1. Executive Summary

The objectives of the CRADA are to:

- Confirm that fiber-resin adhesion is responsible for the observed poor shear properties;
- Determine the mechanism(s) responsible for poor adhesion between carbon fibers and epoxy resins after e-beam curing;
- Develop and evaluate resin systems and fiber treatments to improve the properties of e-beam cured, carbon-fiber-reinforced composites; and
- Develop refined methods for processing e-beam cured, carbon-fiber-reinforced composites.

The CRADA team has been organized into integrated project teams, or IPT's, with each team focused on specific research tasks.

- The Adhesion IPT, led by Dr. Mark Wilenski (Boeing), is focused on understanding why there is characteristic poor adhesion between the fiber and resin in e-beam cured composites, and how to improve the adhesion.
- The Irradiation IPT, led by Vincent Lopata (Acsion), is focused on evaluating the effects of irradiation parameters on composite properties, especially interlaminar shear and toughness.
- The Materials & Processing (M&P) IPT, led by Christopher Janke (ORNL), is focused on developing constituent materials and processing methods that lead to better composite properties, especially resin toughness.
- The Leadership IPT consists of the respective technical IPT leaders and project management staff. It is responsible for coordinating project activities among the three technical IPT's and ensuring that all activities are designed to achieve progress toward accomplishment of the essential project objectives.

The Adhesion IPT is making great strides toward understanding the cause of the reduced mechanical properties of e-beam cured carbon/epoxy composites. The Adhesion IPT is attacking this problem with two complementary philosophies. First, it is striving to generate a scientific understanding of the problem itself. Second, it is using an understanding of those phenomena that *could* be the problem and evaluating solutions based on anticipated issues. This dual approach allows the CRADA to be responsive to the industrial need for a quick solution to this problem while also aggressively pursuing an understanding of the scientific phenomena causing the problem.

The Irradiation IPT has compiled a database of irradiation parameters achievable and support equipment available at the various irradiators on the CRADA team. A round-robin set of experiments has been devised and is now underway to determine what irradiation parameters are important to give optimum composite performance properties. Early indications are that there are formerly unknown parametric irradiation effects on composite properties that are not yet well understood.

The Materials & Processing IPT is currently exploring several strategies for maximizing the fracture toughness of EB curable cationic epoxy resins and composites. These strategies include chain extending the polymer backbone to reduce the cross-link density and the brittleness of the cured resin system, and interleaving prepregs with thermoplastic materials. Additionally, a wide variety of tougheners are being evaluated including those that have previously resulted in toughening thermally cured, brittle epoxy resins.

Despite an unfortunate delay in the execution of a critical subcontract, the CRADA team is now operating at its full expected technical capacity, and is on track to timely achievement of scheduled milestones. The budget has been rebaselined effective 10-1-1999, and budget allocations and cash flow projections appear to be appropriate for the project needs. Some expenditures originally programmed for FY99 were deferred due to the delay in subcontract execution.

ORNL has entered negotiations with the Army Research Laboratory regarding its prospective entry into the CRADA as a new sponsor and team member. All CRADA participants have enthusiastically endorsed ARL's addition to the CRADA team. The ARL funds will be used to modestly expand the project scope, including research that increases the probability of achieving the project objectives, but that was not feasible within the former budget.

2. Adhesion

The Adhesion IPT has gotten a strong start and is making great strides toward understanding the cause of the reduced mechanical properties of e-beam cured carbon/epoxy composites. The Adhesion IPT is attacking this problem with two complementary philosophies. First, it is striving to generate a scientific understanding of the problem itself. Second, it is using an understanding of those phenomena that *could* be the problem and evaluating solutions based on anticipated issues. This dual approach allows the CRADA to be responsive to the industrial need for a quick solution to this problem while also aggressively pursuing an understanding of the scientific phenomena causing the problem.

2.1. Adhesion IPT Mission

The mission of the Adhesion IPT is to improve the adhesion of e-beam cured graphite/epoxy composites so that they meet or exceed their thermally cured counterparts. The researchers will determine the source of the low adhesion in current e-beam cured systems, and will use this understanding to improve their adhesion. Improvement methods will be economical, environmentally friendly, applicable to multiple resin/fiber systems, and will be compatible with the beneficial aspects of e-beam curing.

2.2. Technical Accomplishments

- The following materials were defined as the baseline materials to be used in the CRADA adhesion activities.
  - Tactix 123 with 3phr CD1012 initiator
  - Unsized AS4 fiber with 100% of the commercial surface treatment
- The ITS testing method from MSU was defined as the primary screening test for adhesion between the carbon fibers and epoxy matrices. The Voltage Contrast XPS method used by BP Amoco was evaluated and has shown promising results. Its use as another screening test is being evaluated. AFRL continues to develop the "Cruciform" test for application to carbon fibers and e-beam cured resins. E-beam cured cruciform specimens have been created by AFRL, cured at Boeing, and shipped to AFRL for evaluation.
- Hexcel has provided data comparing neat resin properties with composite mechanical properties for a variety of thermally cured composite systems. E-beam cured neat resin shear and tensile specimens were made at the same time as the cruciform specimens using the "3K" resin system. These are being tested at AFRL for strength and modulus. The AFRL results will be used with the Hexcel data to determine the role bulk matrix properties have on off-

axis properties. Additionally, literature values for neat resin and composite properties for thermally cured composites are being compiled for this purpose.

- To determine the effect nitrogen atoms on the fiber surface have on adhesion, ITS specimens made from BP Amoco fibers that should have very low nitrogen content have been fabricated and are being tested by MSU.
- In an effort to form primary bonds between the carbon fiber surface and epoxy matrix, the use of isocyanate based sizings is being evaluated by both Boeing and UCB/ORNL. Boeing has fabricated ITS specimens with over 25 isocyanate sizing variations. Surface analysis of these specimens has shown that primary bonds to the surface of the fiber have formed. These specimens are being tested at MSU to determine the effect these bonds have had on adhesion as measured by ITS. UCB/ORNL have fabricated approximately 30 specimens with complementary isocyanate variations for test. These specimens are being sent to MSU for test.
- Boeing has created specimens based on both acrylate and sol-gel sizings. These specimens are currently being tested at MSU. Surface analysis of the sol-gel sized fibers is underway.
- UCB Chemicals has provided a large amount of data on the effect of various surfactants on the surface tension of epoxy resins. From these, the most promising surfactants have been chosen and specimens are being fabricated at Boeing.
- Initial studies on the effect of radiation on the fiber surface functional groups has shown that the radiation required to cure e-beam composites does not deactivate the fiber surface. This result will be confirmed in the next quarter. Studies into the effect of surface adsorption of moisture and other species are being conducted and will be complete next quarter.

2.3. Conclusion

The Adhesion IPT has generated a large amount of data and is well on the way to understanding both the problem and solution to the problem at hand. No programmatic issues are foreseen at this time, and it is anticipated that the 12-month milestones will be achieved during the first quarter of FY00. The CRADA Adhesion team is pulling together resources from a variety of sources and is strongly leveraging work from external efforts. This cooperative approach greatly benefits all involved parties and will be continued throughout the program.

3. Irradiation

3.1. Irradiation IPT Mission

The goals of the irradiation IPT are:

- to provide EB processing support for the CRADA;
- to determine the effect of EB processing parameters on material parameters; and
- to determine the EB processing parameters required to give the optimum composite performance properties.

3.2. Technical Accomplishments

3.2.1. Irradiation Parameters Database

A spreadsheet detailing the accelerator parameters and support equipment has been compiled. The accelerator facilities can be characterized into two categories, pulsed electron accelerators (Acsion Industries, E-BEAM Services, and Boeing) and DC electron accelerators (E-BEAM Services and STERIS Isomedix). The available power and voltage of the individual accelerators ranges from 1 MeV to 10 MeV and 0.5 kw to 150 kW. There are limitations on the available combinations of power and voltage, for example 150 kW is available only up to 5 MeV.

Mark Wilenski of Boeing Phantom Works has developed a computer program to theoretically determine the parameters for each accelerator that should influence the composite properties. These accelerator parameters will be determined by experiment.

3.2.2. Round-Robin Experiments on Accelerator Parameters

A series of experiments were carried out at Acsion Industries to look at accelerator parameters that have a significant impact on the chemistry of epoxy polymerization. The experiments looked at the dose per pass and the time duration between passes. These initial experiments looked at the rheological effects on Tactix 123/OPPI (3 phr). The parameters for this set of experiments are detailed in Table 1.

Table 1. Parameters for Preliminary Round-Robin Tests

Conditions	Values
Dose per pass, kGy	25
Scan width, cm	30
Conveyor speed, cm/sec	0.18
Temperatures, ^{o}C	0 and 25
Total dose, kGy	100
Times between passes	AFAP, 10s, 30s, 60s, 2min, 5min
Dose per pass, kGy	5
Scan width, cm	30
Conveyor speed, cm/sec	0.80
Temperature, ^{o}C	25
Total dose, kGy	80
Times between passes	AFAP, 10s, 30s, 60s, 2min, 5min

Figures 1 to 3 show the effects of time duration between passes at various doses per pass and temperature. A strong β peak at approximately 90^{o}C indicates that there is a reduction in crosslinking of the Tactix epoxy resin. A strong β peak occurs at 5 kGy per pass, 5-minute duration between passes and 25 kGy per pass, 2-minute duration between passes at 0^{o}C. Previous work had shown that maximum heat generation occurs at approximately 5 kGy for the Tactix 123/OPPI(3 phr). This dose is also associated with the 50% cure of the epoxy resin. Because there are competing reactions such as polymerization and termination occurring during the crosslinking of the epoxy, these reactions will be affected by the viscosity and time between passes. As the viscosity gets higher and the time between the passes gets longer, the predominant reaction will be the termination reactions. This would lead to a significant decrease in the number of crosslinks occurring, thus a higher β transition. Because the reactions are pseudo-first order, the number of species generated per pass will depend upon the dose per pass. In the case of the 5 kGy per pass experiment, 5 passes would yield a consumption of 97% of the epoxy sites whereas the 25 kGy per pass would yield the equivalent consumption of epoxy sites in one pass. From our results we can see that the 5 kGy per pass, 5-minute duration between passes has a significant impact on the termination step. The other influence factor is the viscosity of the matrix. In the case of the 5 kGy per pass the viscosity will increase significantly with each pass impeding the ability of the epoxy species to react. In the case of the 25 kGy per pass, the production of significant species will occur that they will be close enough to initiate polymerization reactions even though the viscosity is quite high. Reducing the temperature increases the viscosity of the resin and thus lets termination reaction predominant the reaction scheme significantly.

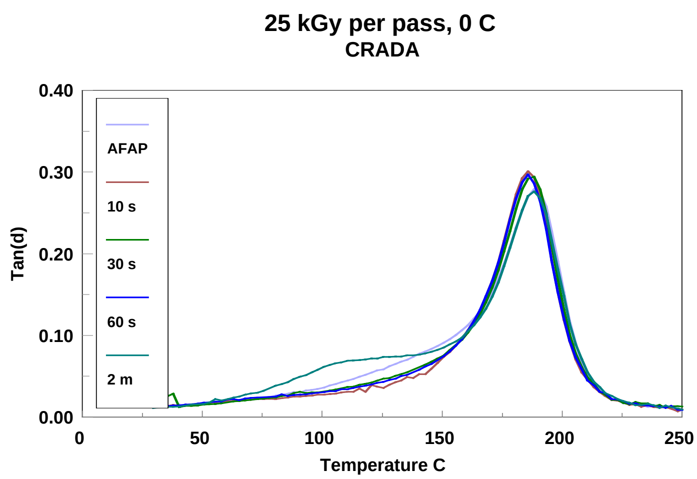

Figure 1. Effect of time delay between passes for irradiation at 25 kGy per pass, 0 C

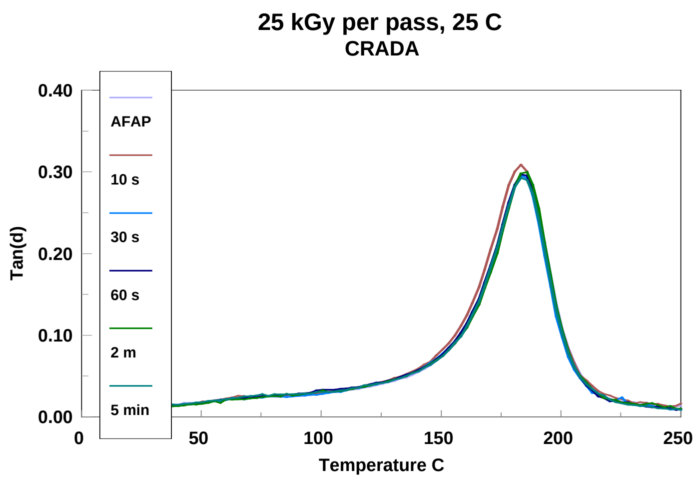

Figure 2. Effect of time delay between passes for irradiation at 25 kGy per pass, 25 C

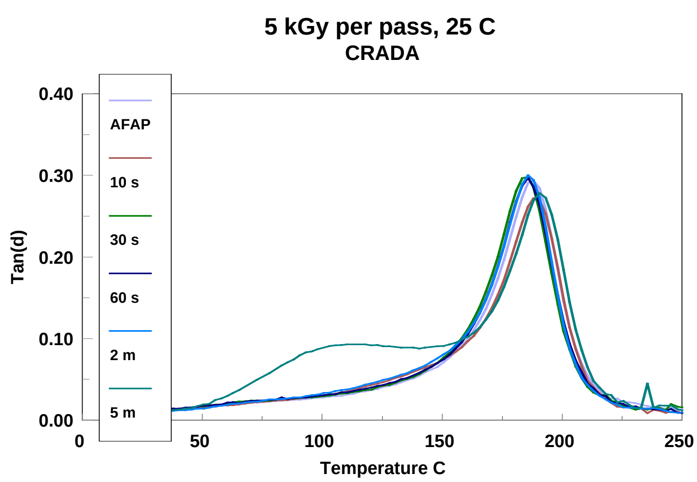

Figure 3. Effect of time delay between passes for irradiation at 5 kGy per pass, 25 C

4. Materials & Processing

The CRADA Materials & Processing IPT is currently exploring several strategies for maximizing the fracture toughness of EB curable cationic epoxy resins and composites. These strategies include chain extending the polymer backbone to reduce the cross-link density and the brittleness of the cured resin system, and interleaving prepregs with thermoplastic materials. Additionally, a wide variety of tougheners are being evaluated including those that have previously resulted in toughening thermally cured, brittle epoxy resins. These toughening options will be screened for their effectiveness by conducting neat resin fracture toughness testing followed by composite testing.

4.1. Materials & Processing IPT Mission

The goal of the M&P IPT is to develop improved EB curable epoxy resin systems and processing methods for producing EB cured composites which meet or exceed the thermomechanical properties of autoclave cured, carbon fiber reinforced composites containing toughened epoxy resins 977-2 or 977-3, or untoughened 3501-6 epoxy (interim target only). To achieve this goal particular emphasis will be placed on overcoming the toughness limitations of the current EB resins without impairing the balance of modulus, strength, thermal stability, and processibility.

4.2. Technical Accomplishments

Several strategies are currently being evaluated for toughening EB curable cationic epoxy resin systems. These toughening approaches include chain extension of the epoxy resin backbone; interleaving of prepregs with thermoplastic materials; high epoxide equivalent weight resins; flexible epoxy resins; thermoplastic particles; inorganic particles; reactive and non-reactive thermoplastic polymers and rubbers; core shell materials; dendritic hyperbranched polymers; acrylate resins; and uniquely shaped epoxy resins. The goal of this activity is to identify options that increase the fracture toughness properties of neat epoxy resins and composites while achieving a satisfactory balance of thermal and mechanical properties.

Preliminary screening of neat resin plaques incorporated with candidate toughening approaches is ongoing. Various epoxy/toughened blends are being formulated using Tactix 123/3 phr CD1012 initiator as the baseline epoxy resin. Following the preparation of these blends, neat resin plaques will be electron beam cured and tested via ASTM D 5045 to determine their respective K_{1c} fracture toughness properties. The top candidates from this evaluation will be further optimized in terms of thermal and mechanical performance, then combined with carbon fiber for composite testing.

5. Project Management

The CRADA project management team exists to serve the technical team and ensure that the various technical activities are coordinated/integrated, and are executed with proper fiscal and temporal discipline. The project team is expected to demonstrate satisfactory progress toward top-level milestones.

5.1. Status of Milestones and Deliverables

Progress toward achieving the project objectives is measured against the milestones and deliverables described in Table 2. The milestones and deliverables are themselves reviewed, on a semi-annual basis, for their appropriateness as indicators of progress toward achieving the project objectives. The first milestone due is the completion of fiber-resin interface chemistry studies on incumbent[1] materials, due in April of 2000. Current projections are that this milestone will be met ahead of schedule.

Table 2. Project Milestones and Deliverables

Milestone	***Metric***	***Deliverable***	***Date***
Fiber-resin interface chemistry studies on incumbent materials complete	Adsorption, deactivation of carbon fiber surface chemistry at specified EB processing conditions quantified & documented	Milestone report including data, analysis, conclusions, recommendations	4-19-00
Interface characterization of incumbent materials complete	Characterization matrix fully populated, ***OR*** source of ILSS deficiency understood	Milestone report including data, analysis, conclusions, recommendations	10-19-00
Incumbent materials processing development complete	Processing matrix fully populated with incumbent materials data	Milestone report including data & processing methods, analysis, conclusions, recommendations	10-19-00
EB compatible fiber surface treatments, chemical agents, and/or resins developed	Coupon data indicating ILSS increased ≥ 15% compared to baseline*	Milestone report including data, analysis, conclusions; IP documented & protected	4-19-01
Composite system optimization complete	Coupon data indicating ILSS increased ≥ 20% compared to baseline* ***OR*** composite optimization matrix fully populated	Final report including data, analysis, conclusions, recommendations; IP documented & protected	4-19-02
Processing development complete	Coupon data indicating ILSS increased ≥ 25% compared to baseline* ***OR*** processing matrix fully populated with new materials data	Final report including data, analysis, conclusions, recommendations; IP documented & protected	4-19-02

* Baseline is best EB processed material properties demonstrated with incumbent materials (same base resin and fiber) before new materials or processes are developed.

[1] "Incumbent" materials are materials that already existed upon commencement of the project.

5.2. Budget Tracking

Tables 3 and 4 below indicate the budget status for funds accounted to and expended by ORNL. Table 3 details quarterly budget status and projections for funds from all sources, including the Department of Energy, other government agency sponsors, and funds-in from industrial partners. Table 4 details quarterly budget status and projections for Department of Energy funds.

The project presently is considerably underspent compared to the original budget baseline. This is primarily attributable to the delay in executing the subcontract with Michigan State University, and does not alarm the project management team. The spend rate is now meeting expectations. Furthermore, revised cost projections show improved cash flow, providing greater flexibility and agility for adjusting resource allocations as the project evolves.

Table 3. ORNL Budget Status, All Funds

Year	Description[2]	1Q	2Q	3Q	4Q	Total	Carryover
FY99	Initial deposit sched			$207,500	$0	**$207,500**	
	Revised deposit sched			$183,107	$48,544	**$231,650**	
	Initial cost ests			$111,807	$59,107	**$170,914**	$36,586
	Revised cost ests			$27,405	$61,764	**$89,169**	$142,481
	Actual costs			$27,405	$61,764	**$89,169**	$142,481
FY00	Initial deposit sched	$165,000	$0	$175,000	$0	**$340,000**	
	Revised deposit sched	$120,000	$131,068	$183,107	$0	**$434,175**	
	Initial cost ests	$84,985	$77,786	$133,684	$79,884	**$376,339**	$247
	Revised cost ests	$132,979	$127,479	$129,679	$119,261	**$509,398**	$67,258
	Actual costs						
FY01	Initial deposit sched	$165,000	$0	$125,000	$0	**$290,000**	
	Revised deposit sched	$153,981	$72,816	$134,563	$0	**$361,359**	
	Initial cost ests	$77,557	$70,857	$70,156	$71,654	**$290,224**	$23
	Revised cost ests	$112,060	$99,531	$98,117	$89,088	**$398,795**	$29,823
	Actual costs						
FY02	Initial deposit sched	$157,500	$0			**$157,500**	
	Revised deposit sched	$178,252	$0			**$178,252**	
	Initial cost ests	$80,342	$77,181			**$157,523**	$0
	Revised cost ests	$105,750	$102,325			**$208,075**	$0
	Actual costs						
Totals	Initial deposit sched	$487,500	$0	$507,500	$0	**$995,000**	
	Revised deposit sched	$452,233	$203,883	$500,777	$48,544	**$1,205,437**	
	Initial cost ests	$242,884	$225,824	$315,647	$210,645	**$995,000**	
	Revised cost ests	$350,789	$329,335	$255,201	$270,113	**$1,205,436**	
	Actual costs	$0	$0	$27,405	$61,764	**$89,169**	

[2] "Initial" refers to deposit schedules and cost estimates in the project proposal. "Revised" refers to deposit schedules and cost estimates that have been updated with information current as of 10-15-1999. Revised cost projections are updated with actual cost numbers for completed fiscal quarters.

Initial cash flow projections differ from current projections for the following reasons.

- Air Force Research Laboratory sponsorship valued at $150k was not included in the initial projections.
- Army Research Laboratory sponsorship is presently in negotiation. A probable value of $105k in government years FY00 – FY02 is included in current estimates.
- Initial plans anticipated $53k expenditure in FY99 associated with the Michigan State University subcontract. The delay in executing that contract deferred FY99 subcontract expenses into FY00. This deferment is a major contributor to the large difference in projected and actual carryover from FY99 to FY00. ORNL staff efforts that required interactions with MSU were also deferred, further increasing the FY99 carryover.
- Initial plans did not account for program office fees levied against DOE funds, nor for mandated Federal Administrative Charges levied against all other contributions. These levies have been programmed into the revised budget.

Table 4. ORNL Budget Status, DOE Funds

Year	Description	1Q	2Q	3Q	4Q	Total	Carryover
FY99	Initial deposit sched			$125,000		**$125,000**	
	Revised deposit sched			$120,000		**$120,000**	
	Initial cost ests			$51,807	$51,807	**$103,614**	$21,386
	Revised cost ests			$19,943	$58,049	**$77,992**	$42,008
	Actual costs			$19,943	$58,049	**$77,992**	$42,008
FY00	Initial deposit sched	$125,000		$125,000		**$250,000**	
	Revised deposit sched	$120,000	$0	$120,000	$0	**$240,000**	
	Initial cost ests	$70,901	$65,702	$67,902	$66,801	**$271,306**	$80
	Revised cost ests	$84,353	$34,557	$69,217	$68,261	**$256,388**	$25,620
	Actual costs						
FY01	Initial deposit sched	$125,000		$125,000		**$250,000**	
	Revised deposit sched	$120,000	$0	$120,000	$0	**$240,000**	
	Initial cost ests	$66,642	$61,943	$59,742	$61,744	**$250,071**	$9
	Revised cost ests	$81,445	$35,971	$63,581	$61,863	**$242,859**	$22,761
	Actual costs						
FY02	Initial deposit sched	$125,000				**$125,000**	
	Revised deposit sched	$120,000	$0			**$120,000**	
	Initial cost ests	$66,700	$58,309			**$125,009**	$0
	Revised cost ests	$73,058	$69,702			**$142,760**	$0
	Actual costs						
Totals	Initial deposit sched	$375,000	$0	$375,000	$0	**$750,000**	
	Revised deposit sched	$360,000	$0	$360,000	$0	**$720,000**	
	Initial cost ests	$204,243	$185,954	$179,451	$180,352	**$750,000**	
	Revised cost ests	$238,856	$140,230	$152,741	$188,172	**$720,000**	
	Actual costs	$0	$0	$19,943	$58,049	**$77,992**	

The industrial partners' in-kind contributions are generally on schedule in accordance with the project plans and needs.

5.3. Accomplishments

- The CRADA was signed by all parties as of April 12, 1999, and officially commenced on April 20, 1999.
- Conducted a press conference with industrial partners and sponsors, announcing commencement of CRADA, on April 20, 1999.
- Conducted CRADA kick-off meeting in Oak Ridge, TN, April 21 – 22, 1999.
- Reviewed rights and responsibilities of CRADA partners and sponsors with all CRADA team members.
- Conducted a CRADA progress meeting in Long Beach, CA, on May 25, 1999, scheduled in coordination with the annual SAMPE spring meeting that is attended by several CRADA team members.
- Organized the technical team into three integrated project teams (IPT's) addressing adhesion, irradiation, and materials & processing.
- Initiated weekly teleconferences at 15:30 eastern time on Thursdays. Each of the technical IPT's teleconferences once per month. A leadership IPT, consisting of the technical IPT leaders and the project managers, teleconferences on the remaining Thursday. The leadership IPT is the "project steering committee" that coordinates project activities.
- Arranged for secure, password-protected, data storage on a website, referred to as CITIS, hosted by Boeing. This site serves as a "common project hard drive" that can be accessed by project participants from any computer with worldwide web access.
- ORNL executed a contract with Michigan State University to perform specified testing and analysis.
- Entered discussions with Army Research Laboratory regarding their stated desire to join the CRADA team.

5.4. Issues

- CITIS database is accessible only by US citizens. One partner, Acsion Industries, employs no US citizens. The data will be provided to Acsion by regular electronic mailings and periodically copying all data to CD which will be sent to Acsion.
- The CRADA team includes several foreign nationals. Compliance with laws restricting the communication of technical information to foreign nationals reduces communication effectiveness among the CRADA team, but is a manageable inconvenience.
- Legal hurdles to contract execution delayed commencement of work by Michigan State University until 8-1-1999. Fortunately the delay does not appear to jeopardize project milestones.

5.5. Scheduled Events

- Semi-annual CRADA meeting, 10-25-1999, hosted by STERIS Isomedix, Chicago.

Appendix

List of Acronyms

AFRL	*Air Force Research Laboratory*
ARL	*Army Research Laboratory*
ASTM	*American Society for Testing and Materials*
CRADA	*Cooperative Research and Development Agreement*
DC	*Direct Current*
DOE	*Department of Energy*
EB	*Electron-Beam*
ILSS	*Interlaminar Shear Strength*
IP	*Intellectual Property*
IPT	*Integrated Project Teams*
ITS	*Interfacial Test System (microindentation method)*
M&P	*Materials & Processing*
MSU	*Michigan State University*
ORNL	*Oak Ridge National Laboratory*
XPS	*X-ray Photoelectron Spectroscopy*