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for

***CHARACTERIZATION OF
CRITICAL FUNDAMENTAL AGING MECHANISMS OF
HIGH TEMPERATURE POLYMER MATRIX COMPOSITES***

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13. ABSTRACT (Maximum 200 words) This program investigated durability and potential critical fundamental aging mechanisms of the high temperature polymer matrix carbon fiber composites, especially crosslinked bismaleimide(BMI) thermosets and thermoplastic polyimide(PI) for the future applications in commercial and military aircraft. The studies involved combined stress, temperature, thermal cycling or thermal spike, moisture, time and oxygen service environment exposure which could lead to complex synergistic environmental-induced degradation mechanisms of composite performance and their critical physical and chemical aging mechanisms in terms of damage initiation and propagation on the molecular, microscopic and macroscopic structural levels in order to develop structural-performance phase diagrams for mechanics model-structural design analyses and associated materials structural optimization at all dimensional levels. Extensive and systematic studies involved two fundamental aging mechanisms, namely (i) the characterization of cure of BMI-carbon fiber composites in service environment with associated microcracking and deterioration of composite mechanical properties and (ii) the effects of thermal-moisture-time environments on the matrix physical damage mechanisms, such as enhanced oxygen diffusion and, also, potential ice formation, in BMI and PI -carbon fiber composites.			
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I. EXECUTIVE SUMMARY

This program investigated durability and potential critical fundamental aging mechanisms of the high temperature polymer matrix carbon fiber composites, especially crosslinked bismaleimide(BMI) thermosets and thermoplastic polyimide(PI) for the future applications in commercial and military aircraft. The studies involved combined stress, temperature, thermal cycling or thermal spike, moisture, time and oxygen service environment exposure which could lead to complex synergistic environmental-induced degradation mechanisms of composite performance and their critical physical and chemical aging mechanisms in terms of damage initiation and propagation on the molecular, microscopic and macroscopic structural levels in order to develop structural-performance phase diagrams for mechanics model-structural design analyses and associated materials structural optimization at all dimensional levels.

In various core test programs developed during the course of the project, the fundamental physical, chemical and mechanical-induced degradation mechanisms were identified in terms of (i) the combined effects of moisture-stress-thermal cycle or thermal spike environments; (ii) the effects of stress-time-temperature environments on the composite creep rupture failure in the absence of chemical degradation; and (iii) the synergistic effects of stress, isothermal temperature, oxygen atmosphere and its flow rate and concentrations upon composite surface degradation. For the thermal-moisture induced physical damage mechanisms the high-precision density measurement is utilized to reveal whether the thermal-moisture-time exposures cause a permanent swelling of the polymer matrix eliminating any memory of molecular glassy-state packing increases as a result of prolonged isothermal exposure (known as "physical aging"), and NMR and microcalorimetry are used to identify ice formation under rapid cooling. In addition, the extensive creep rupture experiments had been conducted at AMEES 600 specimen test facility to ascertain the effects of long time-stress/thermal environments, in the absence of chemical degradation (i.e., oxidation) on the service environment-induced composite dimensional and damage growth mechanisms and, subsequently, to predict service lifetimes from shorter time data using stress and temperature as acceleration vehicles. Detailed comparison between BMI and PI-Carbon fiber composites on short-term strength, creep rupture and failure mode had been made as a function of time under stress, test temperature, geometry factor, stress level, prior aging at high temperature, prior mechanical damage.

For BMI-C fiber composites cure reaction mechanisms and kinetics of the resin system were characterized as a function of cure and service environment conditions in order to predict cure-induced Tg increases and associated matrix and composite mechanical property deterioration. The relationship between the BMI molecular network structure, controlled by composition or initial monomer ratio and time-temperature cure conditions, and its mechanical properties and Tg was studied. The mechanical evaluation of the BMI-carbon fiber composites included the threshold matrix microcrack resistance and fiber-matrix interfacial integrity. Based on earlier studies on the structure-property relations of BMI's and the fiber-matrix interfacial integrity, new fiber surface treatments and subsequent optimal composite cure-conditions were suggested in order to inhibit composite damage initiation thresholds. The chemical characterization of the high temperature aging ($\geq 200^{\circ}\text{C}$) of BMI's as a result of dehydration-induced ether crosslink formation and subsequent decomposition of these

crosslinks causing T_g increases and mechanical property deteriorations was followed.

For PI-C fiber composites the critical hygrothermal induced degradation mechanisms are discussed in terms of:

- (i) PI depolymerization characterization and kinetics and associated mechanical and thermal property deterioration;
- (ii) Moisture evolution induced PI matrix and/or interfacial blistering upon rapid heating resulting from physically entrapped moisture and PI repolymerization.

From the systematic studies on hygrothermal durability, the K3B and AFR700B resin and composite exhibited considerable damage in the form of micro-cavitation, debonding, macroblistering and delamination upon exposure to 250°C hygrothermal spikes. The blistering threshold temperature was monitored at 229°C in the K3B composites. The BMI resin and composite exhibited no damage or property losses after exposure to similar hygrothermal spikes. The physical and chemical structural state of PI matrices such as K3B as a function of hygrothermal exposure were discussed in terms of hydrolytic chemical degradation, moisture vapor-induced physical damage and molecularly locked-in water. Those structural states were characterized by systematic weight monitoring, ²H NMR, and various thermal, mechanical property measurements using D₂O water environment. In conclusion, the most critical hygrothermal induced degradation mechanisms of polyimide, PI, -carbon fiber composites as related to present and future Air Force service environments were matrix blistering and composite delamination. Blistering occurred when the vapor pressure of physically trapped moisture exceeded the yield stress of the PI. From isothermal moisture desorption plots water molecules were locked within PI matrix (K3B and AFR 700B PI's) and were only released at temperatures approaching the dry T_g of the resin, thus causing blistering. Moisture molecular "lock-in" occurred because with increasing temperatures new H-bonding sites within the polymer became accessible to water molecules as the physical structure of the polymer glass expanded. Upon cooling, water molecules were trapped in these new sites and were only released upon heating to a temperature that the site initially became accessible. In the case of AFR 700B PI chemical hydrolysis of the imide and norbornene structures that occurred below 200°C reverted back to the original chemical structure at higher temperature evolving water which further contributed to lowering the blister threshold temperature. These studies also identified blister threshold temperatures and critical moisture contents of those PI matrices and their composites for future Air Force service environments.

In this project, we had identified the most likely potential, critical aging mechanisms that control damage initiation in BMI and PI carbon fiber composites based on the systematic durability evaluation methodology. The critical aging mechanisms involved (i) further cure of BMI-carbon fiber composites with associated T_g increases, mechanical property decreases and enhanced microcrack development in service environment exposure conditions, it was evident that the dehydration induced ether crosslink formation and subsequent rearrangement played a critical role in the chemical and physical network structural changes of BMPM-DABPA BMI resins at high service environment temperatures and long times that could significantly modify the BMI resin thermal and mechanical response and composite resin shrinkage-induced microcrack characteristics, and (ii) hygrothermal induced thermal

and mechanical property deterioration as a result of physical and chemical structural changes in BMI- and PI-carbon fiber composites. The mechanism (ii) was identified from residual property determination of the composites after various thermal cycling simulation programs as a function of temperature, humidity, moisture content, heating/cooling rate, and applied stress. Models on the moisture absorption behavior and hygrothermal induced damage mechanisms, such as matrix blistering and delamination, of the composites and their interrelationship had been suggested.

From real time T_g increase data provided by Boeing HSCT group for commercial BMI-carbon fiber composites (BASF 5260) in isothermal exposures in the 150–200°C range for times up to 8,000 hrs, it was found that the service environment exposure temperature for a T_g increase of $\leq 5\%$ over 120,000 hrs exposure as would be required in commercial aircraft applications could only be 120°C, well below the expected HSCT service environment temperatures. For a more sophisticated prediction of the T_g of the BMI composite matrix as a function of isothermal exposure temperature-time conditions, a semi-empirical expression in terms of chemical cure characteristics and BMI glassy-state diffusion characteristics had been developed

The primary performance issue for BMI-C fiber composites was that they were not fully cured under standard 250°C cure conditions and could continue to cure over prolonged periods of time in service environment at 177°C resulting in matrix embrittlement. However, extrapolation of all available high temperature reaction rate data to the 175-200°C temperature range indicated insignificant further cure and associated BMI embrittlement occurred in the dry, 175-200°C temperature range service environment because of glassy-state diffusion restrictions and decreases in reaction rates of unreacted species at these lower temperatures. Our analyses revealed no change in toughness after 120,000 hours exposure at 175°C and only a 20% decrease at 200°C for the same time period.

From the systematic studies on adhesion between carbon fiber and matrix, all evidence, to date, indicated the C fiber-matrix interface in BMI and PI composites exhibits poor mechanical integrity and was one of the weak links together with resin matrix toughness that was responsible for early microscopic damage initiation and propagation. This poor fiber-matrix interfacial integrity was more serious in BMI-C fiber composites as a result of the imposition of cure induced matrix shrinkage stresses. There had been considerable effort to improve the fiber-matrix interface mechanical integrity for BMI- and PI-C fiber composites using a range of approaches that fall into four major categories: (i) modification of fiber surface energy; (ii) increase in fiber surface functional group concentration; (iii) resin toughening; (iv) additions of fiber sizing..

From the creep rupture studies, the lifetime distribution of BMI 5260/G40-800 was broad, over more than 3 decades of time, e.g., from a few minutes to a few weeks. Prior aging for 2000 hours at 200°C reduced the short term strength by 1/3 and induced a distinct bimodal lifetime distribution probably due to two balanced creep rupture failure modes, such as brittle-like shear crack propagation and crack propagation modified by matrix yielding and crack tip blunting. A bimodal nature and its development by aging was an important feature warning of potential service problems from a low strength 'tail'. Nevertheless, all the results combined for about 100 specimens in all, fitted a single Log Extreme Value distribution. The behavior could thus be described by two parameters, the mode

and a factor indicating variability. The lifetimes of K3B showed a very wide variability. The 85% level produced a large proportion of very early failures indeed many broke on loading. Even at the 75% level there were many early failures. The distribution of lifetimes was clearly bimodal and the second mode in the distribution shifted to a longer lifetime with the lower stress level. Bimodality shown in both lifetime distribution and short term strength distribution as well as changes in the statistical mode development of K3B composites might be due to the competition between brittle and ductile processes, so-called jog splitting and thick shear banding which were distinctive deformation modes observed before the final creep rupture. The maximum elapsed time in this experiment was currently more than 6 years; experiments should be set up to obtain comprehensive distribution data over many years.

Cumulative lists of researchers involved in, and publications and presentations stemming from, this research effort were chronologically summarized in Sections V and VI.

II. INTRODUCTION AND BACKGROUND

Utilization of high temperature polymer matrix-carbon fiber composites for structural applications in future commercial such as High Speed Civil Transport (HSCT) and military aircrafts would be exposed to prolonged, extreme service environment conditions. These complex service conditions of combined stress, time, temperature, thermal cycling, thermal shock, moisture, chemical and atmospheric environment required a thorough understanding of potential physical, chemical and mechanical-induced composite degradation mechanisms, and their synergistic effects that could lead to the most probable critical failure path. An understanding of the critical fundamental aging mechanisms was necessary for credible long-term composite performance predictions from experimentally observed shorter time service-environment induced composite performance deterioration mechanisms. In addition, this understanding would generate more meaningful information for mechanics modeling-structural design analyses and associated materials structural optimization at all dimensional levels.

Two of the leading high temperature, polymer matrix-carbon fiber composites consisting of (i) crosslinked bismaleimide thermosets and (ii) thermoplastic polyimides matrices had been considered for structural applications in commercial and military aircraft models. Based on previous studies, the most likely potential, critical aging mechanisms that control damage initiation of BMI-and PI-C fiber composites had been identified. Two fundamental aging mechanisms to be studied were (i) the relationship between the BMI molecular network structure and composite processing, service environment exposure and mechanical property; specifically, the BMI cure reaction characteristics during composite fabrication and service environment and their effect on physical and chemical molecular network structure and the relationship of this structure to thermal and mechanical properties and how these relations effect the threshold stresses for matrix and fiber-matrix microcracking, (ii) the effects of thermal-moisture-time environments on the physical damage mechanisms and mechanical integrity of BMI and PI-carbon fiber composites; specifically, the polymer physical structure or the molecular packing state of the matrices, that effected gaseous

diffusion, as a function of these environmental exposure conditions together with the physical structure of absorbed moisture within the composite with the view of ascertaining whether ice formation was possible from the absorbed moisture in these environments and whether moisture and temperature-induced depolymerization occurred, especially in PI matrix system. The damage initiation mechanisms on the molecular or microscopic level might be different than those that control the macroscopic damage propagation mechanisms, such as delamination, that led to the ultimate performance deterioration of the composite component.

BMI composite matrices, which were based on the BMDPM-DABPA system were cured in composite production in the 200-250°C range. However, full cure was not attained because of glassy-state diffusion restrictions, and was only attained by post-curing at 300°C/2h, that resulted in a final T_g of near 350°C. In high temperature service environment conditions (>125°C) the undercured BMI composite matrix continued to slowly react which caused a progressively higher T_g , lower composite mechanical performance (up to 50% loss) and an enhanced susceptibility to resin microcracking from resin shrinkage. Boeing Commercial Airplane Group had observed real time T_g increases for commercial BMI-carbon fiber composites (BASF 5260) of up to 70°C after isothermal exposure in the 150-200°C temperature for up to $\sim 10^4$ hours. Also reported were a 50% decrease in impact energy after thermal aging of BMI-carbon fiber composites for 1,000 hours at 190°C, an increase surface ply crack density after isothermal 177°C air exposure for 750 hours for [0/90] laminates, transverse microcrack density increases for 16 ply quasi-isotropic BMI-carbon fiber composites aged isothermally in the 150-204°C range for 16,000 hours as a function of time, temperature and ply depth. Therefore, design confidence and durability predictions of BMI-carbon fiber composites required:

(i) Characterization of:

- Cure reactions and their kinetics in the glassy state;
- The physical and chemical molecular network structure, particularly network defects in terms of unreacted chemical groups;
- The relationship between BMI matrix molecular network structure and its mechanical properties and T_g ;
- The threshold stresses that cause matrix microcracking as a function of composite processing and service environment conditions;
- Composite fiber-matrix interfacial structural integrity; and

(ii) Development of a model that predicted composite thermal and mechanical response and integrity as a function of processing and service environment conditions in terms of BMI chemical cure reaction characteristics and glassy-state diffusion restrictions.

In aerospace applications of high temperature polymer matrix composites hygrothermal performance had been great concerns since those composites that contained absorbed moisture could be exposed to service environment that involved rapid temperature changes. It had been reported that hygrothermal exposure of BMI- and PI-carbon fiber composites had resulted in matrix blistering and composite delamination and significant permanent “dry” T_g decreases after hygrothermal spiking or aging as a results of possible matrix physical and chemical modifications. Obviously, the trapped moisture vapor could cause damage to the composite in the form of matrix microcracking and/or

blistering and/or fiber-matrix interfacial failure, if the moisture could not diffuse-out of the composite in sufficient time prior to moisture vaporization. The moisture vapor pressure might cause the moisture plasticized matrix to swell which might then be permanently frozen-into the glassy-state upon cool-down. The swollen matrix would have a higher glassy-state free volume and exhibit higher associated oxygen and moisture diffusion. In addition, when these moist composites were rapidly cooled to below 0°C it was possible moisture could condense in cavities within the composite with water molecular clusters of >190 water molecules which would then lead to ice formation and irreversible damage as a result of ice formation induced volume increases.

In the 1970's there was considerable effort made to characterize composite damage as a result of moist composites being exposed to extreme thermal service environment conditions on fighter aircraft during a supersonic dash. The aircraft dived from high altitude (outer surface temperature -20 to -55°C) into a supersonic, low-altitude run during which the surface temperature rises in minutes to between 100 and 150°C as a result of aerodynamic heating. On reduction of speed, the outer surface temperature was expected to drop rapidly at rates up to ~500°C/min, thus exposing the epoxy composite to a thermal spike. Simulation of such thermal spikes had been shown to increase the amount of moisture absorbed by the epoxy or epoxy composite. However, after a certain number of consecutive thermal spikes, the amount of moisture absorbed ceased to increase. The entrapped moisture vapor pressure within the composite matrix exceeded the overall moisture plasticized yield stress of the epoxy causing homogeneous swelling of the TGDDM-DDS epoxy matrix. These homogeneous free-volume increased which involved permanent rotational-isomeric population changes within the epoxy network were fixed in the epoxy glass during the rapid cooling after the thermal spike. The additional free-volume within the epoxy allowed water molecules access to previously unavailable H-bond sites. The moisture vapor pressure induced epoxy network swelling was ultimately restricted by network extensibility limitations, thus limiting the number of accessible H-bond sites for interaction with water molecules after a number of thermal spikes. Thermal spike exposure did cause surface microcracking in thicker epoxy and composite specimens as a result of larger service environment temperature gradients and inherent fabrication stresses. In the 1980's moist composites potentially could be exposed to even more severe thermal environments as a result of laser exposure. The presence of composite absorbed moisture was found to significantly modify laser thermal-induced composite damage. Front surface ablation was found to occur in the moist composite if the moist polymer matrix T_g was <100°C. However, through-thickness moisture composite thermal-induced degradation was considerably reduced compared to dry composites, as result of thermal energy by moisture vaporization.

There had been several reports showing significant decreases in PI-carbon fiber composite dry T_g 's of >50°C after exposure to high temperature hygrothermal environments. These observed "dry" T_g decreases could be caused by physically entrapped water molecules in glassy-state that were only released at high temperatures causing plasticization and lowering of the T_g . With increasing temperatures new H-bonding sites within the polymer became accessible to water molecules as the physical structure of the polymer glass expanded. Upon cooling, water molecules could be trapped in these new sites and were only released upon heating to a temperature that the site initially became accessible. On the other hand, polyimides were susceptible to hydrolytic polymer chain scission as

a result of (i) scission of any inherent amide group defects present as a result of non-ring closure to the imide ring and (ii) imide ring opening to amide formation followed by scission of the amide group. Hydrolytic attack of the imide ring reversed the polymerization reaction resulting in the formation of the polyamic acid, followed by chain scission and associated molecular weight and strength decreases resulting ultimately in regeneration of the monomers. The hydrolytic degradation of amide linkages in polymers, particularly at high temperatures in the presence of moisture was well documented. However, there was sparse direct data on the rates of hydrolytic attack of the imide ring. Opening of the imide ring by acidic H^+ protons or alkaline OH^- groups and resultant hydrolytic chain scission, lowering of molecular weight and associated polymer strength loss occurred in aggressive humid-acidic environments. For example, the Navy had experienced severe in service corrosion problems for their bismaleimide-carbon fiber aircraft components as a result of protonic galvanic attack of the maleimide ring. From the viewpoint of imide ring opening there had been a number of literature reports of acid and alkaline catalytic-induced hydrolytic degradation of PI's that resulted in reported decreases in viscosity and by association molecular weight and strength. Certainly, molecular weight decreases were further accelerated by acid-catalyzed oxidative degradation of PI's. Because of the uncertainties of the amount of inherent amide link impurities in the PI's used in the literature studies of PI hydrolytic degradation, it was not possible to ascertain from these studies directly the rates of hydrolytic imide ring opening. However, a group of researchers studied the kinetics of acidic catalyzed hydrolysis of phthalanilic acid using phthalanil model compounds, and their data indicated the imide hydrolysis was 550X slower than the amide hydrolysis in concentrated sulfuric acid.

When physically trapped and/or chemically evolved moisture vapor pressure exceeded the local polymer matrix yield stress during dynamic hygrothermal exposure matrix cavitation would occur. Such matrix cavitation and associated delamination depended on a series of variables such as (i) previous humidity-time-temperature exposure and associated moisture concentration profiles; (ii) component thickness; and (iii) rapid heat-time service environment exposures, such as thermal spikes. A thermoset is more resistant to cavitation and associated macroscopic blistering than a thermoplastic because thermoset cavitation requires rupture of covalent crosslinked molecular segments.

A systematic durability methodology to evaluate the long term performance of these high temperature composites had been applied throughout these studies. The methodology involved initially studying the effects of individual or combined core test service environments upon composite performance in order to identify the most likely synergistic service environments and controlling physical, chemical and mechanical parameters of the ultimate critical failure path. This methodology led to lifetime predictions and materials optimization based on identified mechanisms rather than empiricism. In this project, various core test programs to investigate performance potential of the high temperature composites in terms of (i) thermal cycling, stress and absorbed moisture service environments, (ii) long-time stress, thermal environments where chemical degradation is insignificant, (iii) stress-air flow-time-temperature service environments, and (iv) accelerated hygrothermal aging in a pressure bomb followed by a systematic drying program were developed. The critical hygrothermal induced degradation mechanisms of PI-C fiber composites were further studied in terms of (a) PI chemical depolymerization characterization and kinetics and associated mechanical and thermal property deterioration, (b) Moisture evolution induced PI matrix and/or interfacial blistering upon rapid heating

resulting from physically entrapped moisture and repolymerization of hydrolytically degraded PI that chemically produced water molecules.

III. RESEARCH OBJECTIVES

Based on our previous studies the most likely potential, critical aging mechanisms that control damage initiation in BMI and PI-carbon fiber composites had been identified and a systematic durability evaluation methodology was developed. Our overall durability program goal was to : (i) identify the synergistic critical failure path and its associated performance deterioration mechanisms; (ii) conduct synergistic service environment accelerated performance testing based on the physics and/or chemistry and/or mechanics of the aging mechanisms of high temperature polymeric composites of potential utilization in the high speed aircraft; and (iii) develop fabrication and material optimization procedures to alleviate any performance deficiencies. These would be further complemented by characterizing critical fundamental aging mechanisms on the molecular and microscopic level of BMI and PI-carbon fiber composites in future aerospace stress-time-temperature-moisture-chemical service environments.

IV. TECHNICAL SUMMARY

1. MATERIALS

The BMI resin studied was a commercial system, 4,4' -bismaleimidodiphenyl methane (BMPM)/0,0'-diallyl bisphenol A (DABPA), Matrimid® 5292, Ciba-Geigy. This BMI system was the principal matrix used to fabricate BMI-carbon fiber composites in most of this program. The BMDPM bismaleimide monomer was a crystalline powder with a melting point of 150 - 160°C, whereas the DABPA monomer was a viscous liquid at room temperature. Content of maleimid double bond in BMDPM was 85% of the theoretical value. Content of hydroxyl groups in DABPA was 62%. Molecular mass of the system was 358g/mol and 308g/mol for A and B, respectively. Both components were stored after sealed with dry nitrogen. The two components were mixed and degassed at 130°C and initial cure was at 177°C followed by post-cure cycles up to 300°C.

The PI resin systems studied were:

- (i) Avimid® K3B, DuPont, formed from an aromatic diethyl ester of the pyromellitic diacid and an aromatic diamine in N-methyl-2-pyrrolidone, NMP, and
- (ii) AFR700B is based on a fluorinated PI oligomer with norbornene and primary amine end cap groups, provided by U.S. Air Force Wright Laboratory

The composite materials studied were fabricated with AS-4 or IM-7 carbon fibers in various lay-up configurations. The standard BMI 5292/IM7 composites were cured at 177°C for 1 hr followed by a post-cure for 2 hrs at 200°C and for up to 6 hrs at 250°C unless otherwise indicated. K3B/IM7 composites were consolidated at 360°C using autoclave vacuum bagging process at Boeing Commercial Airplane Group, Seattle.

In some of our studies the BMI 5260 (BASF)-carbon fiber (G80-400) composite was used. This BMI system consists of eutectic BMI mixtures of toluenediamines and 4,4'-methylenedianiline cured with DABPA. A co-polyimide particulate thermoplastic is used as a toughening agent. The composite panels were also processed at Boeing; cured at 190°C for 4 hrs and post-cured at 215°C for 6 hrs.

Various laminate configurations, such as 4-ply [0/90]_{1s}, 8-ply [0/90]_{2s}, 16-ply [0/90]_{4s}, and 16-ply quasi-isotropic [45/90/-45/0]_{2s} balanced symmetric laminates and other specially designed laminates were studied for various experimental tasks. All composite panels were inspected by C-scan before cutting into the test specimens.

2. FUNDAMENTAL AGING MECHANISMS OF BMI-CARBON FIBER COMPOSITES

2.1 Cure Reaction, kinetics and Network Structure Characterization

The cure reaction mechanisms and associated kinetics of BMDPM-DABPA BMI were investigated using systematic Fourier transform infrared spectroscopy, FTIR, and differential scanning calorimetry, DSC, studies as a function of initial monomer ratio and cure time-temperature conditions in order to understand and predict cure-induced T_g increases and associated matrix and composite mechanical property deterioration. [VI- 3,5,14,15,22,28]

The principle findings and conclusions from this program were as follows:

(i) The BMDPM and DABPA monomers reacted in the 100-150°C to reversibly form an "ene" adduct followed by a Diels-Alder slow condensation reaction between maleimide C=C bonds and propenyl C=C bonds, whose product sterically slowed significantly further reaction in this temperature region.

(ii) In the 150-250°C temperature region rapid, free radical polymerization of the C=C bonds occurred, together with slow hydroxyl condensation dehydration to form ether linkages, resulting overall in a complex crosslinked network. FTIR studies showed all the maleimide and allyl C=C bonds are consumed under standard cure conditions at 250°C after 3 hours. However, it was uncertain if all the more sterically restricted propenyl C=C bonds were consumed under these standard cure conditions, as it was difficult to detect such groups by FTIR. The ether crosslink reaction was only ~50% complete after 9 hours at 250°C. That is, the BMI composite matrix was not fully cured under standard recommended commercial cure conditions.

(iii) In the 250-300°C temperature region further cure occurred via slow, glassy-state diffusion controlled dehydration and possibly free radical propenyl C=C bond polymerization.

(iv) However, the ether cross-links decreased in concentration in the 240-300°C temperature range as a function of extended cure time up to 17 hours.

(v) Based on these findings, it was evident that the dehydration induced ether crosslink formation and subsequent rearrangement played a critical role in the chemical and physical network structural changes of BMDPM-DABPA BMI resins at high service environment temperatures and long times that could significantly modify the BMI resin thermal and mechanical response and composite

resin shrinkage-induced microcrack characteristics.

(vi) From the systematic studies on the T_g changes by TMA and the degree of cure by DSC for the BMPM-DABPA (1:1 molar) BMI system, as a function of isothermal exposure temperatures from 130 to 300°C for up to 30 hours, the followings were observed;

- for all cure temperatures the T_g increased rapidly at short times in the liquid state and only increased slowly at longer times in the glassy state as a result of diffusion restrictions,
- there was an abrupt increase in T_g between isothermal 200°C and 250°C cure temperatures over similar time periods, which was consistent with the maximum rates of the double C=C polymerization cure reactions occurring in this range,
- the interrelationship between the degree of cure, α , and T_g as a function of isothermal cure temperature for a constant cure time of 10 hours clearly indicated that the T_g for a specific degree of cure was cure history path dependent, as the isothermal T_g - α plots did not fall on one common plot,
- the poor sensitivity of the degree of cure to the T_g , particularly at the higher cure temperatures indicated that the crosslink reactions in this range did not exhibit as strong ΔH_i exotherms as a lower temperatures. This lack of sensitivity could be associated to the lower heat of reaction of the dehydration reaction that exclusively occurred in the latter stages of cure in the 280-300°C range.
- In the 130-250°C temperature region, the T_g at final cure temperature was essentially independent of cure history path. The T_g was, therefore, not sensitive to any network structural differences that might result from a range viscosity-time cure history profile differences that would affect intermolecular versus intramolecular cure reactions.

(vii) From real time T_g increase data provided by Boeing HSCT group for commercial BMI-carbon fiber composites (BASF 5260) in isothermal exposures in the 150–200°C range for times up to 8,000 hrs, it was found that the service environment exposure temperature for a T_g increase of $\leq 5\%$ over 120,000 hrs exposure as would be required in commercial aircraft applications could only be 120°C, well below the expected HSCT service environment temperatures. For a more sophisticated prediction of the T_g of the BMI composite matrix as a function of isothermal exposure temperature-time conditions, a semi-empirical expression in terms of chemical cure characteristics and BMI glassy-state diffusion characteristics had been developed.

2.2 Network Structure Interrelations with Mechanical, Thermal and Physical Properties

The specific goal of this task was to determine the relationship between BMI matrix molecular network structure and its mechanical, thermal and physical properties, that leads to development of a model that predicts those BMI properties as a function of processing and real service environment conditions in terms of BMI chemical cure reaction characteristics and glassy-

state diffusion restrictions which were discussed in Section 2.1.

The network structure alterations were controlled by initial monomer ratios and cure cycles derived from our current understanding of the cure chemical reactions. T_g , density and weight loss as well as mechanical properties, such as tensile and flexural properties at three temperatures, 23°C, 177°C, and 250°C, of BMI neat resins were determined as a function of BMI composition (four initial monomer ratios) and cure time-Temperature cycle (two standard cure, two low temperature cure and two high temperature cure cycles). [VI- 3,5,14,15,21,28,29,35].

The findings from the studies on the combined effects of BMI initial monomer ratio and cure time-temperature cycle on T_g , density and weight loss supported that the dehydration induced ether crosslink formation and subsequent rearrangement played a critical role in the chemical and physical network structural changes of BMPM-DABPA BMI resins at high service environment temperatures and long times that could significantly modify the BMI resin thermal and mechanical response and composite resin shrinkage-induced microcrack characteristics. Specifically, the results of the studies showed a ~0.2% density decrease; ~0.3 wt% loss; 10% modulus and a 25-40% ductility loss in the 25-177°C temperature range and an increase in equilibrium moisture absorption and diffusivity at 40°C and 70°C as a function of initial monomer compositions, that was associated with ~ 100°C increase in T_g after further cure in the 250-300°C temperature range. These property changes all occurred after all the double C=C bonds of the ene molecule had been consumed. The chemical and physical mechanisms associated with these BMI resin property modifications had to involve thermal dissociation of the ether linkages followed by formation of less flexible crosslinks, such as -C-C-linkages, and a possible increase in overall crosslink density.

In addition, higher initial BMPM monomer concentrations resulted in higher overall densities and T_g , but at the same time, higher equilibrium moisture contents and faster moisture diffusivities for a specific cure cycle, thus indicating a more open/porous molecular and/or nano scale level crosslinked network structure as a result of the stiffer characteristics of the dense BMPM segments. However, the T_g 's of networks cured at 300°C were not influenced by the BMPM initial concentration, as other network structural entities associated with the ether cross-link rearrangement played a more predominant role. Similarly, higher cure temperature or longer time for a given composition resulted in lower overall density, higher diffusivity, higher equilibrium moisture content, and higher T_g . Again, the change was minimal at 300°C cure.

The primary performance issue for BMI-C fiber composites was that they were not fully cured under standard 250°C cure conditions and could continue to cure over prolonged periods of time in service environment at 177°C resulting in matrix embrittlement. However, extrapolation of all available high temperature reaction rate data to the 175-200°C temperature range indicated insignificant further cure and associated BMI embrittlement occurred in the dry, 175-200°C temperature range service environment because of glassy-state diffusion restrictions and decreases in reaction rates of unreacted species at these lower temperatures. Our analyses revealed no change in toughness after 120,000 hours exposure at 175°C and only a 20% decrease at 200°C for the same time period.

2.3 BMI-carbon Fiber Composite Cure History and Associated Matrix Microcracking and Fiber-matrix Interfacial Integrity

The objectives of this task are to ascertain the fiber/matrix adhesion level and the microcracking threshold conditions as a function of cure and service exposure. The poor fiber-matrix interfacial integrity, optimal composite cure conditions and potential new fiber surface treatments were studied in order to enhance composite damage initiation thresholds [IV-3,4,16,21,23,28,33].

During the fabrication and post-cure of BMI-carbon fiber composites significant residual stresses could develop within the composite because of (i) thermal expansion mismatch between the fibers and matrix and (ii) BMI resin shrinkage during cure. Post-curing BMI-carbon fiber composites in the 250-300°C range resulted in matrix microcracking in 0°/90° composite laminates based on BMPM-DABPA (1:1 molar ratio) BMI resins. A variety of analyses including finite element method, a closed form analytical solution, and Monte-Carlo simulation were used to model the combination of macroscopic and microscopic stresses which result from thermal loading. In addition to the modeling, [0° /90°]s BMI/IM7 composites were analyzed using ESEM (Environmental Scanning Electron Microscope). It was found that all laminates were microcracked regardless of cure cycle, if once post-cured. As expected, crack widths grew with decreased fiber volume fraction, and increased with cure advancement. Observation in the ESEM revealed poor adhesion between the IM7 C-fiber and the BMI resin for both cure induced and mechanically induced cracks. No cure induced microcracks were found in the polyimide (K3B)-IM7 C fiber composite, but poor adhesion was observed after mechanical loading.

The adhesion between carbon fiber and matrix had been measured using a variety of techniques. Direct evidence of poor adhesion was obtained by ESEM imaging of Mode I crack opening failure surfaces. The revealed fibers were completely devoid of resin which was seen in adhesive failures. Images of both thermally and mechanically induced cracks also showed a completely adhesive failure. Four point flex testing of composites revealed very poor interlaminar shear strength as evidenced by the mid-plane shear failure of flexure samples with a 28:1 span to depth ratio. IFSS values measured using the Interfacial Testing System (ITS) were less than 10% of the values for standard epoxy/carbon fiber systems. All evidence, to date, indicated the C fiber-matrix interface in BMI and PI composites exhibits poor mechanical integrity and was one of the weak links together with resin matrix toughness that was responsible for early microscopic damage initiation and propagation. This poor fiber-matrix interfacial integrity was more serious in BMI-C fiber composites as a result of the imposition of cure induced matrix shrinkage stresses.

There had been considerable effort to improve the fiber-matrix interface mechanical integrity for BMI- and PI-C fiber composites using a range of approaches that fall into four major categories:

- (i) modification of fiber surface energy;
- (ii) increase in fiber surface functional group concentration;
- (iii) resin toughening;
- (iv) additions of fiber sizing.

However, these studies to date had not resulted in significantly improving the mechanically weak interface deficiency in BMI-C fiber and to a lesser extent PI-C fiber composites. There were a number of reasons for this lack of significant improvement:

- (i) The wide temperature range between composite fabrication conditions and lower extremes of service environment use temperatures produced high fiber-matrix interfacial stresses;
- (ii) Functionally active C fiber surface groups, such as -COOH and -OH groups were lost from the fiber surface in the 275°C temperature region;
- (iii) Lack of thermal stability of many of the thermoplastic sizings during the relatively long time - high temperature composite fabrication conditions and/or lack of sufficient toughness over wide service environment temperature ranges;
- (iv) Loss of fiber strength as a result of fiber surface treatments.

3. THERMAL-MOISTURE INDUCED DEGRADATION MECHANISMS OF BMI AND PI-CARBON FIBER COMPOSITES

3.1 Thermal - Moisture - Stress - Time Exposure Core Test Programs

Present and future polymer-matrix fibrous composite aerospace applications involved combined complex synergistic stress, thermal, moisture, time, radiation and oxygen service environment-induced degradation mechanisms of composite performance. In this program, various controlled exposure core test programs had been developed to simulate or accelerate actual in-service exposure environment conditions and to ascertain if those synergistic service environments caused any composite damage and deteriorated composite residual mechanical properties, thus the critical aging mechanisms that controlled damage initiation in BMI and PI -carbon fiber composites in aerospace applications could be characterize/identify [VI-3,6,14,16,21,28,29,35].

The core test programs developed during this study included:

- (i) Synergistic Thermal Cycling/Thermal Shock-Moisture Effects
 - The effects of thermal cycling (up to 30°C/min) of BMI-C fiber composites (-60°C to +190°C) in HSCT service environments for initially moist composites could be potential core test degradation mechanism. The program consisted of the following exposures, (i) dry-controls: completely dried in vacuum at 23°C, (ii) wet-hot; 95% RH at 80°C and wet-hot & re-dried in vacuum at 23°C, (iii) wet-cold; 95%RH at 23°C; (iv) thermal cycling under humidity (TCH); 95% RH cycled between 23°C and 80°C, (v) thermal cycling under humidity cycle(TCHC); cycled between 95% RH, 23°C and 0% RH 80°C or 0% RH, 180°C, (vi) extended thermal cycling; flight simulation (ETCFS); extended thermal cycles were between temperatures of 23°C, -54°C and 177°C which were the suggested temperature extremes for a Mach 2.4 HSCT. In cases of TCH and ETCFS the applied stress in 4 point flexure mode (up to 20% of σ_f) was also investigated.

As a result of these thermal cycle-moisture exposures, no significant modification in room temperature composite mechanical properties was detected. However, under TCH conditions, the

% moisture absorption in the composite measured at 23°C was always higher than at 80°C, so-called a reverse thermal effect. This moisture absorption behavior was explained in terms of moisture vapor-induced elastic cavity formation. The equilibrium moisture absorption was controlled by both thermodynamic and kinetic reaction of water molecule to the polymer system. From the combined temperature (up to 180°C) and humidity cycle experiment (TCHC) it was found that the moisture absorption in the BMI-carbon fiber composites was independent of previous wet history of the composites.

- The effects of heating and cooling rates (up to 55°C/min) in the HSCT flight simulation cycles (ETCFS) upon composite residual mechanical properties, damage and failure behavior were investigated for BMI 5292/AS-4 (System II), BMI 5260/G40-800 and K3B/IM-7 composites. This cycle contained a wet stage 80% RH, 40°C) and a dry stage (40°C, vacuum). Including a wet stage in each cycle was critically important in simulating actual HSCT application and in monitoring moisture-induced damage. During cycling, moisture absorption and microcracking or delamination behavior was monitored. After a total 82 cycles, glass transition temperature and room temperature residual mechanical properties were determined after dried in vacuum at 40°C. In fact, the weight change monitoring was a sensitive tool in detecting the thermal cycle and/or moisture-induced damage or structural changes in the composite system.

The residual mechanical properties determined at room temperature and at 177°C showed a slight decrease in modulus and strength but a slight increase in the strain to failure for all composites. This softening effect was most pronounced in the wet cycled composites and the BMI 5260/G40-800 carbon fiber composites showed the highest changes. The effects of the applied strain, 0.5% flexural strain were not significant on both the moisture absorption behavior and the residual mechanical properties of both BMI and K3B composites. The most significant results were obtained from the dynamic mechanical analysis scanned to 300°C. In the case of BMI 5260 composites, the T_g of the as-received and the wet-cycled composites was significantly lower, about 12°C, than that of the dry control while that of the dry-cycled composites remained the same, obviously due to the residual or trapped water in the system, but no damage/deformation after the DMA test. However, in the case of K3B composites, the as-received and the wet-cycled samples were all blistered and buckled during DMA scan even though the T_g was not much changed, about 5°C lower. The high temperature induced blistering of the K3B composites was associated with the high moisture vapor pressure exceeding the thermoplastic matrix yield stress and, also, due to an inhomogeneous, localized distribution of water molecules. In the case of K3B thermoplastic matrix the damage was very localized and associated with a larger scale yielding by the high vapor pressure. On the other hand, in the thermoset matrix of BMI, water could be distributed homogeneously and thus the damage could be micro-scale yielding by relatively lower vapor pressure, but in general more significant mechanical property degradation was resulted in.

- The hygrothermal induced damage evolution, property degradation and the related mechanisms were further investigated by a thermal spiking to 250°C from 30°C, either vacuum dry or 90%RH wet stage. A total of 12 spikes was carried out. From this exposure test it was also found that K3B/IM7 composites and neat resin samples failed by blistering when they were

wet, while BMI resins and composites, either wet or dry, showed no visible damage or structural morphological changes. A major blistering temperature was determined at 229°C even though some indications of early micro-cavitation/blistering were observed between 200°C and 225°C. When the trapped moisture vapor pressure exceeded the local polymer matrix yield stress during dynamic hygrothermal exposure matrix cavitation would occur. Such matrix cavitation and associated delamination depended on a series of variables such as (i) previous humidity-time-temperature exposure and associated moisture concentration profiles; (ii) component thickness; and (iii) rapid heat-time service environment exposures, such as thermal spikes. However, BMI-carbon fiber composites exhibited no evidence of blistering for a similar thermal spike. A thermoset was more resistant to cavitation and associated macro blistering than a thermoplastic because thermoset cavitation required rupture of covalent crosslinked molecular segments. Moisture absorption, desorption and diffusion behavior was analyzed and correlated to the physical structural state of materials for both thermoplastics and thermosetting systems. Discussed also included effects of laminate configuration in terms of microcrack formation and the effects of hygrothermal-induced damage; micro-cavitation or blistering.

From the residual mechanical property characterization including tensile, 4-point Flexure, DMA, Open Hole Compression, and Iosipescu Shear testing, the most property degradation was observed in wet spiked K3B/IM7 composites obviously due to micro-cavitation and blistering. Inconsistent behavior between BMI neat resin and BMI/C-fiber composite was noticed and discussed in terms of hygrothermal degradation mechanism.

Dry T_g changes of both neat resins and composites were determined after various exposures. BMI systems showed most changes, i.e., dry T_g drops up to 5°C after wet exposure probably due to residual moisture, but increased about 10°C after spikes mostly due to cure advancement. However, no T_g changes in K3B systems was observed from wet and spike exposures even though density of K3B composite dropped more than 40% due to hygrothermal induced micro-cavitation and blistering. This suggested that the hygrothermal spiking did not cause any chemical de-polymerization in K3B systems.

(ii) Long-time Stress, Thermal Environments in the Absence of Chemical Degradation

Creep rupture experiments were conducted at AMEES 600 specimen test facility to ascertain damage growth and failure times of 4-ply $[0/90]_{1S}$, $[\pm 45^\circ]_{1S}$ and 8-ply $[0/90]_{2S}$ composite laminates as a function of stress level, time and temperature regimes where chemical degradation, such as oxidation, was insignificant. It was also envisioned to predict service lifetimes from shorter time data using stress and temperature as acceleration vehicles. Composite failure times were monitored, and any inherent damage was characterized together with residual mechanical properties

The short term strength of the composites determined by the stair technique, so-called 'Stair Strength' in the same equipment used for lifetime measurements increased significantly with width but it was remarkably insensitive to surface abrasion and to a wide range of pin driven damage when the effective strength was calculated from the undamaged cross-sectional area. The distribution of short term strength of K3B/IM7 composite was distinctly bimodal and broad while the distribution for

BMI5260 composite was much narrower. A yield phenomenon occurred prior to break in most specimens; in the form of a 45° thick shear band on the surface at 90° to the outer fibers; the distribution of stress at this yield was narrow and it may have only one mode.

The creep rupture test protocol involved short term strength combined with lifetime measurements at 3 selected stress levels which aimed for the distribution of creep rupture lifetimes centered around (1) a day, and (2) a year, and for detection of catastrophic change in the creep rupture process at 50% of short term strength. General lifetime behavior fell into two types, (1) a zone where the regression of lifetime with stress was shallow and (2) the extreme of catastrophic degeneration. As these zones were characterized by wide variations in lifetime even at constant stress, the main assessment was of the details of the distribution.

In general, the lifetime distribution of BMI 5260/G40-800 was broad, over more than 3 decades of time, e.g., from a few minutes to a few weeks. Prior aging for 2000 hours at 200°C reduced the short term strength by 1/3 and induced a distinct bimodal lifetime distribution probably due to two balanced creep rupture failure modes, such as brittle-like shear crack propagation and crack propagation modified by matrix yielding and crack tip blunting. A bimodal nature and its development by aging was an important feature warning of potential service problems from a low strength 'tail'. Nevertheless, all the results combined for about 100 specimens in all, fitted a single Log Extreme Value distribution. The behavior could thus be described by two parameters, the mode and a factor indicating variability. The lifetimes of K3B showed a very wide variability. The 85% level produced a large proportion of very early failures indeed many broke on loading. Even at the 75% level there were many early failures. The distribution of lifetimes was clearly bimodal and the second mode in the distribution shifted to a longer lifetime with the lower stress level. Bimodality shown in both lifetime distribution and short term strength distribution as well as changes in the statistical mode development of K3B composites might be due to the competition between brittle and ductile processes, so-called jog splitting and thick shear banding which were distinctive deformation modes observed before the final creep rupture. The maximum elapsed time in this experiment was currently more than 6 years; experiments should be set up to obtain comprehensive distribution data over many years.

Prediction of lifetimes with a semi-empirical model based on the measured phenomena was attempted. Considerable efforts has been made to apply statistical analysis using 'Probability Charts' indicated Log. Extreme Value as the underlying distribution for lifetime.

(iii) Stress-air Flow-time-temperature Service Environments

This core test program was to determine principal composite degradation mechanisms and to predict composite residual strength deterioration from exposure to combined stress, air flow, and composite temperature service environments. A scouting experiment for both BMI 5260/G40-800 and K3B/IM-7 composites, 4-ply [0/90]4S, was conducted at a severe exposure condition, namely hot air flow (200°C), mechanical stress (~ 0.4% max. bending strain) and composite temperature to 200°C.

Surface damage was monitored visually and by optical microscopy, and K3B composites experienced transient melting on the exposed area. Small Spot X-ray Photoelectron Spectroscopy (XPS) analysis conducted on (1) the control (as-received), (2) only temperature-mechanical stress exposed, and (3) hot air blast-temperature-mechanical stress exposed composites indicated, (i) Nitrogen concentration decreased gradually from the control to the exposed composites, especially the hot-air blasted one, which might be possibly related to dissipation of residual NMP, (ii) Oxygen concentration remained almost constant after subtracting oxygen concentrations associated with silicone atoms from release agent and nitrogen atoms from NMP in BMI 5260 composites. On the other hand, K3B composites showed a considerable increase in oxygen concentration for the exposed composites, specially for the hot air blasted one. This might be interpreted as an additional oxidation. These XPS results were subjected to reconfirmation because of the technique's sensitivity.

Effects of residual N-Methyl Pyrollidone(NMP) solvent on long term mechanical performance or durability of PI toughened BMI and K3B composites had to be thoroughly understood prior to predict any thermal aging behavior of the systems. It was uncertain whether potential NMP residual solvent in high temperature polymeric composite matrices was in significant enough concentrations to act as a plasticizer and enhance composite toughness. Certainly, BASF 5260 BMI-C fiber composite were both fabricated from NMP based polymeric solutions. The concern for HSCT applications was that any residual NMP might be lost during service environment conditions leading to a decrease in composite toughness. Previous experimental data indicated it was extremely difficult to remove NMP solvent from high temperature polymer matrices.

(iv) Accelerated hygrothermal aging in a pressure bomb followed by a systematic drying program.: Both neat resin and composite samples were exposed with superheated steam in a pressure bomb at 160°C (pressure generated was about 100 psi) for 1000 hours. D₂O rather H₂O saturation was carried out in these studies in order to conduct ²H NMR studies of D₂O molecular mobility in the PI's. Then, those samples were dried in vacuum at various temperatures up to the wet T_g of the samples. Weight, density, T_g, blistering temperature, and residual mechanical properties were monitored. Dynamic mechanical behavior and NMR analysis were carried out at Air Force Wright Patterson laboratory. Technical objectives, key issues and principal findings are discussed in the following section 3.2.

3.2 Composite and Polymer Matrix Physical, Chemical Structural State and Mechanical Integrity

The critical hygrothermal induced degradation mechanisms of PI-C fiber composites were investigated in terms of (i) PI depolymerization characterization and kinetics and associated mechanical and thermal property deterioration; (ii) Moisture evolution induced PI matrix and/or interfacial blistering upon rapid heating resulting from physically entrapped moisture and PI repolymerization. This program was carried out jointly with Wright Laboratory, AFML.[VI-28,29,35]. In order to ascertain the effects of high temperature hygrothermal environmental exposure upon:

(i) physically trapped moisture;

(ii) chemical hydrolytic degradation;
(iii) residual mechanical, physical and thermal properties;
and (iv) blistering onset temperature;
K3B and AFR700B PI resins were moisture saturated in a pressure bomb at 160°C, 110 psi for 1000 hours and then isothermally dried as a function of time and temperature as described in section 2.1.

The principal findings from this study were:

- It was extremely difficult to remove all the moisture under vacuum from PI's even after drying above 100°C for over 500 hours. The moisture desorption was directly related to the difference between the isothermal drying temperature and the dry T_g for both K3B and AFR700B PI's. These findings indicated that higher T_g PI's retained higher moisture contents for longer times and at higher temperatures, thus making them more susceptible to hydrolytic depolymerization.
- For K3B PI a 1wt% moisture concentration caused a ~25°C T_g decrease which was consistent with T_g plasticization decreases for PI's as a family. In addition, upon drying the initial T_g was retrieved. For AFR700B PI, however, the T_g decreases for 1 wt% moisture was considerably greater namely ~75°C, and further T_g decreases did not occur in the 1-5 wt% moisture concentration range and also, the original dry T_g was not retrieved. These latter observations suggested that chemical hydrolytic degradation of the AFR700B had occurred in addition to physical moisture-induced plasticization.
- The extremely intense secondary glass transition T_{gg} exhibited by AFR700B at ~150°C was plasticized by absorbed moisture indicating the mobile structure was capable of H-bonding. It had been reported that the appearance of this transition only occurred after imidization was complete after curing >300°C and, as such, this peak was associated with norbornene crosslink structures. It had been also reported that such crosslinks were susceptible to hydrolysis at temperatures down to 100°C. More recent report indicated that this secondary glass transition decreased in intensity upon accelerated hygrothermal exposures in the 150-200°C range.
- Accelerated hygrothermal exposure caused dramatic decreases in the flexural "dried" residual mechanical properties of AFR700B PI's with a 70% loss of strength and 85% loss of strain to failure. Such mechanical property deterioration was associate with hydrolytic chain scission of the norbornene based crosslinks. In the case of K3B PI's, smaller decreases occurred in mechanical properties (5% loss of strength and 20% loss of strain to failure) for similar hygrothermal accelerated exposures but at lower drying temperatures.
- In both polyimide neat resin systems, the critical moisture content for blistering was around 0.3~0.4 wt% and the maximum blistering temperature (T_b) was ~425°C for AFR700B and ~300°C for K3B. However, a slight increase in moisture content at near the critical point lowered T_b drastically, about 50 to 100°C, but the change of T_b slowed down with further increase in moisture content.
- In the case of AFR700B/Astroquartz III fiber composite, the overall trend was similar to neat resins but with significantly lower T_b and higher critical moisture content than

those of neat resin. This suggested that the fiber-matrix interface was the main cause of the low T_b , i.e., due to lower fiber-matrix interfacial strength compared to yield strength of resin and/or higher concentration of water molecule at the interface, and the higher critical moisture content might be resulted from the higher diffusivity of water molecule at the interface.

In conclusion, the most critical hygrothermal induced degradation mechanisms of polyimide, PI, - carbon fiber composites as related to present and future Air Force service environments were matrix blistering and composite delamination. Blistering occurred when the vapor pressure of physically trapped moisture exceeded the yield stress of the PI. From isothermal moisture desorption plots water molecules were locked within PI matrix (K3B and AFR 700B PI's) and were only released at temperatures approaching the dry Tg of the resin, thus causing blistering. Moisture molecular "lock-in" occurred because with increasing temperatures new H-bonding sites within the polymer became accessible to water molecules as the physical structure of the polymer glass expanded. Upon cooling, water molecules were trapped in these new sites and were only released upon heating to a temperature that the site initially became accessible. In the case of AFR 700B PI chemical hydrolysis of the imide and norbornene structures that occurred below 200°C reverted back to the original chemical structure at higher temperature evolving water which further contributed to lowering the blister threshold temperature. These studies also identified blister threshold temperatures and critical moisture contents of those PI matrices and their composites for future Air Force service environments. In addition, considerable efforts have been made to understand general moisture degradation of BMI and PI resin mechanical properties and their composite properties and interfacial adhesion properties as a function of cure, moisture content, and fiber volume fraction in case of composites, as well as their interaction effects [VI-33]. Moisture absorption behavior, such as the diffusivity and ultimate moisture content for both the resins and composites of the BMI and PI systems were determined through this study.

Moisture-temperature-time exposures could lead through a range of physical structural state modifications of the polymer matrix and its interface with the fiber which would modify the critical composite mechanical performance threshold. After defining future requirements involved in high temperature composite applications the physical state phase diagram as a function of various hygrothermal durability variables and materials variables was developed, e.g., a 2-D moisture concentration-temperature plots showing various hygrothermal induced polymer physical structural phase, such as homogeneous elastic swelling and inhomogeneous elastic cavitation, both of which are reversible upon removal of moisture, moisture molecular "lock-in", plastic swelling or blistering, and densification etc. Various modified phase diagrams could be developed based on our hygrothermal durability program results.

V. PROGRAM STATISTICS: CUMULATIVE PERSONNEL EFFORTS

1. PI and Co-PI

	Dr. Roger J. Morgan	Professor	7/1/1994 - 1/14/1998
	Dr. Lawrence T. Drzal	Professor	7/1/1994 - 1/14/1998
	Dr. E.Eugene Shin	Specialist	7/1/1994 - 1/14/1998
	Dr. Andre Lee	Professor	7/1/1994 - 1/14/1998
2.	Postdoctoral Research Associate		
	Dr. Jiming Zhou	Post-Doctoral RA	1/15/1996 - 1/14/1998
3.	Graduate Students		
	Mark Wilenski	G.A. (Ph.D.)	8/15/1994 - 1/14/1998
	Jin-Kyu Choi	G.A. (Ph.D.)	8/15/1994 - 1/14/1998
4.	Other Researchers		
	Colin Dunn	Research Specialist	1/15/1995 - 1/14/1998
	Robert Jurek	Research Assistant	1/15/1995 - 1/14/1998
	Eric Walker	Hourly Student	10/1/1995 - 5/31/1996
	Kristin Yorimoto	Summer Student	5/1/1995 - 8/31/1995
	David Knop	Summer Student	5/1/1995 - 8/31/1995
			5/1/1996 - 8/31/1996
	Jason Lincoln	Summer Student	5/1/1996 - 8/31/1996
			5/1/1997 - 8/31/1997
	Emily Phan	Summer Student	5/1/1997 - 8/31/1997

VI. LIST OF PUBLICATIONS AND PRESENTATIONS

1. E.Eugene Shin, Colin Dunn, Roger Morgan, Eric Fouch, Bob Jurek and Judy Chen, "The Durability of Composites for Future Commercial Aircraft Applications," *MRS* 1994 Fall Meeting, Boston, MA, November 29 - December 2, 1994.
2. J-K Choi, Roger Morgan, Eugene Shin and Andre Lee, "Characterization of Cure Reaction of Bismaleimide (BMI) Resins," *March APS meeting*, 20-24 March 1995.
3. Roger Morgan, E.Eugene Shin, Lawrence Drzal, and Andre Lee, "Characterization of Critical Fundamental Aging Mechanisms of High Temperature Polymer Matrix Composites," Annual Report to AFOSR, Grant No. F49620-95-1-0129, August 1995.
4. M.S.Wilenski, E.E.Shin, L.T.Drzal and R.J.Morgan, "Cure Effects on Microcracking in IM7 Fiber/Matrimid 5292® BMI Composite," *Proceedings of the American Society for Composites 10th Technical Conference on Composite Materials*, P271, Santa Monica, California, October 18-20, 1995.
5. E.E.Shin, R.Jurek, L.T.Drzal, R.J.Morgan, J.K.Choi, and A.Lee, "Durability and Critical Fundamental Aging Mechanisms of High Temperature Polymer Matrix Carbon Fiber Composites: PART I," *Proceedings of the ASME Materials Division*, MD-Vol. 69-1, November, 1995 IMECE, ASME P183-189, 1995.
6. E.E.Shin, C.Dunn, E.Fouch, R.J.Morgan, M.Wilenski, and L.T.Drzal, "Durability and Critical

- Fundamental Aging Mechanisms of High Temperature Polymer Matrix Carbon Fiber Composites: PART II," *Proceedings of the ASME Materials Division*, MD-Vol. 69-1, November, 1995 IMECE, ASME P191-200, 1995.
7. Roger J. Morgan, Jin Kyu Choi, Lawrence T. Drzal, Andre Lee, Eugene Shin and Mark Wilenski, "Characterization of Critical Fundamental Degradation Mechanisms of High Temperature Polymer Matrix Composites," Presented at *Fourth Pacific Polymer Conference, Pacific Polymer Federation, ACS*, Koloa, Kauai, Hawaii, Dec.12-16, 1995.
 8. Roger J. Morgan, E.Eugene Shin, Colin Dunn, Lawrence T.Drzal, Andre Lee, Jin-kyu Choi and Mark Wilenski, "Aging Mechanisms of Bismaleimide and Polyimide-Carbon Fiber Composites," Presented at *High Temple Workshop XVI*, Orange Beach, Alabama, Jan.29 - Feb.1, 1996.
 9. JinKyu Choi, Andre Lee, E.Eugene Shin, Roger J.Morgan, "Kinetics and network formation of BMI resins", Presented at March APS meeting, St.Louis, MO, 3/18/96 to 3/22/96.
 10. A.Lee, "Curing kinetics of BMI resins," Presented at *Regional ACS meeting*, Dayton, OH, June 11, 1996.
 11. JinKyu Choi, Andre Lee, Eugene Shin, and Roger Morgan, "Cure Kinetics and Network Formation of Bismaleimide (BMI) Resins," *Proceedings of 28th Central Region, ACS Meeting*, June 1996, Dayton, Ohio, p III-A1.
 12. Roger J. Morgan, "The Structure-Property Relations of Bismaleimide Composite Matrices and Durability of High Temperature Polymer Matrix Composites," Presented at *Gordon Research Conference on Thermosetting High Performance Materials*, Plymouth State College, Plymouth, NH, July 7-11, 1996.
 13. Roger J. Morgan, Jin Kyu Choi, Lawrence T.Drzal, Andre Lee, Eugene Shin and Mark Wilenski, "The Effects of Processing Conditions and Service Environment on the Structure-Property Relations of Bismaleimide Composite Matrices," Presented at *Polymer Processing Society Meeting*, Italy, 1996.
 14. Roger Morgan, E.Eugene Shin, Lawrence Drzal, and Andre Lee, "Characterization of Critical Fundamental Aging Mechanisms of High Temperature Polymer Matrix Composites," Annual Report to AFOSR, Grant No. F49620-95-1-0129, August 1996.
 15. Roger J. Morgan, Eugene E. Shin, Jason E. Lincoln, Jin Choi, and Andre Lee, "The Structure-Property Relations of Bismaleimide Composite Matrices and Durability of High Temperature Polymer Matrix Composites," *Proceedings of the 28th International SAMPE Technical Conference*, November 4-7, 1996, Seattle, WA. Vol. 28, pp 213-223.
 16. E.Eugene Shin, R.J. Morgan, Mark Wilenski, Jiming Zhou, Jason Lincoln, and Lawrence T. Drzal, "The Effects of Processing Conditions and Service Environmental Exposures on High Temperature Polymer Matrix Carbon Fiber Composites," *Proceedings of the 28th International SAMPE Technical Conference*, November 4-7, 1996, Seattle, WA, Vol.28, pp 225-235.
 17. E.Eugene Shin, Roger J. Morgan, Jiming Zhou, Mark Wilenski, Lawrence T. Drzal, "Effects of Processing Conditions and Service Environmental Exposure on Performance of High Temperature Polymer Composites," *Gordon Research Conference on Composite*, Ventura, California, January 5-10, 1997.
 18. Roger J. Morgan, E.Eugene Shin, Jason Lincoln, Robert Jurek, Jin Choi, and Andre Lee,

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VII. CONCLUSIONS

In this project, we had identified the most likely potential, critical aging mechanisms that control damage initiation in BMI and PI carbon fiber composites based on the systematic durability evaluation methodology. The critical aging mechanisms involved (i) further cure of BMI-carbon fiber composites with associated T_g increases, mechanical property decreases and enhanced microcrack development in service environment exposure conditions, it was evident that the dehydration induced ether crosslink formation and subsequent rearrangement played a critical role in the chemical and physical network structural changes of BMPM-DABPA BMI resins at high service environment temperatures and long times that could significantly modify the BMI resin thermal and mechanical response and composite resin shrinkage-induced microcrack characteristics, and (ii) hygrothermal induced thermal and mechanical property deterioration as a result of physical and chemical structural changes in BMI- and PI-carbon fiber composites. The mechanism (ii) was identified from residual property determination of the composites after various thermal cycling simulation programs as a function of temperature, humidity, moisture content, heating/cooling rate, and applied stress. Models on the moisture absorption behavior and hygrothermal induced damage mechanisms, such as matrix blistering and delamination, of the composites and their interrelationship had been suggested.

From the systematic studies on hygrothermal durability, the K3B and AFR700B resin and composite exhibited considerable damage in the form of micro-cavitation, debonding, macroblistering and delamination upon exposure to 250°C hygrothermal spikes. The blistering threshold temperature was monitored at 229°C in the K3B composites. The BMI resin and composite exhibited no damage or property losses after exposure to similar hygrothermal spikes. The physical and chemical structural state of PI matrices such as K3B as a function of hygrothermal exposure were discussed in terms of hydrolytic chemical degradation, moisture vapor-induced physical damage and molecularly locked-in water. Those structural states were characterized by systematic weight monitoring, ²H NMR, and various thermal, mechanical property measurements using D₂O water environment. In conclusion, the most critical hygrothermal induced degradation mechanisms of polyimide, PI, -carbon fiber composites as related to present and future Air Force service environments were matrix blistering and composite delamination. Blistering occurred when the vapor pressure of physically trapped moisture exceeded the yield stress of the PI. From isothermal moisture desorption plots water molecules were locked within PI matrix (K3B and AFR 700B PI's) and were only released at temperatures approaching the dry T_g of the resin, thus causing blistering. Moisture molecular "lock-in" occurred because with increasing temperatures new H-bonding sites within the polymer became accessible to water molecules as the physical structure of the polymer glass expanded. Upon cooling, water molecules were trapped in these new sites and were only released upon heating to a temperature that the site initially became accessible. In the case of AFR 700B PI chemical hydrolysis of the imide and norbornene structures that occurred below 200°C reverted back to the original chemical structure at higher temperature evolving water which further contributed to lowering the blister threshold temperature. These studies also identified blister threshold temperatures and critical moisture contents of those PI matrices and their composites for future Air Force service environments.

From real time T_g increase data provided by Boeing HSCT group for commercial BMI-carbon fiber composites (BASF 5260) in isothermal exposures in the 150–200°C range for times up to 8,000 hrs, it was found that the service environment exposure temperature for a T_g increase of ≤5% over 120,000 hrs exposure as would be required in commercial aircraft applications could only be 120°C, well below the expected HSCT service environment temperatures. For a more sophisticated prediction of the T_g of the BMI composite matrix as a function of isothermal exposure temperature-time conditions, a semi-empirical expression in terms of chemical cure characteristics and BMI glassy-state diffusion characteristics had been developed

The primary performance issue for BMI-C fiber composites was that they were not fully cured under standard 250°C cure conditions and could continue to cure over prolonged periods of time in service environment at 177°C resulting in matrix embrittlement. However, extrapolation of all available high temperature reaction rate data to the 175-200°C temperature range indicated insignificant further cure and associated BMI embrittlement occurred in the dry, 175-200°C temperature range service environment because of glassy-state diffusion restrictions and decreases in reaction rates of unreacted species at these lower temperatures. Our analyses revealed no change in toughness after 120,000 hours exposure at 175°C and only a 20% decrease at 200°C for the same time period.

From the systematic studies on adhesion between carbon fiber and matrix, all evidence, to date,

indicated the C fiber-matrix interface in BMI and PI composites exhibits poor mechanical integrity and was one of the weak links together with resin matrix toughness that was responsible for early microscopic damage initiation and propagation. This poor fiber-matrix interfacial integrity was more serious in BMI-C fiber composites as a result of the imposition of cure induced matrix shrinkage stresses. There had been considerable effort to improve the fiber-matrix interface mechanical integrity for BMI- and PI-C fiber composites using a range of approaches that fall into four major categories: (i) modification of fiber surface energy; (ii) increase in fiber surface functional group concentration; (iii) resin toughening; (iv) additions of fiber sizing..

From the creep rupture studies, the lifetime distribution of BMI 5260/G40-800 was broad, over more than 3 decades of time, e.g., from a few minutes to a few weeks. Prior aging for 2000 hours at 200°C reduced the short term strength by 1/3 and induced a distinct bimodal lifetime distribution probably due to two balanced creep rupture failure modes, such as brittle-like shear crack propagation and crack propagation modified by matrix yielding and crack tip blunting. A bimodal nature and its development by aging was an important feature warning of potential service problems from a low strength 'tail'. Nevertheless, all the results combined for about 100 specimens in all, fitted a single Log Extreme Value distribution. The behavior could thus be described by two parameters, the mode and a factor indicating variability. The lifetimes of K3B showed a very wide variability. The 85% level produced a large proportion of very early failures indeed many broke on loading. Even at the 75% level there were many early failures. The distribution of lifetimes was clearly bimodal and the second mode in the distribution shifted to a longer lifetime with the lower stress level. Bimodality shown in both lifetime distribution and short term strength distribution as well as changes in the statistical mode development of K3B composites might be due to the competition between brittle and ductile processes, so-called jog splitting and thick shear banding which were distinctive deformation modes observed before the final creep rupture. The maximum elapsed time in this experiment was currently more than 6 years; experiments should be set up to obtain comprehensive distribution data over many years.