ORNL/CP-98697

CONF-980572--

THE ELECTRON BEAM CURE OF EPOXY PASTE ADHESIVES

Captain Jeffrey D. Farmer
USAF Advanced Composites Program Office
WL/MLS-OL
McClellan AFB, CA 95652-2510

Christopher J. Janke
Oak Ridge Centers for Manufacturing Technology
Oak Ridge National Laboratory*
Oak Ridge, Tennessee 37831-8048

Vincent J. Lopata
Atomic Energy of Canada Limited, Whiteshell Laboratories (AECL)
Pinawa, Manitoba R0E 1L0
Canada

ABSTRACT

Recently developed epoxy paste adhesives were electron beam cured and experimentally explored to determine their suitability for use in an aerospace-quality aircraft component. There were two major goals for this program. The first was to determine whether the electron beam-curable paste adhesives were capable of meeting the requirements of the U.S. Air Force T-38 supersonic jet trainer composite windshield frame. The T-38 windshield frame's arch is currently manufactured by bonding thin stainless steel plies using an aerospace-grade thermally-cured epoxy film adhesive. The second goal was to develop the lowest cost hand layup and debulk process that could be used to produce laminated steel plies with acceptable properties. The laminate properties examined to determine adhesive suitability include laminate mechanical and physical properties at room, adhesive tack, out-time capability, and the debulk requirements needed to achieve these properties. Eighteen paste adhesives and four scrim cloths were experimentally examined using this criteria. One paste adhesive was found to have suitable characteristics in each of these categories and was later chosen for the manufacture of the T-38 windshield frame. This experimental study shows that by using low-cost debulk and layup processes, the electron beam-cured paste adhesive mechanical and physical properties meet the specifications of the T-38 composite windshield frame.

---

* Managed by Lockheed Martin Energy Research Corporation for the U.S. Department of Energy under contract DE-AC05-96OR22464.

KEY WORDS: Aerospace; Electron Beam Curing; Epoxy Resins

1. INTRODUCTION

The U.S. Air Force Advanced Composites Program Office (WL/MLS-OL), McClellan AFB, Sacramento, CA recently sponsored a project which studied the feasibility of electron beam curing the T-38 composite windshield frame. The T-38 is the U.S. Air Force's primary supersonic trainer. The composite windshield frame is an integral structural part of the windshield assembly system rated to withstand a 1.8 kg bird impact at 740 km/hr. An important step in the design effort for this windshield frame involved a paste adhesive and process optimization study using a series of different electron beam-curable cationic epoxy paste adhesive systems and compatible scrim cloths to bond 301 ½ hard stainless steel. The primary goal of this program was to develop materials that met the windshield frame's requirements, while minimizing layup time before their vacuum bag cure using an electron beam accelerator.

Electron beam curing is a non-thermal, non-autoclave curing process which potentially offers many favorable advantages compared to thermal curing methods (1-5). Electron beam curing has been demonstrated to be capable of very high rates of material processing. This technology can potentially be used to manufacture quality composite parts rapidly and inexpensively at selectable temperatures (ie., room temperature, sub-ambient) using only vacuum pressure. The cost of tooling for some composite parts may also potentially be reduced. When fully developed, it may also eliminate slower, high-temperature, high-pressure curing cycles, harmful chemical hardeners, and volatile emissions that are routine in traditional thermal curing processes. Additionally, it gives the fabricator the ability to manufacture unique products that cannot be built any other way. These include composite parts or tools having little, if any, residual stresses, and composite parts incorporating materials or components which are temperature- and/or pressure-sensitive. A major goal of this program was to determine if these benefits can be realized for a part such as the T-38 composite windshield frame, which has been in production using thermal cure methods for well over three years.

The arch of the T-38 composite windshield frame is composed of 36 sheets of 301 ½ hard, 0.41 mm-thick stainless steel (AMS 5514) bonded together using a thermally-cured EA 9628 NW structural epoxy film adhesive from Hysol of Industry, CA. The fact that the design and strength of the arch represents the significant portion of bird-impact resistance for the windshield frame makes the production of a high-quality arch extremely important. This, as well as the fact the arch is 2.54 cm-thick, made the design of an electron beam cure cycle for this portion of the windshield frame extremely challenging. The first goal was to find a paste adhesive that would meet the minimum strength requirements of the frame. The next goal was to develop an efficient process that would not only generate a part with the required strength but would also be more efficient than the process that is currently in use for the frame. Finally, an electron beam cure process which could penetrate and fully cure the 2.54 cm of material within the arch (approximately 55% steel, 35% adhesive, and 10% prepreg by thickness), was required.

This paper describes the development of the paste adhesive, its layup and cure processes, and selection of the scrim cloth for bonding the stainless steel strips. A paste adhesive was chosen for this program because, in general, it will have much better flow capabilities at room temperature than a film adhesive. One of the program's goals was to develop as efficient a layup process as possible and part of this included room temperature debulks, if at all possible. This paper describes the significant number of lap shear coupons which were fabricated, laid up, electron beam-cured, and tested to develop a qualified adhesive and layup/cure process for bonding the steel within the arch. [A future paper will discuss the work that was done to determine the penetration capabilities of the electron beam, as well as an X-ray beam, to fully cure the adhesive within the arch.]

2. EXPERIMENTAL

2.1 Electron Beam-Curable Cationic Epoxy Adhesives for Bonding Steel

Electron beam-curable cationic epoxy paste adhesives were evaluated for bonding the stainless steel within the arch. All of these adhesives are proprietary systems developed by the Oak Ridge Centers for Manufacturing Technology and AECL. The adhesives are:

Designation	Adhesive Type
14L	Proprietary toughened cationic epoxy
4L	Aluminum oxide toughened cationic epoxy
3G	Proprietary toughened cationic epoxy
2L	Atomized aluminum toughened cationic epoxy
3L	Atomized aluminum toughened cationic epoxy
15L	Proprietary toughened cationic epoxy
16L	Proprietary toughened cationic epoxy
5E	Thermoplastic toughened cationic epoxy
2G	Proprietary toughened cationic epoxy
9L	Proprietary toughened cationic epoxy
8L	Proprietary toughened cationic epoxy
11F	Thermoplastic toughened cationic epoxy
13L	Proprietary toughened cationic epoxy
6L	Calcinated alumina toughened cationic epoxy
12L	Proprietary toughened cationic epoxy
11L	Proprietary toughened cationic epoxy
5L	Calcinated alumina toughened cationic epoxy
10L	Proprietary toughened cationic epoxy

2.2 Manufacture of Electron Beam- and Thermally-Cured Adhesive Lap Shear Coupons

All of the lap shear coupons were tested using 1.6 mm thick 301 ½ hard stainless steel (AMS 5514) as the substrate. In preparation for bonding, the steel was first cleaned, sulfuric acid etched, passivated, and then primed with BR-127 from Cytec Engineered Materials, Inc. Before bonding, the coupons were once again cleaned with a solvent. The electron beam-cured coupons were bonded using the chosen paste adhesive and process (the various processes are listed in Table 1). All of the electron beam-cured paste adhesive coupons were cured using 10 MeV electrons at the 1 kW AECL Whiteshell I-10/I electron accelerator facility. The instantaneous dose rate was 1.5 MGy/s. The thermally-cured coupons were bonded using EA 9628 NW film adhesive and cured for two hours at 121°C under vacuum and 310 kPa pressure at the Physical Sciences Laboratory at McClellan AFB, CA.

2.3 Scrim Cloth used for Bonding Many of the Electron Beam-Cured Paste Adhesive Coupons

Scrim cloths used to bond many of the paste adhesive coupons are listed and described in Table 2. The scrim cloth was used to help ensure a consistent bondline thickness between the two steel substrates.

2.4 Property Testing of Adhesive Lap Shear Coupons

The lap shear coupons were tested in accordance with ASTM D 1002, "Strength Properties of Adhesives in Shear by Tension Loading (Metal-to-Metal)." All of the testing was conducted at the Physical Science Laboratory at McClellan AFB, CA by the same technician. The estimated experimental error for this coupon testing was calculated to be ±5%. Unless otherwise noted, all testing was done at room temperature and all data points presented in this paper represent the average of five test coupons.

3. RESULTS AND DISCUSSION

Before this program, the lap shear strength of the electron beam-cured cationic epoxy paste adhesives had not been measured. Because no information regarding the lap shear strength of the cationic epoxy paste adhesives existed and, therefore, there was no suggested process, it was decided to use the current T-38 composite windshield frame process described above. The steel was first prepared in accordance with the procedures given in Section 2.2. The goal was to develop the strongest adhesive, most efficient layup process, and fastest cure process that would meet the structural requirements for the composite windshield frame.

Figures 1 and 2 show the lap shear strengths of 18 different paste adhesives that were laid up using Process VI (as listed in Table 1 with the exception that numerous paste adhesives were used, not just 11L). Each of the coupons were cured using a dose of 150 kGy. Each one of the data points in these figures represent 4-7 individual coupons tested at room temperature. These figures show a large scatter in the strengths of the different adhesives. Figure 3 shows the best 5 paste adhesives from this original screening compared to the strength of the EA 9628 NW film adhesive. It can be seen that the electron beam-cured paste adhesives are not quite as strong as EA 9628 NW using this preliminary process. Figure 4 also shows that there was a very large variation in the bondline thickness of the five best adhesives (there was an even larger variation within the other 13 adhesives' coupons). Bondlines as thick as 0.4 mm-1.2 mm are known to be weaker than a more "optimum" bondline with a thickness of approximately 0.2 mm. Another reason for requiring a consistently thin bondline thickness is that the dimensional tolerances of the T-38 frame require an adhesive thickness in the range of 0.15 mm - 0.25 mm. One of the major goals for the next set of lap shear coupon tests, therefore, was to achieve a more appropriate bondline thickness.

Figure 5 shows the lap shear strengths for three of the best paste adhesives (as determined from the first round of coupon tests) after using scrim cloth "C" and mechanical pressure to bond the steel (ie., no vacuum). The coupons were cured using two different doses, 100 kGy and 150 kGy. The first point is that the lap shear strengths of the adhesives cured using 150 kGy were lower than the initial results where no scrim cloth was used (Figure 3). The principal cause of this decrease in strength is that the scrim cloth occupies much of the bondline surface area that would otherwise be bonded by the adhesive. The adhesive bonding strength, therefore, is not reduced but the overall strength of the joint is reduced. Figure 6 does show that the coupon bondline thickness is consistently at or below 0.2 mm, as desired. As stated above, the consistency in bondline thickness that comes from using the scrim cloth does come at the price of a lower shear strength. Figure 5 also demonstrates that there is a

33% drop in shear strength when the adhesive is cured using a dose of only 100 kGy rather than 150 kGy. In both of the initial screenings, the 11L performed better than its competitors in terms of shear strength and as well as the others in terms of bondline thickness. All of the paste adhesive were nearly equal in terms of "ease of use" and processing. The 11L, therefore, was chosen as the most promising adhesive for further development.

Figures 7 and 8 show the effects of curing the adhesive with doses greater than 150 kGy. All of the coupons tested for these two figures were cured using the 11L adhesive, under a minimum vacuum of 560mm Hg. The coupons shown in Figure 7 used scrim cloth "B" whereas those for Figure 8 used scrim cloth "A". There is, unfortunately, a difference in the results between the two scrim cloths as can be seen by comparing the two sets of coupons cured using a dose of 250 kGy. It can be seen from this comparison that scrim cloth "A" appears to be the superior choice. (At the point of manufacturing these two sets of coupons this was not yet known). It is seen, nevertheless, that no degradation in the shear strength occurs when the coupons are cured with a dose of up to 250 kGy. There is, however, a noticeable drop off in properties when coupons are processed above 250 kGy and a significant drop above 500 kGy as is seen in Figure 8. (This was an important fact in the design of an electron beam cure process for the arch.)

Figure 9 shows the shear strengths for four sets of coupons bonded using the 11L adhesive, a 150 kGy dose, a minimum vacuum of 560 mm Hg, and four different types of scrim cloths (the scrim cloths are listed and described in Table 2). Each of the scrim cloths produced coupons with a bondline thickness in the desired range of 0.2mm. From this set of tests (and those before it) it is therefore clear that the "A" scrim cloth is the best choice of the four, based upon the lap shear strength testing.

As described earlier, the 25.4 mm-thick arch of the T-38 composite frame is composed of 36 strips of stainless steel whose total thickness is approximately 14 mm. Because of the stainless steel's high specific gravity (≈7.5) one of the program's major questions was whether or not the electron beam could be used to process the adhesive within the desired thickness of steel. An initial look at the lap shear strengths showing the penetration capabilities of the 10 MeV electrons is given in Figure 10. This figure shows that the practical penetration limit of the electrons is somewhere between 4 and 5 millimeters. (Other researchers had stated that 5 mm is the practical limit for electron beam curing through steel.) Many further experiments and measurements regarding the subject of fully curing the adhesive within the arch - as well as the final chosen process - will be given in a future paper.

During the lap shear coupon testing - using the various scrim cloths - it was noticed that numerous voids resulted after processing the coupons under vacuum (as compared to the original no vacuum/no scrim cloth coupons). It was not known whether the voids were: 1) produced by air being "pulled" through the bondline by the applied vacuum, 2) were produced by air trapped within the scrim cloth itself, or 3) produced by expanding voids within the resin while under vacuum. It was thought that little could be done if the effects described in the first or third options were the principal problems (the adhesives had already been degassed). An attempt was made, however, to reduce any chance of air being trapped within the scrim cloth before being applied to the steel substrates. In this set of tests the three scrim cloths were cast with the 11L adhesive on a release film and vacuum bagged for 15-30 minutes at 43°C before being applied to the steel. Figures 11 and 12 show that this process did not improve the lap shear strength of the coupons. A visual inspection also confirmed that approximately the same amount of voids was found in both sets of coupons.

Figure 13 summarizes the lap shear strengths after using the different types of processes to bond the steel substrates with 11L adhesive, various scrim cloths, pressure techniques, and debulk methods. This figure shows that the two superior processes - in terms of simplicity and bond strength - appear to be the ones using the 11L adhesive, without a scrim cloth, while using either vacuum or mechanical pressure for compaction.

Figures 14 through 17 are photographs of the coupons that were processed using a variety of these procedures. Figure 14 shows a photograph of the failed bondline using the EA 9628 NW film adhesive processed under vacuum and 310 kPa pressure. The photo shows that there is adhesive remaining on both surfaces of the steel - a cohesive failure - which is generally the desired failure mode because it typically represents the highest possible shear strength an adhesive can generate. Figures 15 through 17 show coupons which were bonded using the 11L adhesive and: 15) scrim cloth “A” and mechanical pressure, 16) no scrim cloth and vacuum pressure, and 17) scrim cloth “A” and vacuum pressure. It is important to note that these failures were only partially cohesive (approximately 50% on average) with the remainder of the failure being an adhesive failure between the paste adhesive and the primer. It is difficult to notice from the photos but the bondlines of the coupons processed under vacuum were always filled with voids - which significantly reduces the bondline’s strength - whereas the coupons processed under mechanical pressure typically had no voids.

In reality, only minimal direct vacuum is applied to most of the adhesive within the arch ply stack (because of the arch’s thickness, most of the bondlines are sealed off from the vacuum) but pressure is still applied to compact the stack. The void conditions of the two types of processes, therefore, represent the bounds upon the actual conditions that would occur within the arch. It is important to note that the best bondline strength results when no scrim cloth is used - with vacuum or mechanical pressure applied; if scrim cloth “A” is used, there is a reduction in shear strength. It should also be noted that any of these methods are capable of producing bonds stronger than required by the design (21 MPa) and that, at best, the bond strengths were within 13% of the strength obtained when using the autoclave-cured EA 9628 NW film adhesive.

4. CONCLUSIONS

Eighteen different paste adhesives were developed and tested for their ability to bond stainless steel substrates. Based upon hundreds of coupons tested, the 11L adhesive was chosen as the best for this application. Under optimum conditions, this paste adhesive produced bonds that were within 13% as strong as those produced by the baseline material, EA 9628 NW film adhesive. Results from coupons processed under various conditions proved that the highest shear strength could be obtained when no scrim cloth was used. When scrim cloths were used, the lap shear strength typically decreased by 20%. The testing also showed that a minimum dose of 150 kGy was nearly optimum and that doses above 500 kGy significantly reduced the resulting shear strength because of adhesive degradation. In other lap shear coupon testing, coupons processed beneath various thicknesses of steel revealed that the practical penetration limit of the 10 MeV electron beam is between 4 and 5 millimeters.

5. ACKNOWLEDGEMENTS

The authors wish to acknowledge the very important work the following people contributed throughout the research for this paper: Mr. Bob Leach and Mr. Cliff Eberle from Oak Ridge; Mr. Butch Lenzi and Mr. Dan Apostolos from McClellan AFB; Mr. Wayne Stanley, Mr. John Barnard, Ms Minda Chung, Mr. Chris Saunders, and Mr. Mark Simpson from AECL; and Mr. Tom Knobel from E-BEAM Services. This work would not have been possible without the expertise of these professionals.

The authors also wish to express their gratitude to Mr. Richard Warnock of the U.S. Air Force Advanced Composites Program Office for the very generous donation of his time he has made in the preparation and presentation of this paper.

6. REFERNCES

1. C. J. Janke, R.E. Norris, K. Yarborough, S. J. Havens, V. J. Lopata; "Critical Parameters for Electron Beam Curing of Cationic Epoxies and Property Comparison of Electron Beam Cured Cationic Epoxies Versus Thermal Cured Resins And Composites", 42nd International SAMPE Symposium, Anaheim, CA. 42, 477 (1997).

2. C. J. Janke, S. J. Havens, V. J. Lopata, and M. Chung; "Electron Curing Of Epoxy Resins: Initiator And Concentration Effects On Curing Dose And Rheological Properties", 28th International SAMPE Technical Conference, Seattle, WA, 28, 901 (1996).

3. C. J. Janke; "Electron Beam Curing Of Composites Workshop". September 18-19, 1996, Oak Ridge, Tennessee.

4. C. J. Janke, S. J. Havens, G. F. Dorsey, V. J. Lopata; "Toughened Epoxy Resins Cured By Electron Beam Radiation", 28th International SAMPE Technical Conference, Seattle, WA, 28, 877 (1996).

5. C. J. Janke, S. J. Havens, G. F. Dorsey, V. J. Lopata; "Electron Beam Curing Of Epoxy Resins By Cationic Polymerization", 41st International SAMPE Symposium, Anaheim, CA, 41, 196 (1996).

Process	Description
I	Adhesive: 11L, Dose: 150 kGy Scrim: "A" Process: debulk resin/scrim at 43C and cured under 560mm Hg vacuum
II	Adhesive: 11L, Dose: 150 kGy Scrim: none Process: cured under 560mm Hg vacuum
III	Adhesive: 11L, Dose: 150 kGy Scrim: "A" Process: debulk resin/scrim at 43C and cured using mechanical pressure
IV	Adhesive: 11L, Dose: 150 kGy Scrim: "A" Process: cured under 560mm Hg vacuum
V	Adhesive: 11L, Dose: 150 kGy Scrim: "C" Process: cured using mechanical pressure
VI	Adhesive: 11L, Dose: 150 kGy Scrim: none Process: cured using mechanical pressure
EA9628	Adhesive: Film Process: Autoclave cured using 560mm Hg vacuum and 0.31 Mpa

Table 1 Description of processes used to manufacture the lap shear coupons.

Scrim	Description
A	Flexible woven fabric, 0.1mm thick with openings of 2.5mm
B	Stiff woven fabric, 0.13mm thick with openings of 2.5mm
C	Flexible knit fabric, 0.13mm thick with openings of 0.5mm
D	1 Copper wire, 0.38mm thick

Table 2 Description of scrim cloths used to bond many of the lap shear coupons.

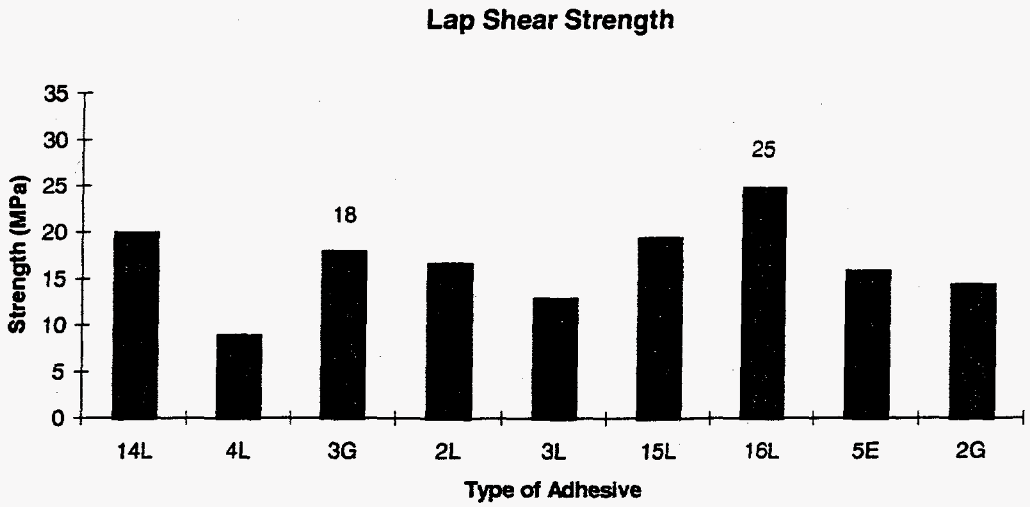

Fig. 1 Adhesive lap shear strengths from the initial screening test.

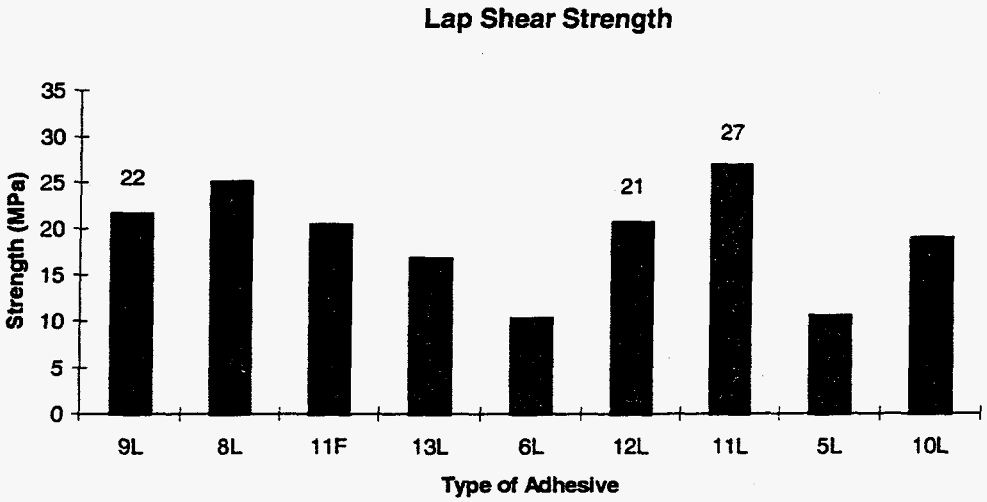

Fig. 2 Adhesive lap shear strengths from the initial screening test.

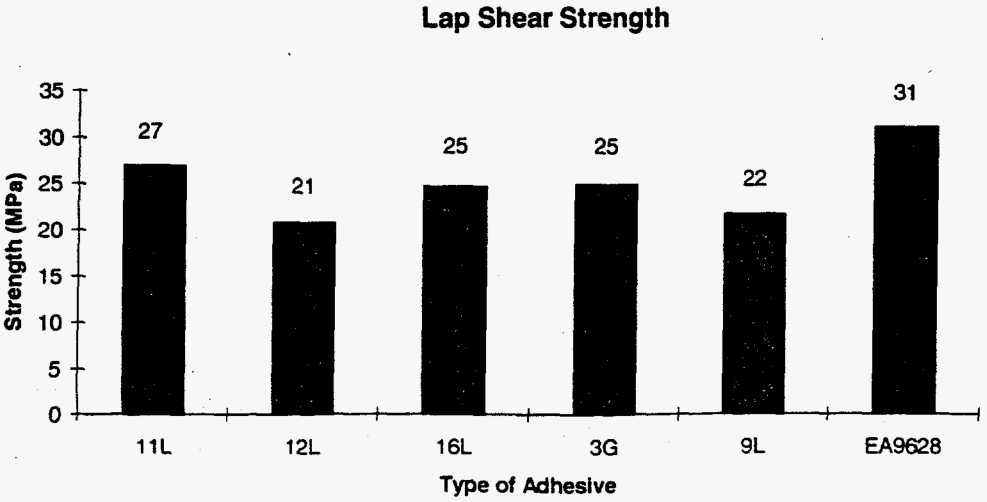

Fig. 3 Best adhesive lap shear strengths from the initial screening test compared to EA 9628.

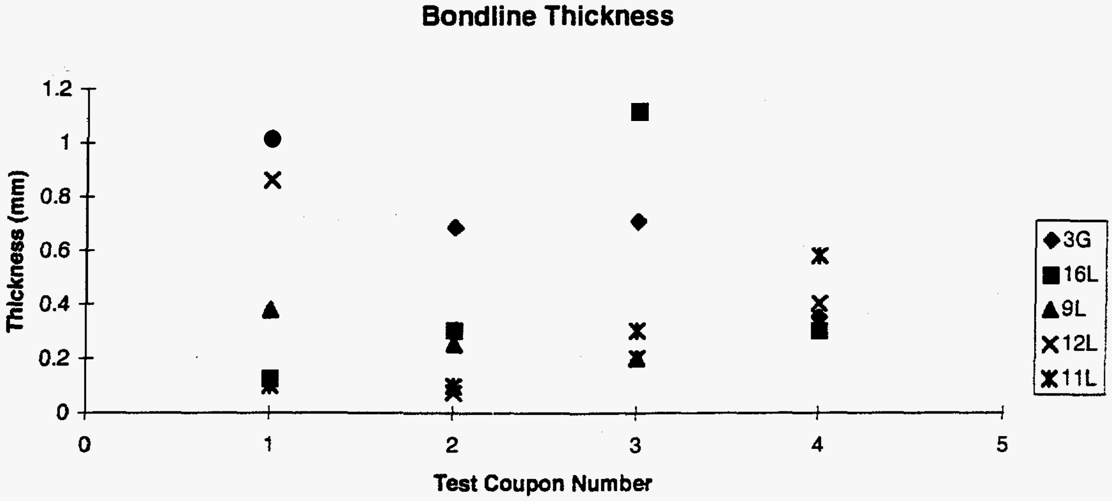

Fig. 4 Bondline thickness from the initial lap shear coupons.

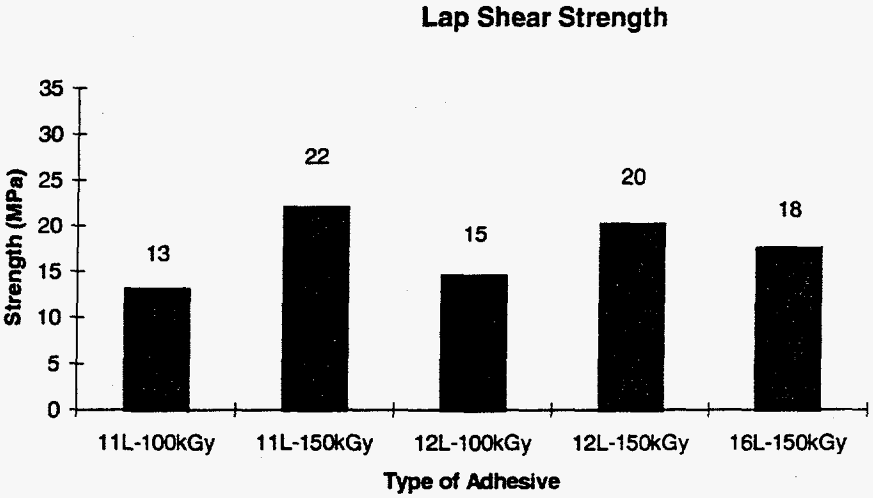

Fig. 5 Lap shear strength of the best adhesives with scrim cloth "C" at two different cure dosages.

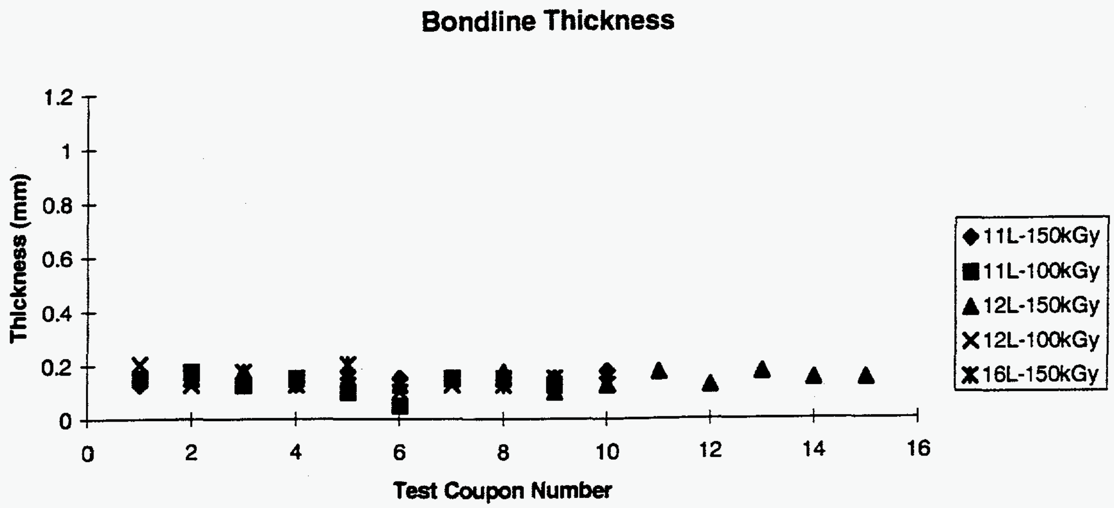

Fig. 6 Bondline thickness of the best adhesives using scrim cloth “C”.

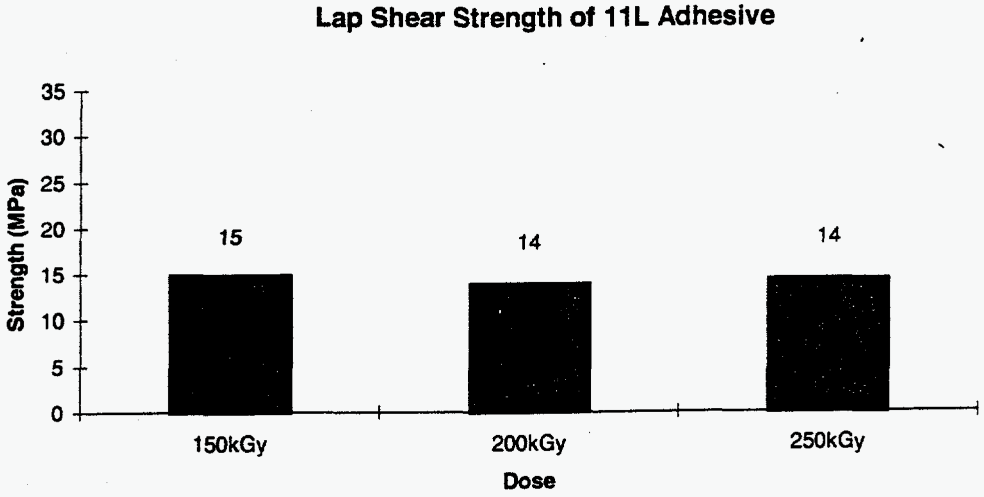

Fig. 7 Lap shear strength of the 11L adhesive with scrim cloth “B” at various cure dosages.

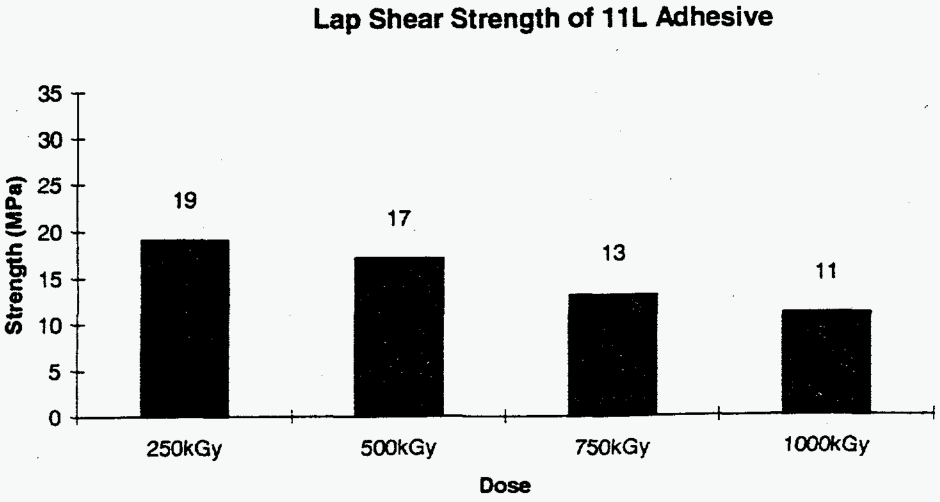

Fig. 8 Lap shear strength of the 11L adhesive with scrim cloth “A” at various cure dosages.

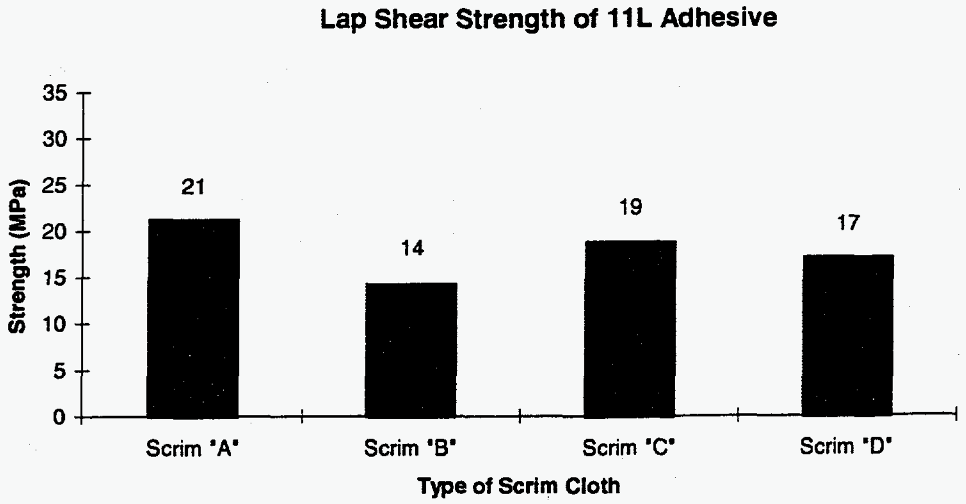

Fig. 9 Lap shear strength of the 11L adhesive using various scrim cloths and 150 kGy dose.

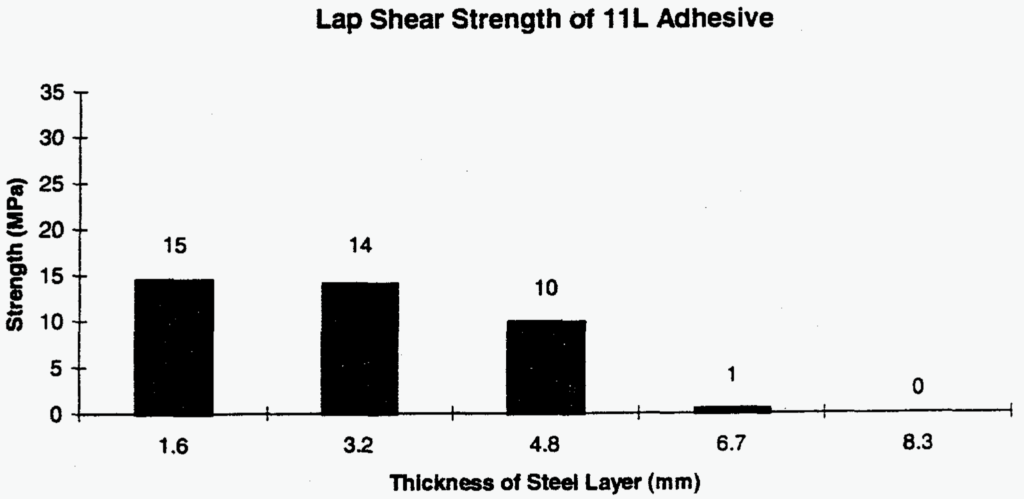

Fig. 10 Lap shear strength of the 11L adhesive with scrim cloth "B" after being irradiated below various thicknesses of stainless steel.

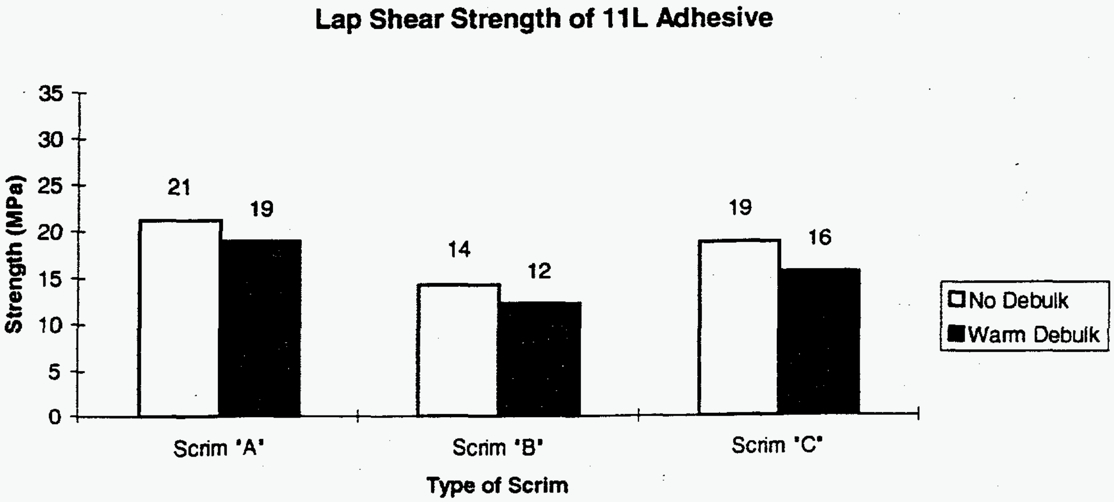

Fig. 11 Lap shear strength of the 11L adhesive using various scrim cloths and debulk cycles.

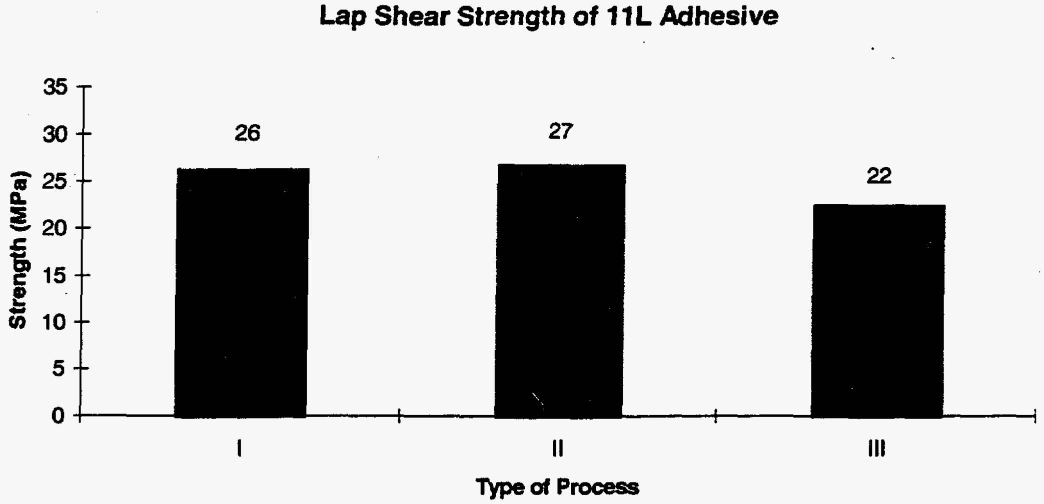

Fig. 12 Lap shear strength of the 11L adhesive using various processes.

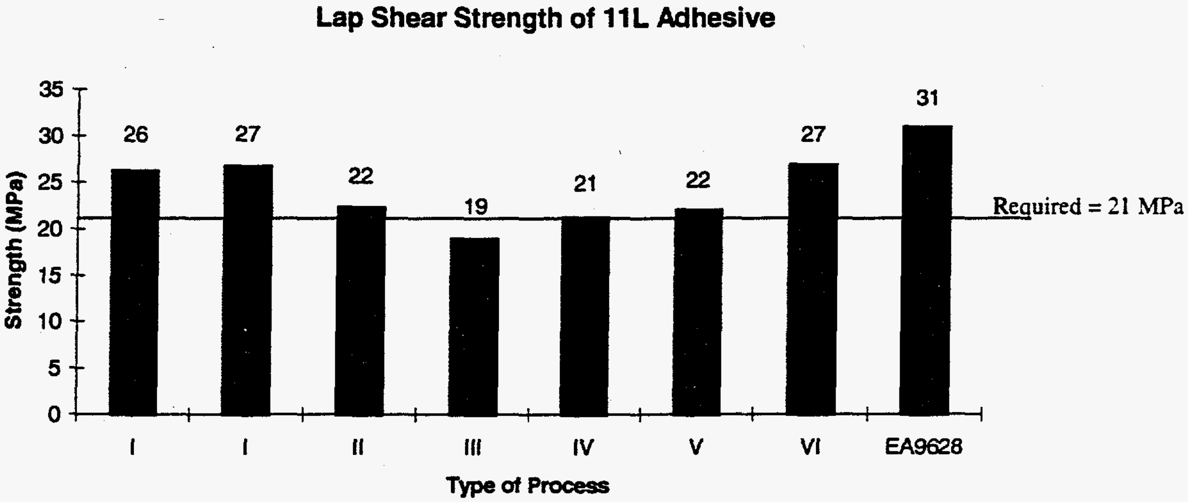

Fig. 13 Lap shear strength of the 11L adhesive using various processes compared to EA 9628.

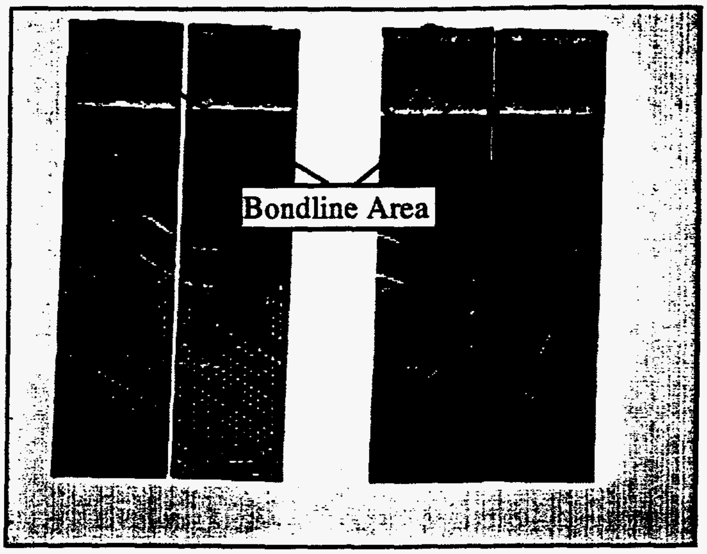

Fig. 14 Lap shear tested coupons using the EA 9628 film adhesive.

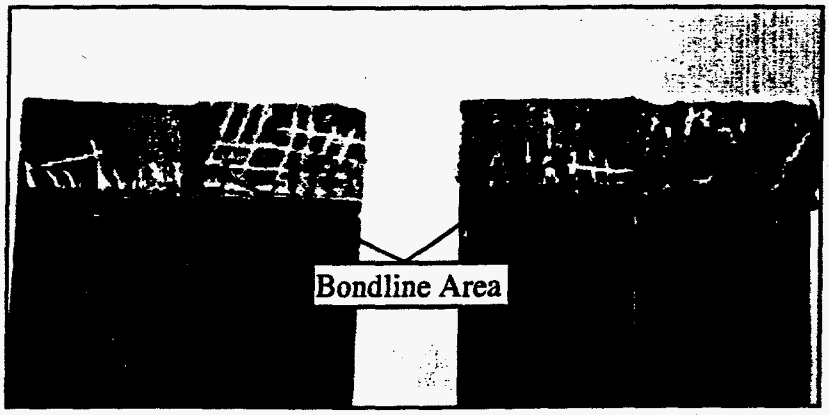

Fig. 15 Lap shear tested coupons using the 11L paste adhesive.

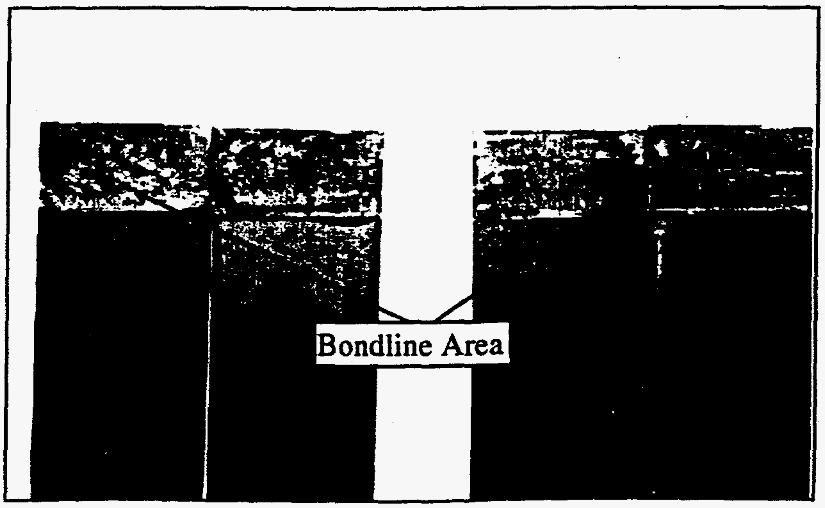

Fig. 16 Lap shear tested coupons using the 11L paste adhesive.

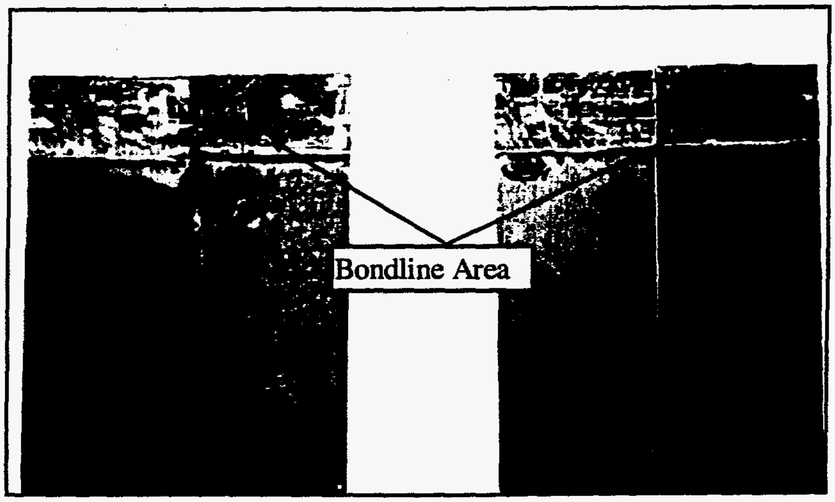

Fig. 17 Lap shear tested coupons using the 11L paste adhesive.