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Spring Materials Research Society (MRS) - Meeting
in San Francisco, California, April 8-12, 1996

Prepared by the
*Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831
managed by
Lockheed Martin Energy Research Corp.
for the
U.S. DEPARTMENT OF ENERGY
under Contract No.
DE-AC05-96OR22464

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ABSTRACT

Adhesive bonding/joining through microwave radiation curing has been evaluated as an alternative processing technology. This technique significantly reduces the required curing time for the adhesive while maintaining equivalent physical characteristics as the adhesive material is polymerized (crosslinked). This results in an improvement in the economics of the process. Testing of samples cured via microwave radiation for evaluation of mechanical properties indicated that the obtained values from the single lap-shear test are in the range of the conventionally cured samples. In general, the ultimate tensile strength, σ_B, for the microwave processed samples subjected to this single lap-shear test was slightly higher than for conventionally cured samples. This technology shows promise for being applicable to a wide range of high volume, consumer goods industries, where plastics and polymer composites will be processed.

KEY WORDS: Composite Bonding, Adhesives, Microwave Processing, Single Lap-Shear Test.

INTRODUCTION

The intent of this work was to produce high quality bonds with a substantial reduction in the required cure time. The bonds were to have mechanical and physical properties equivalent to conventionally cured samples. The experimental results of this work indicate that the cure time is substantially reduced by the application of microwave radiation when compared to thermal curing. Substrate materials discussed in this work are glass and a urethane-based composite with glass fiber reinforcement (SRIM-part). Glass substrates (annealed soda lime silicate slides) were bonded via microwave radiation curing of epoxy to eliminate the variable represented by the absorption of microwave energy by different substrates. This permits, as a first step, the study of the coupling characteristic of the pure neat adhesive resin independent of any “lossy” effect of the substrates. Lossy is a material characteristic or property indicated by a large tangent delta which means electrically very resistive and consequently couples very efficiently to microwave radiation.

In spite of the original intention to study only pure neat resin (BFGoodrich EXP 582E adhesive), it was decided to extend the study to include resin additives. These would enhance the coupling efficiency to microwave radiation and possibly improve the kinetic reaction rate during the curing process of the adhesive. Adhesives used were 100% Goodrich 582E (epoxy based), 582E plus 10 wt% $Zr0_2$, 582E plus 20 wt% $Zr0_2$, 582E plus 25 wt% $Zr0_2$. Further compositions consisted of 582E plus 10 wt% Tosoh-Soda (Tosoh-Soda: 80 wt% $Zr0_2$ and 20 wt% Al_20_3; herewith referred to as TZ), 582E plus 25 wt% TZ, 582E plus 0.1 wt% carbon black powder, 582E plus 0.3 wt%

carbon black powder, 582E plus 1.0 wt% carbon black powder, and 582E plus 10 wt% carbon black powder.

The effects of additives were studied only to achieve further reductions in the required cure time when compared to microwave processed samples without additives through the improved lossy characteristics of the doped adhesive. The effects of these additives on thermally cured adhesives was outside the scope of this work, therefore, property changes resulting from chemical changes as a result of the additive are not addressed.

The data presented in this paper with respect to adhesive additives will be limited to carbon black powder. The basis for this is that previously published results [1] indicated that zirconia or Tosoh-Soda (TZ) will not improve the microwave energy deposition into the adhesive during the curing process.

SAMPLE PROCESSING AND RESULTS

For sample preparation and subsequent microwave processing of these samples, the various types of substrates were coated using the adhesive compositions noted above. In order to maintain uniform bond line thickness a few glass beads of 30 mil diameter were embedded in the adhesive. Subsequently, all samples were exposed to varying power levels of microwave radiation. At selected time intervals during the processing, substrates were visually inspected to determine acceptance for degree of polymerization (crosslinking). Figure 1 shows typical exposure times versus input power for glass and urethane substrates and the adhesive without additives. Indicated also in this figure is the effect of a high dosage of microwave energy with the subsequent generation of bubbles in the adhesive region. The result of this art of microwave processing is a substantial reduction in the required curing time of the samples. Figure 2 indicates the dependence of the required adhesive curing time on the input microwave power in a 2.45 GHz environment using the identical adhesive condition as in Figure 1. Also noted is the first order power law for this specific material. Substrate type, adhesive composition, exposure time, forward power, and reflected power were recorded for each trial in this experimental program.

The microwave system used was a Cober SF6 power supply which provided up to 5.5 kw of 2.45 GHz radiation into the 61 x 61 x 61cm multimode cavity. Depending on the requirements of the specific process or the part to be processed, any applicator may be used to accomplish a suitable joint. However, depending on part geometry and the joint area geometry, an applicator can be properly designed to accomplish a suitable power density in the required area which optimizes the energy incident on the required area. An analysis of the data reveals that in all cases, epoxy cure time approximately followed theory in that as electric field intensity increased, cure time decreased [2]. The experimental data empirically indicates that power (P) varies as the inverse square root of the curing time of the adhesive. The interrelationship between adhesive cure time and incident microwave power was discussed in [1]. Summarizing the results of that work, it may be stated that two regions in the experimental data are recognizable. In the high power region the experimental data indicates that the power varies as the inverse square root of the cure time, while for the low power data, the input power is inversely proportional to the exposure or cure time. Through analyzing the experimental data presented in Figure 2, urethane substrate/adhesive without additive, an appropriate empirical function was determined which describes these data to a high degree of accuracy. The empirical relationship which describe the observed data is a power law function with an exponent essentially of negative 0.5 and a constant term of approximately 1400.

Figures 1 and 2 show data obtained for the various systems investigated. The first system investigated was the glass/substrate/epoxy-based adhesive without additives. Cure times ranged from less than one minute to over twenty minutes. Samples with urethane-glass fiber substrates, exhibited cure times which ranged from nine minutes to twenty-five minutes. This is very attractive when compared to a conventional cure time of forty-five minutes.

The selection of an acceptable curing time is dependent upon the industry and manufacturing environment where this technology will be utilized. Because there is a maximum power level above which bubble generation will take place, a minimum permissible curing time to achieve full crosslinking exists. For example, the data depicted in Figure 1 suggests a reasonable and acceptable curing time of between 5 and 15 minutes for many high rate manufacturing environments, as apposed to 45 - 60 minutes for conventional cure.

As expected, for each kind of substrate/adhesive system studied, the required curing time decreased with an increase in the level of the microwave input power, and with an increase in the concentration of the active additive in the adhesive system that responded favorably to the microwave energy deposition. Figure 3 clearly indicates this effect. Our current knowledge indicates that microwave curing will occur within a third to a quarter of conventional curing time. Results, obtained to date with the 582E adhesive indicate an approximate cure time of fifteen minutes or less through exposure to microwave radiation.

During the experimental work, it was noticed that a decrease in the reflected microwave power as a function of curing time occurred; and eventually, this reflected power leveled off and became steady-state. An explanation of this phenomenon may be the deposition of the microwave energy into the adhesive, resulting in the molecular crosslinking process. This changes the lossy characteristic of the adhesive, resulting in a change in the degree of polymerization. When the reflecting power levels off, this may be an indication that crosslinking is largely finished and the curing of the sample is approaching completion. Also, during the processing of the specimens only a marginal increase in the urethane-glass fiber composite substrate temperature was noticed. Further studies are needed in this area to better understand the mechanisms of microwave energy deposition as a function of the molecular crosslinking process.

Characterization of Joint Mechanical Strength

The characterization of the bond strength in the processed samples was determined using single lap-shear samples. Figure 4 shows a schematic of this test. A standard Instron Tensile testing machine, Model 1125, was used to perform this testing. In this evaluation, only urethane-glass substrates were studied.

From the previous study [1] of the cure time together with the subsequent evaluation of the joint mechanical strength, it was noted that when a physically (visually) acceptable joint was obtained, failure occurred as a fiber tear "peel" of the urethane substrate. This condition may be observed in Figures 5 and 6. From these results it was determined that discrete regions of the prior power density versus cure time curve (Fig. 1) needed to be evaluated and related to joint mechanical strength. For this reason four discrete regions on the power density vs. cure time curve were selected for further study. This data is summarized in of Tables I and II.

As seen in Table I, relatively little variation in σ_B (ultimate tensile strength) was observed in the samples with processing times (curing times) from 10 to 40 minutes. In general, the average σ_B ranged from a value of 2600 psi to 3000 psi. For certain specific cases σ_B was as high as 3150 psi. A satisfactorily microwave processed sample when submitted to the single lap-shear test demonstrated a fiber tear "peel" type fracture directly on the urethane substrate as indicated in Figure 5. For the case of no additives in the adhesive and for short curing time with high input power a low average of 1918 psi was observed for σ_B. Upon the initial visual observation of these tested parts, it was observed that a nonuniform formation of bubbles occurred in the adhesive in the joint area, as seen, for example, in Samples A10 and A18 as shown in Figure 6.

In some samples, in spite of the bubble formation directly in the adhesive located in the joint area, a satisfactory value of the joint strength was obtained. For example, in samples A18 and A10 (Figure 6) it is clearly observed that at least half of the joint area is covered by bubbles, a partial "peel" fracture in the substrate is observed in these samples when they were submitted to the single lap-shear test. The "peel" region in the substrate occurred in the area which lacked bubbles. Surprisingly good values of joint mechanical strength were observed even though a high density of bubble formation occurred in some sections of the joint region.

A comparison of samples containing 0.1 wt% carbon black powder and 1 wt% carbon black powder indicated, in general, a good overlapping of σ_B values. The “**short**” cure time samples upon visual observation showed a lower density of bubbles in the interfacial region which could account for the increased σ_B when compared with the above non-additive samples processed at equal conditions (short time and high power). It appears that the presence of carbon black in the adhesive partially inhibits the formation of bubbles in the interface region. For samples not containing voids, fracture occurred by near surface fiber tear of the composite. Since the failures were cohesively through the adherend, any improvements in adhesive mechanical properties due to the incorporation of carbon would not be measurable in this study.

As observed in Table I, there may exist a maximum of σ_B with respect to cure time. This maximum may be observed within the range of moderate cure time (14-17 and 20-25 minutes), for all the microwave processed specimens. For the short sample cure time, a plausible explanation for this observed phenomena may be based on the high electric-field intensity and the subsequent high energy deposition which results in the generation of a high density of bubbles. For the long sample cure time, the observed results may be explained based on the extended/extensive exposure to microwave radiation resulting in possibly over-processing of the polymer (e.g. molecular degradation, increasing the adhesive brittleness, etc.).

The next analysis of mechanical strength data is shown in Table II. Shown in this table are the total crosshead displacement (δ) of the Instron tensile testing machine versus microwave sample processing characteristics. The complexity of the test geometry of single lap-shear samples (e.g. two nonaligned substrates bending in the joint area during testing, as indicated in Figure 4, stresses in the joining region which are difficult to define, and an adhesive with unknown material characteristics, etc.) makes the term "strain" for this specific case not applicable as known academically. The test length of the specimen may be described as a multiple component system in series. For this reason, it is important to describe it only in terms of the total crosshead deformation/displacement (TCHD) of the sample system in the single lap-shear test.

For comparison reasons the total crosshead displacement (δ) was evaluated for all the samples/series with and without adhesive additives at σ_B, and at a load of 1000 lbs. The TCHD at σ_B will indicate the maximum tolerable deformation that the system can withstand at maximum load. The TCHD at a load of 1000 lbs. was selected as a reference value which corresponds to a stress of approximately 2000 psi which is well below the ultimate strength (material is still physically sound) and is located at the lower limit of the range of observed mechanical strength data.

As seen in Table II, the addition of an adhesive additive such as carbon increases δ both at σ_B and at 1000 lb. load. The variation seen in TCHD between 0.1 wt % and 1 wt % carbon data is found to be negligible for σ_B and at a 1000 lb. load. No clear trend of the TCHD values was observed as a function of the curing characteristic (cure time) for all systems evaluated.

Table III presents the consolidated data obtained on conventionally cured and microwave cured samples in this experimental work. Data for ultimate tensile strength, total TCHD at ultimate strength, and TCHD at 1000 lbs. load is summarized in this table. In general, the data indicates nearly equivalent results for the conventional and microwave processed samples when comparing σ_B. Table III also demonstrates that higher maximum ultimate tensile strength (σ_B) values were consistently obtained for the microwave processed samples compared with the conventionally cured samples. This was observed with and without additives to the adhesive. The data indicates that the microwave processed samples possess ultimate strengths slightly higher or equivalent values than the conventionally cured specimens. As measured, the TCHD for the conventionally processed samples showed a significantly lower value than those obtained for microwave processed samples at corresponding equal load values. The greatest difference in TCHD was observed to occur when comparing conventionally cured and microwave processed samples (especially those specimens with high carbon additive in the adhesive). This indicates that the conventionally processed samples show higher rigidity/stiffness when submitted to the single lap-shear test. A complete, fundamental comparison between mechanical properties of conventionally processed and microwave processed samples is not possible within the scope of this work. For example, in the single lap-shear test, the system under study, (despite equivalent predrying processing of the substrates) may be assumed to be a multiple component system with each component acting in series. When this system is exposed to different processing methodologies (microwave vs. conventional) the affect on each system component (two segments of substrate transmitting forces at each end of a nonaligned adhesive joint region) can be significantly different and a function of what these segments undergo in each process methodology. Another indication of different sample characteristics caused by process methodologies may be found in the samples which experienced total peel failure. Visually, the new surface (cohesive composite failure) of the microwave processed samples shows more resinous characteristic than the conventionally processed samples.

Figures 7-9 represent data obtained in a single lap-shear test for conventionally cured samples and microwave processed samples cured over different levels of input power and for different lengths of time (short, moderate, and long cure times). Data expressed in Figures 7-9 represents load not stress. Associated with each curve is the corresponding ultimate tensile stress (σ_B). When σ_B is evaluated, it must include the joining area which varies very slightly from sample to sample.

It is clear from the data on the diagrams (Fig. 7-9) that conventionally cured samples demonstrate a higher rigidity than all the microwave processed samples. From these diagrams it is clear that the higher the concentration of carbon in the adhesive, the larger is the deformation that the tested system can tolerate. Within each figure, data can be compared or analyzed to determine trends since all specimens were subjected to similar processing conditions (power level and cure time). In Figure 8 (**moderate** cure time) four specimens with varying adhesive formulation and processing are compared. Clearly recognizable is an increase in the TCHD as a function of carbon content in the adhesive. Since the samples were subjected to very nearly the same processing conditions, the different results may be attributed directly to the adhesive carbon content. It is evident that the carbon content affects the tolerable state of deformation. Similar conclusions may be drawn from Figures 7 and 9 for the short and long curing times.

From Figures 7-9, in spite of the similarity of the general shape of load versus deformation curves for the conventional and microwave cured samples, it is clear that the conventionally cured samples exhibit a more elastic behavior than do the microwave processed samples, which exhibit more plastic behavior. It is not clear what the reasons are for this difference and it is not possible within the scope of this work to draw any conclusions. This may be attributable to the complex stress state present in the test samples due to the test configuration of the specimens.

For a comparison of microwave vs. conventionally processed samples, a possible explanation for obtained results is discussed below. The higher degree of deformation under load for the microwave processed samples is based on the ability for the long wavelength microwave radiation (possessing faster depth of penetration through the substrate sample than conventionally curing processes) to interact directly at the interface throughout the complete curing process. The relatively fast energy deposition in the joint area is enhanced by the intrinsic polar characteristic of the adhesive at early stages of the curing process. Under these conditions, it is expected that a better chemical bond may be made between the epoxy and urethane directly at the interface boundary. The above results are directly analogous to those observed during the process of glass-ceramic joining. In this process, conventionally made glass-ceramic joints experience mechanical bonding and not diffusional bonding; however, exposure to microwave radiation results in complete diffusion bonding and in many cases the joint is not visible in a SEM.

Basic microscopy of the substrate/adhesive interface indicates a nonhomogeneous distribution of the glass fiber in the substrate. We thus assume that a nonhomogeneous fiber distribution exists through the substrate. From the microscopy it is observed that fiber concentration exists in the form of bundles surrounded by resin. This nonuniform distribution of glass fibers throughout the substrate will severely distort the microwave electric field present in the substrate and the substrate joint region. This nonuniform electric field will almost certainly result in localized high electric field intensity (hot spots) in regions of low composite dielectric constants.

Vast improvements may be possible in the optimization of this process including adhesive reformulation to increase the lossy nature of the adhesive and speed the reaction kinetics of the microwave process. No reformulation of the adhesive was undertaken in this study beyond the inclusion of particulate additives known to be good microwave energy enhancers. Any changes in the chemical constituency of the adhesive to reduce the thermal cure time are expected to also decrease the required microwave cure time due to the excellent coupling characteristic of the epoxy adhesive to a broad spectrum of microwave energy.

CONCLUSION

- The application of microwave technology for joining of substrates using epoxy based adhesives will significantly reduce the curing time to only a third to a quarter of the conventional cure time. This is accomplished while maintaining equal or slightly higher values of the ultimate tensile strength obtained through the single lap-shear test.

- Microwave processed samples, when tested as single lap-shear specimens exhibit less rigidity but more plasticity than do conventionally processed samples.

- Coupling of the Goodrich EXP 582E epoxy based adhesive to the 2.45 GHz microwave radiation is extremely efficient. This coupling characteristic is enhanced by an additive such as carbon black.

- Total crosshead displacement (TCHD) for conventionally processed samples exhibit a significantly lower value than those obtained for microwave processed samples at correspondingly equal load values. Clearly recognizable is also an increase in the TCHD as a function of carbon content in the adhesive for the microwave processed samples.

- Microwave processed samples with an additive such as carbon black powder exhibit more plasticity than those without an additive. As additive concentration in the adhesive increases so does plasticity. In all cases increased plasticity was observed with equal or greater ultimate tensile strength (σ_B).

- This technology may be extended to multiple-layered panels or components.

ACKNOWLEDGMENT

Research was performed at Oak Ridge National Laboratory and sponsored by the Office of Transportation Material, U.S. Department of Energy, under contract No. DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

REFERENCES

1. F. L. Paulauskas, T. T. Meek, C. D. Warren, SAMPE International Technical Conference Proceedings, 27, 114 (1995).

2. T. T. Meek, J. of Materials Science Letters, 6, 638 (1987).

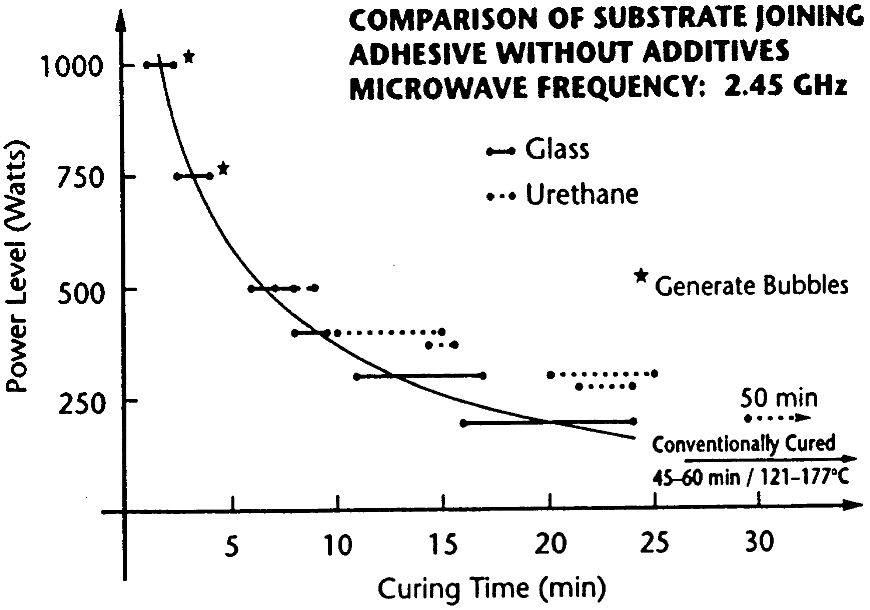


Figure 1. Curing time vs power level.

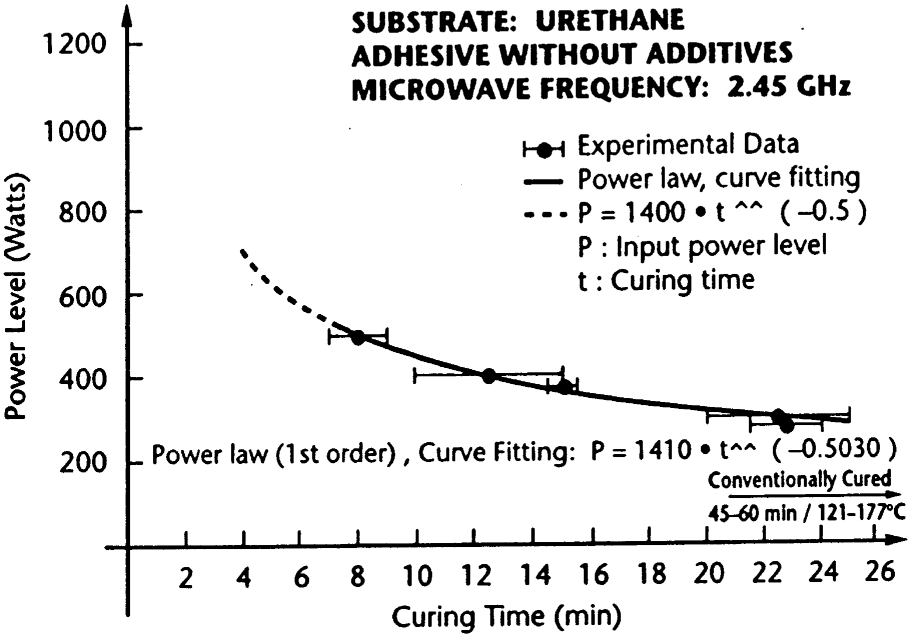


Figure 2. Curing time vs power level. Power law approximations.

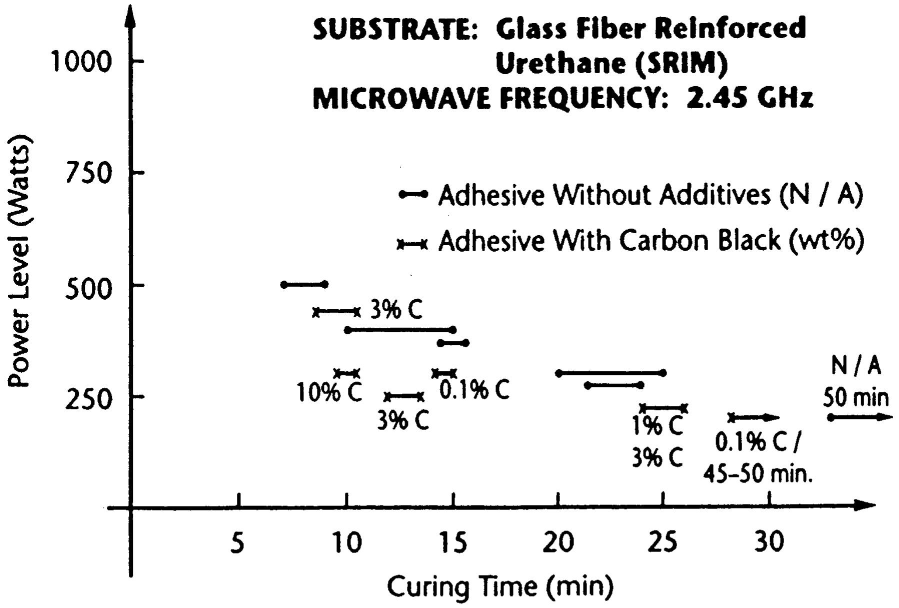
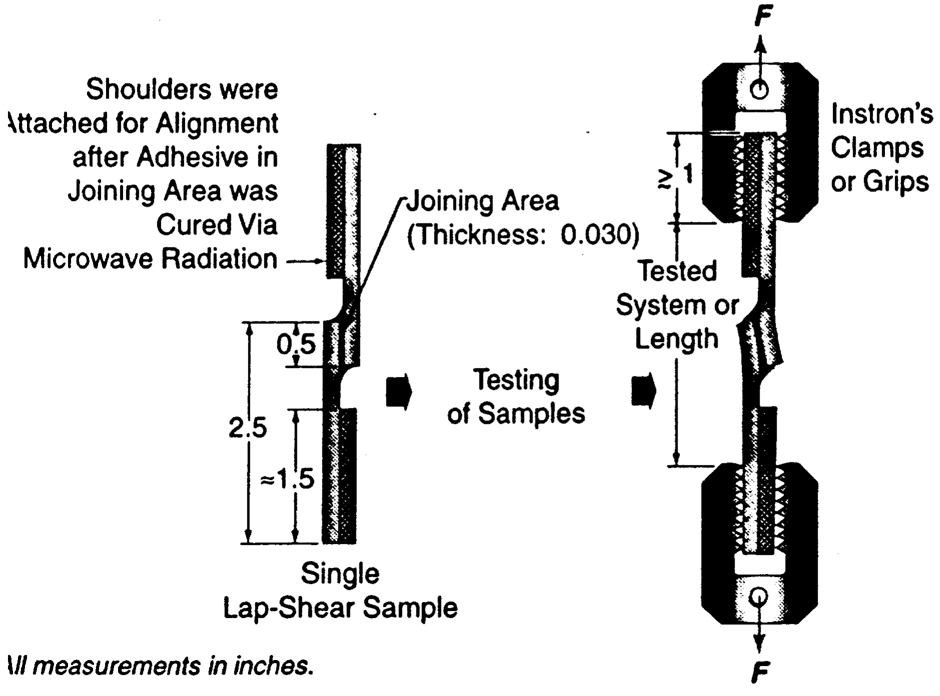


Figure 3. Curing time vs power level.



All measurements in inches.

Figure. 4. System Deformation / Displacement In The Single-Lap-Shear Test

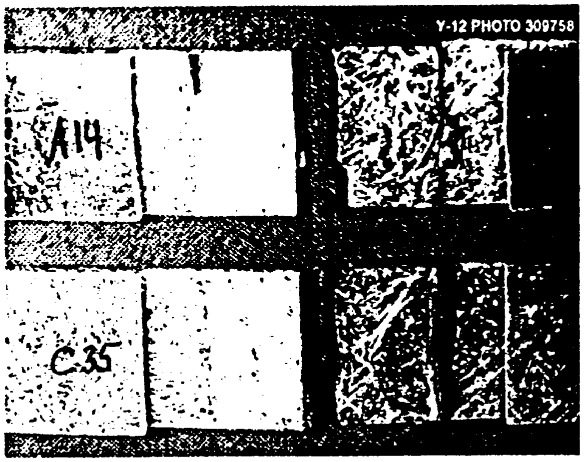


Figure 5. A satisfactorily microwave processed sample, when submitted to a single lap-shear test, demonstrated a fiber-"peel"-type fracture directly at the substrate surface.

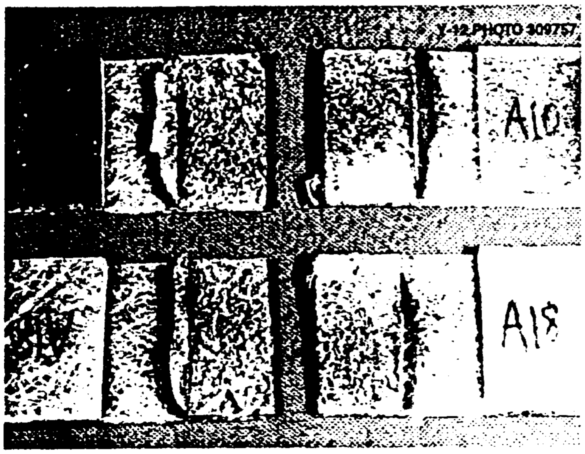


Figure 6. Microwave processed samples showing localized bubble formation in the adhesive joint area. Under test conditions these samples demonstrated partial peel-type fracture with good values of mechanical strength.

Table I. Single Lap-Shear Test Data of Microwave Process Samples
Urethane / Glass Composites Substrates. Adhesive (epoxy based): 582E
Ultimate Tensile Strength (σ_B) vs Microwave Cure Time (CT)

	Adhesive without Additives			**Adhesive with 0.1 wt% carbon**			**Adhesive with 1.0 wt% of Carbon**		
Curing characteristic	Cure time range (min)	σ_B, psi average	σ_B, psi range	Cure time range (min)	σ_B, psi average	σ_B, psi range	Cure time range (min)	σ_B, psi average	σ_B, psi range
Short Cure Time	10 – 13	—[1]	3130 ↕ 1450	10 – 11	**2874**	2950 ↕ 2800	—	—	—
Low-Moderate Cure Time	14 – 17	**2875**	2950 ↕ 2800	14 – 16	**2733**	3000 ↕ 2600	12.5 – 14	**2772**	2930 ↕ 2620
Moderate Cure Time	20 – 25	**2950**	3150 ↕ 2840	19 – 23	**2885**	3100 ↕ 2600	25 – 30	**2720**	2900 ↕ 2600
Long Cure Time	≈ 40	**2745**	2900 ↕ 2600	≈ 30	**2662**	2800 ↕ 2550			
	average:	**2845**		average:	**2802**		average:	**2755**	

[1] Majority of samples in this series were unacceptable (bubbles in joining area).

Table II. Single Lap-Shear Test Data of Microwave Process Samples
Urethane / Glass Composites Substrate. Adhesive (epoxy based): 582E
Total Cross-head Displacement (δ) vs Microwave Cure Time (CT)

	Adhesive without Additives			**Adhesive with 0.1 wt% carbon**			**Adhesive with 1.0 wt% of Carbon**		
		δ, inch, average			δ, inch, average			δ, inch, average	
Curing characteristic	Cure time range (min)	at σ_B	at 1000 lbs load	Cure time range (min)	at σ_B	at 1000 lbs load	Cure time range (min)	at σ_B	at 1000 lbs load
Short Cure Time	10 – 13	—[1]	—[1]	10 – 11	**0.0859**	0.0495	—	—	—
Low-Moderate Cure Time	14 – 17	**0.0646**	0.0354	14 – 16	**0.0806**	0.0472	12.5 – 14	**0.0800**	0.0473
Moderate Cure Time	20 – 25	**0.0721**	0.0371	19 – 23	**0.0755**	0.0401	25 – 30	**0.0850**	0.0533
Long Cure Time	≈ 40	**0.0606**	0.0378	≈ 30	**0.0731**	0.0438			
	average:[2]	**0.0652**	0.0368	average:[2]	**0.0790**	0.0457	average:[2]	**0.0819**	0.0495

[1] Majority of samples in this series were unacceptable (bubbles in joining area).
[2] Average of all acceptable samples in all series.

Table III. Comparison Of Single Lap-Shear Test Results
Conventionally Cured Samples vs Microwave Processed Samples

	Conventionally cured samples (45 min at 150° C)		Microwave Processed Samples					
			Adhesive without additives		Adhesive with 0.1 wt % carbon		Adhesive with 1.0 wt % carbon	
	avg.	(range)	avg.	(range)*	avg.	(range)*	avg.	(range)*
Ultimate Tensile Strength (σ_B), psi	2736	2840 ↕ 2406	2845	3100 ↕ 2600	2802	3100 ↕ 2600	2755	2930 ↕ 2600
Total Cross-Head Displacement, at Ultimate Strength (σ_B), in.	0.0546		0.0652		0.0790		0.0819	
Total Cross-Head Displacement at 1000 lbs load, in.	0.0333		0.0368		0.0457		0.0495	

*Approximate range.

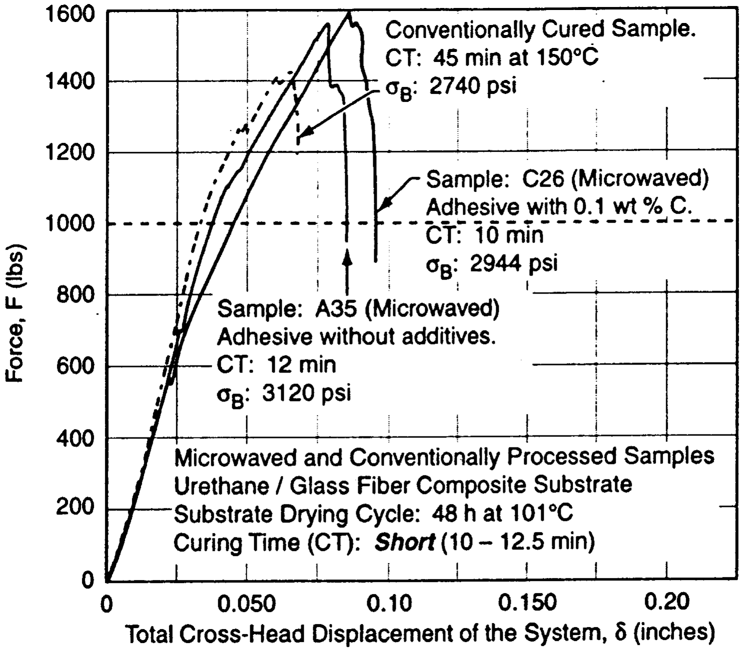


Figure 7. Single Lap-Shear Test Diagram

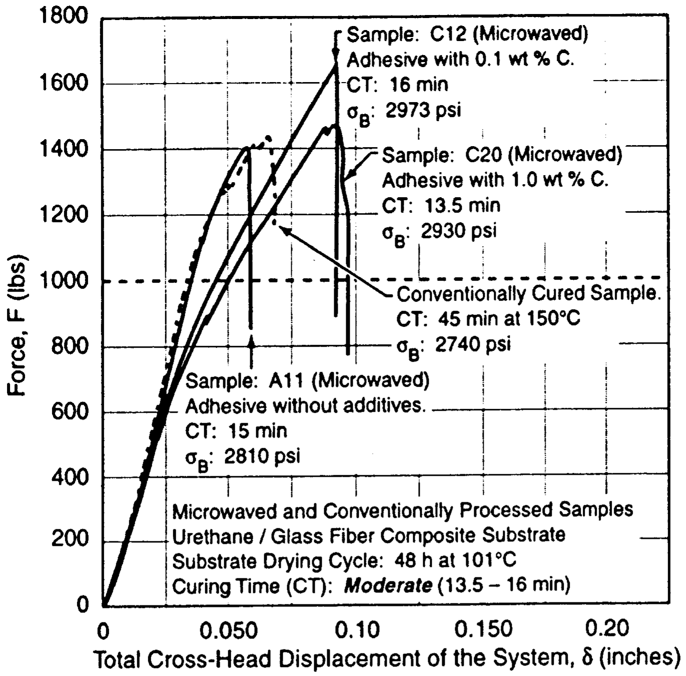


Figure 8. Single Lap-Shear Test Diagram

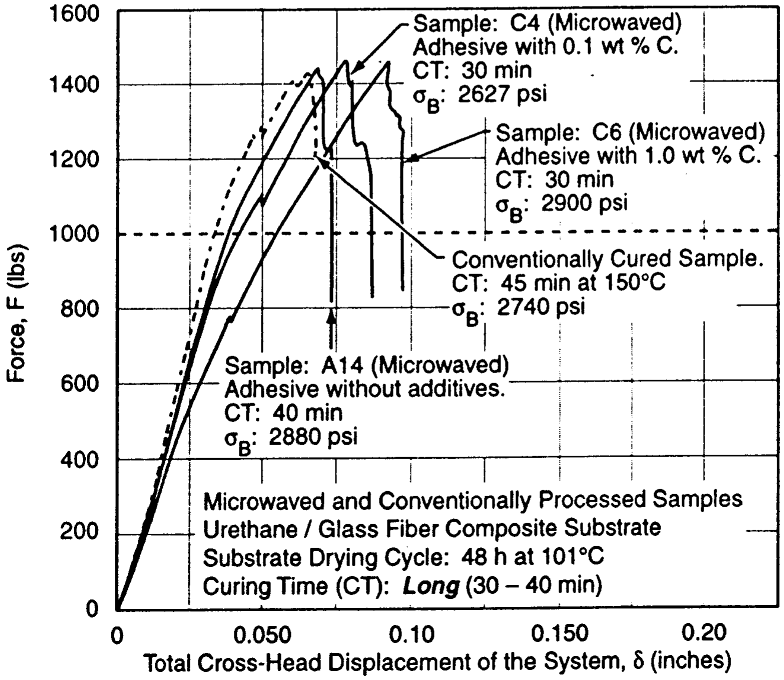


Figure 9. Single Lap-Shear Test Diagram