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Abstract

Polymer-matrix composite material and structural adhesive repair and manufacturing have significant environmental costs. These costs were recently documented based on current and anticipated future Department of Defense (DOD) use of these materials. The principal issues for reducing the environmental impact and its associated cost are (1) reduction in hazardous waste by eliminating shelf-life limitations, (2) reduction in nitrogen oxides by replacing global heating of the part with localized heating, (3) reduction in volatile organic compound (VOC) emissions by accelerated curing and containment, and (4) reduction in hazardous waste by minimizing production debris through processing step management. The predicted reduction in hazardous waste, which affects both raw materials and waste-disposal costs, is 78% for composite materials and 95% for adhesives. Nitrogen oxides and VOC emissions can be reduced by 100% and 50% by replacing autoclave curing with radiation curing. Electron-beam (E-beam) curing has successfully been applied to E-beam-curable prepegs, adhesives, and vacuum-assisted resin transfer molding (VARTM) resins while maintaining process-specific viscosities and application-specific thermal performance. For the first time, there is credible evidence that E-beam-curable resin systems can be formulated to have sufficient toughness while maintaining other required process and performance criteria. In this work, both free radically and cationically cured E-beam resin systems have been formulated.

Acknowledgments

This research was supported in part by the U.S. Department of Defense (DOD), through the Strategic Environmental Research and Development Program (SERDP). The authors gratefully acknowledge the assistance of Diane Kukich, editorial coordinator at the University of Delaware, Center for Composite Materials (UD-CCM), in editing this report.

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Table of Contents

List of Figures

List of Tables

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1. Introduction

The electron-beam (E-beam) accelerator is a source of ionizing radiation that can generate ionic species, free radicals, and molecules in excited states capable of initiating and sustaining polymerization. Depending on the chemistry of the resin system being irradiated, polymerization can occur by free-radical as well as ionic mechanisms. The polymerization of acrylic/methacrylic systems, maleic and fumaric polyester resins, and thiolene systems proceeds via free-radical mechanisms without initiators. E-beam-induced polymerization of nitroethylene proceeds via anionic mechanisms, and epoxies are polymerized cationically with the appropriate catalyst under E-beam irradiation. Of these systems, free-radical-cured systems based on acrylate and methacrylate functionality and cationically cured epoxies catalyzed using diaryliodonium or triarylsulfonium salts like diphenyliodium hexalfluoroantimonate or triarylsulfonium hexalfluoroantimonate have shown the most promise for composites applications. Acrylate/methacrylate-based free-radical-cured systems have been studied extensively. These systems provide high reactivity, and they have good stiffness, good control over processing viscosity, and very long shelf life.

Among the shortcomings associated with such systems are high cure shrinkage (8–20%), the potential for oxygen inhibition, and low glass transition (T_g) relative to high-temperature thermally cured epoxies. Cationically cured epoxies require a photoinitiator to enable polymerization. Cationically cured epoxies offer low shrinkage; exhibit high T_g; are not inhibited by oxygen; and do not require curing agents, as do their thermally cured counterparts. On the other hand, cationic systems tend to cure more slowly than acrylate/methacrylate systems, and the photoinitiators are easily poisoned by nucleophilic contaminants, which can often be found on the surfaces of reinforcing materials or as part of epoxy resin compositions.

In this work, both free radically and cationically cured E-beam resin systems are being formulated. Cationic systems have been employed primarily for prepreg resin formulation, as discussed in section 2, while free-radical systems based on interpenetrating polymer networks have been used to formulate vacuum-assisted resin transfer molding (VARTM) resins and adhesives, as discussed in sections 3 and 4, respectively.

2. E-Beam Prepreg Resin Formulation

2.1 Introduction to E-Beam Prepreg Resin Formulation. Cationic resin formulation efforts follow a basic building-block approach to develop new toughened E-beam-curable resins for composite matrix materials. Sufficient quantities of the new resin are produced to develop chemical and mechanical properties, evaluate repair on an aircraft structure, and demonstrate the producibility of one structural component.

Over the past 5 years, hundreds of model formulations of E-beam-curable resins have been prepared. Using epoxy backbone and functionality, the structure/property relationships of E-beam-curing resins have been similar to those of thermal-curing resins. In addition, over 75 modifiers have been tried, with little success in improving the property of the resins. With thermoplastic and elastomeric toughening, either single or multiple phases, the modified resins still exhibit the high cross-link density characteristics of the epoxy continuous phase.

It is believed that chain extension of the epoxy continuous phase is critical to enable the modifiers to nucleate their energy dissipation. This has not yet been attempted with E-beam-curing resins. It is important that a ductile fracture pattern be achieved. It is also important to lower the cross-link density to allow for plastic flow and to raise the composite interlaminar shear strength by increasing shear bonding.

The primary function of modifiers is to toughen the resin. The addition of modifiers to the rigid extenders should not reduce the resin modulus at elevated temperature. For cationic curing epoxies, the modifier requirements are as follows:

- an epoxy-compatible low-molecular-weight oligomer or monomer;

- a nonnucleophillic, aromatic, or heterocyclic ring in the backbone; and
- stability at ambient temperature.

The modifier can be either a difunctional coreactant with a very high percent of reactivity or a multifunctional modifier.

The objective of this task is to reformulate the E-beam-curing cationic resin, CAT-M, and associated adhesives to extend the toughness, durability, and thermal performance to meet 250 °F/wet service for aircraft repair and remanufacturing. To date, cationic resins for prepreg applications meet T_g and modulus goals but provide very poor interlaminar strength and toughness.

All matrix resins and adhesives are modified epoxies (a blend of four epoxies—Dow 742, 556, 332, and 439) cured using diphenyliodonium hexaflouroantimonate cationic catalyst. The first stable species, a Bronsted acid of $H^+ SbF_6^-$ along with H^+F^-, is believed to be responsible for breaking the epoxy ring, ionizing the hydroxyl, and propagating via homopolymerization, which is the same as thermal cure (Figure 1).

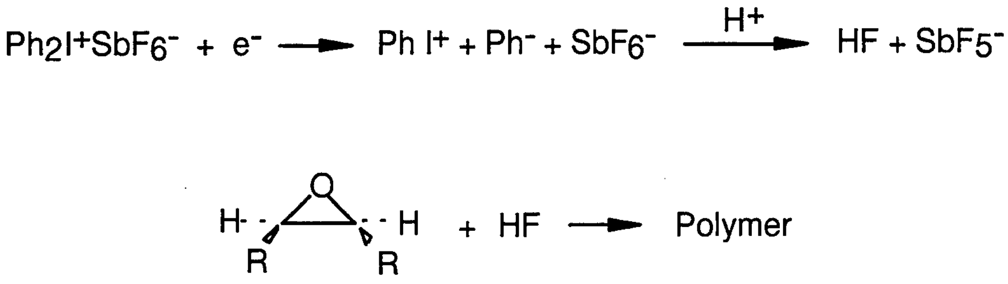

Figure 1. Example of Cationic-Based Epoxy Initiation Reaction.

Although the propagation steps (Figure 2) and the chemistry are the same as in thermal cure, the mechanism to cure to a high level of completion in a solid state with electronically excited molecular species is unknown.

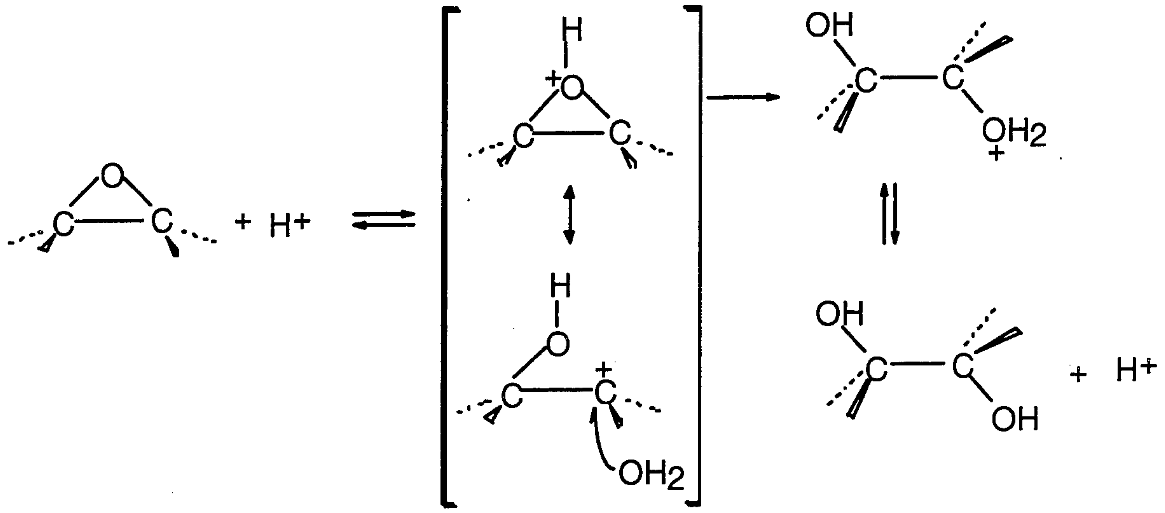

Figure 2. Example of Cationic-Based Epoxy Propagation Reaction.

Trace water in the raw material can result in a 1,2 diol or glycol, which can react with groups to form a highly cross-linked brittle matrix. Cationic resins need to be toughened before they are of practical value, especially for aircraft applications. The most common way to achieve toughening is to coreact alcoholic hydroxyls in situ during curing. However, the usual reduction of modulus and T_g will occur. As with thermal curing, a balance between toughness and T_g or modulus is needed. Although the propagation mechanism is the same as in thermal cure, radiation-induced excited molecular intermediates drive the reaction to completion in the solid state. Thermal homopolymerization cures follow classic time, temperature, transformation (TTT) diagrams, where T_g is no more than 20 °C higher than T_{cure}. However, E-beam curing totally violates the classic TTT diagrams and T_g can routinely be as much as 150 °C higher than T_{cure}.

2.2 E-Beam Prepreg Resin Selection Criteria. The following are the criteria used for prepreg resin downselection. Studies found that each resin formulation had to pass all the tests indicated. If one test failed, no further testing was conducted for that particular formulation.

(1) Radiation Cure Properties (determined from gamma calorimetry):

- Gelation < 40 kGy. All of the cationic-initiated epoxies that were studied evidence gelation at doses less than 15 kGy.

- Curing dose < 120 kGy. Curing dose depends on the type of the initiator used.

(2) Dynamic Mechanical Analysis (DMA):

- DMA modulus > 350 ksi (2.4 GPa). The modulus of most epoxy resins is about 450 ksi (3.1 GPa). However, the modulus slowly drops off as temperatures approach the T_g.

- T_g > service temperature + 30 °C.

(3) DMA After 2 hr at 177 °C Postcure:

- Postcure DMA modulus < 10% different from DMA modulus prior to postcure. This test is to gauge the degree of cure from the initial E-beam curing. A difference between the two values of greater than 10% indicates that significant residual uncross-linked species remained after the initial cure.

(4) DMA After 24-hr Water Boil:

- Weight gain < 3%.

- DMA modulus after water boil < 10% different from DMA modulus prior to conditioning.

- Wet T_g > service temperature + 20 °C.

2.3 E-Beam Prepreg Resin Formulation Approach. The goal of this formulation effort was to improve the toughness of baseline resins. Two types of toughening agents were added to the epoxy formulations: (1) polyethersulfone (PES) and (2) thermoplastic acrylic. The two best formulations, T-11 and T-14, were selected for further evaluation based on the gamma calorimetry and DMA data. Gamma calorimetry was used to determine the gel point. The E-beam dose at which the temperature begins to rise is defined as the gel point. DMA was used to determine the T_g. Downselected resins had to meet the requirements listed in section 2.2 prior to toughness evaluation.

A series of nine model formulations was investigated (Table 1), including a dendrimer (Boltorn EZ, obtained from YLA, Inc.) that is an epoxy-terminated polyol with a viscosity of about 25,000 cps at ambient temperature. Reactive liquid rubbers such as Hycar rubber and related tougheners provide a neat balance of properties if precipitated during cure into a second phase with particle size in the 1–5 μm range. In E-beam curing, the precipitation of the rubbery phase was not achievable due to instant gelation. Therefore, the second-phase emulsion must be accomplished in the liquid state prior to cure. Several epoxies with varying polarities, with and without modifiers, were formulated with the dendrimer and screened via ultraviolet cure. All formulations cured to clear single-phase castings. The model expected to have the best chance of second-phase formation, M-25, was E-beam-cured along with M-24 as a control. Hydrogenated Bis-A (1510), which results in cycloaliphatic structures, accelerates reactions compared to its nonhydrogenated counterpart (332). However, all of the experiments performed to date indicated that there was no phase separation in these samples.

The cured Model M series resins were tested by DMA, as shown in Table 2. M-22 was left in the oven overnight and gelled; no DMA data were obtained. Comparing M-21 and M-23 with controls (M-11, M-13, and M-16), the multifunctional chain extender used in M-21 looks very encouraging. Past models with difunctional reactants indicated incomplete reaction. Although the initial modulus and T_g are lower for M-21 than for the controls, a 50% retention of modulus at higher temperature, 150 °C, was observed for M-21. The modifier used in M-21 warrants further investigation. This modifier can be added to prepreg and adhesive resins but will not be used for the VARTM resins because of its excessively high viscosity.

Table 1. Model Formulations

M Series	11	13	16	21	22	23	24	25
332	100	94	100	60	70	80	—	—
556	—	—	—	—	—	—	70	70
1510	—	—	—	—	—	—	30	30
Chain extender-1 (GP)	—	—	—	15	—	—	—	—
Chain extender-2 (GP)	—	—	—	—	30	20	—	—
Dendrimer Boltorn-EZ	—	—	—	—	—	—	—	8
TBBPA	5	—	—	—	—	—	—	—
542	—	6	—	—	—	—	—	—
DPI-1	2.8	2.8	2.8	2.5	2.5	2.5	3	3

Notes: GP = No Significance. Nomenclature only.
TBBPA = Testbromobisphenol A.
DPI-1 = Diphenyliodiumhexaflouroantimonate.

Table 2. DMA Data

M Series	11	13	16	21	23	24	25
T_g (°C)	170	170	175	140	150	150	125
Temperature at 50% of modulus	143	118	96	152	107	142	125
Flexural modulus (ksi) [GPa]	261 [1.8]	305 [2.1]	345 [2.4]	256 [1.77]	147 [1.0]	207 [1.4]	262 [1.8]

The difunctional chain extender used in M-23 reduces the initial modulus by 50%. This model will be eliminated unless significant toughening is observed in the resins. M-24 and M-25, with 8% dendrimer incorporation, were poorer in elevated-temperature properties. The results showed the expected plasticization from the modifier. The dendrimer did not precipitate as a second phase. The latest data indicate that the key to obtaining a successful precipitation of dendrimer lies in the blending of the single-phase epoxies used, including not only the types of epoxies but also the proportion of each epoxy in the blend. Two blends of single-phase epoxy with the modifier precipitated out as a second phase after curing are currently being investigated and show promise. These resins will be E-beam-cured and evaluated.

As expected, both types of thermoplastic modifier reduce the rate of curing, although thermoplastic (TP) acrylic appears to affect it less. TP acrylic is a micropulverized powder added like a filler and is a dispersed second phase with a partially solubilized and bonded particle interface. It did not chemically inhibit curing. Both T-11 and T-14 resins contain TP acrylic as a toughening agent. The DMA spectroscopy results for the two resins cured at 200 kGy are shown in Figures 3–6 for dry and wet (48-hr water boil) T-11 and dry and wet T-14. Dry T_g from E* for both systems is around 200 °C; wet T_g is about 170 °C. However, the DMA curves for T-14 are much better than for T-11, especially the much smaller β peak from the tan δ curve of T-14. The β peak in the DMA is likely the low-molecular-weight components produced from the low-dose (<10 kGy) E-beam, which was used to prevent cracking of the sample during cure. Such short segmental chains created during the low-dose pass affect the final mechanical properties. However, in the case of composite curing, the exotherm during curing will likely dissipate through the carbon fibers, which should prevent the low-molecular-weight components, such as the β peak, from forming.

2.4 E-Beam Prepreg Resin Formulation Results. The resins that met the downselection criteria were further evaluated for initial mechanical properties. The dynamic moduli of the neat resins were also measured in a Rheometrics RDS-II dynamic mechanical spectrometer from the torsion of rectangular coupons. One set of coupons of each resin type was conditioned in a humidity cabinet set at 66 °C/95% relative humidity until saturated with moisture. Another coupon set of each resin type was desiccated prior to testing. The tests on dry and wet specimens were run at a scan rate of 5 °C/min. From plots of the data (Figures 3–6), it is apparent that the only unambiguous measure of T_g temperature can be obtained from the tan δ curves. The T_g's from the tan δ curves for dry and wet specimens of T-11 are 230 °C and 218 °C, respectively. The corresponding dry and wet T_g's for T-14 are 220 °C and 205 °C, respectively; they are very similar to the aforementioned DMA data. The wet T_g is therefore only slightly lower than the corresponding dry T_g for each material, although the shoulder in the tan δ curves becomes more

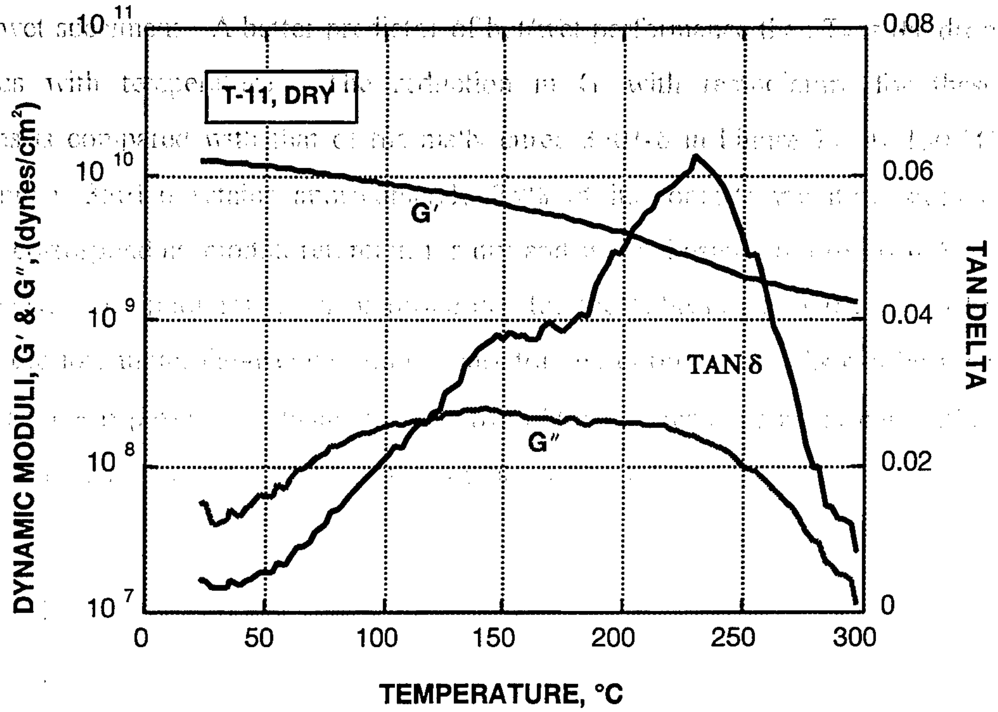

Figure 3. Dynamic Mechanical Spectroscopy Results for Dry T-11 Resin.

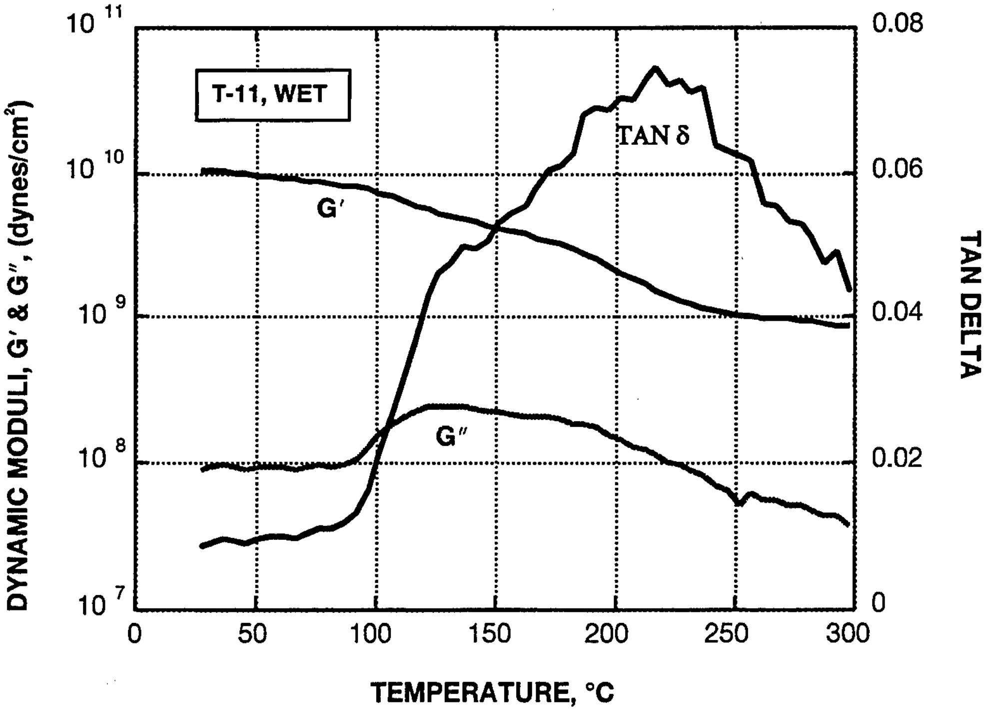

Figure 4. Dynamic Mechanical Spectroscopy Results for Wet T-11 Resin.

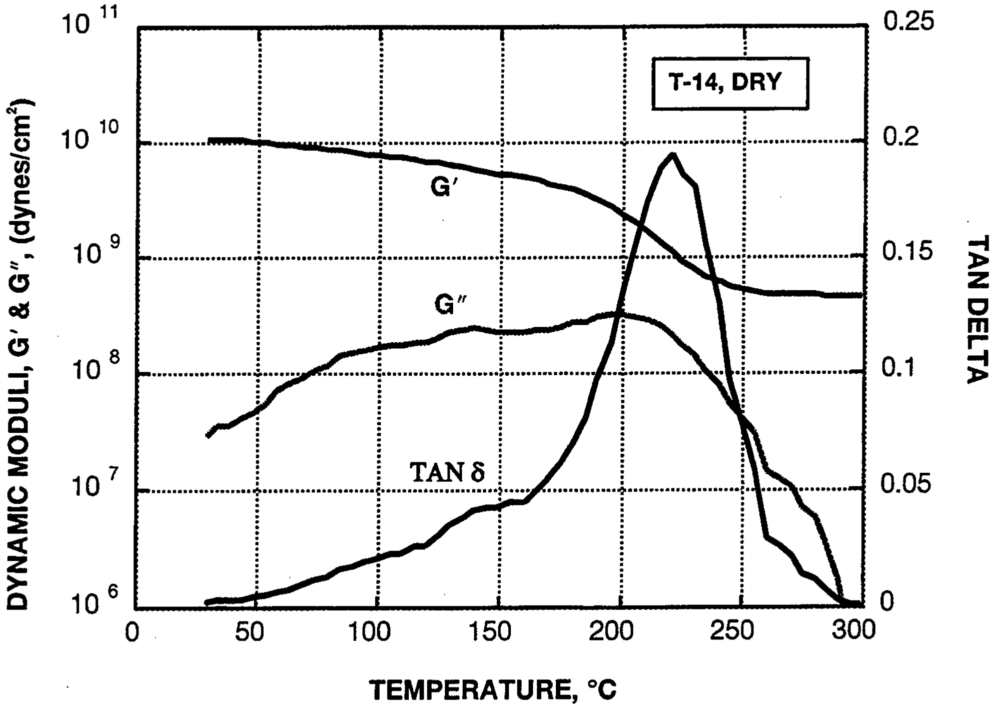

Figure 5. Dynamic Mechanical Spectroscopy Results for Dry T-14 Resin.

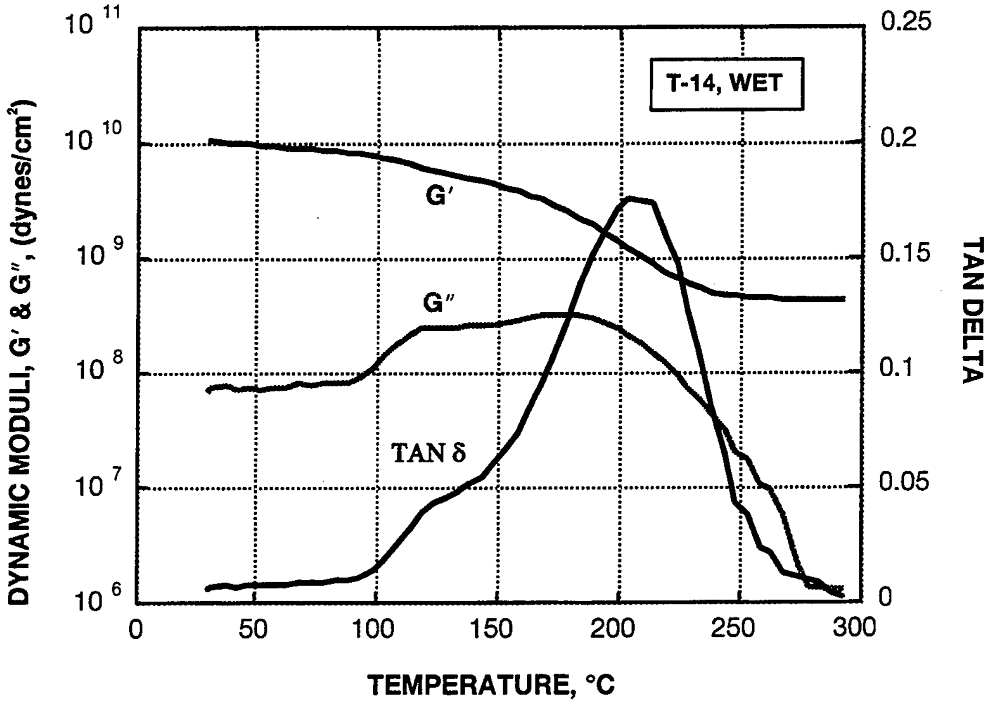

Figure 6. Dynamic Mechanical Spectroscopy Results for Wet T-14 Resin.

pronounced in the wet specimens. A better predictor of hot/wet performance than T_g is the drop in storage modulus with temperature. The reduction in G' with temperature for these E-beam-cured resins is compared with that of thermally cured 3501-6 in Figure 7. At 150 °C (300 °F), for example, 3501-6 retains approximately 75% of its room-temperature storage modulus, while the corresponding moduli retention for dry and wet E-beam-cured resins is 50% and 42%, respectively. The poor retention of properties for the E-beam-cured resins can be attributed again to the low-molecular-weight components formed during cure. As can be seen from the RDS curves, the β peaks are similar to those from DMA. This experiment correlating the storage modulus with temperature is repeated for composite specimens.

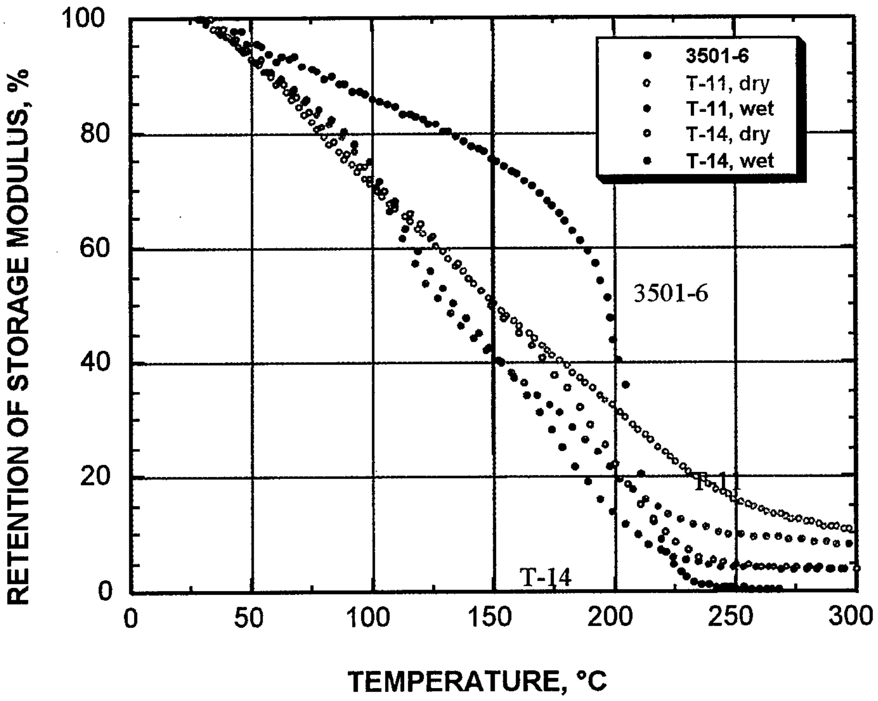

Figure 7. Retention of Dynamic Storage Modulus of Neat T-11, T-14, and 3501-6 at Various Temperatures.

2.4.1 Resin Density and Shrinkage. The resin density and shrinkage of T-14 are shown in Table 3. The difference in the cured and uncured resin density is negligible. The T-14 resin did not shrink but expanded slightly after curing at an E-beam dose of 200 kGy. Similar behavior

Table 3. Physical Properties of T-14 Resin

Density (g/ml)	Condition	Volumetric Shrinkage (%)	Linear Shrinkage (%)
1.2124	Uncured	—	—
1.2121	E-beam: 200 kGy	−0.025	−0.008
1.2123	E-beam: 200 kGy thermal: 2 hr at 200 °C	−0.008	−0.003

was observed for the resin postcured at 200 °C for 2 hr after E-beam curing. The postcure was conducted to relieve residual stresses caused by the high-energy E-beam curing.

2.4.2 Differential Scanning Calorimetry. A cross section of the resin plaques, T-11 and T-14, revealed a variation in color from the surface (reddish brown) to the midplane (yellowish brown).. Samples from both of these areas were analyzed by DSC. The sample from the T-11 interior of the plaque did not display any exotherm on heating in nitrogen up to 300 °C; however, the sample from the surface of the plaque displayed an exotherm (~3.3 mcal/mg) beginning at about 100 °C, indicating an advancement of cure with the thermal energy supplied. Similar results were observed for the T-14 sample. The center of the T-14 appeared to be fully cured when analyzed by DSC; however, the surface of the T-14 panel underwent additional cure in the DSC, exhibiting an exotherm of approximately 9.5 cal/g and peaking at about 135 °C. The color of the surface specimen also changed from reddish brown to yellow at the end of the run. These results indicate a nonuniform cure through the thickness of the as-received plaque, with the degree of cure higher in the interior than at the surface.

2.4.3 Fracture Toughness. The fracture toughness of the neat resin was determined from compact tension tests in accordance with American Society for Testing of Materials (ASTM) E399-83. Test specimens with dimensions shown in Figure 8 were sectioned from the resin plaque, and notches were machined as indicated. One batch of specimens was then dried for a minimum of 48 hr in a vacuum oven at 40 °C and tested under ambient conditions. Two more batches of specimens were isothermally aged at 121 °C—the T-11 for 54 hr, the T-14 for 102 hr, and both for 168 hr—and tested at room temperature. At least five specimens were tested for the

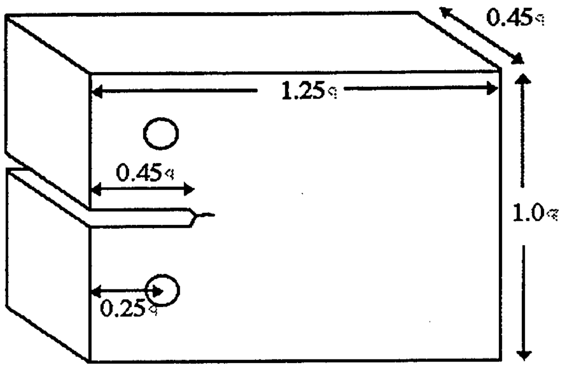

Figure 8. Schematic of Compact Tension Test Specimen (Dimensions in Inches).

unaged baseline and each aging condition, and data were collected for four crack extensions in each specimen to give a minimum of 20 measurements of fracture toughness for each specimen batch. The test results are shown in Tables 4 and 5 for T-11 and T14, respectively. The data are fairly consistent and indicate a slight increase in fracture toughness with aging, possibly due to the additional thermal cure that occurs under these conditions. The fracture toughness of the unaged T-14 material is approximately 40% higher than that of unaged T-11.

2.4.4 Flexural Properties. Flexural test specimens were sectioned from the T-11 plaque with faces perpendicular to the x and z directions. The latter specimens bowed after being sectioned, suggesting that cure shrinkage at the midplane of the plaque is greater than that at the surface (also observed in DSC studies). The results of flexural tests on as-fabricated (and vacuum dried) specimens, performed under ambient conditions, are summarized in Table 6. Although the midplane of the plaque appears to have a higher degree of cure than the surface, the results from Table 6 indicate no significant differences in the flexural properties of the two regions. However, the properties appear to be lower than the corresponding flexural stiffness and strength of neat thermally cured 3501-6 epoxy.

One batch of T-14 flexural test specimens was conditioned at 66 °C/95% relative humidity (RH) until saturated with moisture, while a second set was desiccated prior to testing.

Table 4. Fracture Toughness of T-11 Resin

Specimen No.	Conditioning	Fracture Toughness (psi.in$^{0.5}$)				Average (±s.dev.)
		KQ_1	KQ_2	KQ_3	KQ_4	
T-11-15	Dried 48 hr at 40 °C in vacuum oven	265	271	282	255	245 ± 30
T-11-17		285	240	277	257	
T-11-20		215	229	301	279	
T-11-12		221	232	228	224	
T-11-14		215	211	207	204	
T-11-02	Aged 54 hr at 121 °C in air	271	285	291	281	278 ± 12
T-11-08		284	287	287	270	
T-11-19		254	273	278	269	
T-11-01		274	278	276	258	
T-11-04		262	289	302	291	
T-11-03	Aged 168 hr at 121 °C in air	292	297	299	301	293 ± 15
T-11-10		273	286	290	284	
T-11-11		281	294	294	288	
T-11-13		302	307	323	295	
T-11-16		246	290	297	298	
T-11-18		309	309	301	285	

Three-point flexural tests were conducted at ambient temperature and 82 °C for both wet and dry T-14 specimens, with a minimum of six specimens for each material/test condition. The results are summarized in Figures 9 and 10. The flexural strengths are not as high as expected (or observed for thermally cured epoxies such as 3501-6), which may be due to the significant void content of the neat resin plaques. The flexural stiffness of the neat resin shows a significant decline with temperature at relatively low temperatures. For example, the flexural stiffness of dry T-14 is 410 ksi at room temperature; this modulus drops to 79% and 57% of the room-temperature values, respectively, at temperatures of 82 °C (180 °F) and 104 °C (220 °F).

2.5 E-Beam Prepreg Resin Conclusions. Incorporation of dendrimers into a single-phase epoxy was successful. The dendrimer precipitated in the epoxy mixture as a second phase, resulting in resin with greater ductility and toughness than conventional one-phase epoxy. Investigations of model formulations will continue, in an effort to optimize dendrimers and chain

Table 5. Fracture Toughness of T-14 Resin

Specimen No.	Conditioning	Fracture Toughness ($psi.in^{0.5}$)				Average (±s.dev.)
		KQ_1	KQ_2	KQ_3	KQ_4	
T-14-05	Dried 48 hr at 40 °C in vacuum oven	326	340	365	398	342 ± 19
T-14-11		330	340	347	327	
T-14-14		331	349	359	368	
T-14-17		328	340	350	361	
T-14-18		334	337	337	354	
T-14-19		330	304	334	313	
T-14-02	Aged 102 hr at 121 °C in air	425	373	384	378	378 ± 20
T-14-03		360	396	391	394	
T-14-04			316	355	384	
T-14-09		397	401	367	374	
T-14-13		359	365	377	385	
T-14-21		377	378	381	382	
T-14-01	Aged 168 hr at 121 °C in air	328	375	377	371	370 ± 15
T-14-06		351	360	353	381	
T-14-07		379	371	388	403	
T-14-08		363	366	368	377	
T-14-12			355	371	374	
T-14-15		367	366	386	388	

formulations, the most promising one will be selected for further development. This formulation will be used to prepreg AS4 carbon fibers at YLA, Inc. A small run (10 lb) of prepreg will be produced for initial evaluation of the prepreg quality and E-beam processing cycles. Additional prepreg will be manufactured for full characterization of the final prepreg system. The characterization will include physical and mechanical analyses at ambient and elevated wet temperatures. Photomicrographs and failure analyses using scanning electron microscopy (SEM) will also be conducted to characterize the quality of composite laminate and fiber/matrix interface properties.

Table 6. Room-Temperature Flexural Properties of Neat T-11 Resin

Specimen Category	Specimen No.	Flexural Strength (ksi)	Average (ksi) (s.dev.)	Flexural Modulus (Msi)	Average (Msi) (s.dev.)
A	T-11-X01	7360	—	0.445	—
	T-11-X05	7005	6625	0.437	0.433
	T-11-X06	6650	(635)	0.425	(0.008)
	T-11-X09	6435	—	0.427	—
	T-11-X10	5680	—	0.431	—
B	T-11-Z10	6985	—	0.422	—
	T-11-Z01	6540	6810	0.383	0.389
	T-11-Z03	6885	(355)	0.384	(0.019)
	T-11-Z07	7270	—	0.379	—
	T-11-Z02	6380	—	0.375	—
C	T-11-Z06	7890	—	0.405	—
	T-11-Z09	7020	7640	0.402	0.397
	T-11-Z05	9510	(1435)	0.408	(0.016)
	T-11-Z08	6150	—	0.374	—

Notes: A = Specimens cut perpendicular to x-axis.
B = Specimens cut perpendicular to z-axis and tested with surface from the plaque midplane in tension.
C = Specimens cut perpendicular to the z-axis and tested with the original plaque surface in tension.

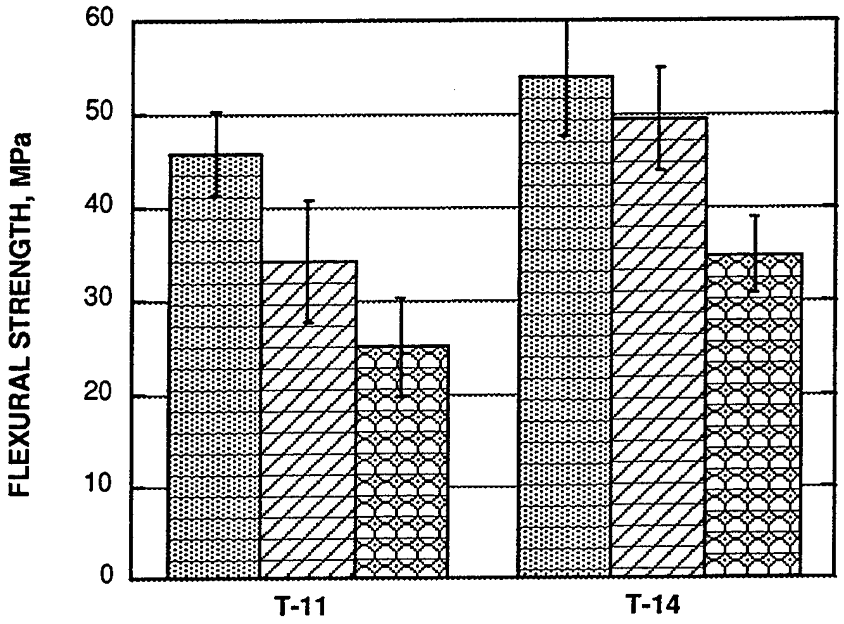

Figure 9. Flexural Strength of Neat T-11 and T-14, Dry and After Saturation, With Moisture at 66 °C/95% RH.

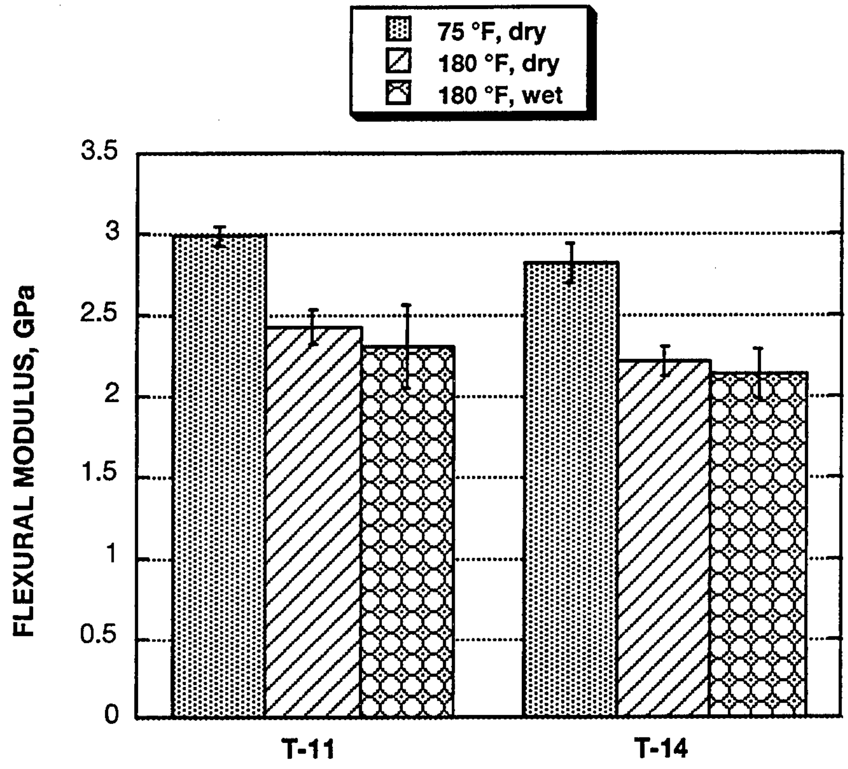

Figure 10. Flexural Modulus of Neat T-11 and T-14, Dry and After Saturation, With Moisture at 66 °C/95% RH.

3. E-Beam VARTM Resin Formulation

3.1 Introduction to E-Beam VARTM Resin Formulation. VARTM has become an important composites processing technique. In the VARTM process, the liquid resin converts into a nontacky solid during cure. Curing is accomplished via chemical reactions between monomers, which leads to the formation of a three-dimensional network. Energy for this process can be supplied in various forms, such as heat or radiation. There are various sources for radiation, including microwave, infrared (IR), ultraviolet (UV) light, and E-beam. Thermal curing has traditionally been preferred over radiation curing for fabricating thick polymer-matrix composites because of the limited penetration depth of radiation and the high cost of radiation equipment. However, recent developments and better E-beam equipment has revived interest in radiation curing. In addition to reduced processing time, E-beam curing offers many advantages over traditional thermal curing, including the following:

- unlimited material shelf life,
- reduced energy consumption,
- curing at selectable temperatures,
- curing of complex-shaped parts with inexpensive tooling,
- line-of-sight cure,
- shorter curing time,
- lower health risk, and
- reduced cure shrinkage.

In order to take advantage of E-beam curing, the developed resin should form a partially cured structure that can be easily transported for complete curing by E-beam. In addition, resins that can be processed using nonautoclave techniques such as VARTM and RTM should be developed to realize the significant cost savings associated with this technique.

3.2 E-Beam VARTM Resin Selection Criteria. The most important requirement for VARTM resins is a viscosity of less than 500 cps at processing temperature. Presently available and commercially used VARTM resins are based on epoxy or vinyl ester. The presence of unsaturated bonds in vinyl-ester resin allows curing by several different methods. Vinyl-ester resins have T_g's around 250 °F, but they exhibit very low toughness compared to commercially available epoxy resins. On the other hand, thermally cured epoxy resins designed for VARTM often have a low T_g. The primary objective of this research is to develop a new generation of toughened VARTM resins with the following properties:

- viscosity less than 500 cps at processing temperature,

- T_g between 250 °F and 350 °F,

- fracture toughness above that of presently available resins,

- ability to be cured thermally as well as by radiation,

- unlimited shelf life,

- environmental friendliness, and

- commercial availability or easily scaleable monomers.

3.3 E-Beam VARTM Resin Formulation Approach. Radiation can initiate free-radical or ionic polymerization. In this program, a new generation of radiation-cured systems based on free-radical curing is examined. This novel system uses interpenetrating polymer network (IPN) synthesis. Figure 11 shows the chemistry of the developed resin forming the IPN. In addition, work has been performed to develop cationic systems for VARTM application.

The curing process of an epoxy-vinyl-based IPN system, as shown in Figure 11, involves step-growth as well as free-radical polymerization. The step-growth reaction takes place between epoxy and amine, while free-radical curing brings about polymerization in the vinyl group. As shown in Figure 11, the resin is a mixture of difunctional epoxy; tetrafunctional amine, a unique monomer with epoxy and vinyl functionality; and divinyl monomers. The resin mixture is cured initially at low temperature, where the epoxy-amine forms a polymer network, while the vinyl monomer remains unreacted inside the network. The epoxy end of the unique monomer used in the resin becomes a part of the epoxy-amine network upon initial thermal curing, while the vinyl end remains pendant on the network. This constitutes a C-stage structure. The C-stage material is then cured completely by E-beam to form a second network of vinyl

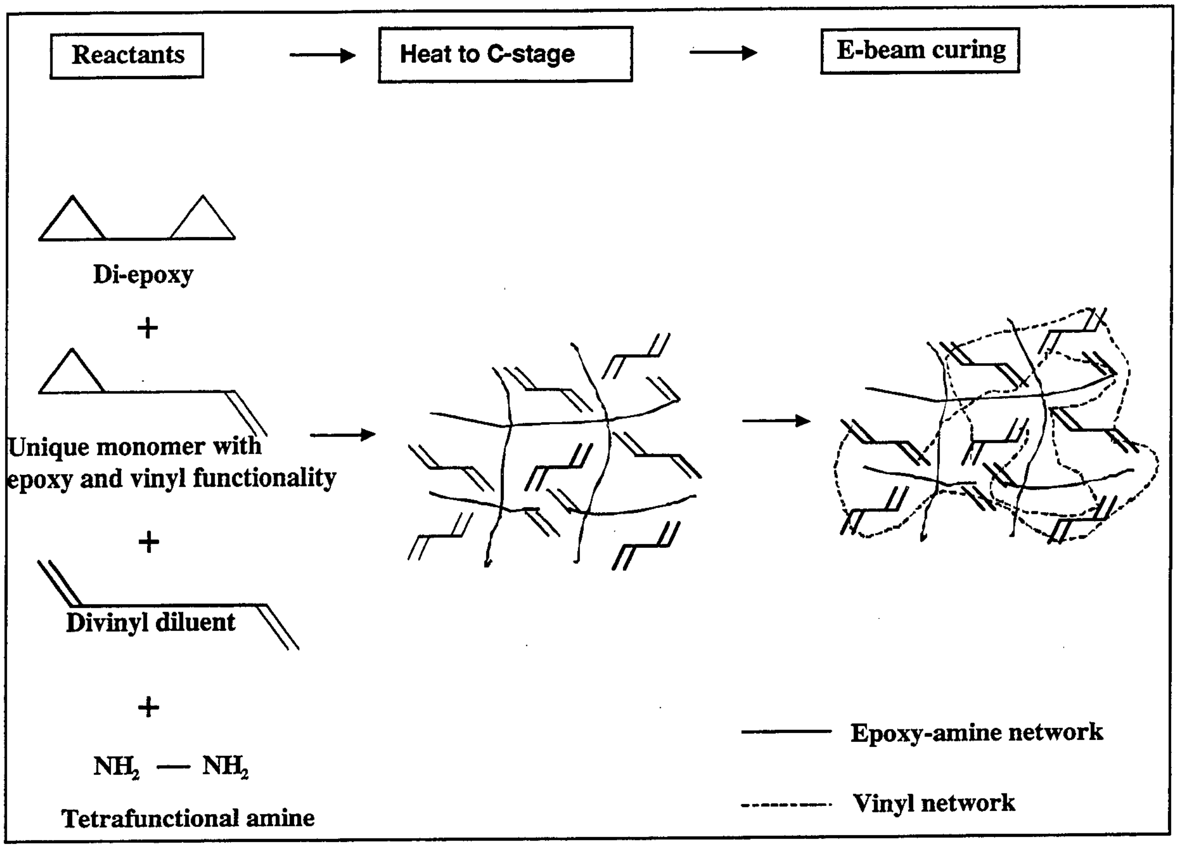

Figure 11. Chemistry of an IPN-Based VARTM Resin.

monomers or diluents. The polymerization of pendant vinyl groups along with the diluents provides co-continuity between the two networks. The combination of two networks forms an IPN. Since the two polymer networks were formed sequentially, it can be called a sequential IPN.

The advanced feature of this formulation approach is that the resin can be tailored in various ways to meet any specific property requirement. By varying the functionality of the epoxy monomer, the cross-linking density of the C-stage system—and, hence, the T_g of the cured system—can be varied. The number of pendant double bonds on the epoxy-amine network can also be varied, which affects the cross-linking density of the vinyl network with the epoxy-amine network. The effect on the property of the cured system when the diluent is changed is also measurable. The resin system shown in Figure 11 meets the viscosity requirement of the

VARTM process and also provides a T_g temperature in the range of 250 °F. To approach a T_g of 350 °F, the cross-linking density of the C-stage network and the number of pendant double bonds were varied. The composition of formulated high-T_g resin was varied to form a high-T_g resin with moderate viscosity and a high-T_g resin with low viscosity. The toughness of these materials does not meet the standard set by epoxy-based VARTM resins. To improve the toughness of developed IPN-based VARTM resins, two approaches were taken (Figure 12):

(1) synthesis of a new homo- or copolymer by varying the reactive diluent and

(2) modification of the existing polymer through the addition of a second polymeric component.

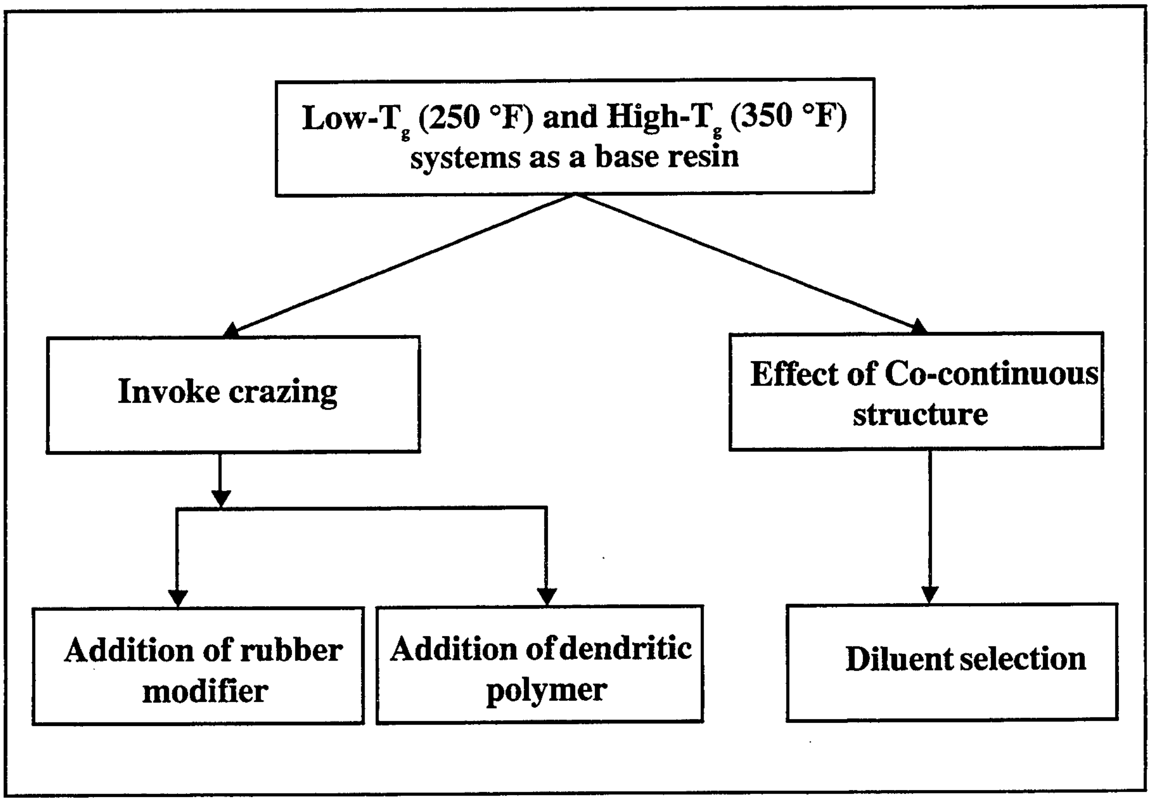

Figure 12. Approach Used to Toughen the VARTM Resin.

The first approach involved the use of diluents with different functionalities as well as different backbone structures. The second approach is also called blending. Rubber is the most commonly employed blending agent for the toughening of polymers. It provides a disperse phase into a rigid plastic matrix and also provokes yielding of the matrix material. As a result, the blend shows considerably higher fracture toughness than the parent polymer. However, in order to achieve satisfactory performance, a certain degree of chemical interaction between the resin and the modifier is required to improve the interfacial adhesion. To overcome this limitation, a compatible rubber agent whose functionality is adjusted according to the chemical nature of the matrix was added. In addition to the use of a rubber modifier, the second approach also involved the use of dendritic polymers. These polymers have a functionality compatible with the matrix that makes them soluble in uncured resin. However, during curing, they precipitate from the solution and phase separate. The second phase results in overall toughening of the two-phase blend.

3.4 E-Beam VARTM Resin Formulation Results

3.4.1 Resin Synthesis. As mentioned earlier, the developed resin based on an IPN system is made up of two parts: the step-growth epoxy-amine part and the free-radical-curable vinyl part. The base resins used in the study are CCM1, CCM2, and CCM3 (Table 7). They all contain diluents but no rubber modifier. CCM1 is a low-T_g resin with low viscosity. CCM2 and CCM3 are the base resins with high T_g. The viscosity of CCM2 is lower than that of CCM3.

Table 7. Base Resin Properties

Resin	T_g	Viscosity (cp)		
		30 °C	40 °C	50 °C
CCM1	Low (250 °F)	200	170	95
CCM2	High (350 °F)	340	135	125
CCM3	High (350 °F)	1050	550	200

The replacement of diluents or addition of a modifier to these developed resins to increase the toughness created a series of resins. The features and properties of diluents and rubber modifiers investigated are shown in Table 8.

Table 8. Rubber Modifiers and Diluents Used for Toughening

	Features	Viscosity (25 °C)	Functionality
D1	Hard and high T_g	8 cps	Di-
D2	Aromatic backbone	—	Di-
D3	Flexible	—	Mono-
D4	Flexible and high-impact strength	25 cps	Di-
D5	Cyclic group with high T_g	11 cps	Mono-
D6	Low shrinkage	67 cps	Di-
R1	High elastomer content and high viscosity	1,500-2,500 poise	Di-
R2	High elastomer content and moderate viscosity	40-80 poise	Di-
R3	High elastomer content and moderate viscosity	20 poise	Di-

The series of resins formulated using these constituents and base resin is tabulated with their composition in Table 9. Each number in parentheses suggests the overall weight percentage of that component in a resin mixture. Each of these sets was mixed thoroughly and degassed before being cured at low temperature to form a C-stage structure. The C-stage material was then exposed to E-beam for complete curing.

3.4.2 Determination of E-Beam Dose. To determine the optimum E-beam dose required for cure, Fourier transform infrared (FTIR) spectroscopy was employed. Several samples of one formulation were C-staged and then exposed to varying levels of E-beam dose. The conversion obtained as a result of E-beam exposure was then measured and compared. The range of E-beam dose selected was from 0.5 Mrad to 30 Mrad because most of the radiation-cured systems evaluated thus far cure between 7 and 25 Mrad. The plot of E-beam dose vs. percentage conversion of vinyl group is shown in Figure 13. The conversion increases rapidly with an increase in E-beam dose for low doses. Once the E-beam dose increases beyond 2 Mrad, the increase in conversion slows down. Since the increase in dose also increases process cost, a

Table 9. Developed Resin Composition

Set	Base Resin	Diluents (Overall Percentage)		Modifier (Overall Percentage)
CCM4	CCM1	D1 (30)	D2 (20)	R1 (5)
CCM5	CCM1	D1 (30)	D2 (20)	R1 (10)
CCM6	CCM2	D1 (30)	D2 (20)	R1 (5)
CCM7	CCM2	D1 (30)	D2 (20)	R1 (10)
CCM8	CCM3	D1 (25)	D2 (25)	R1 (5)
CCM9	CCM3	D1 (25)	D2 (25)	R1 (10)
CCM10	CCM1	D1 (30)	D2 (20)	R2 (10)
CCM11	CCM1	D1 (30)	D2 (20)	R3 (10)
CCM12	CCM2	D1 (30)	D2 (20)	R2 (10)
CCM13	CCM2	D1 (30)	D2 (20)	R3 (10)
CCM14	CCM3	D1 (25)	D2 (25)	R2 (10)
CCM15	CCM3	D1 (25)	D2 (25)	R3 (10)
CCM16	CCM1	D3 (30)	D2 (20)	—
CCM17	CCM1	D4 (30)	D2 (20)	—
CCM18	CCM1	D5 (30)	D2 (20)	—
CCM19	CCM1	D6 (30)	D2 (20)	—
CCM20	CCM2	D3 (30)	D2 (20)	—
CCM21	CCM2	D4 (30)	D2 (20)	—
CCM22	CCM2	D5 (30)	D2 (20)	—
CCM23	CCM2	D6 (30)	D2 (20)	—
CCM24	CCM3	D3 (25)	D2 (25)	—
CCM25	CCM3	D4 (25)	D2 (25)	—
CCM26	CCM3	D5 (25)	D2 (25)	—
CCM27	CCM3	D6 (25)	D2 (25)	—

tradeoff exists between conversion and process economy. Based on that, for the present work, a dose of 20 Mrad was selected as optimum.

3.4.3 Viscosity Evaluation. Resin viscosity is an important factor in VARTM processing. The viscosity of the developed resin was measured at the beginning of the curing process at three temperatures. Viscosity experiments were carried out on a Brookfield Model LVDV II + digital viscometer. Sample temperature was controlled with the Brookfield small-sample adapter and Brookfield bath/circulator model TC-200. The viscometer consists of a fixed outer cylinder and a spindle that rotates at a constant angular velocity. The spindle is connected to a torque spring,

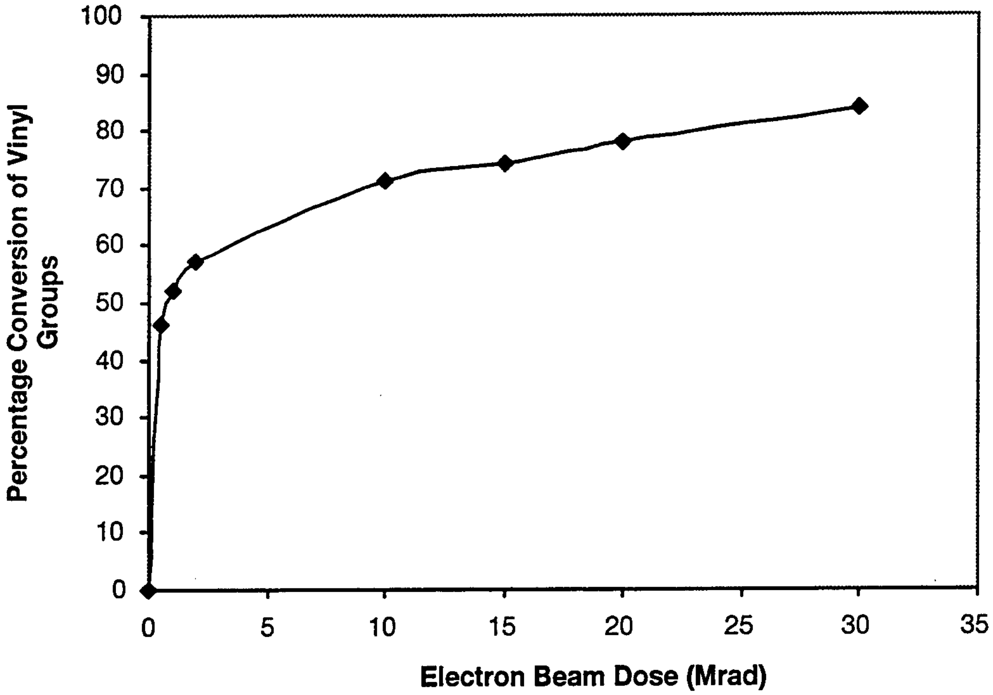

Figure 13. Percentage Conversion of Vinyl Group as a Function of E-Beam Dose.

which measures the frictional resistance offered by the sample. The viscometer converts the resistance into viscosity.

All components of the synthesized resin, except the curing agent, were mixed and heated to the desired temperature. The curing agent amine was added after the equilibrium temperature was reached. Approximately 10 ml of sample was measured and used for viscosity analysis. After the addition of amine, initial viscosity was measured. Viscosity data were collected at various temperatures.

3.4.4 T_g Measurement. The T_g of the cured resin was measured using a DuPont 983 Dynamic Mechanical Analyzer (DMA) interfaced with a DuPont 9900 thermal analyzer. A sample with dimensions of approximately 30 mm × 10 mm × 2.5 mm was prepared from the cured resin matrix. The specimens were placed in the test grips, and the arm displacement was zeroed. The heater assembly surrounding the sample provided a uniform temperature environment.

The DMA was run in fixed-frequency mode at 1 Hz. The peak-to-peak amplitude was kept between 0.1 and 0.3 mm. The sample was heated at 5 °C/min to the final temperature of 200 °C. The shear storage and loss moduli obtained were stored as a function of temperature.

3.4.5 ***Fracture Toughness Measurement.*** The energy required to fracture the cured material surface was measured using the ASTM D5045 method. The test is designed to characterize the toughness of plastics in terms of the energy per unit area of crack surface or critical strain energy release rate, G_{1C}, at fracture initiation.

Specimens for toughness testing were prepared according to the ASTM standard. The sample was then sectioned to meet ASTM standards. The next step in preparing the specimen after cutting is notching to initiate the crack. Once the notch was made, it was measured and checked according to the ASTM standard. For each set under investigation, five specimens were prepared. One specimen from each set was left unnotched to serve as a control specimen and to enable determination of a compliance calibration curve.

3.4.6 CCM1-Based Systems. Figure 14 shows the initial viscosity of all the systems based on CCM1 resin at various temperatures. The initial viscosity of all sets decreases with an increase in temperature. They all exhibit viscosity significantly below the criteria required for VARTM processing.

The viscosity, T_g, storage modulus E', G_Q, and K_Q data for CCM1-based resins are shown in Table 10. Empty entries in the table indicate that the analysis was underway at the time of this report. The combined analysis gives a broader view on the performance of the resin. CCM4 and CCM5, the systems with a rubber modifier added, show no change from the base resin in terms of T_g. The plot of storage modulus and loss modulus as a function of temperature for the CCM4 system is shown in Figure 15. At T_g, the material becomes rubberlike. Hence, the loss modulus shows a peak at Tg temperature. For the CCM4 system, T_g is well exhibited by a distinct peak of loss modulus at 120 °C. Although the viscosity of the CCM5 resin is higher than that of the base resin CCM1, it is significantly lower than required by VARTM processing. The addition of 10-weight-percent (wt%) R1 rubber to the system increases the fracture toughness of the base

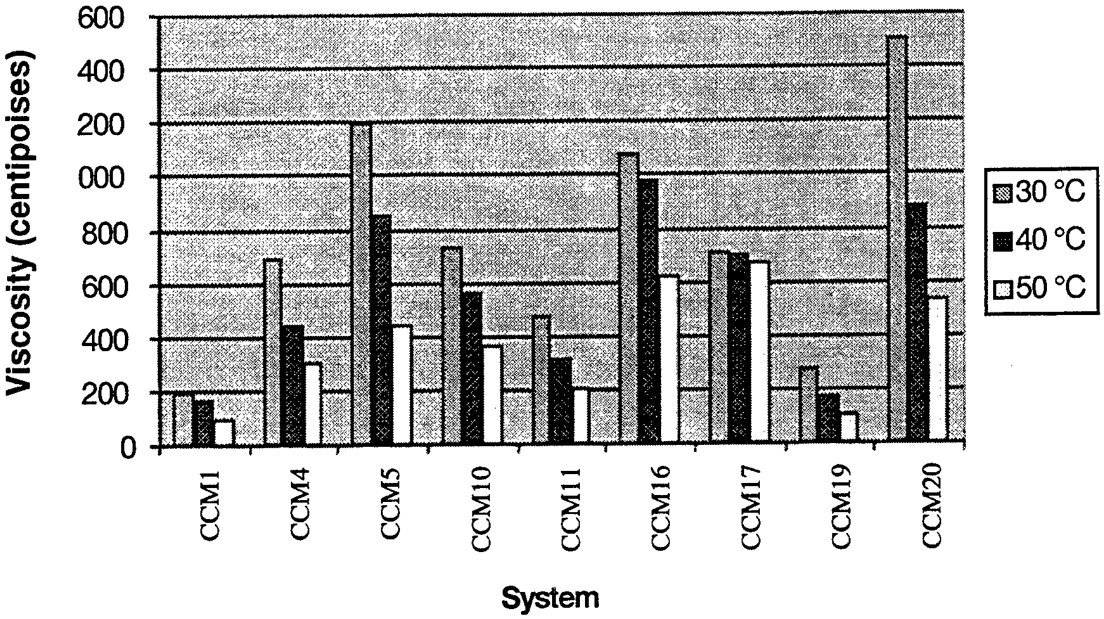

Figure 14. Viscosity Analysis of CCM1-Based Modified Systems.

Table 10. Properties of CCM1-Based Modified Resins

	Viscosity (cps)			T_g (°C)	E' at Room Temperature (GPa)	G_Q (J/m^2)	K_Q (MPa.m$^{0.5}$)
	30 °C	40 °C	50 °C				
CCM4	693	450	307	117	3.25	—	—
CCM5	1200	850	450	120	2.15	883.86	2.034
CCM10	735	565	363	95	—	—	—
CCM11	475	315	210	120	2.5	464.82	1.452
CCM16	1080	985	625	85	2.25	2458.84	—
CCM17	720	710	680	70	3.0	3959.72	—
CCM18	275	175	112	116	2.8	—	—
CCM19	1512	885	540	72	2.5	4330.16	3.532

resin by approximately 134%. The addition of low-viscosity rubber R3 to the base resin, CCM1, also results in a T_g of about 120 °C. However, the critical strain energy release rate at the fracture initiation is less than that of the base resin.

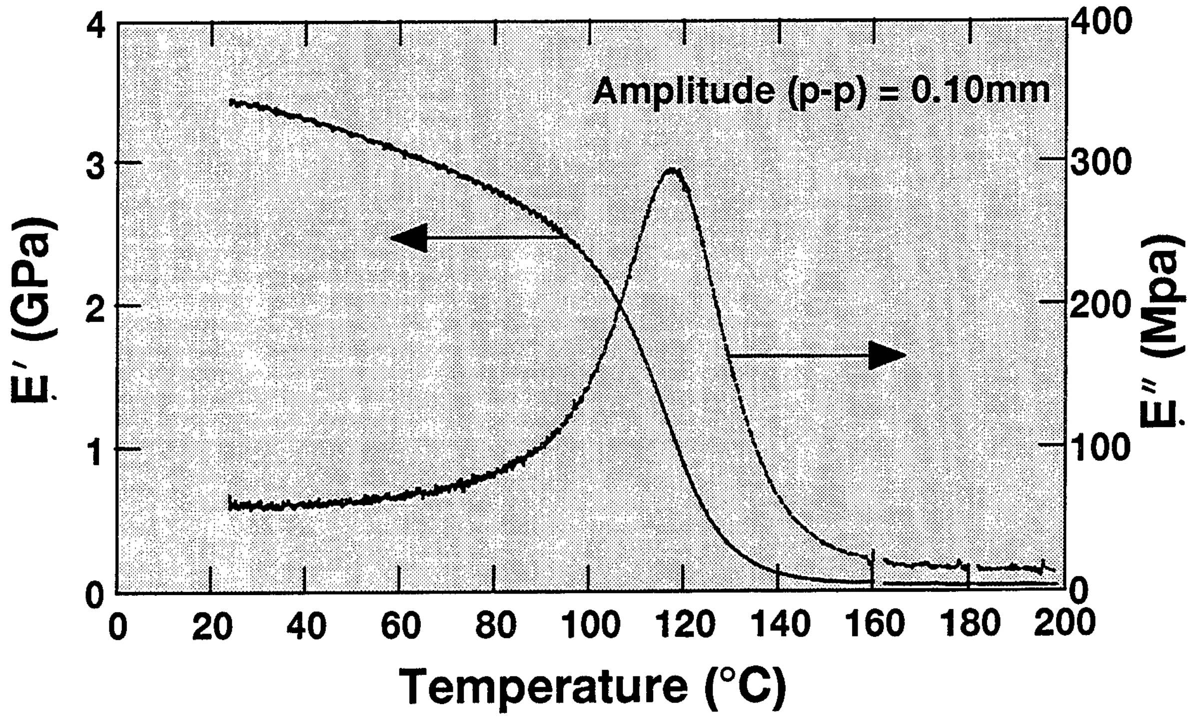

Figure 15. DMA Analysis of the CCM4 Resin System.

The effect of replacing the diluent of the CCM1 resin resulted in a low T_g of the modified system. The diluents D3, D4, and D6—corresponding to resin systems CCM16, CCM17, and CCM19, respectively—resulted in T_g below 100 °C. These diluents were used because of their flexible backbones. The resin systems with these flexible diluents failed at high fracture energy. They exhibited fracture toughness values 4 to 6 times higher than those of the base resin, but at the expense of the T_g. The resin system CCM18 exhibited a T_g value similar to that of the base resin. The plot of storage and loss modulus as a function of temperature for the CCM18 system is shown in Figure 16. The storage modulus shows the elastic energy stored by the system. Generally, the storage modulus of the system decreases with the increase in temperature. As seen in Figure 16, for the CCM18 system, the storage modulus remains unchanged up to 100 °C. This characteristic of the system indicates higher fracture toughness. Most of the developed systems showed acceptable storage modulus at room temperature.

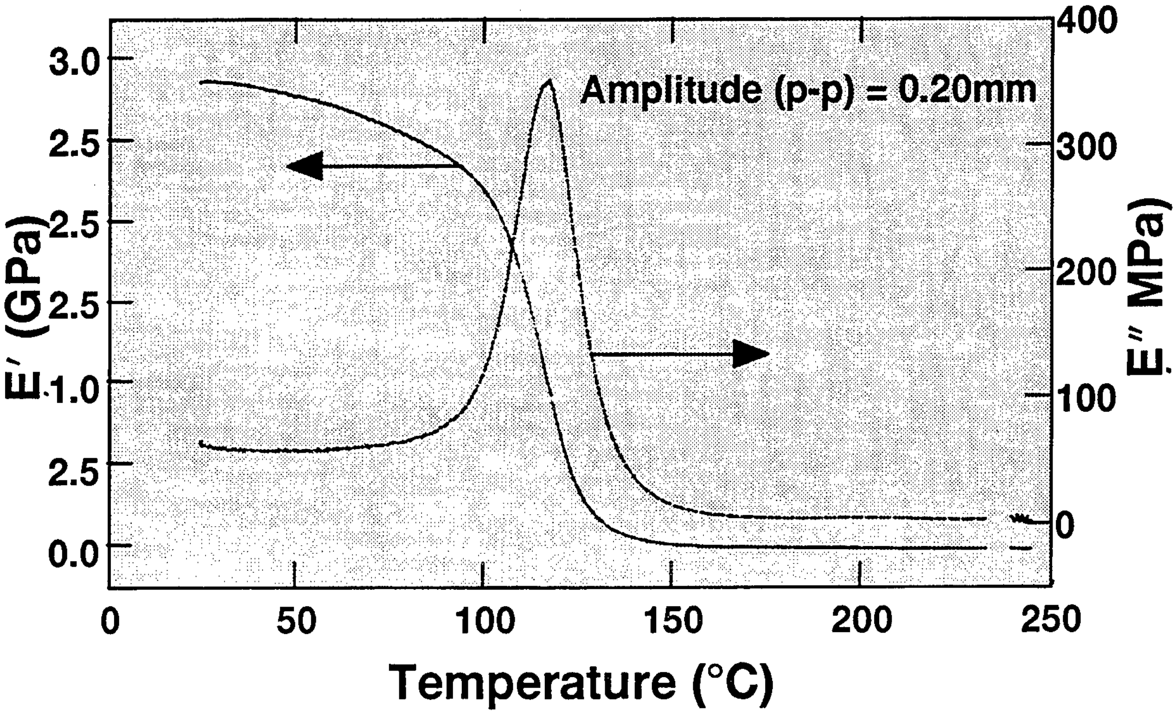

Figure 16. Storage and Loss Moduli as a Function of Temperature for the CCM18 Resin.

3.4.7 CCM2-Based Systems. The CCM2 resin is a high-T_g low-viscosity resin. The modifications used for the CCM1 system were also applied to the CCM2 system. The viscosity analysis of the modified CCM2 system is shown in Figure 17. The results of fracture toughness and viscosity analysis along with T_g analysis are shown in Table 11. The cured CCM2 resin has higher cross-linking than the CCM1 resin, which gives a higher T_g for the CCM2 resin. However, the increase in cross-linking density reduces the toughness of the system. It has been shown that the addition of rubber to a highly cross-linked system does not provide significant improvements in toughness [1]. However, the system under investigation, CCM2, does not fall in that highly cross-linked category. Hence, little attempt was made to increase the toughness via the addition of rubber modifiers. The addition of 5 wt% rubber (CCM6) to the CCM2-based resin yields a fracture toughness of 487.22 J/m^2. Further addition of rubber modifier results in deterioration of toughness.

Another common approach to increase the toughness of the highly cross-linked materials is to blend them with the ductile tough materials. Here, a similar concept was adopted in the form

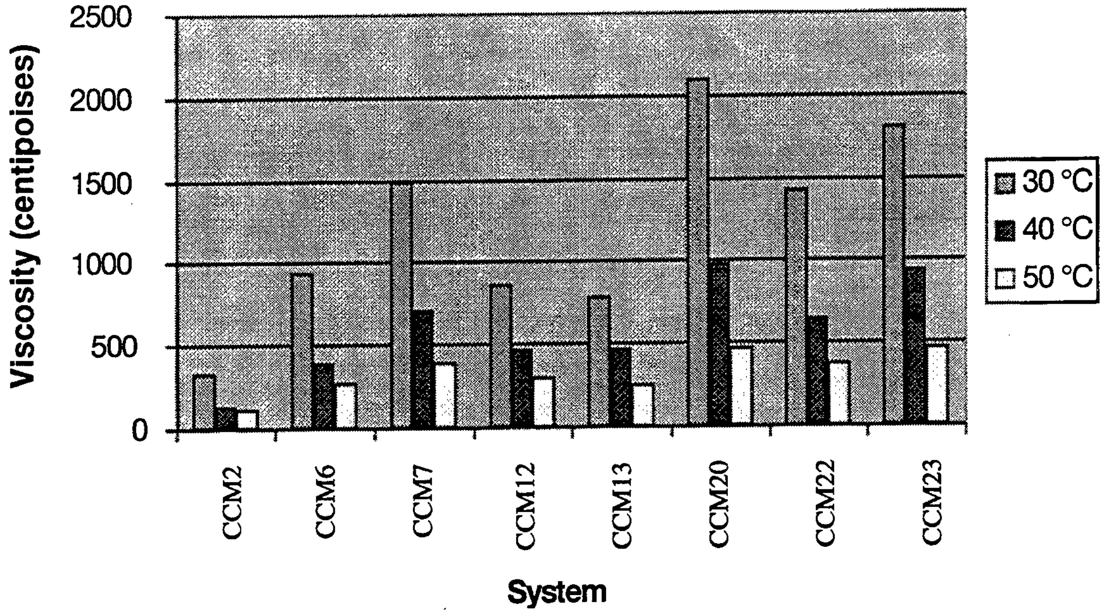

Figure 17. Viscosity Analysis of CCM2-Based Modified Systems.

Table 11. Properties of CCM2-Based Modified Resins

	Viscosity (cps - 50 °C)	T_g (°C)	E' at Room Temperature (GPa)	G_{IC} (J/m^2)	K_{IC} (Mpa.m$^{0.5}$)
CCM6	267	148	2.15	487.22	1.625
CCM7	392	150	2.5	289.35	1.079
CCM12	309	142	1.75	—	—
CCM13	264	152	—	367.93	—
CCM20	465	99	3.0	315.45	—
CCM22	375	155	1.55	379.11	1.268
CCM23	467	75	2.0	—	—

of diluent replacement. The CCM20 to CCM24 resins show the effect of diluent on T_g. Since, the CCM21 resin could not be cured, it is not included in Table 11. The use of diluent with flexible backbone such as D4 and D6 reduced the T_g of the base resin dramatically. The addition of D5 diluent with cyclic backbone to the base resin (CCM22) imparts toughness similar to the CCM13 system with rubber modifier R3. Figure 18 shows the storage and loss moduli as a function of temperature for the CCM7 system. The plot of loss modulus vs. temperature shows a

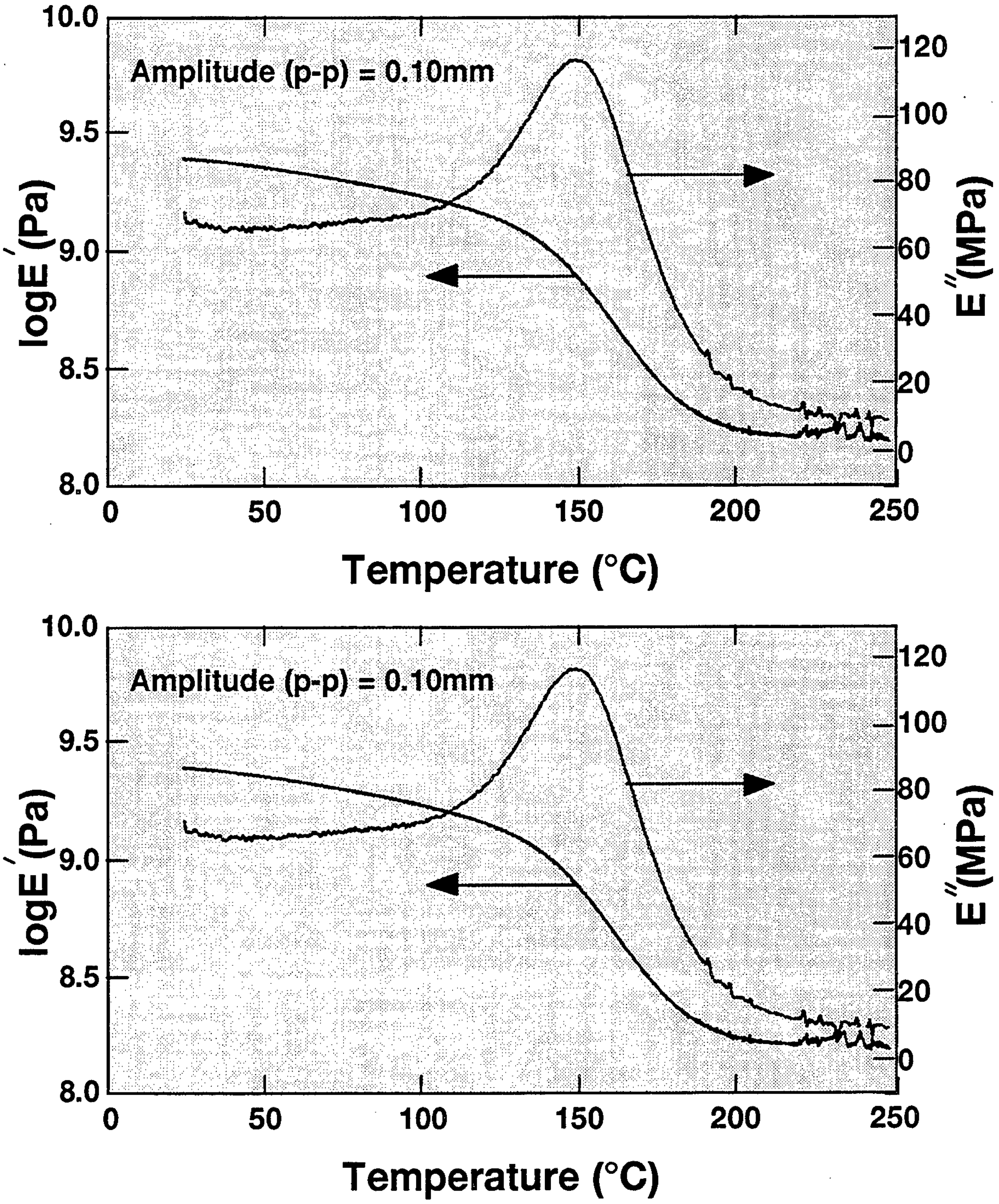

Figure 18. Plot of Storage and Loss Modulus for the CCM7 System.

single peak at 150 °C for the rubber-modified CCM7 system. The storage modulus values for the other systems are shown in Table 11.

3.4.8 CCM3-Based Systems. The CCM3 system is similar in C-stage structure to the CCM2 system. However, the diluent content makes this system viscous compared to CCM2. The initial viscosity of the CCM3-based modified resin at various temperatures is shown in Figure 19. The VARTM process allows the use of temperatures higher than room temperature. At 50 °C, the viscosities of the modified resins fall close to the limit for VARTM processing.

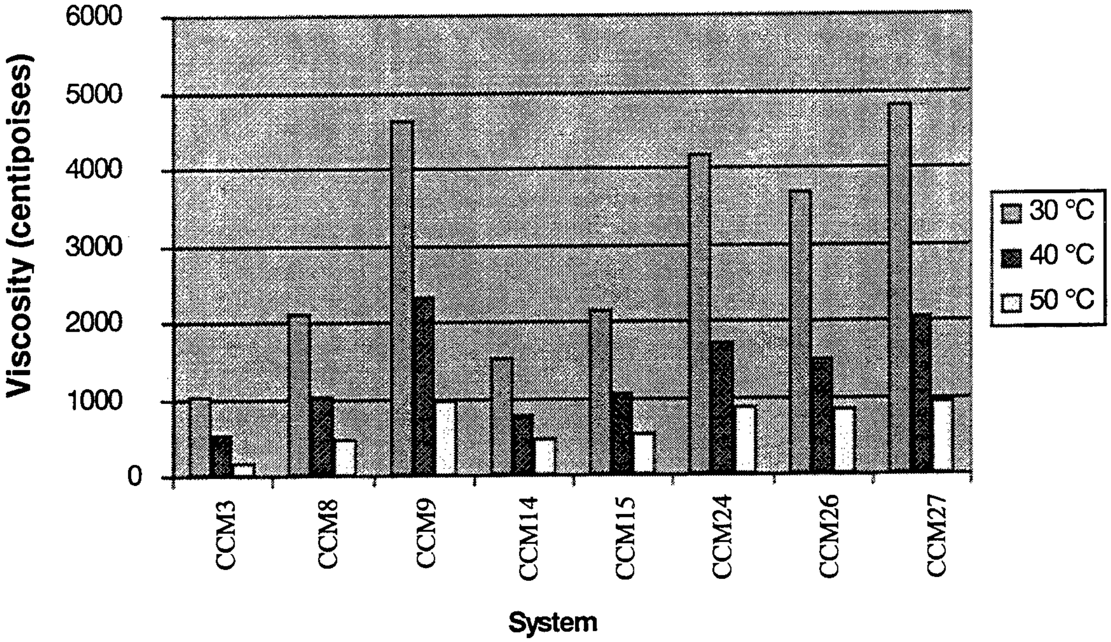

Figure 19. Initial Viscosity of the CCM3-Based Toughened Systems.

Table 12 shows the rheological, thermomechanical, and mechanical properties of CCM3-based modified systems. CCM15 resin is the base resin CCM3 with the addition of rubber modifier R3. This system exhibited high toughness but low T_g. CCM26, the system containing the D5 diluent, demonstrated an excellent T_g. The toughness of the CCM26 system is also comparable to that of the rubber-modified CCM14 resin. The DMA analysis of cured the

Table 12. Properties of CCM3-Based Modified Resins

	Viscosity (cp at 50 °C)	T_g (°C)	E' at Room Temperature (GPa)	G_{IC} in (J/m^2)	K_{IC} (Mpa.m$^{0.5}$)
CCM8	505	160	3.15	—	—
CCM9	1,000	156	2.6	—	—
CCM14	495	144	2.65	472.49	—
CCM15	565	139	2.75	647.42	—
CCM24	900	—	—	233.46	1.0227
CCM26	860	165	2.15	472.22	1.492
CCM27	950	120	2.85	—	—

CCM26 system is shown in Figure 20. The CCM3-based systems all show exceptionally high values of storage modulus at room temperature, as shown in Table 12.

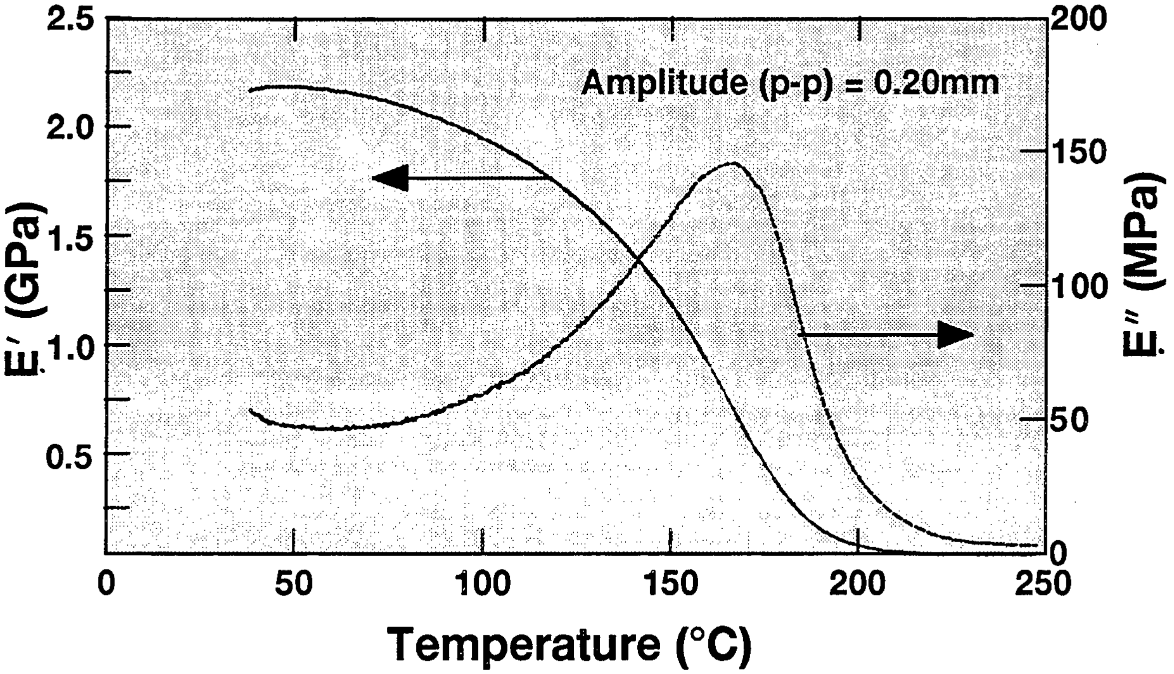

Figure 20. Thermomechanical Analysis of CCM26 (CCM3 With Diluent D5 Added).

3.5 E-Beam VARTM Resin Conclusions. The toughening of base free-radical-cured VARTM resin was carried out by the addition of a rubber modifier and replacement of the diluent. The addition of high-viscosity rubber R1 to low and high-T_g resins increased the toughness without affecting the T_g. Although the viscosity was also increased, it remained within the range required by the VARTM process. The addition of moderate-viscosity rubber (R2 and R3) did not demonstrate the performance achieved with the R1 rubber modifier.

The approach of replacing the diluent of the base resin to increase the toughness was selected because the diluents form a co-continuous structure upon curing, which, in turn, governs the properties of the cured resin. The selection of diluents with a flexible backbone such as D3, D4, and D6 yielded high toughness, but at the expense of T_g. The appropriate diluent was one with a cyclic or hard backbone (e.g., D5). The resin mixture with the D5 showed an increase in toughness without sacrificing the thermomechanical properties of the cured material.

Overall, most of the modified systems exhibited viscosity within the range required for VARTM processing. They achieved or surpassed the T_g of vinyl-ester resin, while providing the high toughness of epoxy-based VARTM resin.

Future work is aimed at the use of dendritic polymers to increase the toughness of the base resin. Also, the issue of combining the rubber modifier with the diluent is unexplored. Significant potential exists to increase the toughness of the base resin if a tough diluent such as D5 can be combined with a rubber modifier such as R1. Microscopic examination of the toughened material will also be addressed in future work. Two of the resins previously described will be used to fabricate composite panels using AS4 fabric preforms and will become the baseline system in the development of E-beam VARTM resins.

Cationically cured systems are also being evaluated, with the most promising formulation being VAEB-8, which exhibits resin shrinkage of less than 2%, a dry T_g of 150 °C, and a wet T_g of 125 °C. Composite laminates for evaluation will be fabricated using VAEB-8 injected at 55 °C into AS4 fabric preforms and E-beam cured.

Work continues in the development of cationic VARTM systems to attain a better balance of viscosity, pot life, and retention of an elevated-temperature modulus.

4. E-Beam Repair Adhesive Formulation

4.1 Introduction to E-Beam Repair Adhesive Formulation. The ability to perform effective repairs of composite structures on military structures will be governed to a large extent by the properties of the repair adhesives. Previous research [2] has shown that there are no E-beam adhesives that match the performance standards of thermally cured epoxies. This may be attributed to a number of factors. Notably, the inability to effectively toughen the E-beam resins results in adhesives with poor resistance to peel and delamination. Hence, the development of adhesives in this program mirrors the other E-beam resin development efforts in that a major goal is to toughen the existing E-beam systems so that they can be used as structural adhesives. Furthermore, adhesive materials must be available in a variety of product forms to provide flexibility in repair and remanufacturing operations. These product forms include two-part pastes, one-part pastes, supported and unsupported films, and low-viscosity liquids. Initial efforts have focused on development of toughened two-part pastes and infinite-shelf-life one-part pastes and films. To date, the greatest success has been in formulating two-part adhesives based on the CCM series of IPN-based E-beam resins.

4.2 E-Beam Repair Adhesive Selection Criteria. The adhesives currently being used for thin-walled structural repair will be evaluated to provide baseline property values. Most repairs of these types employ either 250 °F or 350 °F curable epoxy film adhesives or two-part pastes. These materials have been well characterized. Table 13 gives some typical target values for adhesive formulations based on the properties of thermally cured adhesive baselines. The goal will be to approach these performance target values for each relevant product form.

Critical properties to be measured and tabulated will include characterization of the adhesive T_g (dry and wet), elastic constants, strength, and toughness, as well as adhesive bond properties for metal-metal, composite-composite, and composite-metal joints. The properties of the new

Table 13. Adhesive Formulations

Property	Target Value
T_g temperature	95–105 °C
Service temperature	82–95 °C
Tensile modulus (RT)	3.0 GPa
Metal-Metal Bonds	
Lap-shear strength RT (Al-Al)	35–43 MPa
Lap-shear strength service temperature	16–28 MPa
Floating roller peel	8–11 KN/m
Sandwich peel	75–100 Nm/m

resins will be compared to those of the baseline thermally cured adhesives to assess relative performance. The results of the mechanical testing will be augmented by corresponding chemical and physical characterization of the resins.

Lap-shear strength for both aluminum-aluminum and composite-composite joints was the primary screening evaluation. Adhesives that matched or approached the performance of their thermally cured counterparts were selected for further evaluation. This screening procedure also permitted rapid feedback on performance deficiencies in certain instances. For downselected candidates, the bonded adhesive joints will be evaluated using climbing drum peel (ASTM D1781), lap-shear (ASTM D1002), wedge-crack extension (ASTM D3762), and other testing, as deemed necessary, to gain confidence in the properties of newly developed materials.

4.3 E-Beam Repair Adhesive Formulation Approach. As discussed earlier, two major classes of radiation-curable systems will be used in this program. These include the low-shrinkage C-stageable free-radical CCM systems based on epoxy and urethane chemistries, as well as the cationically cured CAT-M systems. During this task, activities will focus on modifying these systems to improve fracture toughness. The team developed these systems by formulating toughening agents into the base resins, as is typical of a second-phase toughener, or via novel approaches to toughening based on resin chemistry, whereby flexible linkages are incorporated into the radiation-curable resin backbone.

The untoughened s-IPNs have good strength properties but are quite brittle. However, these systems may be toughened through a number of methods. In thermally cured epoxies, toughness is improved by the addition of rubber, which is chemically bonded into the network through reactive end groups [3]. The rubber components that were studied for adhesives evaluation included various butadiene-nitrile liquid rubbers, dendritic polymers, and preformed particles. Also, suitable diluents were used to modify base formulations to control the viscosity of formulated adhesives. Table 14 lists the modifiers and diluents that were used in this work.

Table 14. Modifiers and Diluents for Adhesives Formulation

ID	Description	Functionality
M1	CTBN - Epoxy adduct	Epoxy
M2	CTBN - Epoxy adduct	Epoxy
M3	CTBN - Epoxy adduct	Epoxy
M4	CTBN - adduct (low viscosity)	Epoxy
M5	CTBN - adduct (low viscosity)	Epoxy
M6	CTBN	Carboxy
M7	ATBN	Amine
M8	ATBN	Amine
M9	ETBN - styrene blend	Epoxy - vinyl
M10	ETBN	—
M11	Polester polyol – epoxy	Epoxy
M12	Polester polyol – epoxy	Epoxy
M13	CORE-shell acrylic	—
D1	Low-viscosity methacrylate	Methacrylate
D2	Viscosity D1-methacrylate	Methacrylate
D3	Low-Viscosity mono methacrylate	Methacrylate
CE1	Epoxy chain extender	—
CE2	Epoxy chain extender	—

Base resin formulations for the IPN-based adhesives were similar to those described earlier. However, diluent and modifier selection were used to control processing and cure properties. The diepoxide that was selected is the bis-phenol-A-based epoxy, EPON 828, provided by Shell Chemical, Inc. Along with the selected bis (p-aminocyclohexyl) methane, PACM, the epoxy demonstrates a T_g of approximately 175 °C. This temperature is suitable for adhesive repair of Army materials; however, the T_g of the epoxy network can be increased through the addition of a high-function (tetrafunctional) amine or aromatic amines. PACM, an aliphatic amine provided by Air Products, Inc., is selected because of the importance of the environmental impact of the resin formulations. PACM is less caustic and hazardous than alternative aromatic amines.

4.3.1 ***Epoxy Adhesive Toughening.*** As with most pure epoxy networks, the E-beam-cured EPON 828/PACM/methacrylate network is very brittle. Consequently, the material is inadequate for most adhesive applications. Improving the toughness of these s-IPN blends is key to creating an alternative cure adhesive by this approach. Other research efforts have demonstrated the challenges associated with toughening epoxy resins, especially cationic epoxy resins that are cured through E-beam methods [2, 4]. However, toughening of brittle epoxy networks has been accomplished by Kinloch, Riew, and others over the past decade [5]. The body of work in toughening of epoxy networks has demonstrated that brittle thermosets can be toughened without a significant sacrifice in T_g through two approaches: the addition of rubber and the addition of chain extenders.

The first method of toughening involves the addition of a second phase, commonly a rubber or TP, to the thermoset. A functionalized rubber is added to the uncured epoxide/amine mixture and co-cured with the epoxy network. During cure, the rubber becomes insoluble in the growing epoxy network and separates into rubber domains. The small rubber concentration [6] in the network causes discrete rubber particles (0.2–5 μm) to form inside the network [7–9]. These rubber particles improve toughness by changing the energy absorption of the matrix and inhibiting premature failure of the thermoset, which often results from small defects. Alternatively, the second phase is added as rubber or TP particles. The size, surface binding, and concentration of the particles greatly influences the toughness of the thermoset [7, 8]. Often, the surface of the particles is coated with an adhesion promoter to enhance the interaction between the thermoset and the filler. Generally, the addition of discrete particles for toughening is less effective than the addition of reactive rubbers [3].

The second method of toughening thermosets is to add chain extenders to the network [9]. The average distance between cross-links is a key parameter governing the toughness of the network. Through insertion of a fraction of oligomers into the network, the average number of cross-links per unit volume is reduced, providing greater flexibility to the network although usually at the expense of the T_g.

Toughening of s-IPNs has been evaluated using a reactive rubber and a reactive dendrimer. Upon curing, both the rubber and the dendrimers phase-separate into discrete rubber domains. Although cure conditions reportedly affect the formation of the rubber domain size and, consequently, the overall matrix toughness, the impact of cure conditions has not yet been evaluated in this study. A maximum toughness enhancement in a pure-epoxy matrix is obtained with rubber loading between 8% and 12% by weight. Dendrimer suppliers report that optimum toughness of epoxy formulas of these materials is also 10% by weight. For the purposes of this report, a number of reactive rubber and dendrimer-like polymers were explored; the tested materials are listed with their characteristics in Table 14.

4.3.2 Infinite Shelf-Life Formulation Methods. Base formulation of experimental one-part adhesive resins is designed by controlling the extent of reaction of the epoxy matrix. The issue of gelation in condensation-type reactions where monomer A-A reacts with monomer B-B and B_3N can be predicted and controlled. Gelation is the point when an infinite network exists. The gel point can be predicted from the number and functionality of the monomers present in the condensation reaction. The following is an example of a condensation reaction:

$$A{+}A + B_3N \rightarrow A\text{-}A\text{-}BNBB\text{-}AA\text{-}BBNB\text{-},$$

where B_3N is trifunctional ($f = 3$). The critical point for gelation (α_c), defined as the point extent of conversion of “B” required to form an infinite network, is defined as follows:

$$\alpha_c = 1/(f - 1).$$

Thus, controlling the extent of reaction conversion is achieved by controlling either the amine functionality or the epoxy functionality of the system. A blend of mono- and multifunctional amines generates a high-molecular-weight soluble hyperbranched polymer. The stability of such a molecule is dependent upon the reaction completion of the epoxide/amine. Alternatively, monofunctional epoxides can be added to the mixture to decrease the probability of infinite network formation.

Initial experiments demonstrated that limiting the epoxy network formation in EPON 828/PACM/dimethacrylate adhesives produces a processible material with high stability. The epoxy network was thermally cured in the presence of the free-radical monomers to create a paste-like substance. The amine was suitably end-capped to prevent premature gelation but permit network formation during E-beam radiation. These materials were then evaluated for shelf-life stability using FTIR. The results are reported in subsequent sections.

4.4 E-Beam Repair Adhesive Formulation Results. The toughness of model adhesive formulation was evaluated using single-edge notch flexure specimens. The tests were performed in accordance with ASTM D5045. The effect of 5% rubber addition to base IPN resins was, in some instances, dramatic. The toughness was increased subtantially for many of the modifiers that were examined. In two cases, toughness increased by nearly a factor of 2. Further research is needed to optimize the toughness improvements in these resin systems, and this work is presently ongoing. However, the ability to toughen these E-beam resins is significant and is a major accomplishment to date. The improved toughness should have a direct impact on the performance of joints produced using these modified resins. The mechanical properties of the adhesives have been tested on composite lap-shear specimens. Prepared samples were tested as both green and fully cured adhesive specimens. The results are shown in Tables 15 and 16.

From the mechanical data, it is evident that the bond strengths of the E-beam adhesives are adequate. Composite failure was observed in all samples, except for CAO1, which is a one-part adhesive formulation. The toughened one-part adhesive, CAO2, demonstrated both better adhesive strength and better toughness than the untoughened case. The source of this improvement has not yet been determined.

Table 15. Double-Notch Lap-Shear Results

Sample ID	Bond Strength	T_g (°C)
CA5	2000±100 PSI	120
CA6	2300±100 PSI	121
CAO1	1550±100 PSI[a]	90[b]
CAO2	2000±100 PSI	88[b]
Dexter Hysol EA9394	3200±100 PSI	78

[a] Sample failed in the bondline.

[b] Epoxy network not fully cured (FTIR).

Table 16. Lap-Shear Results

Sample ID	Bond Strength	T_g (°C)
CA1 (2-pt)	2900±100 PSI	120
CA2 (2-pt)	2750±100 PSI	121
CA3 (2-pt)	3100±100 PSI	120
CA4 (2-pt)	3400±100 PSI	121
Dexter Hysol EA9394	3700±100 PSI	78

The T_g of each of these adhesive samples was also measured using DMA. The results are also listed in Tables 15 and 16. The target T_g of a 250 °F adhesive is well within the scope of this effort. Work is currently being done to further increase the T_g of the network by modifying the acrylate network content and the ratio of epoxy to acrylate in the mixture.

Since these adhesives produced joints that exceeded the strengths of the composite adherends, further tests were performed on aluminum-aluminum lap joints to determine the ultimate properties of the adhesive. Aluminum (7075-T6) coupons were surface-treated prior to bonding. The surface treatments employed were all chromate-free to maintain the goal of environmentally friendly bonding and repair methods. In this case, the aluminum was etched using the P-2 process. For comparison, joints were also bonded using commercially available adhesives. FM73 and EA9628 were selected as film adhesives, and E9394 was used as a two-part paste formulation.

The results of the aluminum-aluminum lap-shear testing (Table 17) are very encouraging. The strengths are higher than what has been reported for previously developed E-beam adhesives. They also approach the film-adhesive baselines. The large degree of scatter must be addressed during production of our best candidate materials. Failure analysis of the joints revealed less than consistent degrees of cure, indicating uneven E-beam irradiation. This issue will be addressed during future work.

Table 17. Joint Strengths of Aluminum-Aluminum Single-Lap Joints (D-1002)

Sample ID	Lap-Shear Strength	T_g
MA3	3000	127
MA4	3130	120
MA5	3700	115
MA6	5627	118
MA23	2793	100
MA24	1829	106
MA43	1183	87
MA73	2503	99
Hysol EA9394	3000	78[a]
Cytec FM73	5875	116[b]
Hysol EA9628	5670	122[c]

[a] Material safety data sheet. Hysol EA9394, Dexter Aerospace Materials Division, Pittsburg, CA, 1997.

[b] Chester, R. Personal communication. Aeronautical and Maritime Research Laboratory, Melbourne, Australia, 1998.

[c] Product data sheet. Hysol EA9628, Dexter Aerospace Materials Division, Pittsburg, CA, 1997.

4.5 E-Beam Repair Adhesive Conclusions. Future efforts will concentrate on optimizing the downselected resin formulations to achieve the desired joint properties. Specifically, the base adhesive resins will be reformulated and more joints will be produced to expand the existing database and reduce the inconsistency of the joint strengths. These optimized resins will be further formulated to include fillers, adhesion promoters, thixotropes, and other materials used in traditional adhesives.

Research must also continue to develop improved one-part film adhesives. In the first year of the program, the feasibility of shelf-life-stable one-part resins was demonstrated. This approach must be continued to provide stable adhesives with performance comparable to the two-part resins described here. These efforts are underway, and some promising candidate systems have been derived. Once these materials have been produced, appropriate product forms will be produced and distributed for evaluation of properties.

Further mechanical evaluation of optimized adhesive joints will be performed. These will include testing at elevated and subambient temperatures, fatigue, and joint fracture toughness. These data will provide added confidence in the properties of these adhesives and allow for comparison to traditional thermally cured adhesives. Furthermore, work will continue to monitor the aging characteristics of these resins to assess their shelf life.

5. Resin Aging Study

5.1 Introduction to Resin Aging Study. Many adhesive and composite material systems cure slowly during storage prior to use, as discussed in section 2.3. For these systems, processing and performance requirements can be met only within the designated storage period or shelf life (Figure 21). Shelf life is generally documented under a required level of reduced-temperature storage. Shelf-life restrictions are determined for each resin system by evaluating changes in the characteristics of the resins or components of two-part resin systems under various storage conditions. The limitations are based on maintaining characteristics that allow suitable processability and quality of the cured materials. Resins or components of resin systems that have exceeded shelf life are partially cured, can no longer be used, and are considered hazardous waste.

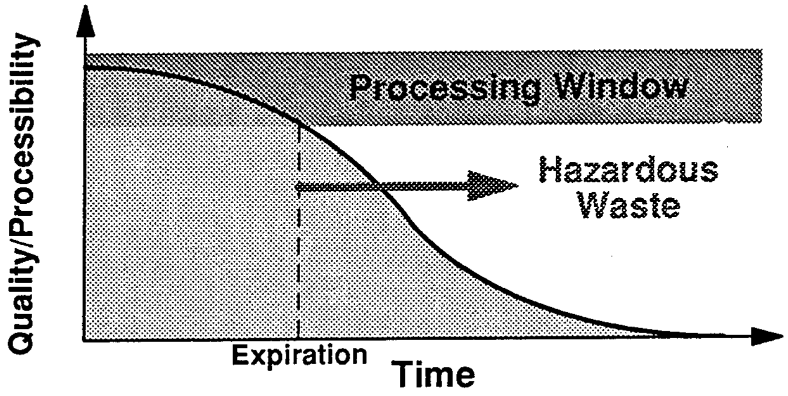

Figure 21. Shelf Life Expires When Material Processing Characteristics No Longer Meet Specification Limits.

Common materials used for composite repair in DOD applications are one- and two-part epoxy adhesives and resins, epoxy film adhesives, and glass- or carbon-fiber/epoxy prepregs. The one-part systems have all the materials needed to achieve full cure and must be stored under controlled-temperature conditions to slow the curing process. The two-part systems must be mixed to cure at expected rates; however, the epoxy part (Part A) can cure by itself, although at a slower rate. Shelf-life limits for these materials are typically 6–12 months. The new formulations are designed for cure by E-beam or induction processing and should have an extended shelf life. In particular, the formulations for E-beam cure are expected to have an infinite shelf life. An aging study is being performed to verify these expectations.

5.2 Approach to Resin Aging Study. In the context of this repair effort, aging studies to identify the changes in characteristics of the resins and components are relevant to evaluating the shelf-life capabilities of current materials and proposed replacement materials. In this study, extent of cure is being determined at room temperature for current commercial adhesives, films, and prepregs that are used in repairing polymeric composites in defense applications. Resin systems formulated at the U.S. Army Research Laboratory (ARL) and University of Delaware, Center for Composite Materials (UD-CCM) that could potentially be used in Army repair applications are also being evaluated. Evaluation of existing resin systems was initiated when the relevance of the materials to the study had been determined. Resin systems formulated as part of the repair program are integrated into the aging study on an ongoing basis. Consequently, materials are aged for different amounts of time based on when they were integrated into the study.

The approach used in this study is to monitor the degradation of a particular functional group that is important to the shelf life of that particular sample. To monitor this degradation of a functional group, FTIR spectroscopy is applied. In FTIR, each excitation mode (vibration, stretching, overtone, etc.) of a chemical bond in the sample absorbs energy at a characteristic wavelength. The change in intensity of absorbance is related to the change in concentration of a chemical functional group. At first, the mid-infrared (MIR) range, 4000 cm^{-1} to 400 cm^{-1}, was used to monitor the samples. Due to the spectral overlap that occurs in this region for the amine peak, the near-infrared (NIR) spectrum, from 7000 cm^{-1} to 4000 cm^{-1}, was used to monitor the amine peak. Eventually, NIR was also used to monitor epoxy and acrylate peaks.

The materials currently in the aging study are listed in Table 18 with reactive functional groups and approximate excitation wave numbers monitored. The functional groups of particular interest for the resins in this study are primarily amines, epoxies, and acrylates.

Table 18. Aging Study Materials

Sample	Source	Functional Group	Wave Number
9390 part A of two-part epoxy system	Hysol	Epoxy	916
9390 part B of two-part epoxy system	Hysol	Primary Amine	6510
AF163-2OST epoxy adhesive film	CytecFiberite	Epoxy	916, 4530
9628.045 PSFK epoxy adhesive film	Hysol	Epoxy	916, 4530
R6376 epoxy prepreg	Northrop	Epoxy	916, 4530
JDW71 one-part epoxy/methacrylate	Army Research Laboratory	Methacrylate	945, 6150
JDW72 one-part epoxy/methacrylate	Army Research Laboratory	Methacrylate	945, 6150
SBIR-ARL1 one-part epoxy	Merlin Technologies, Inc.	Epoxy	916

The sample preparation could differ slightly, depending on the initial state of each material (prepreg, adhesive film, liquid resin, solid resin) and the range of wave numbers used. As shown in Figure 22, all the samples are compressed between two 25-mm-diameter NaCl transparent crystal windows. For liquid resin systems, except for SBIR-ARL1, no additional preparation was needed before placing the sample on the crystal. In the MIR range, the adhesive film samples and the prepreg sample were diluted in acetone. The resin/acetone solution was then added to the crystal, and the acetone was allowed to evaporate off the crystal, leaving only the resin. The SBIR-ARL1 resin system was also diluted in acetone before being placed onto the crystal because the sample is not a liquid but a solid. A spacer was used between the crystals to regulate the thickness of each sample and to reduce evaporation losses. For the MIR range, a Teflon spacer was used for all materials. For the NIR range, a lead spacer was used for resin systems and no spacer was needed for adhesive films. After the sample was compressed between the NaCl crystals, it was placed in a cell holder for the duration of the study. At appropriate intervals, spectra were obtained to evaluate extent of cure. Between measurements, the samples were stored in a desiccator at room temperature.

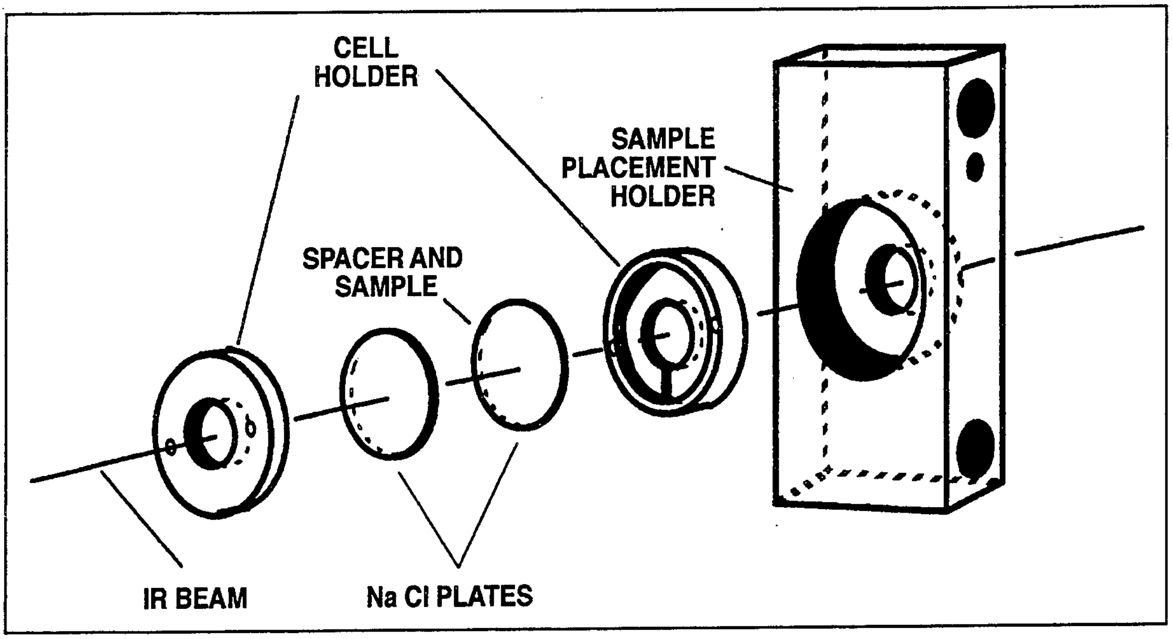

Figure 22. Exploded View of Sample Between NaCl Windows in the Sample Holder.

5.3 Results of Resin Aging Study. The effects of aging are evaluated using the fraction converted or extent of cure based on heights of significant peaks in the absorbance spectra. Figure 23 serves as an example for the AF163-20ST adhesive file. The peak at a wave number of 916 cm^{-1} is monitored as a function of time with a notable reduction in height.

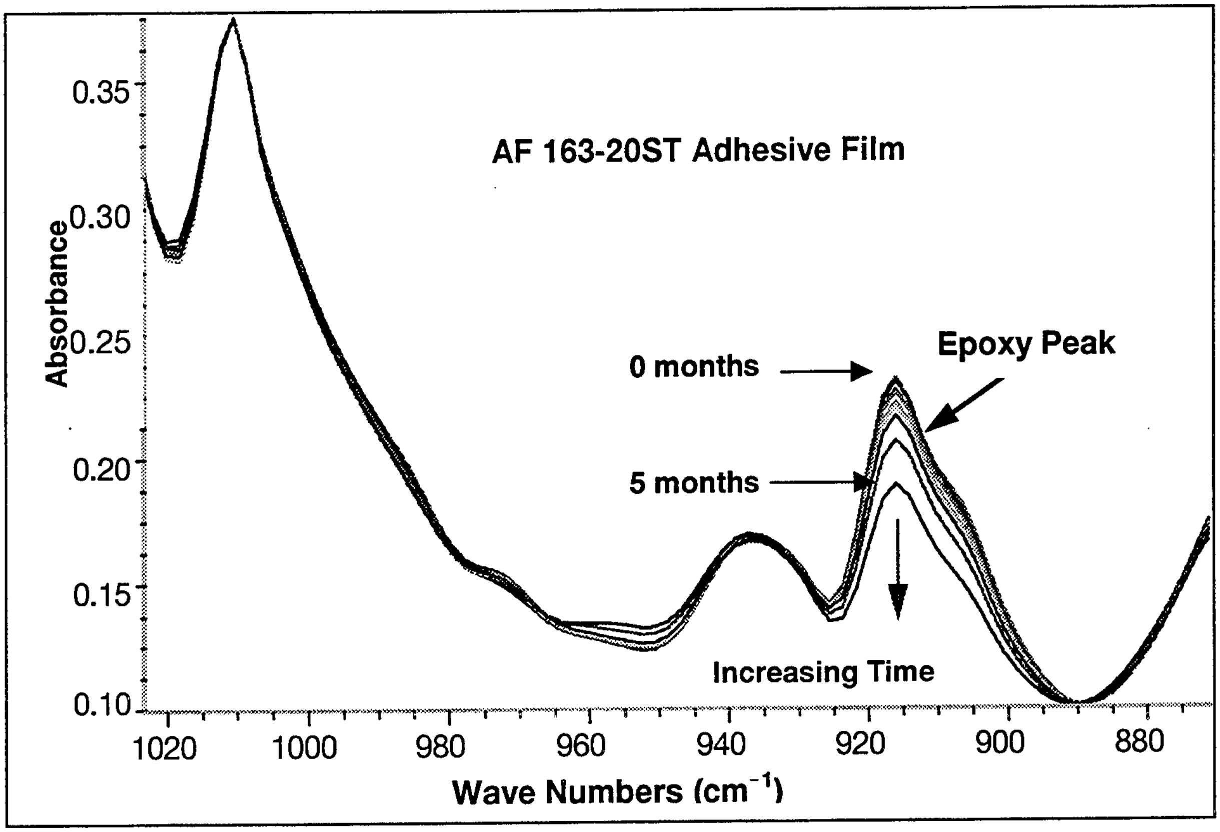

Figure 23. MIR Absorbance Spectra for AF163-20ST Adhesive Film. Note the Reduction in the 916 Peak Over a 5-Month Period.

To quantify the results, peak height relationships vs. time are studied using the following formulas:

$$\alpha(t) = 1 - A(t)/A(0) \qquad \text{(NIR: } 7000\ cm^{-1} \text{ to } 4000\ cm^{-1}\text{),}$$

and

$$\alpha(t) = 1 - A(t)/A(0) \bullet A_{ref}(0)/A_{ref}(t) \qquad \text{(MIR: } 4000\ cm^{-1} \text{ to } 400\ cm^{-1}\text{),}$$

where

α = fraction that reflects extent of cure,

A = absorbance peak height of the reactive functional group,

t = time, and

A_{ref} = absorbance peak height of a reference peak.

In the IR range, evaporation and dimensional changes could have a profound effect on the results; therefore, a reference peak is used. The reference peak selected should be a peak of a particular functional group within the sample that does not have any reactivity. In the NIR region, no reference peak is needed, since evaporation effects are reduced and dimensional changes are small. Changes with time are addressed by using the baseline method. For NIR, transmittance is assumed to be constant or to vary linearly between the shoulders of a peak. Changes in the transmittance are treated as being uniformly affected by time.

Results to date for the aging study are shown in Table 19 for the MIR range and Table 20 for the NIR range. Sources of variability for these data include ambient effects on the specimen during sample preparation, any changes in the desiccant over time, and changes in the crystal windows over time. For example, the NaCl windows can become fogged with absorbed moisture [10]. For short-term projects (one day), such effects are negligible; however, for long-term studies, these effects may be significant. Variability of ±5–10% is not uncommon in FTIR spectroscopy. Dimensional changes affect the results, and these changes tend to be more significant for MIR, where typical cell thicknesses are 0.01 to 1 mm, than for NIR, where cell thicknesses range from 0.1 to 10 mm [10]. The response of the material to each type of analysis varied; so, each material is discussed separately with observations regarding variability.

Table 19. Extent of Cure for MIR Range Observations

Products	Time (weeks)					
	1–2	4–6	8–10	12–14	16–18	20–22
Hysol 9390 part A of two-part epoxy system	0.0	1.3	10.0	15.8	13.5	21.9
AF163-20ST epoxy adhesive film	21.1	25.6	36.2	53.2	56.2	73.3
Hysol 9628.045 PSFK epoxy adhesive film	5.4	0.0	0.0	7.5	0.0	11.1
R6376 epoxy prepreg	15.6	57.0	70.8	78.0	77.1	—
JDW71 one-part epoxy/methacrylate	0.0	0.0	0.0	—	—	—
JDW72 one-part epoxy/methacrylate	0.0	0.0	0.0	—	—	—
SBIR-ARL1 epoxy	2.9	3.1	—	—	—	—

Table 20. Extent of Cure for NIR Range Observations

Products	Time (weeks)					
	1–2	4–6	8–10	12–14	16–18	20–22
Hysol 9390 part A of two-part epoxy system	1.5	0.90	5.3	1.8	—	—
Hysol 9390 part B of two-part epoxy system	1.1	2.7	3.2	4.3	6.9	5.9
AF163-20ST epoxy adhesive film	13.2	25.9	37.9	—	—	—
Hysol 9628.045 PSFK epoxy adhesive film	4.4	8.5	4.4	0.0	2.0	—
R6376 epoxy prepreg	16.6	44.5	36.6	46.4		—
JDW71 one-part epoxy/methacrylate	3.0	6.1	—	—	—	—

5.3.1 Hysol 9390. Hysol 9390 is a commercial two-part epoxy system. The two parts, Part A containing epoxy and Part B containing amine, are both liquids that are mixed prior to use. Part A can begin to cure without the addition of Part B, causing the primary limitation on shelf life for this system. Part B is expected to have less effect on aging. Part A was evaluated using both MIR and NIR. In both cases, significant changes in the spectra are observed, although at different times. The NIR results lag behind the MIR results, and differences in the sources of variability may have an effect on the cure timeline. Hysol 9390 Part B was evaluated using the reaction of an amine functional group. Due to the spectral overlap that occurs in the MIR region for the amine peak, only the NIR spectrum was used. Only small changes are noted in the NIR results for Part B. More rapid changes would be expected following mixing of the two parts for Hysol 9390.

5.3.2 AF163-20ST. AF163-20ST is a commercial adhesive film. For MIR, the film was dissolved in acetone and the solution put on the NaCl window and allowed to dry. For NIR, a piece of the film was placed directly on the NaCl window. Results from both MIR and NIR show significant effects of aging on the extent of cure.

5.3.3 Hysol 9628.045 PSFK. Hysol 9628.045 PSFK is a commercial adhesive film. Hysol 9628.045 PSFK has not aged significantly, and the results fluctuate. The aging of this sample is somewhat surprising. The sample contains both epoxy and amine; therefore, aging should occur at a more rapid rate. One explanation for the fluctuation in the results for this sample and others is that the baselines for the peaks under study change over time, causing errors in quantifying the results. In the MIR spectra for Hysol 9628.045, there is a clear indication that the baselines have changed. Effects of the acetone solvent drying may be important. Future work includes the same specimen preparation for MIR with a thorough drying procedure in a vacuum oven.

5.3.4 R6376 Prepreg. R6376 prepreg is a reformulation of an epoxy prepreg. Significant effects of aging on extent of cure are observed in both MIR and NIR. Greater variability in the NIR results may be due to a thinner specimen than is desirable. For both wave number ranges, the specimen is prepared by dissolving the resin from the prepreg and then drying the solution on the crystal window. This produces a specimen of appropriate thickness for MIR but a rather thin specimen for NIR.

5.3.5 ***CAO1.*** CAO1 is a one-part epoxy/methacrylate system formulated at ARL. No changes were observed in the MIR range. Variability was high in the NIR range (most likely an effect of significant effects in the baseline). There is a concern regarding the peak selected for measurement. Based on Horalek et al. [11], a double-bond acrylate peak is being evaluated, but more study is needed to confirm this selection.

5.3.6 ***CAO2.*** CAO2 is also a one-part epoxy/methacrylate system formulated at ARL. No changes were observed in the MIR range. NIR evaluation of this material was begun at the same time as the CAO1 material, and the effects of baseline variability were so pronounced that no measurements were recorded.

5.3.7 ***SBIR-ARL1.*** SBIR-ARL1 is a one-part epoxy formulated by Merlin Technologies, Inc., as part of an SBIR program with ARL. Initial results may indicate changes in extent of cure based on MIR observations. No NIR measurements are available for this material.

5.4 Resin Aging Study Conclusions. Preliminary results indicate that new formulations show promise to provide extended shelf life. In several cases, these are very preliminary conclusions, as the new formulations have been part of the aging study for relatively short periods of time. The aging study will continue into the next year of the program and will include downselected materials that have been formulated. As part of the aging study, work will continue on evaluating the effect of solvents, such as acetone, in the specimen preparation for MIR and on the effect of baseline drift.

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13. ABSTRACT ***(Maximum 200 words)***

Polymer-matrix composite material and structural adhesive repair and manufacturing have significant environmental costs. These costs were recently documented based on current and anticipated future Department of Defense (DOD) use of these materials. The principal issues for reducing the environmental impact and its associated cost are (1) reduction in hazardous waste by eliminating shelf-life limitations, (2) reduction in nitrogen oxides by replacing global heating of the part with localized heating, (3) reduction in volatile organic compound (VOC) emissions by accelerated curing and containment, and (4) reduction in hazardous waste by minimizing production debris through processing step management. The predicted reduction in hazardous waste, which affects both raw materials and waste-disposal costs, is 78% for composite materials and 95% for adhesives. Nitrogen oxides and VOC emissions can be reduced by 100% and 50% by replacing autoclave curing with radiation curing. Electron-beam (E-beam) curing has successfully been applied to E-beam-curable prepegs, adhesives, and vacuum-assisted resin transfer molding (VARTM) resins while maintaining process-specific viscosities and application-specific thermal performance. For the first time, there is credible evidence that E-beam-curable resin systems can be formulated to have sufficient toughness while maintaining other required process and performance criteria. In this work, both free radically and cationically cured E-beam resin systems have been formulated.

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