesive out-time
APPT	atmospheric pressure plasma treatment
CC	compliance calibration
DCB	double cantilever beam
DGEBA	diglycidyl ether of bisphenol A
DMA	dynamic mechanical analysis
DOE	design of experiments
FEP	fluorinated ethylene propylene
FTIR	Fourier-transform infrared
MBT	modified beam theory
MCC	modified compliance calibration
MSFC	Marshall Space Flight Center
NDE	nondestructive evaluation
NIAR	National Institute for Aviation Research
PBT	preparation to bond time
PTFE	polytetrafluoroethylene

NOMENCLATURE

a	delamination length from the loading point to the crack tip
E'	storage modulus
h	adherend thickness
R	resistance
t	adhesive layer thickness
T_g	glass transition temperature

TECHNICAL PUBLICATION

THE INFLUENCE OF MANUFACTURING PROCESS PARAMETERS ON ADHESIVELY BONDED JOINTS: AN EVALUATION OF SURFACE PREPARATION, CURE PROFILE, AND ADHESIVE OUT-TIME

1. INTRODUCTION

1.1 Background

In the fabrication of an adhesively bonded joint in a polymer matrix composite structure, there are several process parameters that can potentially affect joint performance. Certification of an adhesively bonded joint is not trivial and can depend heavily on application. The traditional building block approach can be relied upon to certify an adhesively bonded joint, but several interferences inherent to the nature of adhesively bonded joints can present significant challenges. Contamination is a significant concern and detrimental levels of contaminants, principally siloxanes (sometimes generically referred to as 'silicones'), can be extremely difficult to detect.[1] While bondline defects where an air gap is present (i.e., a classical delamination) can typically be detected via nondestructive evaluation (NDE), a reliable NDE method for identifying weak bond regions (where an adhesive bond exists but said bond region exhibits reduced mechanical performance compared to the nominal) does not currently exist. Furthermore, the practice of creating an intentional weak bond region for the purposes of validating an NDE method is also a challenge, though at least one method has been patented by researchers at Boeing.[2] While a proof test approach could be used to mitigate these concerns to some extent, achieving an adequate proof for an adhesively bonded joint in a given structure can often be challenging, if not infeasible. Given these issues, a suitable certification approach for adhesively bonded joints must rely heavily on well-established process controls and subscale testing. In order to establish adequate process controls, relevant process parameters and their influence on adhesively bonded joint performance must be well understood. This study aims to characterize the effects of several key process parameters relevant to adhesively bonded joint manufacturing in the interest of defining process windows for the material systems and surface preparation approach considered herein.

1.2 Study Design and Scope

Adhesively bonded joint manufacturing gives rise to several potentially critical process parameters. For the purposes of this study, the authors selected a subset of said potentially critical parameters based primarily on in-house experience and needs. However, the process parameters examined herein are, for the most part, general in nature and should be pertinent to a wide range of adhesively bonded joint approaches, configurations, and applications. To assess the criticality

of the process parameters of interest both individually and in combination, a full-factorial design of experiments (DOE) approach was used. The process parameters considered in this study are summarized in Table 1, with the particular levels evaluated shown in italics.

Table 1. Summary of process window development DOE for adhesively bonded joints.

Process Parameters		Adhesive Age (mo)	Adhesive Out-Time (d)	Laminate Age (mo)	Prep to Bond Time (d)	Cure Temp. (°F)	Plasma Treatment
Levels	Low	<6 (+0)	*<3 (+0)*	*<1 (+0)*	*0 (+0)*	*200 (–10/+10)*	*No*
	Mid	Null	Null	Null	Null	*250 (–10/+10)*	Null
	High	*12 (–0/+1)*	*40 (–0/+3)*	12 (–0/+1)	*14 (–0/+3)*	*300 (–10/+10)*	Yes

Note that this DOE is intended for a secondarily bonded joint with a 250 °F curing adhesive. A cobonded approach, for example, would warrant the evaluation of additional process parameters (such as prepreg age, prepreg out-time, vacuum level during cure, etc.). Because several of the terms used to denote process parameters in this study could entail some degree of ambiguity, the following descriptions outline said process parameters as defined herein:

- Adhesive age: elapsed time between date of material manufacture and date of bonding, where aging environment is cold storage.
- Adhesive out-time: cumulative time adhesive has incurred outside of cold storage prior to bonding, where exposure environment is composites fabrication facility.
- Laminate age: elapsed time between date of laminate cure and date of bonding, where aging environment is composites fabrication facility.
- Preparation to bond time: elapsed time between time of peel-ply removal and time of bonding, where exposure environment is composites fabrication facility.
- Cure temperature: hold temperature during cure cycle.
- Plasma treatment: atmospheric pressure plasma treatment (APPT).

Among these descriptions, several details are notable—primarily, in relation to the aging/exposure environments considered. For adhesive age, the aging environment is straightforward (in sealed packages in cold storage). For adhesive out-time, laminate age, and preparation to bond time, the aging/exposure environment was chosen to be the composites fabrication facility used for manufacturing operations carried out in this study. This environment was selected in lieu of an environmental chamber in the interest of more closely replicating the conditions (in particular, relative humidity, temperature, ultraviolet (UV) radiation, and potential airborne contaminants) that full-scale composite hardware would face in the same facility. Characteristics of the composites fabrication facility used in this study are further detailed in section 2.3.

The scope of this study, though extensive, was subject to limitations with respect to budget and schedule. In particular, these limitations prevented the evaluation of effects due to extended laminate age. In the context of this study's construct, this would have likely provided insight with respect to the critical issue of pre-bond moisture in the adherends.[3–7] The effects of extended laminate age (and pre-bond moisture) will be evaluated in future work.

2. EXPERIMENTAL

2.1 Material Selection and Surface Preparation Approach

In the interest of material selection and developing a baseline surface preparation approach, the authors relied heavily on a review of the available literature, expert elicitation (both within NASA and among peers in industry), and in-house experience. Based on this evaluation, the following takeaways became clear:

- For a given adhesively bonded joint application, material selection and surface preparation approach are interdependent and should be considered as such.
- With respect to surface preparation, operator independence (automation is preferable where relevant and feasible) should be sought after in the interest of limiting the potential for variability and contamination.
- A simple, straightforward surface preparation approach that minimizes the number of operations and processing materials used is highly desirable.

Among the myriad options for surface preparation techniques, the use (and removal) of a peel ply, when properly selected and utilized, can largely satisfy each of the key considerations mentioned above. Peel plies are commonly considered in surface preparation schemes for composite structures[4,6,8,9] due to their ability to provide for surface roughness in a uniform manner as well as some degree of protection against contamination. Prior to cure, peel plies are applied to surfaces to be bonded, then typically left on said surfaces of the cured component until immediately prior to bonding. Upon removal, which ideally should take place immediately prior to bonding within a contamination-controlled environment, peel plies leave behind a roughened surface that can provide for mechanical interlock in an adhesively bonded joint. Peel plies can be either dry or preimpregnated with a suitable resin system (preimpregnated peel plies may also be referred to as 'prepregged' or 'wet' peel plies). Upon removal, both dry and prepregged peel plies are intended to provide for a freshly fractured surface with enhanced surface free energy. Prepregged peel plies can provide for a resin-rich fractured surface, where the reinforcing fibers in the primary structure are unlikely to be exposed during peel ply removal.[6,10] This can be an advantage of using a prepregged peel ply, given that exposed, clean fiber surfaces, which are more likely to be left behind after removal of a dry peel ply, may lead to poor adhesion in bonded applications.[11] As previously mentioned in this section, peel plies, dry or prepregged, can also provide some measure of protection against contamination, as the surfaces to be bonded are covered throughout the life of the composite component prior to bonding. It should be recognized, however, that the extent of protection can vary with the type of peel ply used: A thin, loosely woven, dry peel ply will likely offer minimal protection, while a thick, tightly woven, prepregged peel ply may effectively act as a sacrificial outer ply.

The use of peel plies does not come without potential pitfalls. Given their more traditional use in composites applications, where eventual bonding operations are not a consideration and

where ease of removal is key, many commonly used peel plies are coated with a release agent. These release agents, which are commonly silicone- or polytetrafluoroethylene (PTFE)-based, can be left behind after peel ply removal and subsequently act as contaminants in applications where bonding is eventually completed. Nylon-based peel plies can be particularly difficult to remove without the aid of a release agent, while polyester- and fiberglass-based peel plies can typically be safely removed (i.e., without damaging the underlying composite structure) without the need for a release agent. Hart-Smith, et al. chronicled the potentially detrimental effects of released nylon peel plies in bonding applications in the widely circulated paper "The Curse of the Nylon Peel Ply."[11]

In light of the considerations detailed in this section, a commercially available prepregged peel ply (Solvay FM® 3500 EZP [epoxy with glass fabric carrier]) was selected for use in the surface preparation approach used herein. A widely used intermediate modulus carbon fiber/mid-toughened epoxy matrix system in unidirectional tape form (Hexcel IM7/8552-1) was used for the laminate adherends. Solvay FM® 209-1M epoxy film adhesive was used for bonding. The following baseline surface preparation/bonded assembly fabrication approach was used in this study:

(1) Co-cure FM 3500 EZP on surfaces to be bonded during IM7/8552-1 adherend cure.

(2) Immediately prior to bonding, remove FM 3500 EZP from IM7/8552-1 adherend surfaces to be bonded.

(3) Apply FM 209-1M and secondarily bond adherends.

Note that several traditionally used components of surface preparation in composites are absent from this approach: No solvents are used and no direct physical contact (as would be necessary with manual abrasion, wiping, or otherwise) is made with surfaces to be bonded. This minimization of contact with surfaces to be bonded, coupled with the operator dependence inherent to this approach, significantly reduces the potential for contamination during bonding operations. As previously noted, the presence of prepregged peel ply on surfaces to be bonded offers protection throughout part processing, which is especially significant in the context of a large-scale component that could be exposed to handling, machining, NDE, assembly, etc., prior to adhesive bonding.

Given the nature of this study, the execution of the baseline surface preparation/bonded assembly fabrication approach was intentionally altered as necessary to evaluate the process parameters and levels of interest. Most notably, where plasma treatment was considered, surfaces to be bonded received plasma treatment following peel ply removal and prior to bonding.

2.1.1 Atmospheric Pressure Plasma Treatment (APPT)

Plasma treatment processes are used for surface preparation in a wide variety of applications, including adhesive bonding with polymer matrix composites. Plasma treatment exposes a surface to a cloud of ionized gas, where ions, electrons, and free radicals collide with the surface to be bonded with enough energy to break existing molecular bonds. This process yields an increase in surface free energy and, depending on substrate composition, can add functional groups to surfaces that were previously largely chemically inactive. While a variety of plasma treatment approaches

exist, APPT is among the most viable in terms of ease-of-implementation and scalability (APPT lends itself well to automation), both of which are critical considerations for adhesive bonding of large-scale composite structures. In contrast to other methods of plasma treatment, which can require vacuum pressure and/or feedstock gases such as argon or nitrogen, APPT can be carried out in open air with only clean air as the feedstock gas. Given the advantages of APPT, considerable interest in developing, understanding, and utilizing the technology exists within government, industry, and academia alike. Thanks to this interest, fundamental work has been carried out to optimize process parameters and demonstrate the capabilities of APPT with respect to adhesive bonding in composite structures applications.[12–17] In particular, researchers at Boeing have developed APPT process parameters using a Plasmatreat Openair-Plasma® system. Table 2 summarizes these process parameters.

Table 2. Summary of APPT process parameters for Plasmatreat Openair-Plasma system.

Source	Plasma Jet Configuration	Distance between Jet and Substrate (in)	Raster Speed (in/sec)	Improvement (via plasma) in Mode I Fracture Toughness over Control
Encinas et al.[16]	Single flume rotational jet (Plasmatreat RD1004)	0.24	0.39	≈100%
Tracey et al.[9,17]	Single flume rotational jet (Plasmatreat RD1004)	0.5	1 and 6	206% for 1 in/sec raster 196% for 6 in/sec raster
Tracey[12]	Single flume rotational jet (Plasmatreat RD1004)	0.5	1, 6, 9, and 12	206% for 1 in/sec raster 196% for 6 in/sec raster 183% for 9 in/sec raster 203% for 12 in/sec raster

In view of the work summarized in Table 2, a Plasmatreat Openair-Plasma system was chosen for this study in test groups where plasma treatment was considered on surfaces to be bonded. In particular, a Plasmatreat RD1004 single flume rotational jet with a 17° nozzle was used along with a Plasmatreat FG5001 generator. The distance between jet and substrate was fixed at 0.5 in and a raster (scan) speed of 5 in/sec was used. APPT was automated via a 3-axis gantry, as shown in Figure 1.

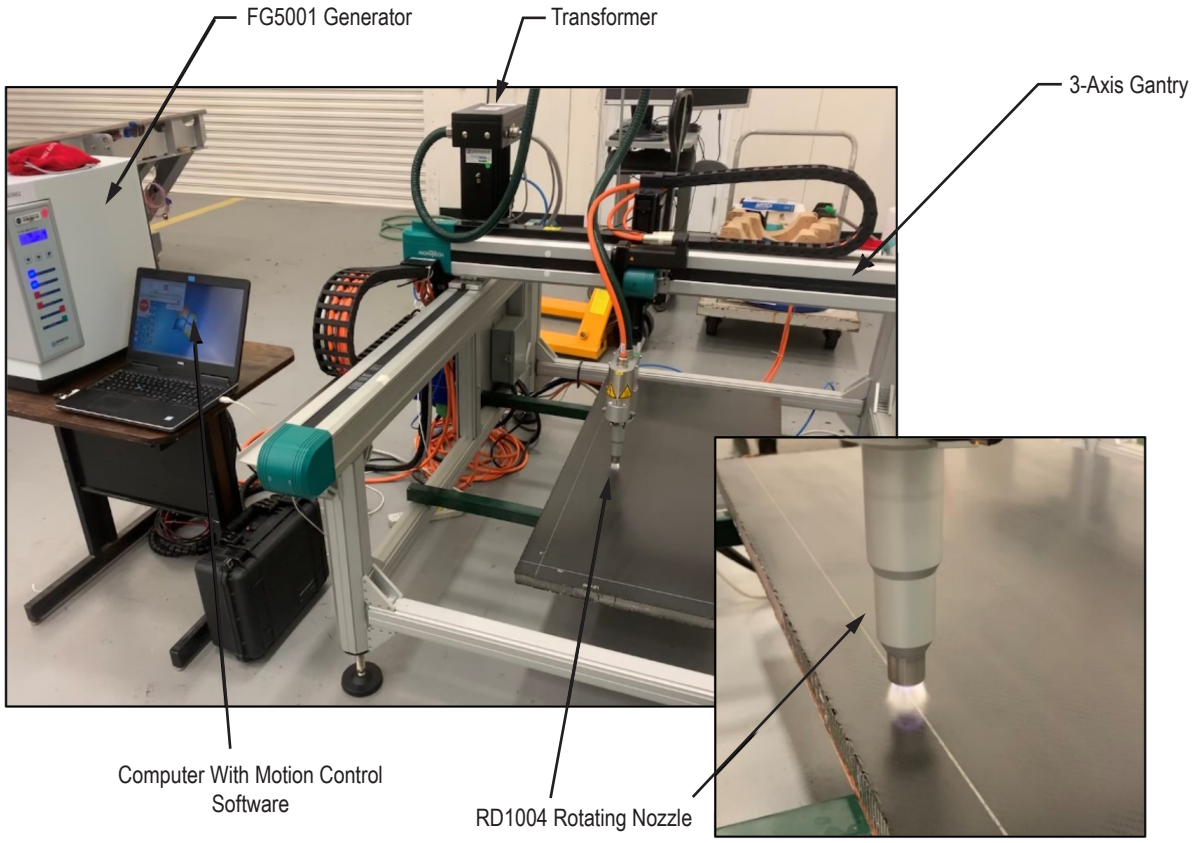


Figure 1. NASA Marshall Space Flight Center (MSFC) automated system for atmospheric pressure plasma treatment (APPT).

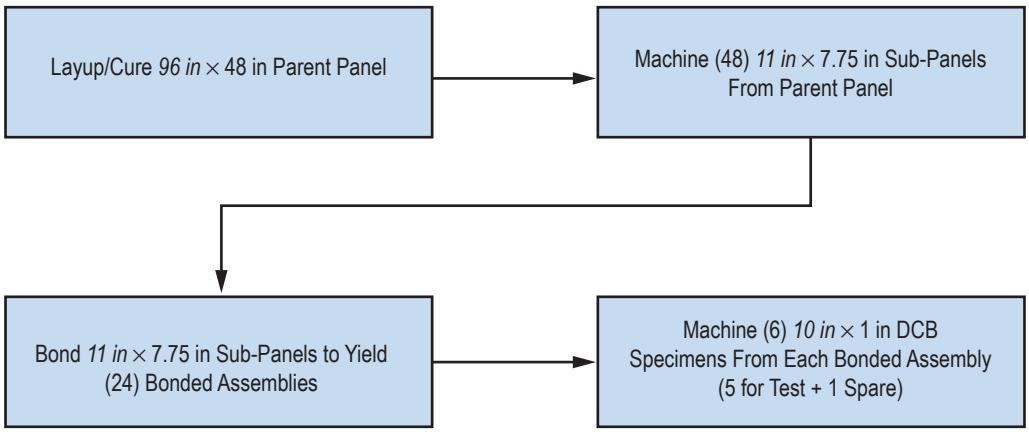
2.2 Test Method Selection

In terms of evaluating the effects of the aforementioned process parameters of interest, several options exist with respect to test methods. While the single lap shear test can be tempting to use, primarily due to its ease-of-implementation (coupons are simple to prepare; data collection is straightforward), there are significant drawbacks associated with this test method. Hart-Smith,[18] Davis and Bond,[19] and Bardis and Kedward[8] have reported that the lap shear test verifies only short-term bond strength and is a poor indicator of durability in an adhesively bonded joint. While manufacturing process parameters have a significant influence on the durability of an adhesively bonded joint, the same cannot necessarily be said with respect to short-term bond strength. In this way, process parameters that could be critical in terms of durability may not appear to be significant with respect to short-term bond strength. As such, a test method capable of assessing durability, and therefore, manufacturing process parameters, is more appropriate than a lap shear test. Among the test methods capable of assessing durability, the Mode I fracture toughness test using the double cantilever beam (DCB) specimen has been shown to be the most effective and the most sensitive in evaluating the effects of adhesively bonded joint manufacturing process parameters.[20] Given its sensitivity to minute modifications and/or variations in bonded joint processing, the

Mode I fracture toughness test using the DCB specimen can be thought of as a "canary in a coal mine" in that, if a process parameter changes, this test will likely show it. In view of these considerations, the Mode I fracture toughness test using the DCB specimen was chosen to evaluate process parameters for adhesively bonded joint manufacturing in this study.

2.3 Bonded Assembly Fabrication

A single parent panel (96 × 48 in in size) was manufactured in order to facilitate fabrication of the bonded assemblies considered in this study. Prior to parent panel layup, the Invar (an iron-nickel alloy also denoted as FeNi36 or 64FeNi) tooling surface was coated with Loctite® Frekote 700-NC™. Given that this Invar tool is commonly used in the normal course of operations at NASA MSFC, a single coat (rather than 2–3 coats, which would generally be used to prepare a new tooling surface) of Frekote 700-NC was manually applied to the tooling surface prior to parent panel layup. One ply of FM 3500 EZP was applied to the tooling surface prior to IM7/8552-1 layup. IM7/8552-1 layup was carried out via automated fiber placement (AFP). In programming for the AFP layup, care was taken to stagger course start points to avoid stacking course-to-course seams through the thickness. Following IM7/8552-1 layup, another ply of FM 3500 EZP was applied to the bag side of the layup. A composite caul sheet, also coated with a single layer of Frekote 700-NC, was used on the bag side of the layup. The parent panel was cured in an autoclave at 350 °F and 50 psi, with a 120 min hold at said temperature and pressure. Following cure, sub-panels were machined from the parent panel and stored in sealed bags. Said sub-panels were then used to fabricate the bonded assemblies from which DCB test specimens were ultimately machined. Figure 2 outlines this process flow.



Note: The italicized dimensions for the parent panel, sub-panels, and DCB specimens correspond to the 0° fiber direction.

Figure 2. Process flow used to fabricate DCB test specimens considered in this study.

Bonded assemblies from which test specimens were ultimately taken were fabricated by secondarily bonding 11 × 7.75-in, pre-cured sub-panels (IM7/8552-1, $[0]_{12}$) together with FM 209-1M film adhesive. Figure 3 shows a schematic of the bonded assemblies. Note that the 0.0005-in fluorinated ethylene propylene (FEP) was used as a non-adhesive insert to create an initiation site for delamination growth. The partial-coverage FEP layer was applied between the film adhesive layer and one adherend. Placement of the FEP layer in the context of the DCB specimens ultimately machined from the bonded assemblies can be seen in Figure 3(b).

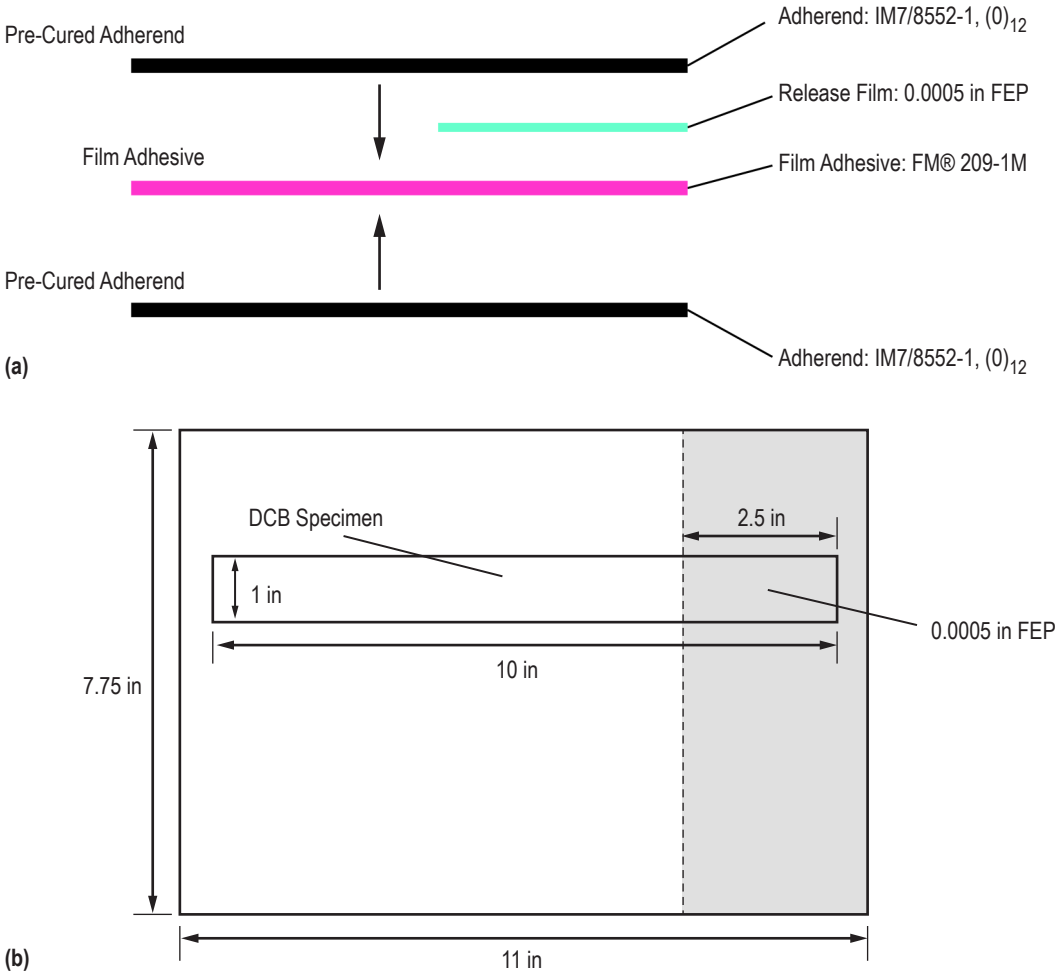


Figure 3. Overview of bonded assemblies fabricated to yield DCB test specimens: (a) bonded assembly schematic and (b) plan view of bonded assembly.

The following general operations were used to fabricate bonded assemblies for this study. As previously noted in section 2.1, the execution of the baseline bonded assembly fabrication approach was intentionally altered as necessary to evaluate process parameters and levels of interest in this study.

(1) Immediately prior to bonding, remove FM 3500 EZP from IM7/8552-1 adherend A.
   – If APPT is to be used, carry out APPT following FM 3500 EZP removal as dictated by test group.

(2) Apply FM 209-1M to IM7/8552-1 adherend A.

(3) Debulk film adhesive on IM7/8552-1 adherend A for minimum of 10 min.

(4) Apply 0.0005-in FEP partial coverage layer to film adhesive (see Figure 3(b) for placement detail).

(5) Remove FM 3500 EZP from IM7/8552-1 adherend B.
   – If APPT is to be used, carry out APPT following FM 3500 EZP removal as dictated by test group.

(6) Place IM7/8552-1 adherend B onto film adhesive/IM7/8552-1 adherend A to create bonded assembly.

(7) Debulk bonded assembly overnight (minimum of 12 h) prior to cure.

(8) Bag assembly for cure with minimum of two thermocouples contacting assembly edges near film adhesive layer.

(9) Cure under full vacuum (> 27 in Hg) in oven per designated cure cycle.
   – For 200 °F cure groups: heat to 200 °F at 3–5 °F/min, hold at 200 °F for 90 min, then cool to below 150 °F at no greater than 5 °F/min.
   – For 250 °F cure groups: heat to 250 °F at 3–5 °F/min, hold at 250 °F for 90 min, then cool to below 150°F at no greater than 5°F/min.
   – For 300 °F cure groups: heat to 300 °F at 3–5 °F/min, hold at 300 °F for 90 min, then cool to below 150 °F at no greater than 5 °F/min.

Each assembly was bonded with the tool side of the laminate adherends oriented toward the film adhesive. This practice was undertaken to better ensure consistency among test groups. Although both laminate adherend surfaces (tool side and bag side) were tooled in this case, the authors preferred to avoid any potential interferences associated with mixing tool side and bag side surfaces at the bonded interface. This is particularly relevant regarding the use of Frekote 700-NC. While this release agent was applied to both the Invar tooling surface and the composite caul sheet, it is conceivable that Frekote 700-NC could interact differently with these two surfaces with respect to adhesion to the surfaces and the potential for transfer to the cured adherends. At the outset of this study, the authors hypothesized that even if Frekote 700-NC introduced contaminants on the surfaces of cured adherends, the presence (and ultimate removal) of the sacrificial FM 3500 EZP layer would preclude transfer of contaminants to IM7/8552-1 surfaces to be bonded. The testing carried out herein accounts for any effects of said potential contamination due to the standard usage of Frekote 700-NC.

Bonding operations were carried out at NASA MSFC in a composites fabrication facility. This facility, which can be characterized as a large volume high bay, is climate controlled and continuously monitored for temperature, relative humidity, and airborne particulate count. The facility is also regularly monitored for airborne silicones via aluminum fallout plates. Clean aluminum plates are placed face up toward the ceiling in several locations throughout the facility. Each week, the plates are swabbed and checked for silicones via benchtop Fourier-transform infrared (FTIR) spectroscopy. The following sections show temperature and relative humidity profiles in the composites fabrication facility during the key periods of this study. Over these same key periods there was no evidence of airborne silicones (i.e., the weekly checks via FTIR showed no evidence of silicones).

2.3.1 Extended Surface Preparation-to-Bond Time

Where extended preparation to bond time was considered, FM 3500 EZP was removed and the IM7/8552-1 adherends were allowed to sit uncovered and unshielded in the composites fabrication facility for the duration of the aging period. As shown in Figure 4, adherends were oriented with surfaces to be bonded face up so as to maximize exposure to the room environment (e.g., airborne particulates, potential contaminants, UV radiation, relative humidity, and temperature). This approach was taken to evaluate the effects of open time following peel ply removal and prior to adhesive application.

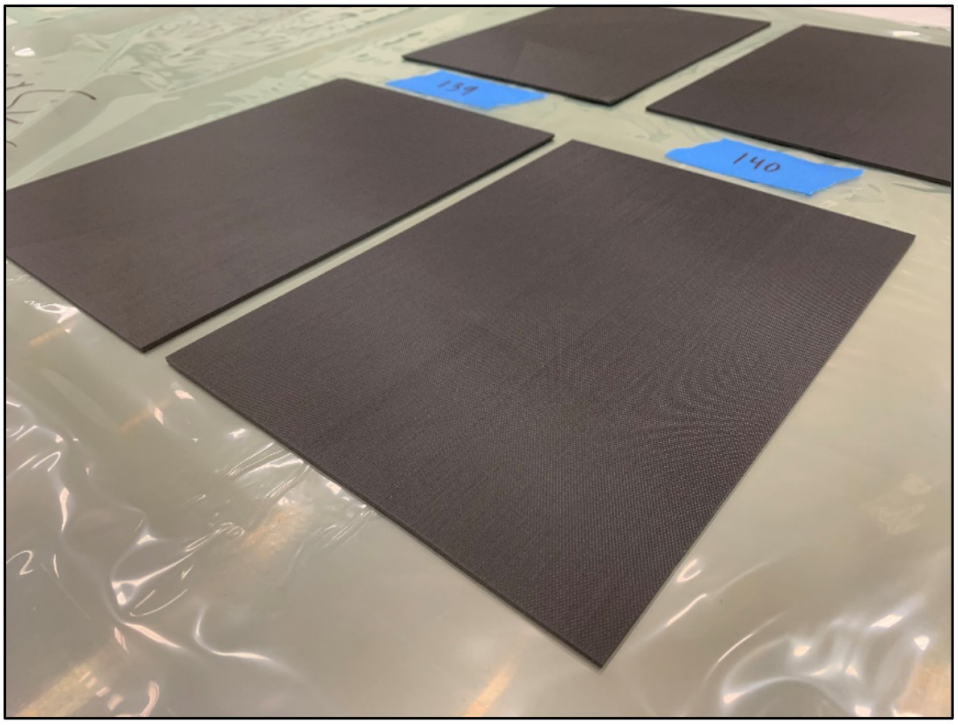


Figure 4. Precured adherends, with peel ply removed, for extended preparation to bond time groups during aging period in NASA MSFC composites fabrication facility.

Where APPT was considered in conjunction with extended preparation to bond time, APPT was carried out at the end of the aging period (i.e., immediately prior to adhesive application) in an effort to simulate a bonded joint fabrication scenario in which APPT cannot be successfully carried out immediately following peel ply removal (for example, due to a general power failure or operational failure of the APPT system). This particular scenario informed the length of the extended preparation to bond time aging period considered herein, where 14 days was selected as a conservative length of time during which operational issues with the APPT system could be remedied. Note that, in cases where APPT was not considered in conjunction with extended preparation to bond time, a 14-day period of open time following peel ply removal is arguably excessively conservative. Using the surface preparation approach considered in this study, adhesive can likely be applied within a matter of minutes following peel ply removal in most scenarios. However, at the outset of this study, the authors chose to proceed with the understanding that (pending results) a more realistic period of extended preparation to bond time may need to be considered in future work. Though this approach entailed some degree of risk, it also presented the potential reward of establishing a wider-than-likely-necessary processing window with respect to preparation to bond time.

Figure 5 shows relative humidity and temperature data as measured in the composites fabrication facility during the extended preparation-to-bond-time aging period considered in this study. Note that the relative humidity levels are at the upper end of typical composites fabrication facility requirements, which are commonly 60%–65%. As such, this study considers the upper range of relative humidity levels for typical operations in a composites fabrication facility.

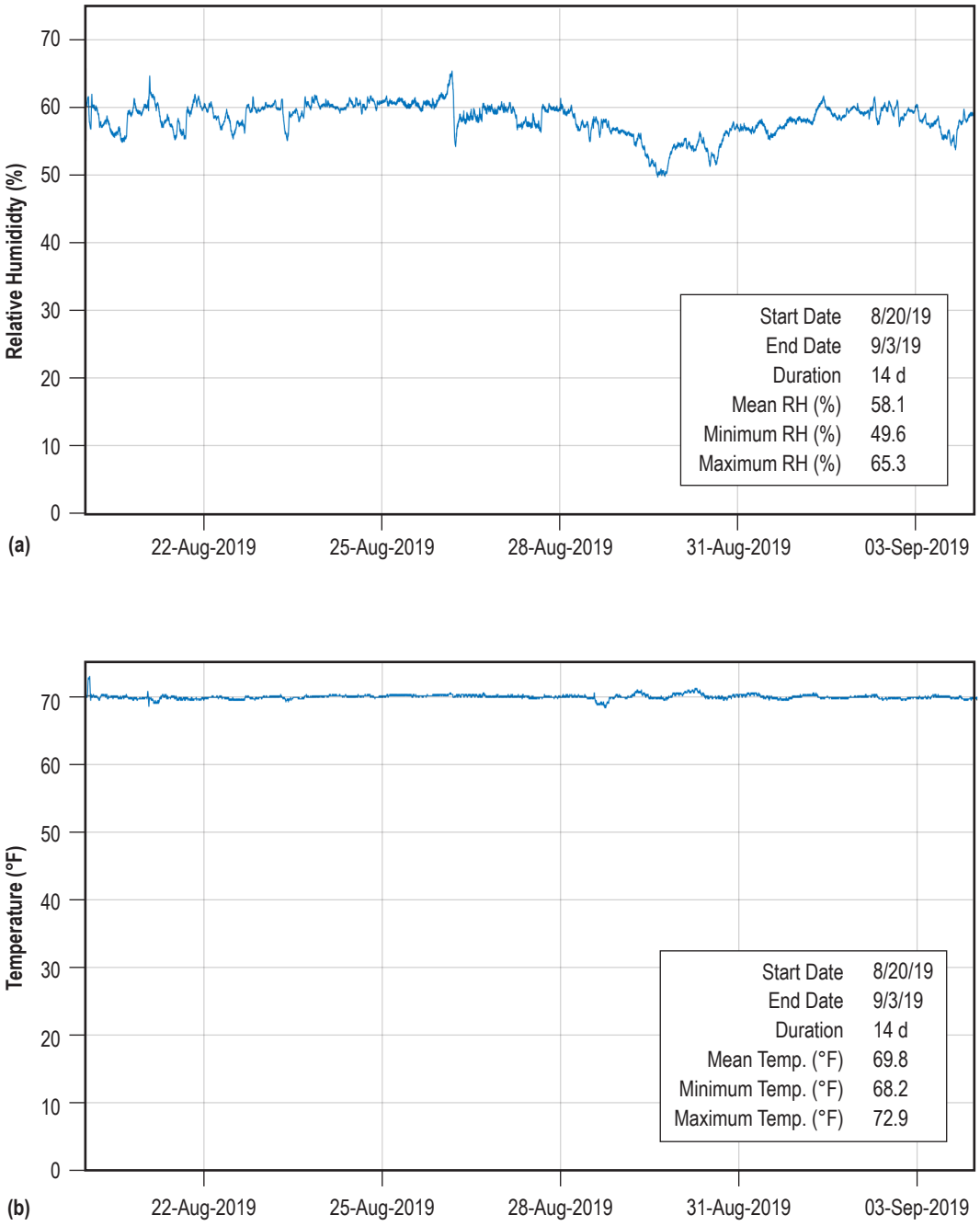


Figure 5. Environmental conditions for extended preparation-to-bond-time groups: (a) relative humidity data and (b) temperature data for NASA MSFC composites fabrication facility.

2.3.2 Extended Adhesive Out-time

While material out-time can be defined generically as cumulative time out of proper storage conditions (in the case of FM 209-1M, sealed and stored at or below 0 °F), the effects of out-time accumulation ultimately depend on material usage/storage conditions during said accumulation

period. For example, out-time can accumulate while the material is in use (i.e., applied to core material during sandwich structure layup) or while the material is simply stored awaiting use (i.e., in a sealed bag while the material is allowed to thaw). While both scenarios fit within generic definitions of material out-time, they can notably differ from one another with respect to both the likelihood of occurrence during the normal course of operations in composites manufacturing and the associated effect on material performance. In the context of the adhesively bonded, joint-fabrication approach considered in this study, out-time accumulation, while the adhesive is in use, is inherently minimal. In contrast, out-time accumulation, while the adhesive is sealed and stored at room temperature awaiting use, is not avoidable, though it can be managed. This holds true regardless of end use or manufacturing approach. As such, this study focused on out-time accumulation while the material was sealed and stored at room temperature awaiting use, which, given the commonality of this consideration, provides for applicability to a wide range of manufacturing processes where adhesive out-time is a concern.

Where extended adhesive out-time was considered, FM 209-1M was cut to size for eventual bonded assembly fabrication and sealed in polyethylene bags. As shown in Figure 6, said film adhesive was then stored at room temperature in the composites fabrication facility for a period of 40 days (10 days beyond the manufacturer's stated maximum out-time of 30 days, in an effort to be conservative). This approach was taken to simulate adhesive storage upon removal from cold storage and prior to use where the material would remain in a sealed bag until time of use.

Figure 6. Film adhesive for extended adhesive out-time groups during aging period in NASA MSFC composites fabrication facility.

Figure 7 shows relative humidity and temperature data as measured in the composites fabrication facility during the extended out-time period considered in this study. Like the extended surface preparation-to-bond time groups, relative humidity levels for the extended adhesive out-time groups represent the upper range of relative humidity levels for typical operations in a composites fabrication facility.

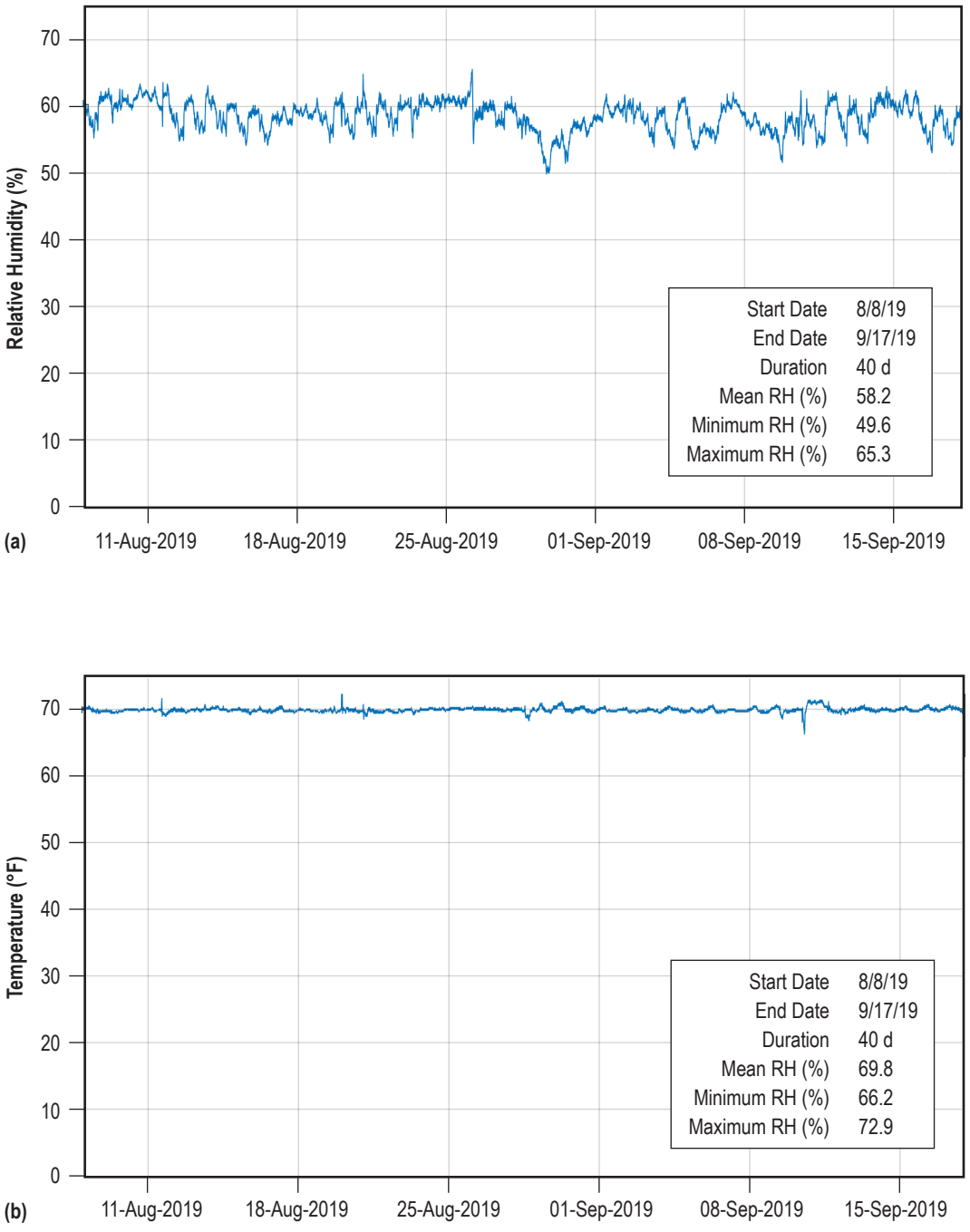


Figure 7. Environmental conditions for extended adhesive out-time groups: (a) relative humidity data and (b) temperature data for NASA MSFC composites fabrication facility.

2.4 Mode I Fracture Toughness Testing

Mode I fracture toughness tests using the DCB specimen were completed at the National Institute for Aviation Research (NIAR). Tests were carried out in accordance with ASTM D5528.[21] ASTM D5528 is intended for use with monolithic unidirectional composite laminates with single-phase matrices, which reflects the round-robin testing carried out in the development of the standard. However, the standard acknowledges that the test method may have applicability to other configurations as long as potential interferences are taken into consideration.[21] While potential interferences may be present and should be accounted for, it is noted that Mode I fracture toughness test using the DCB specimen is commonly used to evaluate assemblies where two composite adherends are bonded together.[4,8,9,16,17]

In the case of this study, where the intent of the test program dictated that DCB specimens simulate a secondarily bonded joint with film adhesive between two precured adherends, the potential for multiple apparent fracture toughness values, due to the presence of multiple materials and interfaces, is noted. This is accounted for by considering Mode I fracture toughness values together with associated failure modes (since fracture toughness values by themselves could potentially be misleading in this case). ASTM D5573[22] covers the classification of failure modes in adhesively bonded composite joints. These conventions are used herein, albeit with several considerations that should be noted. Only three principal failure modes are considered in this study: interfacial failure (also referred to as adhesive failure in ASTM D5573), cohesive failure, and substrate failure. While ASTM D5573 distinguishes between cohesive failure and thin-layer cohesive failure, for the sake of simplicity, a single classification of cohesive failure is considered herein. Similarly, a single classification of substrate failure is used, rather than making the ASTM D5573 distinction between fiber tear failure and light fiber tear failure (note that stock break failure, the remaining potential substrate failure mode established by ASTM D5573, is not relevant in this study).

Hinges were bonded to DCB specimens using a room temperature curing adhesive. The use of a room temperature curing adhesive is notable in this case, as its use avoided advancing the cure of the film adhesive in the DCB specimens themselves, particularly in the 200 °F cure temperature group, where the film adhesive was intentionally under-cured. Specimens were loaded at 0.08 in/min to advance the delamination 0.12–0.2 in from the tip of the non-stick insert, unloaded at 1 in/min, then reloaded at 0.08 in/min to advance the delamination an additional 2–3 in. Delamination length was tracked and correlated to the load-displacement record. Upon test completion, specimens were loaded at 1 in/min to completely separate the two adherends. Adherends were photographed and stored to allow for further evaluation of fracture surfaces.

3. RESULTS AND DISCUSSION

3.1 Mode I Fracture Toughness Data Reduction

ASTM D5528 identifies three data reduction methods for calculating Mode I fracture toughness values from the DCB test: modified beam theory (MBT), compliance calibration (CC), and modified compliance calibration (MCC) methods.[21] Each of these methods yields fracture toughness values as a function of delamination length, including initiation (delamination onset) and propagation (stable delamination growth) fracture toughness values. ASTM D5528 recommends the MBT method, as it proved to be the most conservative among the aforementioned data reduction methods in round-robin testing.[23,24] In keeping with this recommendation, the MBT method was used for Mode I fracture toughness data reduction herein.

Given the nature of this study, which intends to evaluate the integrity of a bonded interface with respect to a range of process parameters, propagation fracture toughness values are considered. As illustrated in Figure 8, a mean Mode I propagation fracture toughness was calculated for each test specimen. This mean value was taken over a 1–2 in delamination length range where delamination growth was principally stable. This same delamination length range was used to evaluate and quantify failure modes (discussed in section 3.2). Using this approach, Mode I fracture toughness values and corresponding failure modes for each test group can be considered in direct relation to one another. While propagation fracture toughness values are considered herein, initiation fracture toughness values are also highlighted per ASTM D5528. Deviation from linearity is the point at which the load versus opening displacement curve becomes nonlinear, visual onset is the point at which delamination is observed visually on specimen edge, and 5% offset/max corresponds to the intersection of the load versus opening displacement curve and a 5% (increase in compliance) offset curve unless this intersection occurs after the maximum load point (in which case, the maximum load point is used to calculate fracture toughness).

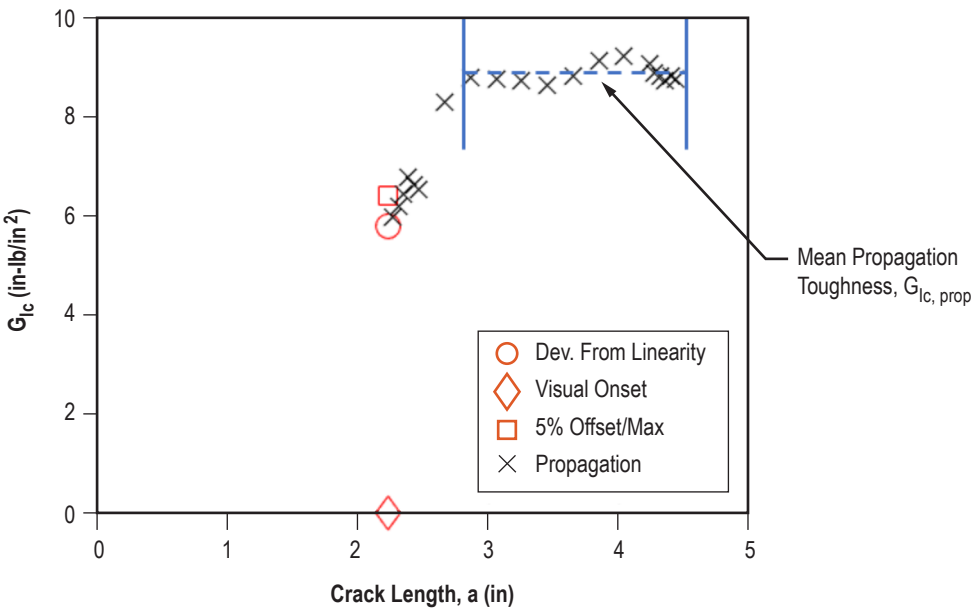


Figure 8. Typical delamination resistance curve (*R* curve) as observed in this study.

The aforementioned data reduction methods identified in ASTM D5528 do not directly account for a dissimilar adhesive layer, as is present in the DCB coupons considered in this study (in the form of film adhesive used to bond the two precured adherends). However, the work carried out by Fernlund and Spelt,[25] and Bardis and Kedward[4] showed that adhesive layer effects can be neglected so long as the following conditions are met where Mode I fracture toughness values are calculated as:

$$\frac{a}{h-t} > 8 \tag{1}$$

where

a = delamination length from the loading point to the crack tip
h = adherend thickness
t = adhesive layer thickness

In this study, where delamination length was no less than 2 in at the beginning of the test and was commonly near 3 in where delamination growth stabilized, adherend thickness measured an average of 0.086 in, and adhesive layer thickness measured an average of 0.01 in, the condition shown in equation (1) is easily met. As such, the presence of the adhesive layer for the purposes of calculating Mode I fracture toughness values is neglected in this study.

3.2 Failure Mode Analysis

Post-test images were taken of each DCB test specimen in order to evaluate and quantify failure modes. As noted in section 2.4, three principal failure modes were considered: cohesive failure (within the film adhesive; includes both cohesive failure and thin-layer cohesive failure per ASTM D5573), substrate failure (within adherend, includes both fiber tear failure and light fiber tear failure per ASTM D5573), and interfacial failure (at film adhesive/adherend interface; also referred to as adhesive failure in ASTM D5573). Note that adhesive failure is considered to be an unacceptable failure mode for a bonded joint, given that it is generally associated with relatively poor and unpredictable fracture performance. This concept is further detailed in section 3.4.

In each test group considered in this study, failure occurred in one of two combinations: interfacial (primary) and cohesive (secondary) or cohesive (primary) and substrate (secondary). Figure 9 shows detailed examples of these failure modes where failure occurred via interfacial and cohesive failure, while Figure 10 shows examples where failure occurred via cohesive and substrate failure.

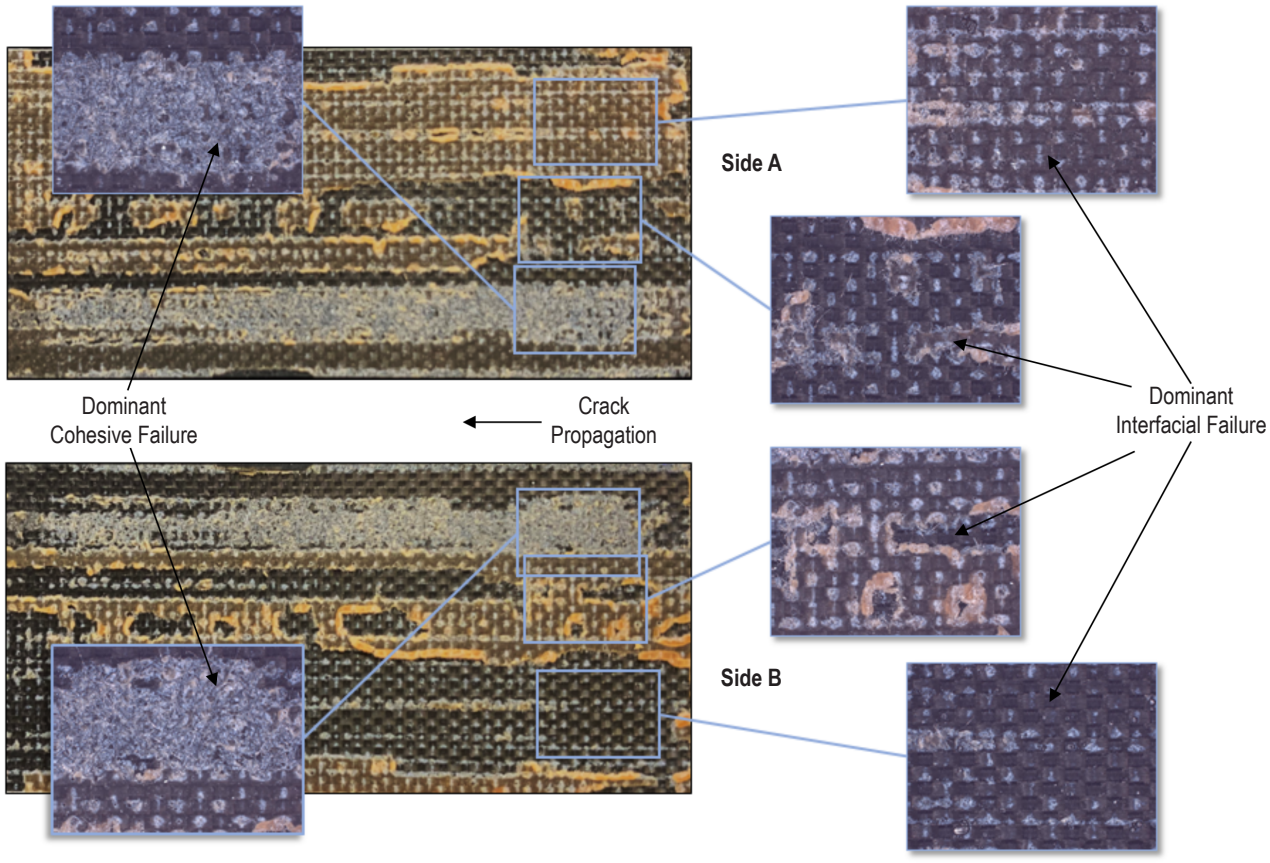


Figure 9. Detailed view of failure modes where failure occurred via combination of interfacial and cohesive failure. Note that images show corresponding fracture surfaces (denoted as Side A and Side B) from a given test specimen.

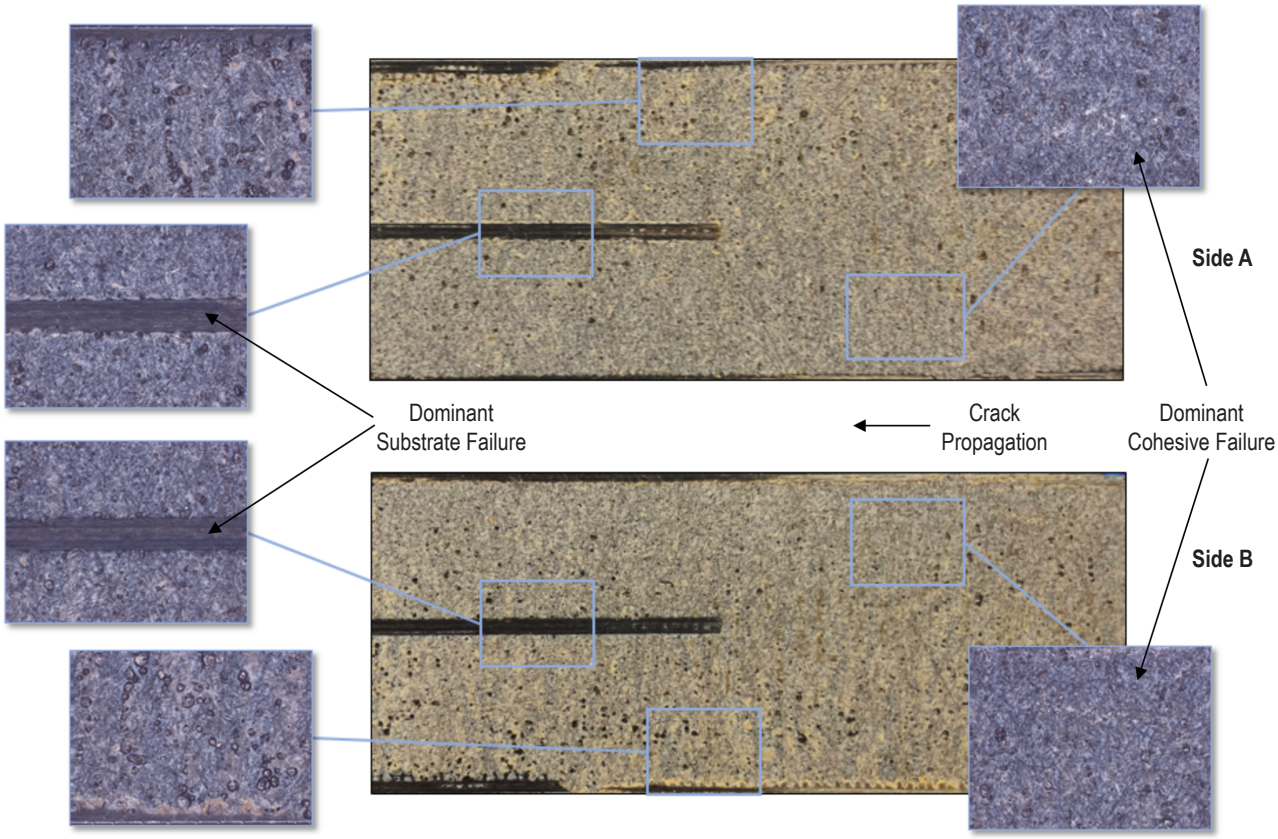


Figure 10. Detailed view of failure modes where failure occurred via combination of cohesive and substrate failure. Note that images show corresponding fracture surfaces (denoted as Side A and Side B) from a given test specimen.

Images were processed via digital image analysis using ImageJ software to quantify the three aforementioned principal failure modes by percentage area. Images were cropped so as to consider only the 1–2 in delamination length range where the aforementioned Mode I propagation fracture toughness values were taken. In general, images had thresholds assigned to isolate failure mode areas of interest (using micrographs on corresponding fracture surfaces, as shown in Figures 9 and 10, to anchor failure mode assignment), though the interfacial failure regions necessitated a slightly different threshold technique than the more straightforward cohesive and substrate failure regions. In particular, a color deconvolution routine was necessary to isolate areas of cohesive failure in instances where failure occurred via a combination of interfacial and cohesive failure. This additional image processing was generally not necessary for the more starkly contrasted regions in instances where failure occurred via a combination of cohesive and substrate failure. Note that the threshold assignment process is not absolutely quantitative; that is, while automated threshold routines were used, some degree of judgment is required to appropriately assign thresholds commensurate with the failure modes observed. Once the images had thresholds assigned, pixel counts were taken to quantify failure mode areas of interest in comparison to total image area. Figure 11 details the image processing approach used to quantify failure modes in this study. Percentage failure modes are further discussed in section 3.4 and are provided in comprehensive detail in (app. A).

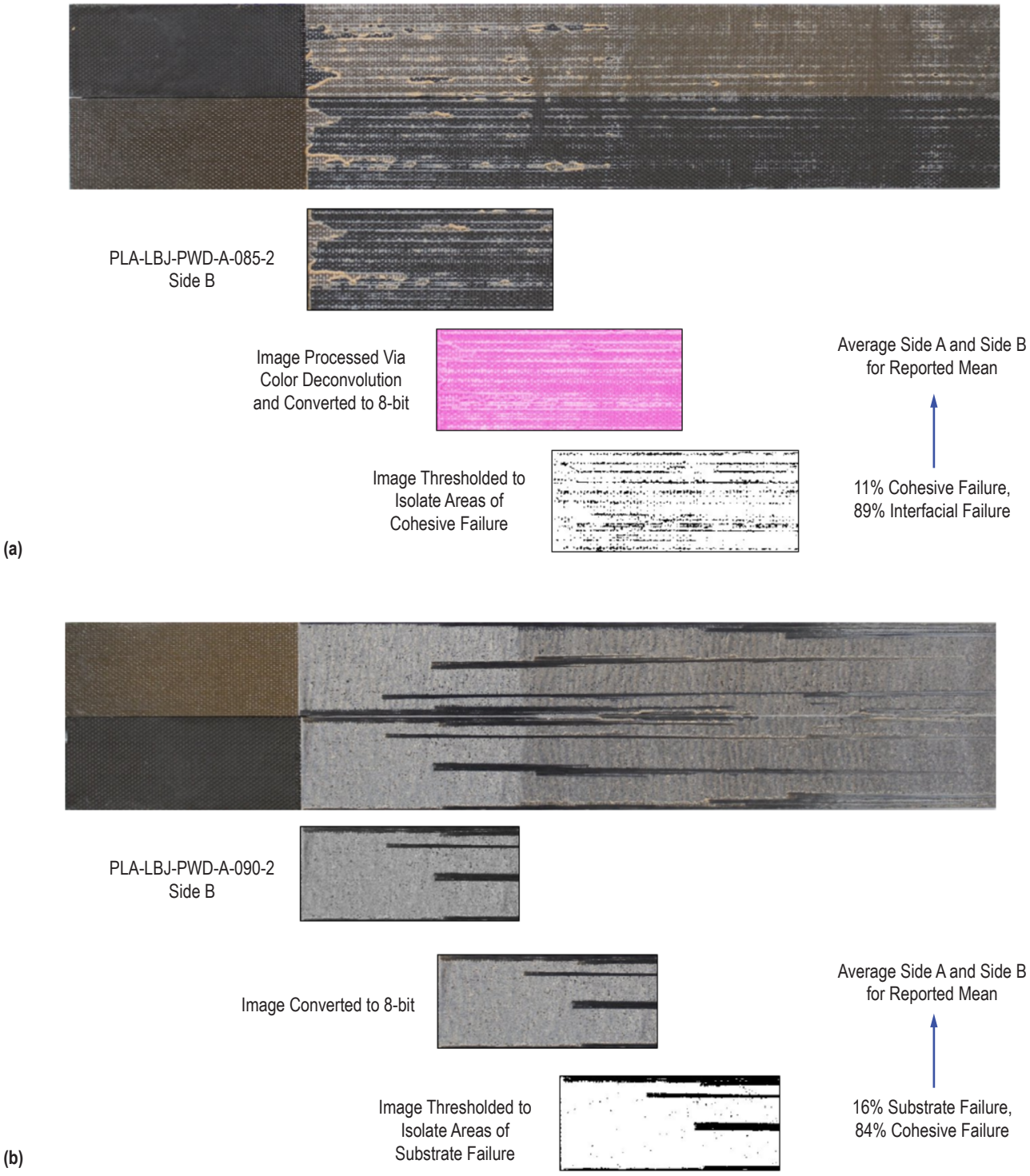


Figure 11. Image processing approach used to quantify failure modes: (a) technique used where failure occurred via combination of interfacial and cohesive failure and (b) technique used where failure occurred via combination of cohesive and substrate failure.

3.3 Mode I Fracture Toughness Test Results

Table 3 shows Mode I propagation fracture toughness values and percentage failure modes. Given the nature of this study's design, which uses a full-factorial DOE approach, further evaluation of the data presented in Table 3 is warranted. The influence of the process parameters considered herein on Mode I fracture toughness is examined in detail in section 3.3, while the relationships between fracture toughness and failure modes are further evaluated in section 3.4.

Table 3. Mode I fracture toughness test results.

Adhesive Age (mo)	Adhesive Out-Time (d)	Prep to Bond Time (d)	Cure Temperature (°F)	APPT	G_{IC}, prop. (in-lb/in^2)	% Cohesive Failure	% Interfacial Failure	% Substrate Failure
12	0	0	200	No	3.98 ± 1.09	15 ± 11*	85 ± 11	0 ± 0
12	0	0	200	Yes	3.01 ± 0.51	10 ± 2	90 ± 2	0 ± 0
12	0	0	250	No	8.65 ± 0.43	87 ± 4	0 ± 0	13 ± 4
12	0	0	250	Yes	8.60 ± 0.31	84 ± 4	0 ± 0	16 ± 4
12	0	0	300	No	9.48 ± 0.35	88 ± 4	0 ± 0	12 ± 4
12	0	0	300	Yes	8.94 ± 0.27	81 ± 2	0 ± 0	19 ± 2
12	0	14	200	No	4.05 ± 0.77	13 ± 6	87 ± 6	0 ± 0
12	0	14	200	Yes	3.75 ± 1.39	15 ± 11*	85 ± 11	0 ± 0
12	0	14	250	No	8.81 ± 0.42	87 ± 7	0 ± 0	14 ± 7*
12	0	14	250	Yes	9.09 ± 0.54	96 ± 1	0 ± 0	4 ± 1
12	0	14	300	No	8.75 ± 0.63	89 ± 6	0 ± 0	11 ± 6*
12	0	14	300	Yes	8.71 ± 0.39	92 ± 4	0 ± 0	8 ± 4*
12	40	14	200	No	4.11 ± 0.62	13 ± 3	87 ± 3	0 ± 0
12	40	14	200	Yes	5.96 ± 0.94	17 ± 4	83 ± 3	0 ± 0
12	40	14	250	No	9.00 ± 0.36	87 ± 3	0 ± 0	13 ± 3
12	40	14	250	Yes	8.69 ± 1.18	80 ± 11	0 ± 0	20 ± 11*
12	40	14	300	No	8.09 ± 0.98	74 ± 16	0 ± 0	26 ± 16*
12	40	14	300	Yes	8.81 ± 0.72	90 ± 8	0 ± 0	10 ± 8*

*Coefficient of variation is 50% or greater. Data should be considered with caution given excessive scatter.

3.3.1 Regression Analysis

To better characterize the influence of each process parameter and formally determine which process parameters affect Mode I fracture toughness in a statistically significant manner, a general least squares regression was fit to the data gathered in this study. A single continuous response variable, Mode I propagation fracture toughness, was considered and four factors (all fixed) were considered: (1) preparation to bond time, (2) adhesive out-time, (3) cure temperature, and (4) APPT. Because extended adhesive out-time was considered only in combination with extended preparation to bond time, adhesive out-time was nested within preparation to bond time. All other factors were treated as non-nested. So that the difference between each factor mean and a factor reference mean was considered, (1, 0) factor coding was used. In addition to the four factors considered, two covariates were also considered: (1) ramp rate to hold temperature and (2) hold duration. These two parameters were not directly evaluated in this DOE, but data captured during processing was incorporated into the regression model so as to evaluate their influence, if any. Table 4 summarizes the factors and covariates considered in the regression model.

Table 4. Summary of factors and covariates considered in general least squares regression model.

Factor or Covariate	Process Parameter (units)	Type	Levels	Values
Factor	Preparation to Bond Time, PBT (d)	Fixed	2	0,* 14
Factor	Adhesive Out-time (d)	Fixed, nested within PBT	2	0 (at 14 d PBT),* 40 (at 14 d PBT)
Factor	Cure Temperature (°F)	Fixed	3	200, 250,* 300
Factor	APPT	Fixed	2	No,* Yes
Covariate	Ramp Rate (°F/min)	NA	Not directly considered	Continuous, taken from processing data
Covariate	Hold Duration (min)	NA	Not directly considered	Continuous, taken from processing data

*Factor Reference Mean

Upon generating the regression model, residuals were evaluated to confirm the validity of the model used. The residuals versus fitted values plot in Figure 12(a) shows that residuals are randomly distributed on both sides of 0 with no discernable pattern, while the residuals versus observation order plot in Figure 12(b) shows that no trends exist with respect to order. The normal probability plot and histogram, Figures 12(c) and (d) respectively, show that the residuals are normally distributed. Together, these takeaways confirm that the regression model is valid.

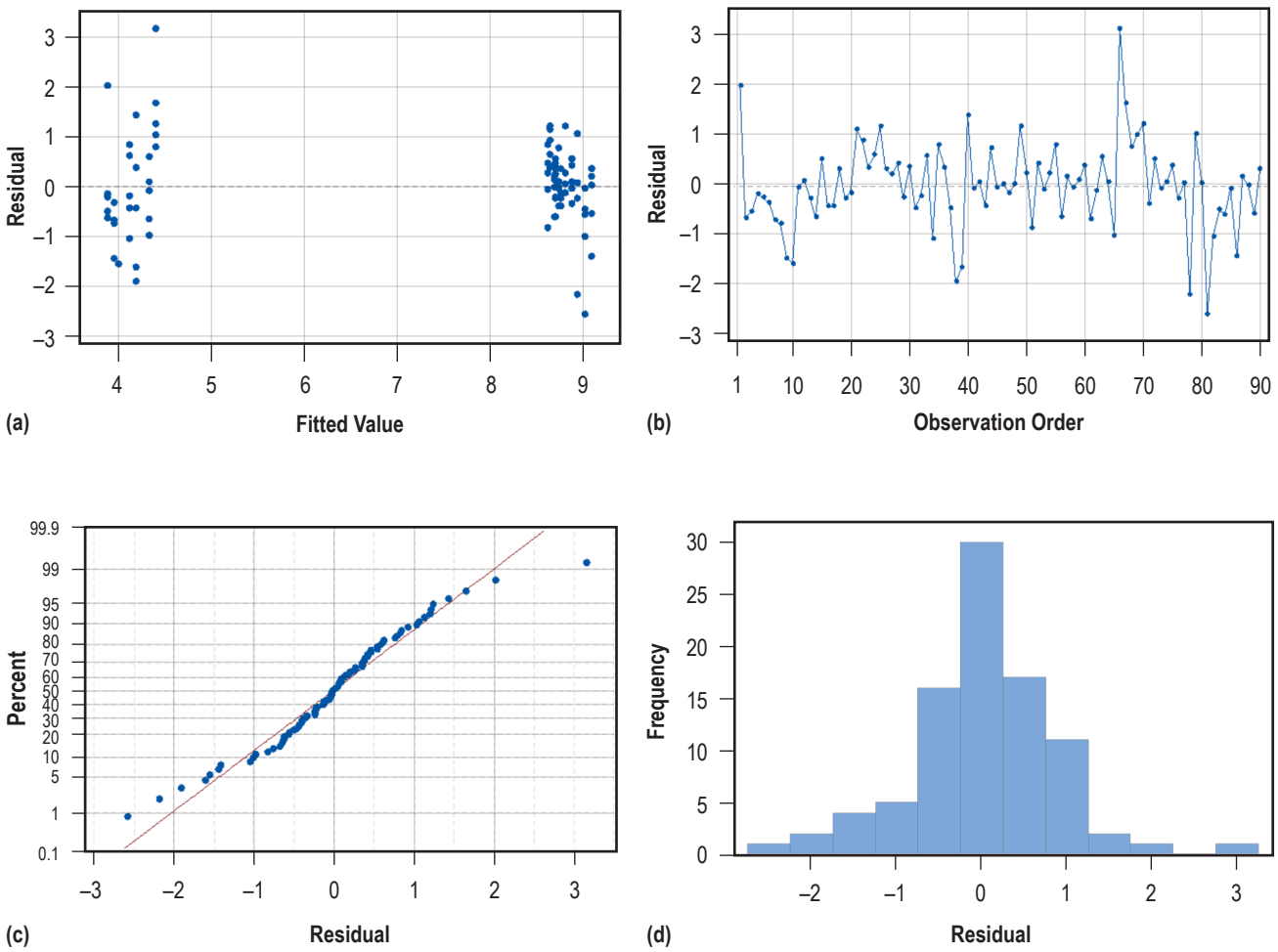


Figure 12. Plots used to verify validity of regression model: (a) residuals versus fits, (b) residuals versus order, (c) normal probability plot of residuals, and (d) histogram of residuals.

P-value analysis was used to determine whether each of the factors and covariates considered in the regression model exhibited a statistically significant influence on the response variable of interest: Mode I propagation fracture toughness. The null hypothesis in this context is that no association exists between a given factor or covariate and the response variable. If a p-value returned is less than an established significance level, taken as 0.05 herein,[26–29] it can be concluded that a statistically significant association exists between the datasets of interest at the established significance level. P-values are often considered in a binary manner with a line of demarcation established at the chosen significance level, but it should be recognized that p-values are continuous (from 0 to 1) and should be considered accordingly. For example, there is little difference between p-values of 0.052 and 0.048, but if a 'hard' line is drawn at a significance level of 0.05, these two p-values would lead to different conclusions. P-values returned from the regression analysis carried out in this study are shown in Table 5. Figure 13 shows main effects and interaction plots that accompany the test results and regression analysis discussed here.

Table 5. P-values returned from regression analysis, where null hypothesis is that no association exists between the process parameter of interest and Mode I propagation fracture toughness.

Process Parameter (units)	Level	P-Value
Preparation to Bond Time, PBT (d)	0	–
	14	0.745
Adhesive Out-time (d)	0 (at 14 d PBT)	–
	40 (at 14 d PBT)	0.393
Cure Temperature (°F)	200	0.000
	250	–
	300	0.743
APPT	No	–
	Yes	0.727
Ramp Rate (°F/min)	Covariate; Not Directly Considered	0.912
Hold Duration (min)	Covariate; Not Directly Considered	0.774

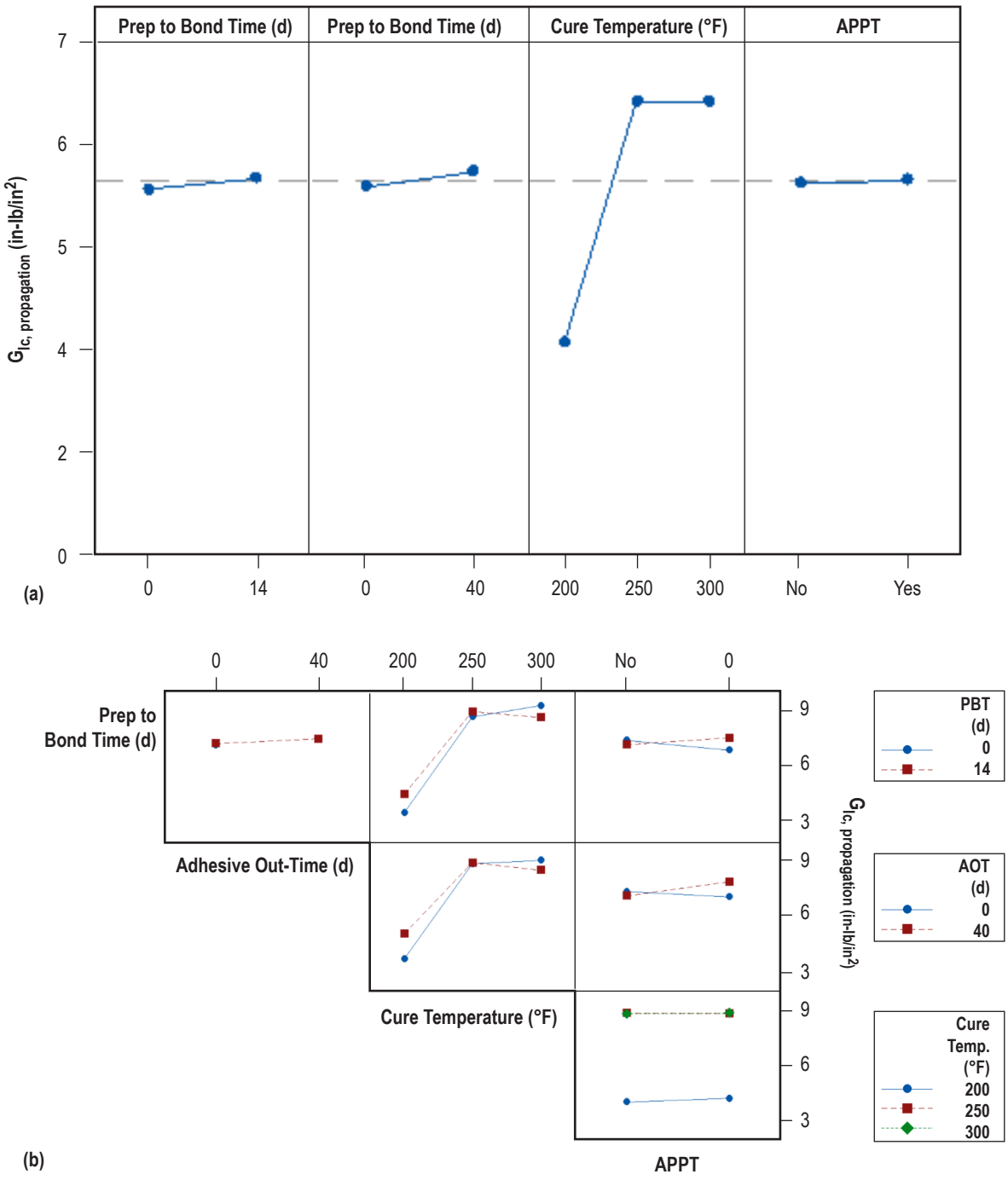


Figure 13. (a) Main effects plot and (b) interaction plot from DOE considered herein. Note that PBT corresponds to preparation to bond time and AOT corresponds to adhesive out-time.

As evidenced by the results presented in Table 3 and Figure 13, and confirmed by the p-values shown in Table 5, the only convincing influence on Mode I fracture toughness observed in this study is cure temperature of 200 °F. The remaining process parameters, including cure temperature (250 °F and 300 °F), preparation to bond time (up to 14 days), adhesive out-time (up to 40 days), APPT, ramp rate, and hold duration, did not prove to significantly influence Mode I fracture toughness. In several cases, however, additional consideration is warranted in the interest of accurately describing the data presented here.

3.3.2 Effects of Cure Temperature

As shown in Table 3 and Figure 13, a cure temperature of 200 °F led to dominant interfacial failure and corresponding significant reductions in Mode I propagation fracture toughness. Given that the FM 209-1M film adhesive considered herein is marketed as a 250 °F curing system, this result is not unexpected. However, the authors chose to proceed with the evaluation of this particular level given some uncertainty with respect to the relationship between degree of cure, glass transition temperature, and fracture toughness. Blackman, et al.[30] showed a correlation between increasing glass transition temperature and increasing Mode I fracture toughness in DCB specimens bonded with an epoxy paste adhesive. However, Utaloff, et al.[31] demonstrated a more complex relationship between fracture toughness and glass transition temperature, where toughening effects in neat diglycidyl ether of bisphenol A (DGEBA)-based epoxies were shown to depend not only on curing conditions, but also on the characteristics of the base material itself, crosslinking modifiers, and toughening agents. In some resin system configurations, an increase in fracture toughness (in this case) was shown to correspond to a decrease in glass transition temperature, but in others, increases in both fracture toughness and glass transition temperature were observed. These studies demonstrate a complex relationship between degree of cure, glass transition temperature, and fracture toughness; a relationship that also appears to be material specific. However, by considering the effects of crosslinking separately from the effects of toughening agents, the relationship can be better understood. Additional crosslinking generally leads to increases in both glass transition temperature and fracture toughness, while the addition of toughening agents generally leads to an increase in fracture toughness but can lead to a decrease in glass transition temperature.

The results gathered in this study are clear in that a 200 °F hold for 90 min is not sufficient to develop an adequate bond between the film adhesive and precured composite substrate. While the low cure temperature groups also exhibited some cohesive failure in the film adhesive layer, this failure mode is clearly secondary to interfacial failure. Given this, it is not reasonable to evaluate the fracture toughness of the film adhesive in the 200 °F cure temperature groups against that in the 250 °F and 300 °F cure temperature groups. In the 250 °F and 300 °F cure temperature groups, where the dominant failure mode is cohesive failure, no significant change in Mode I propagation fracture toughness is observed between the two cure temperatures. In the interest of more comprehensively characterizing the film adhesive considered in this study, dynamic mechanical analysis (DMA) runs were carried out at each of the three cure temperatures of interest. A dual cantilever clamp configuration was used with a load frequency of 1 Hz. For each cure temperature, two distinct DMA runs were carried out to populate Table 6: a cure run (that mimics cure cycle used in bonded assembly fabrication) to evaluate gel time and a subsequent temperature sweep to evaluate glass transition temperature of the cured adhesive. A minimum of two replicates were considered at each

cure temperature, with average values reported in Table 6. For the gel time values presented in Table 6, it is advisable to consider trends with respect to these values rather than the absolute values themselves.

Table 6. Summary of DMA on FM® 209-1M film adhesive. Note that storage modulus is represented by E'.

Cure Temperature (°F)	For Cure Run			For Temperature Sweep	
	Ramp Rate (°F/min)	Time at Hold Temperature (min)	Gel Time,* Tan Delta Peak (min)	Ramp Rate (°F/min)	T_g, Shoulder (°F)
200	3	90	126	3	179
250	3	90	67	3	291
300	3	90	68	3	293

*From start of ramp.

Figure 14 shows representative DMA runs for each of the three cure temperatures considered. Note that storage modulus (E') values are normalized by the initial storage modulus value for each run. Like the gel time values reported in Table 6, time values associated with the cure runs presented in Figure 14 should be considered in comparison with one another rather than on an absolute basis.

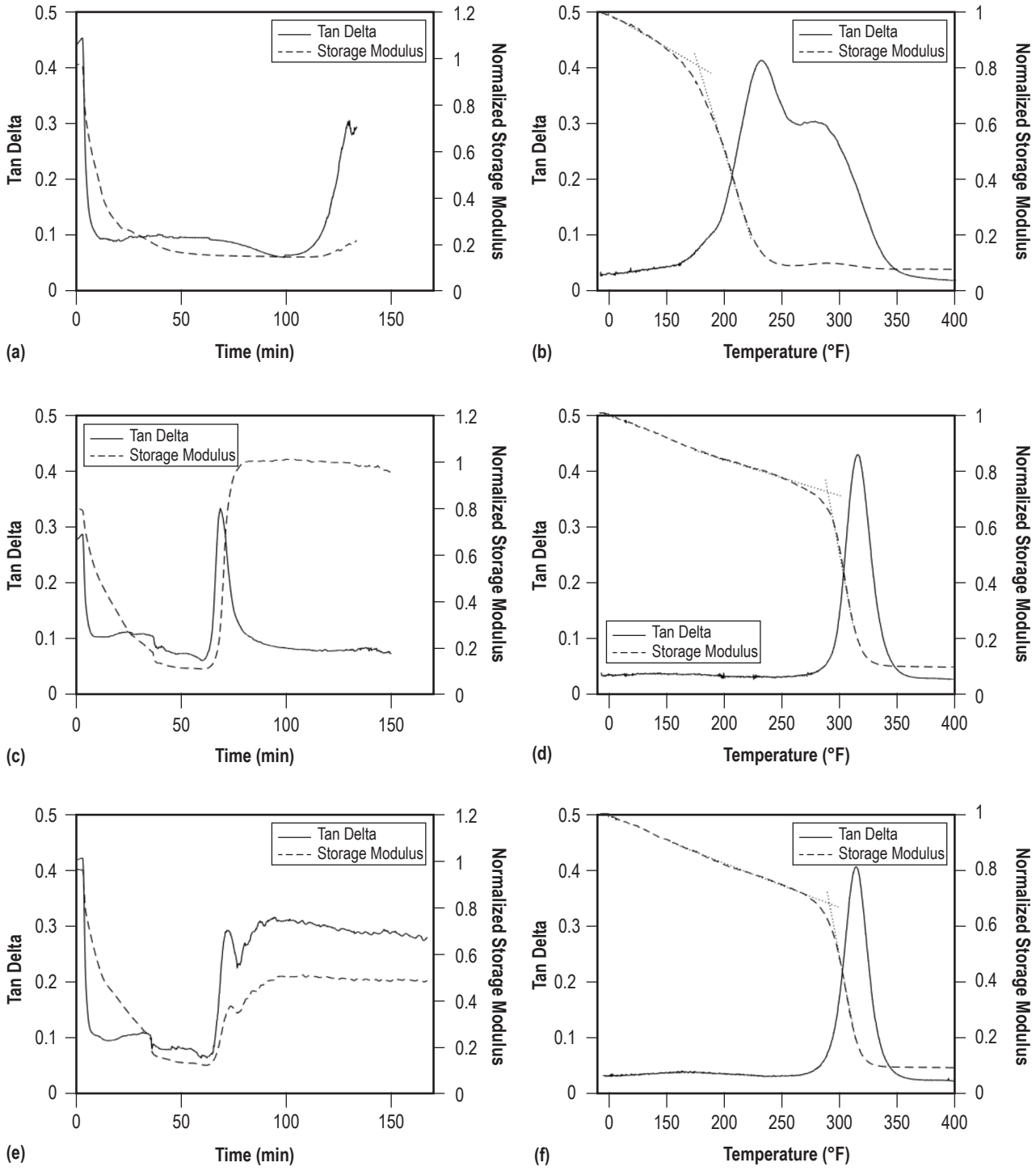


Figure 14. Dynamic mechanical analysis (DMA) runs for FM 209-1M film adhesive. For 200 °F cure temperature: (a) cure run and (b) temperature sweep. For 250 °F cure temperature: (c) cure run and (d) temperature sweep. For 300 °F cure temperature: (e) cure run and (f) temperature sweep. In temperature sweeps, note that dotted lines identify E' shoulder for glass transition temperature (T_g) determination.

While the data presented here may not fully describe the relationship between degree of cure, glass transition temperature, and fracture toughness for FM 209-1M, it is clear that a cure temperature threshold likely exists between 200 °F and 250 °F (where hold time is 90 min). Below this threshold, the bonded system is susceptible to interfacial failure and above this threshold, the bonded system is shown to be adequate.

Though not directly evaluated in this study, it is reasonable to consider that extending the hold time beyond 90 min (to allow for additional crosslinking and promote a higher degree of cure) in a low temperature cure scenario would likely help to remediate the issues observed in the 200 °F cure temperature groups. This is critical given that in practice, lower-than-nominal cure temperatures are commonly encountered, especially in large-scale bonding operations that necessitate out-of-autoclave/out-of-oven cure processes (e.g., the use of heat blankets).

3.3.3 Effects of Preparation to Bond Time

Preparation to bond time, which was evaluated at 0 days (where bonding occurred immediately following peel ply removal) and 14 days, shows no statistically significant influence on Mode I fracture toughness. Though some interaction can be observed with cure temperature and APPT in Figure 13, the changes in Mode I fracture toughness are small (< 10%) and the trends are not consistent with one another. As such, the effects of preparation to bond time on Mode I fracture toughness are considered to be minimal if present at all.

3.3.4 Effects of Adhesive Out-time

With respect to adhesive out-time, a moderate increase in fracture toughness was observed when APPT was used in the 200 °F cure temperature groups. This increase, which can be directly observed in the interaction plot, principally accounts for the trend seen in the main effects plot as well. The p-value returned in regression analysis (0.393) suggests that adhesive out-time is not a statistically significant influence on fracture toughness overall, but the p-value returned when directly comparing datasets from the 200 °F cure temperature groups with extended adhesive out-time with and without APPT (0.008) indicates that these two datasets are indeed distinct from one another. In the 200 °F cure temperature test groups with extended adhesive out-time, the group treated with APPT shows Mode I propagation fracture toughness values notably higher than would otherwise be expected given dominant interfacial failure. Figure 15 shows representative fracture surfaces from these two test groups (without and with APPT).

Figure 15. Representative fracture surfaces from 200 °F cure temperature test groups with extended adhesive out-time (40 days): (a) without APPT and (b) with APPT.

Despite both test groups showing dominant interfacial failure, the group with APPT exhibited a 45% increase in Mode I propagation fracture toughness over the group without APPT. While the underlying cause is not clear from the results gathered in this study, it is clear that the group with APPT shows a more tortuous crack path during fracture. While the fracture plane in the group without APPT largely remained at the same film adhesive/adherend interface, the fracture plane in the group with APPT jumped back and forth from one interface to the other. This likely led to the increase in apparent fracture toughness, though caution should be taken when considering the implications of this increase. While a more tortuous crack path is generally preferable (given the associated increase in delamination resistance), in this case, it could be an artifact of the combination of process parameters considered.

3.3.5 Effects of APPT

As observed in Table 3 and Figure 13, the use of APPT did not meaningfully influence fracture toughness in the test groups considered in this study. Upon considering the significant improvements in Mode I fracture toughness observed by others, as shown in Table 2, using the same APPT configuration and similar (if not the same) operational parameters, this takeaway is particularly curious. However, taking a broader view of the results gathered in this study offers a degree of clarity.

Where cure temperatures of 250 °F or 300 °F are used, it is apparent that the material systems and baseline surface preparation approach (without APPT) used here are sufficient to force failure away from the bonded interfaces. In these cases, improved adhesion between the film adhesive and

precured adherends is not necessary; the interfaces are 'good enough' without APPT. Although APPT could conceivably be leading to an improvement in adhesion at the interfaces, the test groups considered herein are effectively masking any such improvements.

For the 200 °F cure temperature groups where interface failure is dominant and improvements in adhesion offered by APPT should not be masked, it appears that any improvement in adhesion offered by APPT is not sufficient to overcome the apparently dominant effects of insufficient cure temperature. Despite potential improvements in adhesion at the interfaces, the film adhesive is not able to adequately bond to the precured adherends.

It is hypothesized that with the material systems and surface preparation approach considered herein, even when adequate cure temperatures are used, APPT could be beneficial in certain critical situations not included in the scope of this study. Whether the well-established issue of prebond moisture in adherends[3,5,6,32] can be remedied by APPT is of particular interest to the authors moving forward and will be addressed in future work.

3.3.6 Effects of Ramp Rate and Hold Duration

As discussed in section 3.3.1, ramp rates and hold durations were tracked during bonded assembly fabrication but were not directly considered as factors in this study's DOE. The target ramp rate was set at 3 °F/min and as-measured values ranged from 2.1 °F/min to 4.2 °F/min. The target hold duration was set at 90 min and as-measured values ranged from 79–132 min. The latter as-measured hold duration value, 132 min, occurred in the 250 °F cure temperature groups with extended adhesive out-time and extended preparation-to-bond time (which showed no discernible differences relative to comparable test groups). As shown in Table 5, neither ramp rate nor hold duration exhibited a statistically significant influence on Mode I fracture toughness. While this takeaway is significant in the context of setting allowable tolerances in larger-scale bonding operations (where target ramp rates and hold durations are often much more difficult to maintain), it should be recognized that the test data gathered does not represent a scenario where ramp rates and/or hold durations vary with location throughout a given bonded assembly (which could lead to potentially detrimental non-uniform glass transition temperatures, fracture toughness values, and/or residual stresses throughout the part).

3.3.7 Effects of the use of Frekote 700-NC™

As noted in section 2.3, Frekote 700-NC was used as a mold release agent on the parent panel tooling used to produce the adherends for each of the test groups considered herein. As such, the effects of the use of Frekote 700-NC on the integrity of the bonded interfaces of interest were indirectly evaluated across this study. Considering the Mode I fracture toughness test results and associated trends gleaned in this study on the whole, it can be observed that Frekote 700-NC showed no apparent adverse effects on the eventual bonded interfaces evaluated in this study. This shows that even if Frekote 700-NC leaves behind release agent on cured adherends, the use and removal of FM 3500 EZP is sufficient to protect eventual bonding surfaces from this potential source of contamination.

3.4 Fracture Toughness in relation to Failure Modes

Mode I propagation fracture toughness values are plotted as a function of percentage failure modes in Figures 16, 17, and 18. A strong linear correlation is observed between fracture toughness and percentage cohesive failure ($R^2 = 0.971$), where Mode I propagation fracture toughness is shown to increase with increasing amounts of cohesive failure. The relationships between fracture toughness and the other two principal failure modes considered here, substrate failure and interfacial failure, are not as neatly defined but are nevertheless telling. Small amounts (< 20%) of substrate failure correspond to the upper range of fracture toughness values measured in this study, while large amounts (> 90%) of interfacial failure correspond to the lower range of fracture toughness values measured. Given that failure typically occurred in one of two combinations, either cohesive (primary) and substrate (secondary), or interfacial (primary) and cohesive (secondary), it should be noted that the influence of substrate failure and interfacial failure can be indirectly observed in the relationship between fracture toughness and cohesive failure. Where cohesive failure is dominant (and substrate failure is secondary), relatively narrow scatter in fracture toughness can be observed for a given amount of cohesive failure (or substrate failure). However, where interfacial failure is dominant (and cohesive failure is secondary), fracture toughness varies relatively widely for a given amount of interfacial failure (or cohesive failure). This builds on the well-established knowledge that interfacial failure is undesirable for its tendency to yield relatively unpredictable (and typically low, as is the case here) fracture toughness values.

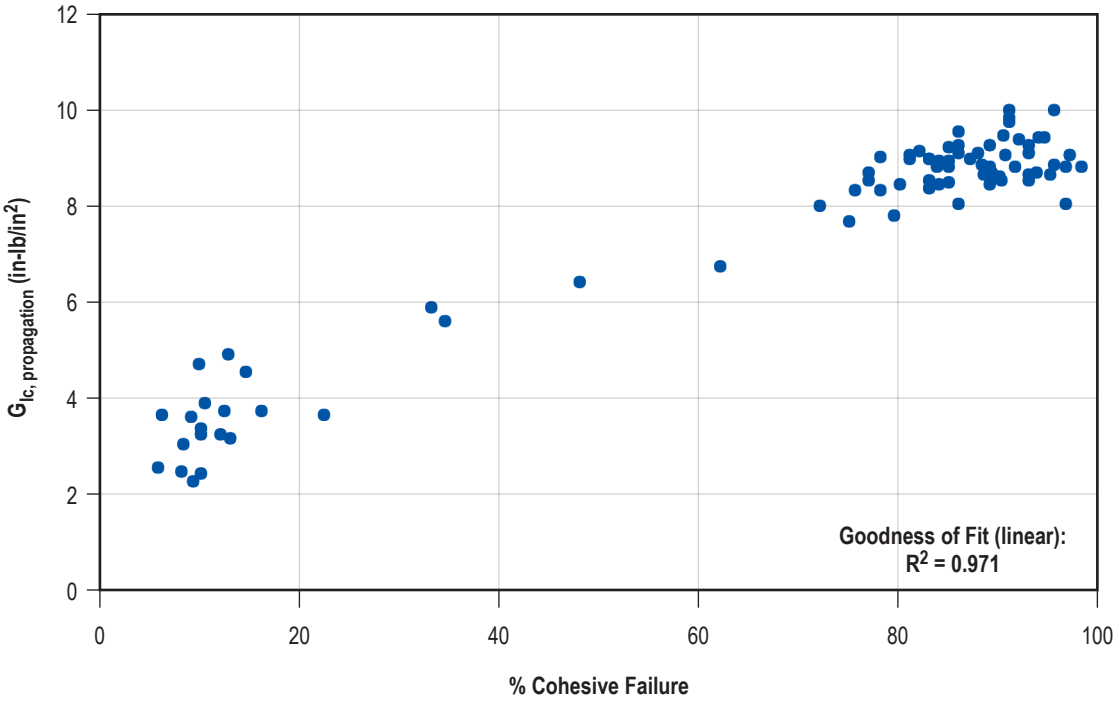


Figure 16. Mode I fracture toughness as a function of percentage cohesive failure. Note that results exclude test groups where cure temperature was 200 °F, adhesive out-time was 40 days, and prep-to-bond time was 14 days; results in these groups are anomalous and are considered to be an artifact of the combination of process parameters considered (see section 3.3.4 for details).

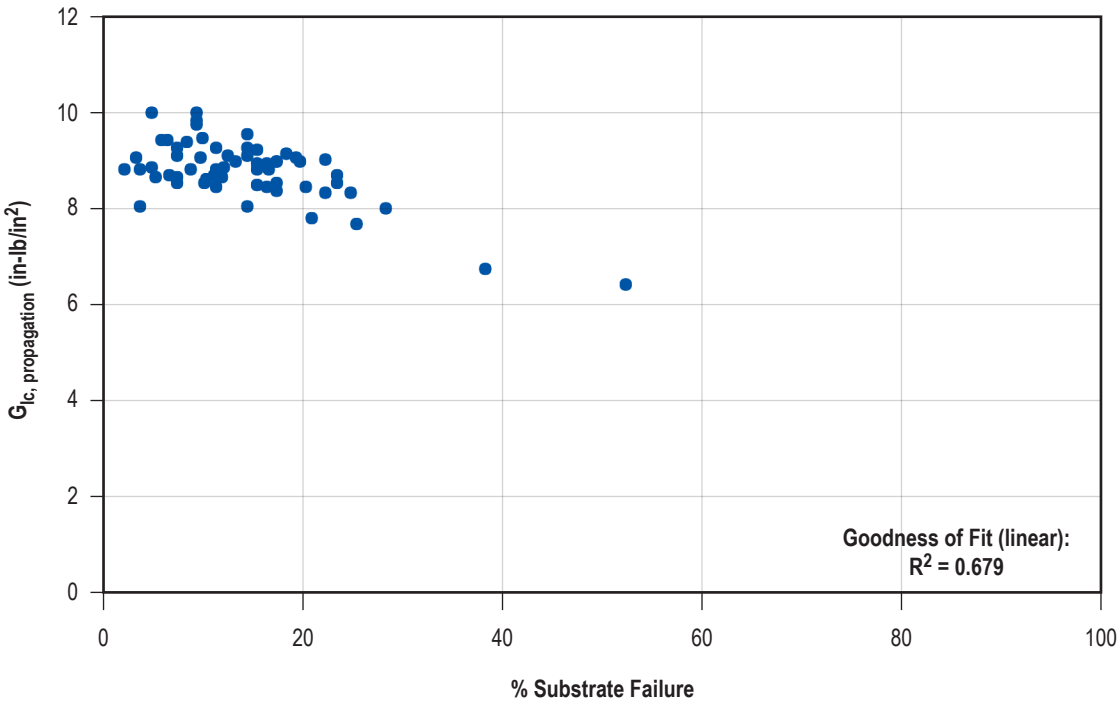


Figure 17. Mode I fracture toughness as a function of percentage substrate failure. Note that results exclude test specimens where no substrate failure occurred.

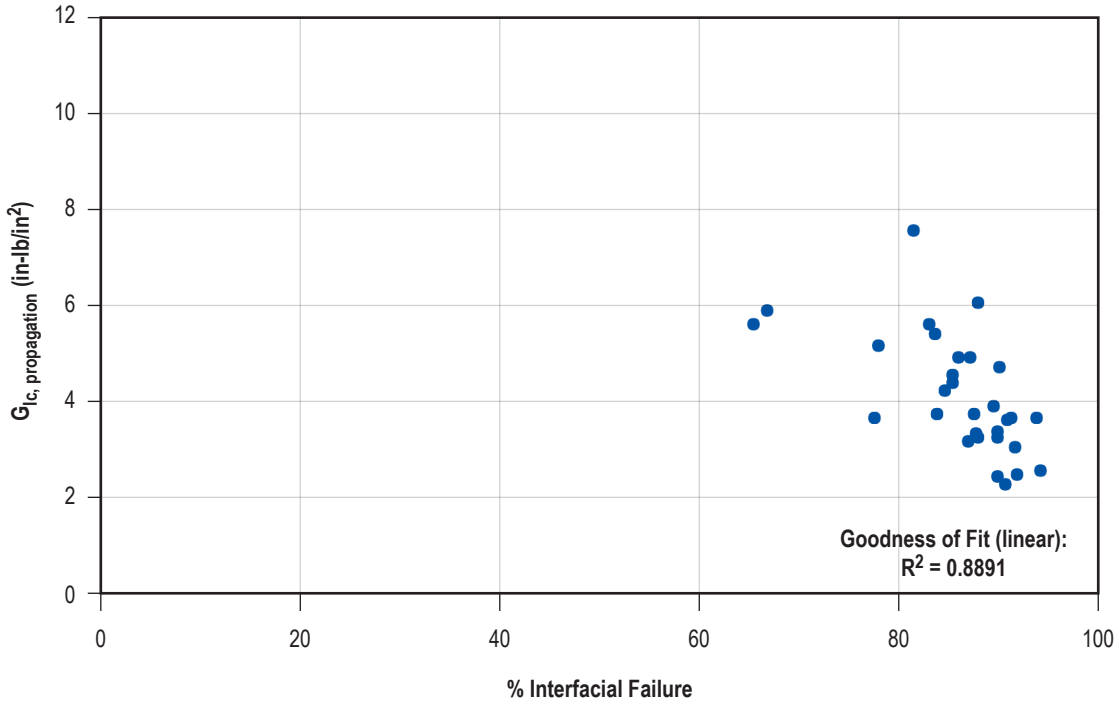


Figure 18. Mode I fracture toughness as a function of percentage interfacial failure. Note that results exclude test specimens where no interfacial failure occurred.

4. CONCLUSIONS

The work carried out in this study provides for several key conclusions with respect to the bonded system considered herein. In general terms, adhesively bonded joint performance using the materials, surface preparation technique, and overall bonding approach is not highly sensitive to manufacturing process parameters. This is largely a testament to the materials (well-established, commercially available, and used per manufacturer recommendations) and surface preparation technique (straightforward, repeatable, and largely operator-independent) selected for this study. While no two adhesively bonded joint applications are likely to be the same, the general considerations with respect to material selection and surface preparation approach outlined in this study are widely applicable.

Among the process parameters/levels evaluated in this study, only an excessively low cure temperature of 200 °F led to significant degradation of the bonded interface. A cure temperature threshold likely exists between 200 °F and 250° F, but in view of the data collected in this study, cure temperature should not be a concern as long as it is held between the appreciably wide window of 250 °F to 300 °F. At both temperatures, fracture was shown to occur away from the bonded interface via a combination of cohesive and substrate failure. Though not directly evaluated herein, the lower bound of this window can likely be further lowered by extending the hold time (thus allowing for additional crosslinking and promoting a higher degree of cure) when cure temperature does not reach 250 °F.

The effects of preparation to bond time (of up to 14 days) and film adhesive out-time (of up to 40 days) on Mode I fracture toughness and failure mode are considered to be minimal if present at all. One notable exception was shown in the case where preparation to bond time was 14 days, adhesive out-time was 40 days, and cure temperature was 200 °F, but as discussed in detail in section 3.3.4, the improvement in fracture toughness without a discernible shift in failure mode (compared to corresponding test groups) is likely an artifact of the combination of process parameters considered in this case.

Interestingly, the use of APPT did not show a significant influence on Mode I fracture toughness or failure mode. This takeaway is curious given the typically drastic improvements via APPT shown in other studies, but can be explained by the materials, baseline surface preparation technique (i.e., without APPT), and bonding approach used herein providing bonded interfaces that are sufficient to force failure away from the bonded interface without APPT. In this way, any potential effects of APPT, a surface treatment that directly influences only the bonded interface and not the substrate or film adhesive, have likely been effectively masked. APPT could prove beneficial in certain critical scenarios not addressed by this study, namely, where pre-bond moisture is present in the adherends, and will be further evaluated in future work.

Along with the process parameters explicitly evaluated in this study, the effects of ramp rate, hold duration, and the use of Frekote 700-NC as a mold release agent on parent panel tooling were indirectly considered in each test group. Neither ramp rate nor hold duration exhibited a statistically significant influence on Mode I fracture toughness. Considering the results and associated trends gleaned in this study on the whole, standard usage of Frekote 700-NC as a mold release agent showed no apparent adverse effects on the eventual bonded interfaces.

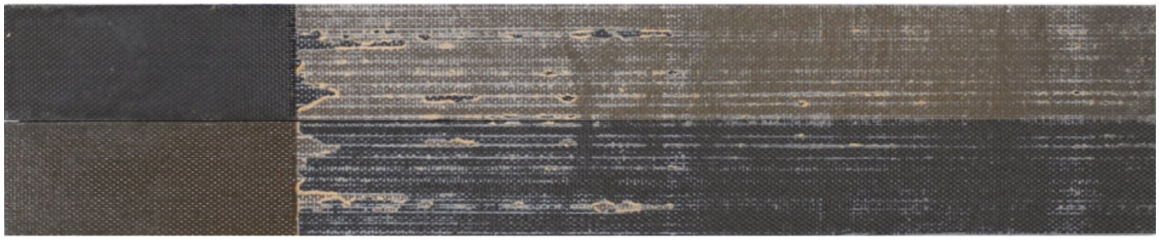
With respect to fracture toughness in relation to failure modes, Mode I fracture toughness is shown to correlate well with percentage cohesive failure (directly proportional; goodness of fit for linear regression: 0.971) with relatively little variation in Mode I fracture toughness for a given percentage of cohesive failure. That is, percentage cohesive failure is a reliable indicator of Mode I fracture toughness. The relationship between Mode I fracture toughness and percentage interfacial failure is telling but is not as reliable; a higher degree of interfacial failure generally relates to lower Mode I fracture toughness, but there is relatively large variation in Mode I fracture toughness for a given percentage of interfacial failure. This reinforces the well-established knowledge that interfacial failure is undesirable due to its tendency to yield characteristically low and relatively unpredictable fracture toughness values.

Note that the conclusions presented herein reflect the fact that no airborne silicones were detected in the composites fabrication facility at any point over the duration of this study. The potential presence of airborne silicones in any composites fabrication facility (whether used for parent component manufacture, storage, or bonding) should be carefully monitored, as adverse effects not captured by this study (since no silicones were present) could manifest themselves if airborne silicones are present.

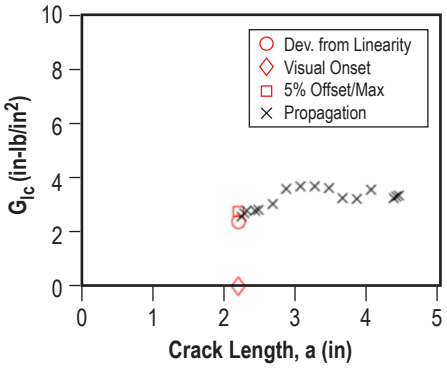
APPENDIX A—TEST RESULTS IN DETAIL

Detailed summaries of each of the test groups are presented in this appendix. Note that fracture surface images and *R*-curves are representative of the test group of interest, while the Mode I propagation fracture toughness values and percentage failure modes are mean values.

Test Group ID	Adhesive Age (mo)	Adhesive Out-Time (d)	Laminate Age (mo)	Prep to Bond Time (d)	Cure Temp. (°F)	APPT
PLA-PWD-LBJ-A-085	12	0	0	0	200	No

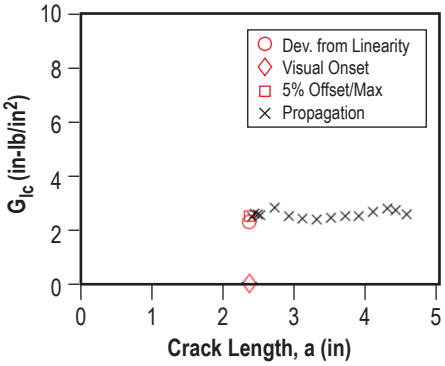


Test Group Summary (Mean Values, Based on 5 Specimens)	
$G_{Ic,\ prop.}$ (in-lb/in^2)	3.98 ± 1.09
% Cohesive	15
% Substrate	0
% interfacial	85

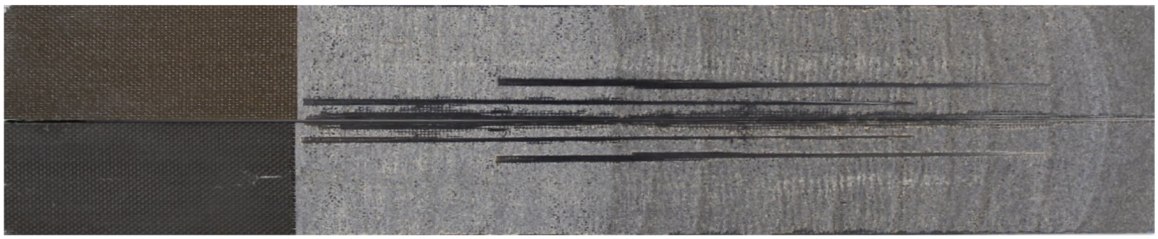


Test Group ID	Adhesive Age (mo)	Adhesive Out-Time (d)	Laminate Age (mo)	Prep to Bond Time (d)	Cure Temp. (°F)	APPT
PLA-PWD-LBJ-A-086	12	0	0	0	200	Yes

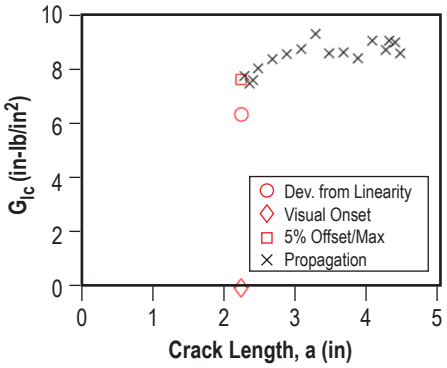
Test Group Summary (Mean Values, Based on 5 Specimens)	
$G_{Ic,\ prop.}$ (in-lb/in^2)	3.01 ± 10.51
% Cohesive	10
% Substrate	0
% Interfacial	90



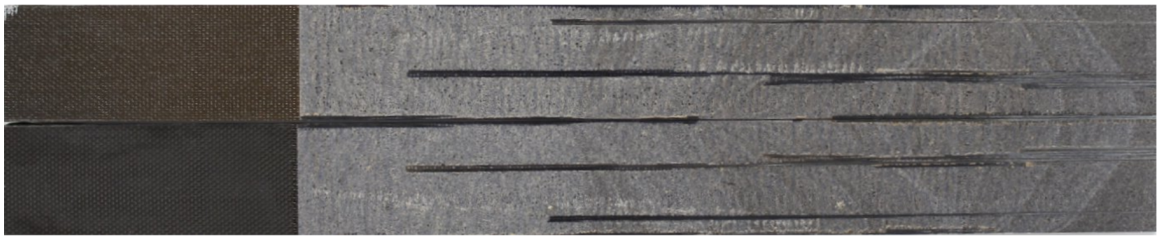
Test Group ID	Adhesive Age (mo)	Adhesive Out-Time (d)	Laminate Age (mo)	Prep to Bond Time (d)	Cure Temp. (°F)	APPT
PLA-PWD-LBJ-A-087	12	0	0	0	250	No



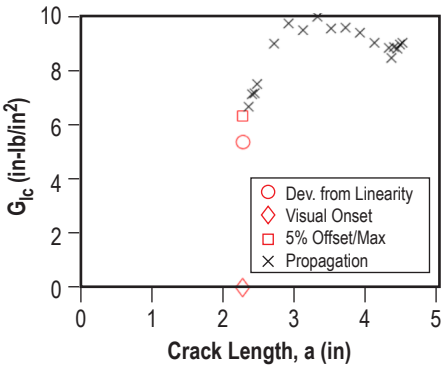
Test Group Summary (Mean Values, Based on 5 Specimens)	
$G_{Ic,\ prop.}$ (in-lb/in^2)	8.65 ± 0.43
% Cohesive	87
% Substrate	13
% Interfacial	0



Test Group ID	Adhesive Age (mo)	Adhesive Out-Time (d)	Laminate Age (mo)	Prep to Bond Time (d)	Cure Temp. (°F)	APPT
PLA-PWD-LBJ-A-088	12	0	0	0	250	Yes

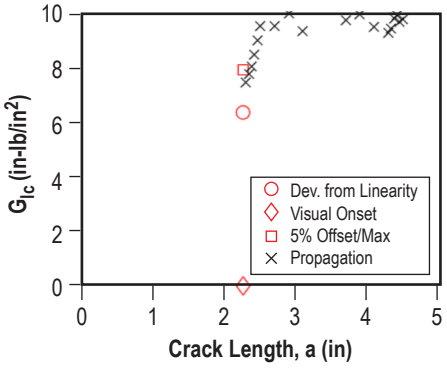


Test Group Summary (Mean Values, Based on 5 Specimens)	
$G_{Ic,\ prop.}$ (in-lb/in^2)	8.60 ± 0.31
% Cohesive	85
% Substrate	15
% Interfacial	0

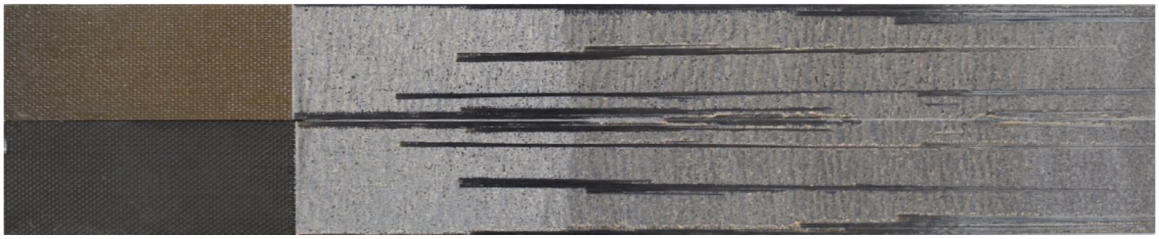


Test Group ID	Adhesive Age (mo)	Adhesive Out-Time (d)	Laminate Age (mo)	Prep to Bond Time (d)	Cure Temp. (°F)	APPT
PLA-PWD-LBJ-A-089	12	0	0	0	300	No

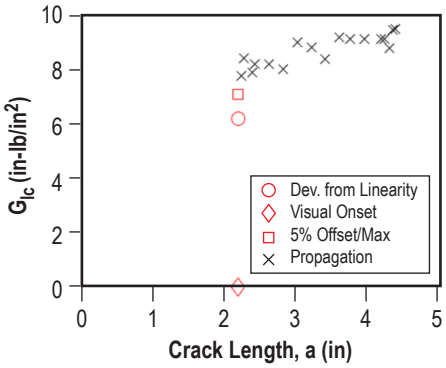
Test Group Summary (Mean Values, Based on 5 Specimens)	
$G_{Ic,\ prop.}$ (in-lb/in^2)	9.48 ± 0.35
% Cohesive	88
% Substrate	12
% Interfacial	0



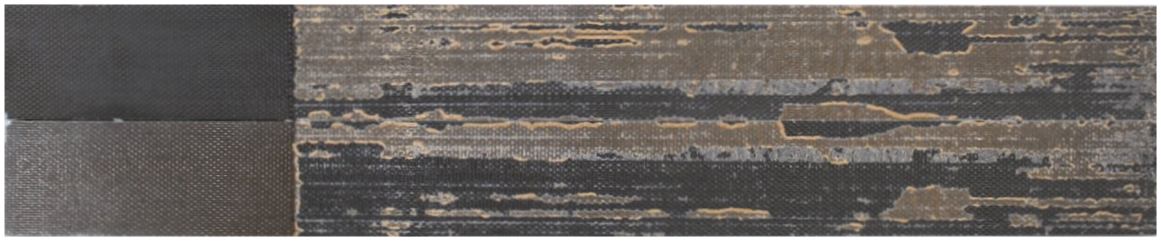
Test Group ID	Adhesive Age (mo)	Adhesive Out-Time (d)	Laminate Age (mo)	Prep to Bond Time (d)	Cure Temp. (°F)	APPT
PLA-PWD-LBJ-A-090	12	0	0	0	300	Yes



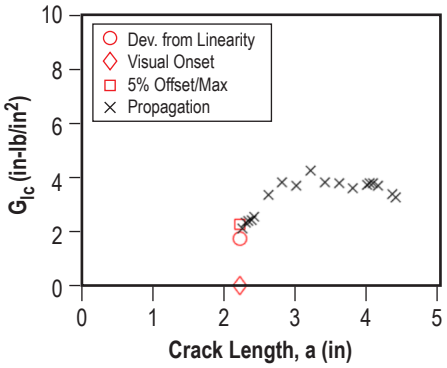
Test Group Summary (Mean Values, Based on 5 Specimens)	
$G_{Ic,\ prop.}$ (in-lb/in^2)	8.94 ± 0.27
% Cohesive	81
% Substrate	19
% Interfacial	0



Test Group ID	Adhesive Age (mo)	Adhesive Out-Time (d)	Laminate Age (mo)	Prep to Bond Time (d)	Cure Temp. (°F)	APPT
PLA-PWD-LBJ-A-097	12	0	0	14	200	No

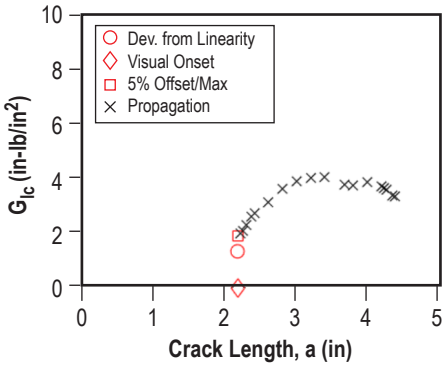


Test Group Summary (Mean Values, Based on 5 Specimens)	
$G_{Ic,\ prop.}$ (in-lb/in^2)	4.05 ± 0.77
% Cohesive	13
% Substrate	0
% Interfacial	87



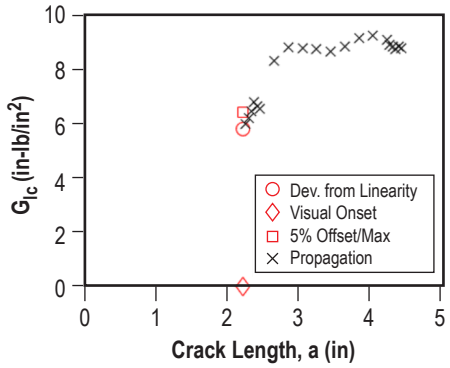
Test Group ID	Adhesive Age (mo)	Adhesive Out-Time (d)	Laminate Age (mo)	Prep to Bond Time (d)	Cure Temp. (°F)	APPT
PLA-PWD-LBJ-A-098	12	0	0	14	200	Yes

Test Group Summary (Mean Values, Based on 5 Specimens)	
$G_{Ic,\ prop.}$ (in-lb/in^2)	3.75 ± 1.39
% Cohesive	15
% Substrate	0
% Interfacial	85



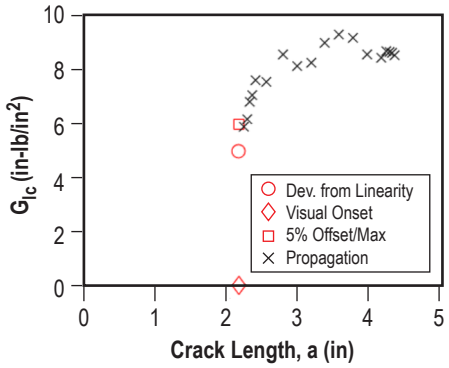
Test Group ID	Adhesive Age (mo)	Adhesive Out-Time (d)	Laminate Age (mo)	Prep to Bond Time (d)	Cure Temp. (°F)	APPT
PLA-PWD-LBJ-A-099	12	0	0	14	250	No

Test Group Summary (Mean Values, Based on 5 Specimens)	
$G_{Ic,\ prop.}$ (in-lb/in^2)	8.81 ± 0.42
% Cohesive	87
% Substrate	13
% Interfacial	0



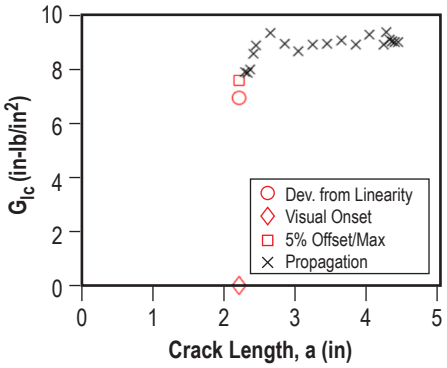
Test Group ID	Adhesive Age (mo)	Adhesive Out-Time (d)	Laminate Age (mo)	Prep to Bond Time (d)	Cure Temp. (°F)	APPT
PLA-PWD-LBJ-A-100	12	0	0	14	250	Yes

Test Group Summary (Mean Values, Based on 5 Specimens)	
$G_{Ic,\ prop.}$ (in-lb/in^2)	9.09 ± 0.54
% Cohesive	97
% Substrate	3
% Interfacial	0

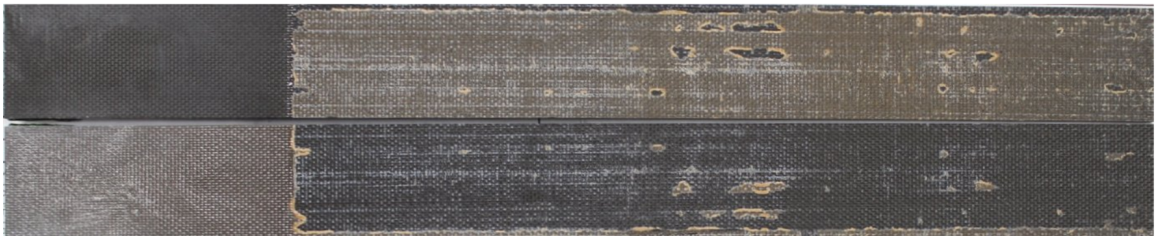


Test Group ID	Adhesive Age (mo)	Adhesive Out-Time (d)	Laminate Age (mo)	Prep to Bond Time (d)	Cure Temp. (°F)	APPT
PLA-PWD-LBJ-A-101	12	0	0	14	300	No

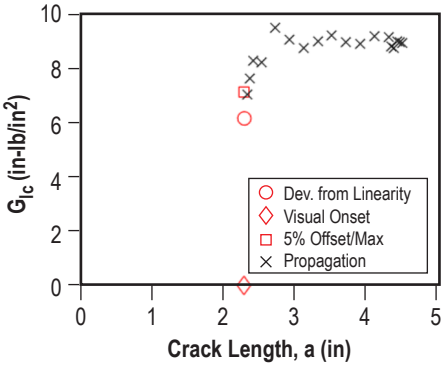
Test Group Summary (Mean Values, Based on 5 Specimens)	
$G_{Ic,\ prop.}$ (in-lb/in^2)	8.75 ± 0.63
% Cohesive	89
% Substrate	11
% Interfacial	0



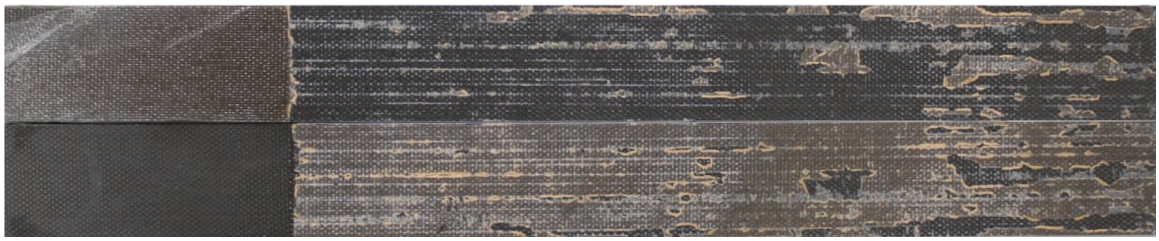
Test Group ID	Adhesive Age (mo)	Adhesive Out-Time (d)	Laminate Age (mo)	Prep to Bond Time (d)	Cure Temp. (°F)	APPT
PLA-PWD-LBJ-A-102	12	0	0	14	300	Yes



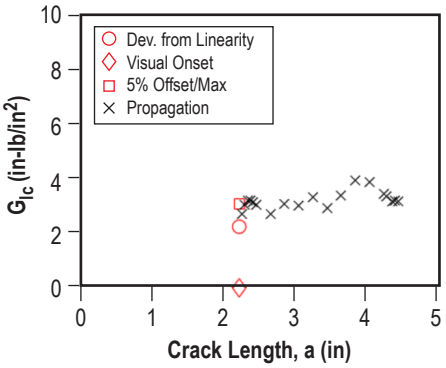
Test Group Summary (Mean Values, Based on 5 Specimens)	
$G_{Ic,\ prop.}$ (in-lb/in^2)	8.71 ± 0.39
% Cohesive	92
% Substrate	3
% Interfacial	0



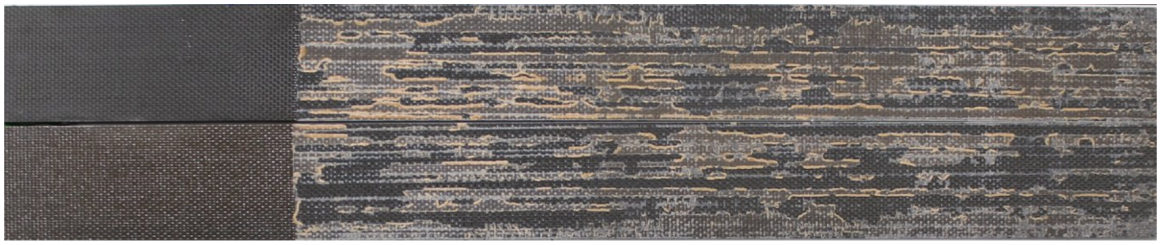
Test Group ID	Adhesive Age (mo)	Adhesive Out-Time (d)	Laminate Age (mo)	Prep to Bond Time (d)	Cure Temp. (°F)	APPT
PLA-PWD-LBJ-A-139	12	40	0	14	200	No



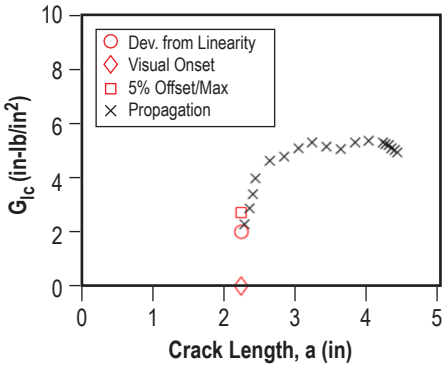
Test Group Summary (Mean Values, Based on 5 Specimens)	
$G_{Ic,\ prop.}$ (in-lb/in^2)	4.11 ± 0.62
% Cohesive	13
% Substrate	0
% Interfacial	87



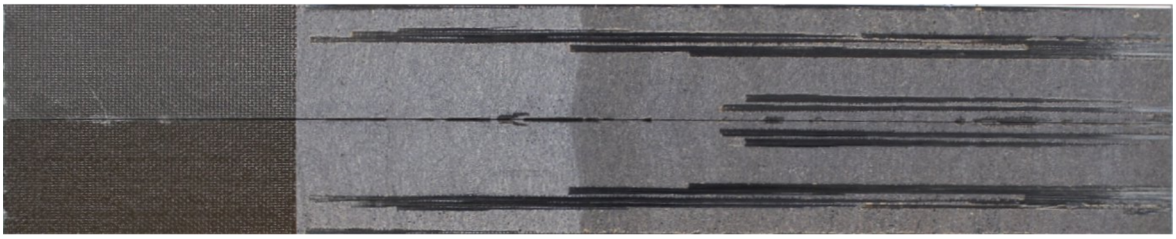
Test Group ID	Adhesive Age (mo)	Adhesive Out-Time (d)	Laminate Age (mo)	Prep to Bond Time (d)	Cure Temp. (°F)	APPT
PLA-PWD-LBJ-A-140	12	40	0	14	200	Yes



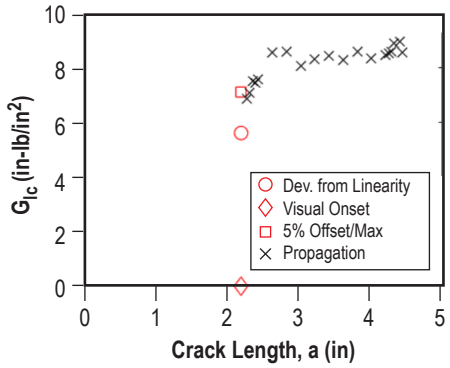
Test Group Summary (Mean Values, Based on 5 Specimens)	
$G_{Ic,\ prop.}$ (in-lb/in^2)	5.96 ± 0.94
% Cohesive	17
% Substrate	0
% Interfacial	83



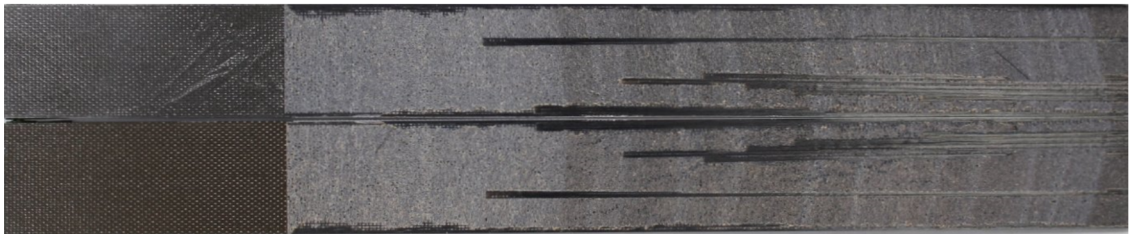
Test Group ID	Adhesive Age (mo)	Adhesive Out-Time (d)	Laminate Age (mo)	Prep to Bond Time (d)	Cure Temp. (°F)	APPT
PLA-PWD-LBJ-A-141	12	40	0	14	250	No



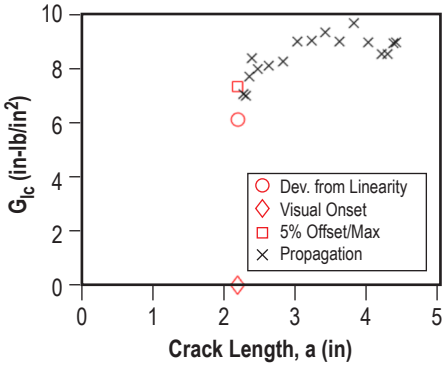
Test Group Summary (Mean Values, Based on 5 Specimens)	
$G_{Ic,\ prop.}$ (in-lb/in^2)	9.00 ± 0.36
% Cohesive	13
% Substrate	0
% Interfacial	87



Test Group ID	Adhesive Age (mo)	Adhesive Out-Time (d)	Laminate Age (mo)	Prep to Bond Time (d)	Cure Temp. (°F)	APPT
PLA-PWD-LBJ-A-142	12	40	0	14	250	Yes

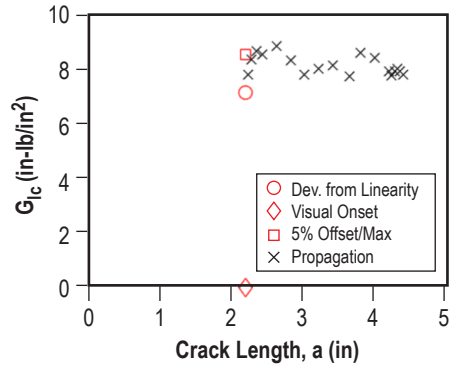


Test Group Summary (Mean Values, Based on 5 Specimens)	
$G_{Ic,\ prop.}$ (in-lb/in^2)	8.96 ± 1.18
% Cohesive	80
% Substrate	20
% Interfacial	0



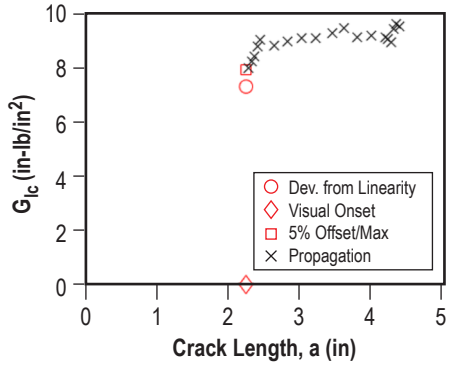
Test Group ID	Adhesive Age (mo)	Adhesive Out-Time (d)	Laminate Age (mo)	Prep to Bond Time (d)	Cure Temp. (°F)	APPT
PLA-PWD-LBJ-A-143	12	40	0	14	300	No

Test Group Summary (Mean Values, Based on 5 Specimens)	
$G_{Ic,\ prop.}$ (in-lb/in^2)	8.09 ± 0.98
% Cohesive	74
% Substrate	26
% Interfacial	0



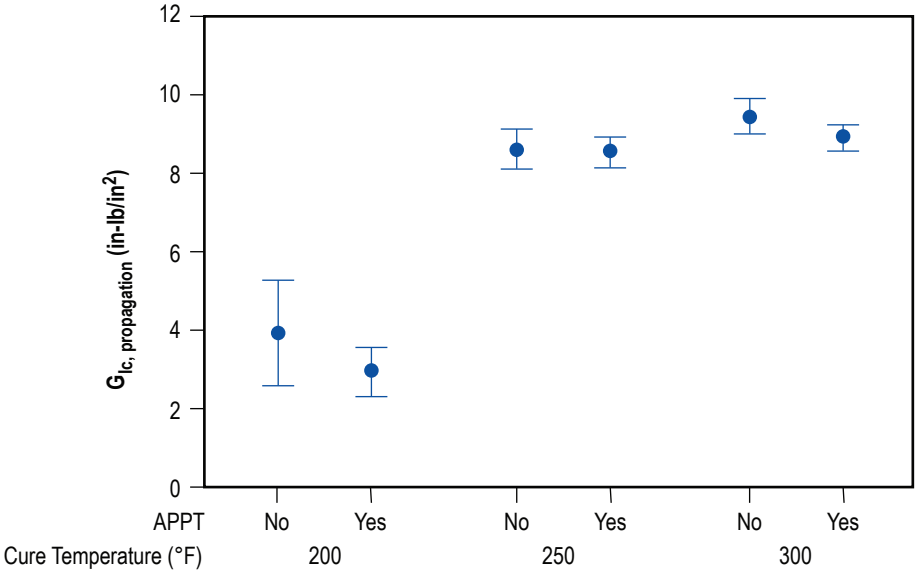
Test Group ID	Adhesive Age (mo)	Adhesive Out-Time (d)	Laminate Age (mo)	Prep to Bond Time (d)	Cure Temp. (°F)	APPT
PLA-PWD-LBJ-A-144	12	40	0	14	300	Yes

Test Group Summary (Mean Values, Based on 5 Specimens)	
$G_{Ic,\ prop.}$ (in-lb/in^2)	8.81 ± 0.72
% Cohesive	90
% Substrate	10
% Interfacial	0

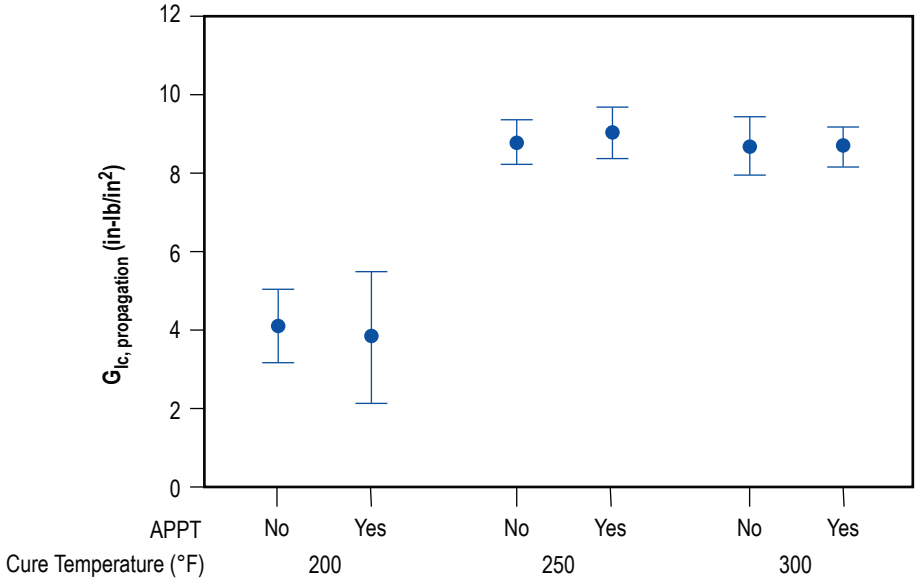


APPENDIX B—PROCESS PARAMETER COMPARISONS IN DETAIL

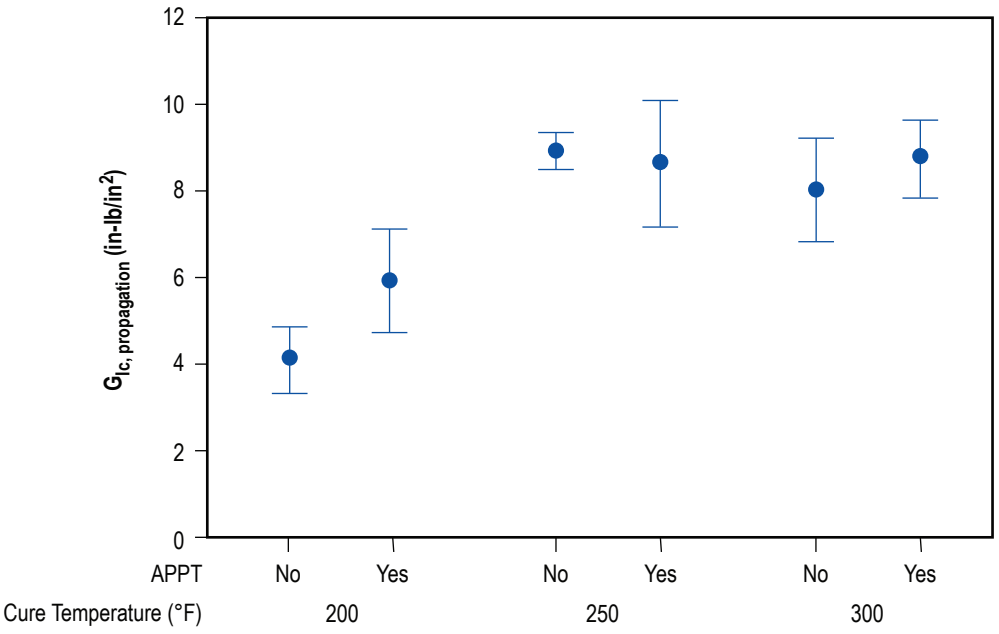
In-depth comparisons among the process parameters considered in this study are presented in this appendix. These comparisons are presented via interval plots, which show mean values and 95% confidence intervals on said mean values. Note that mean values and confidence intervals are based on datasets with 5 data points in each test group (n = 5) and outliers (if present) have not been screened or excluded.



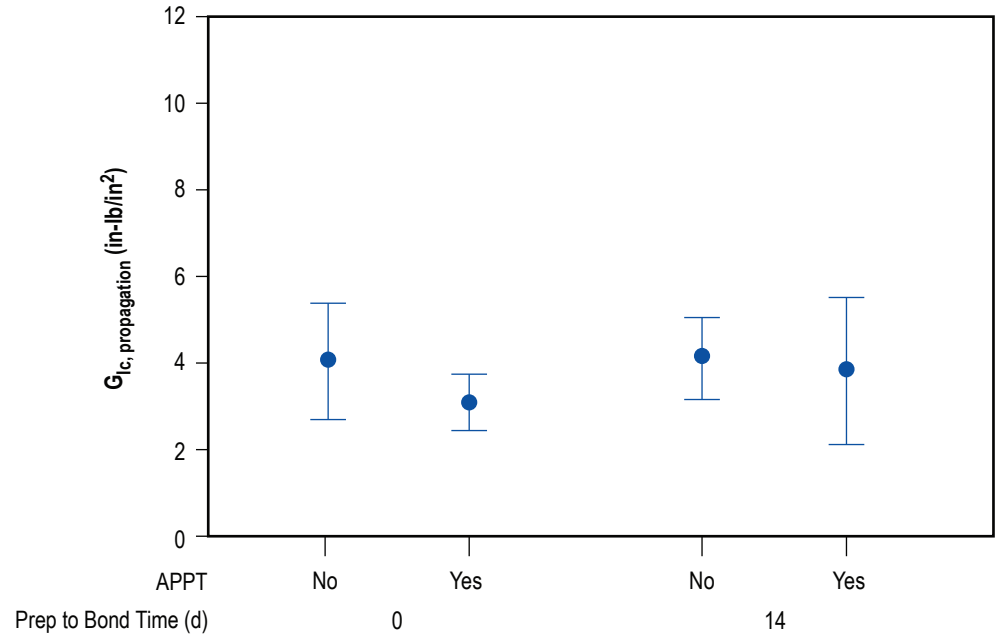
Individual standard deviations are used to calculate the intervals.
Results include rows where 'Prep to Bond Time (d)' = 0 and 'Adhesive Out-Time (d)' = 0.



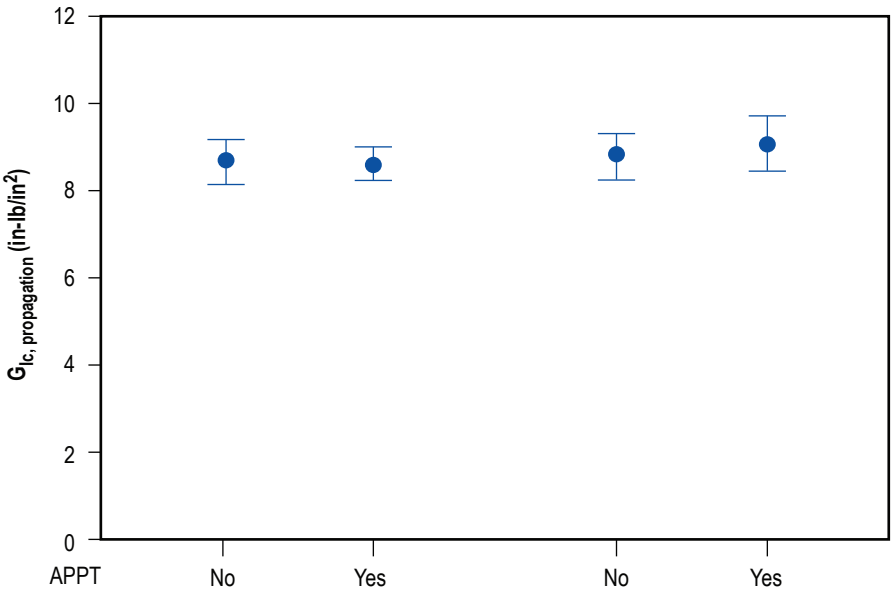
Individual standard deviations are used to calculate the intervals.
Results include rows where 'Prep to Bond Time (d)' = 14 and 'Adhesive Out-Time (d)' = 0.



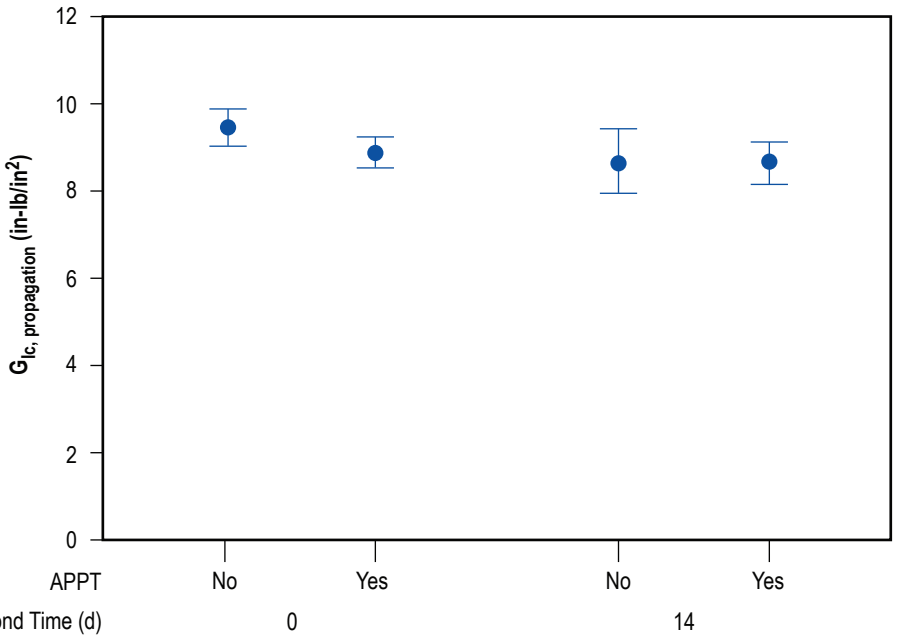
Individual standard deviations are used to calculate the intervals.
Results include rows where 'Prep to Bond Time (d)' = 14 and 'Adhesive Out-Time (d)' = 40.



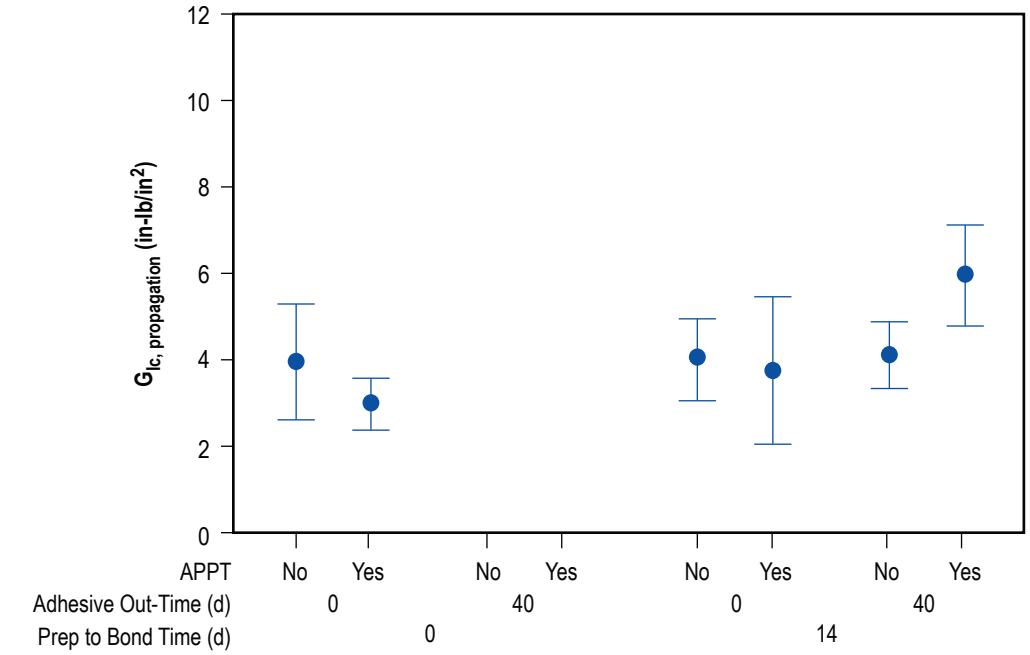
Individual standard deviations are used to calculate the intervals/
Results include rows where 'Cure Temperature' = 200 and 'Adhesive Out-Time (d)' = 0.



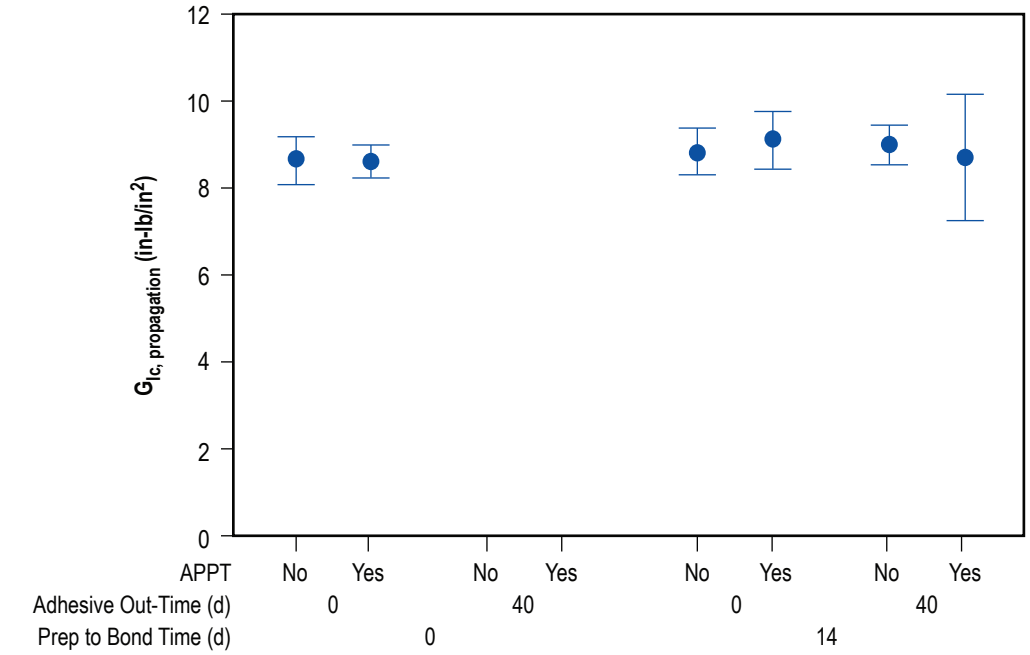
Individual standard deviations are used to calculate the intervals.
Results include rows where 'Prep to Bond Time (d)' = 250 and 'Adhesive Out-Time (d)' = 0.



Individual standard deviations are used to calculate the intervals.
Results include rows where 'Cure Temperature (°F)'=300 And 'Adhesive Out-Time (d)' = 0.



Individual standard deviations are used to calculate the interval.
Results include rows where 'Cure Temperature (°F)'=200.



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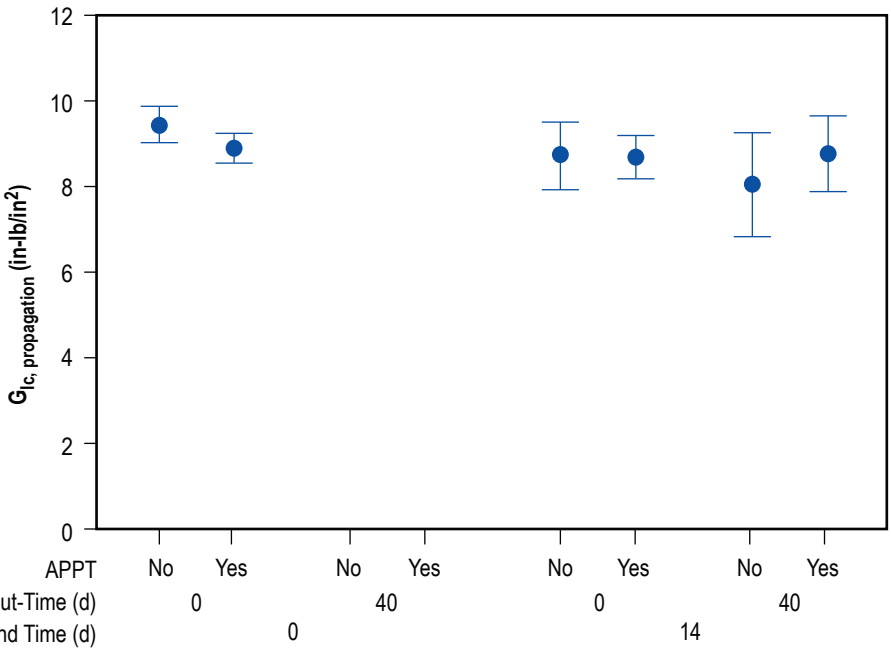
Results include rows where 'Cure Temperature (°F)'=250.



Individual standard deviations are used to calculate the intervals.
Results include rows where 'Cure Temperature (°F)'=300.

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14. ABSTRACT

A number of manufacturing process parameters can affect mechanical performance in an adhesively bonded joint. A suitable certification approach must rely heavily on well-established process controls given the challenges inherent to the nature of adhesively bonded joints in polymer matrix composite structures. In order to establish adequate process controls, relevant process parameters and their influence on joint performance must be well understood. This study characterizes the effects of adhesively bonded joint manufacturing process parameters in the interest of defining process windows for widely used material systems and surface preparation techniques.

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adhesively bonded joints, polymer matrix composites, composite structures, certification, process parameters, fracture toughness

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