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POLYMER BLENDS

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FINAL REPORT - VOLUME 1

BY: MICHAEL JAFFE

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13. Three generations of PBI and polyimide blends have been evaluated for use as high temperature matrix resins for carbon fiber composites in aerospace applications. To enable property testing, a neat resin molding cycle was developed to produce plagues with less than 2% void volume. Phthalic anhydride end-capping of the PBI was shown to significantly reduce crosslinking as measured by the change in Tg after high temperature exposure. This reduction in end-group chemistry provided for maximum thermoplasticity of the blend during molding. Thermo-oxidative stability studies indicated that at 600F and above, the weight loss of the blend was approximately proportional to its PBI content. Attempts to mitigate this effect by incorporating 6F moiety into the PBI backbone were unsuccessful. Phosphoric acid treatment of 85/15 molded blend samples was shown to provide a four-fold increase in weight retention. However this effect was due to surface oxidation barrier effect. A series of nine copolymer polyimides were synthesized and evaluated. The blend of 10/90 ecPBI/6FcoPI-2 was chosen to be moved forward for aerospace evaluations. The blend with end capped chemistry was scaled up in steps from gram quantities to 50 kilograms. Prepregging of the neat resin onto plain weave AS-4 carbon fabric and onto AS-4 unidirectional tape was successfully demonstrated by YLA Incorporated. Three prepregging trials produced a total of 1450 linear feet of fabric and over 450 feet of unidirectional prepregs. Composite laminate fabrication was demonstrated by both Lockheed and Hoechst Celanese. Composite properties were demonstrated which either approached or exceeded GE Aircraft Engines specifications for PMR-15 composites.

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FOREWORD

This is the final report for Contract F49620-88-C-0014, "Polymer Blends," sponsored by the Defense Advanced Research Projects Agency and monitored by the Air Force Office of Scientific Research. The entire report is being submitted in two volumes. Volume 1 of this report will discuss the polymer blend research and development activities under this contract from its initiation in November 1987 through May 1991. Volume 2, enclosed, will describe Lockheed's large part fabrication and evaluation program.

The materials development was performed by the Hoechst Celanese Research Division, Summit, New Jersey with end-user large part fabrication development and testing being performed by the Lockheed Aeronautical Systems Company, Burbank, California and the General Electric Aircraft Engine Company, Cincinnati, Ohio. Polyimide polymer optimization was done at the Virginia Polytechnic Institute under Dr. James McGrath. Drs. Frank Karasz and William MacKnight of the University of Massachusetts were technical consultants to the program to insure an understanding of the blend science and observed results.

The program sponsor within DARPA was Dr. Richard Loda the program monitor for the Air Force was Dr. Charles Lee. The principal investigator for Hoechst Celanese was Dr. Michael Jaffe. Drs. Robert Boschan and Richard Griffin were the focal points for Lockheed and GE, respectively.

Volume 1 Polymer Blend Research and Development

1.0 INTRODUCTION

1.1 Background

A polymeric matrix resin is needed for advanced aerospace, fiber reinforced composite and adhesive applications which is readily processible to large parts while meeting thermo-oxidative and thermo-mechanical requirements at temperatures above 400°F. Under the DARPA/AFOSR "Improved Structural Polymer Alloy and Composite Program" (1984-1987) it was concluded that miscible blends are a viable way to modify and tailor resin properties offering cost, flexibility and time savings advantages when compared to new chemistry. In particular, polybenzimidazole (PBI) was found to be miscible with a range of polyimides, including the thermoplastic polyimides, thereby potentially leading to a viable, new class of high temperature, thermoformable resins for 371°C (700°F) applications. The Polymer Alloy and Composite Program also established a framework to systematically identify and verify miscible polymer pairs, utilizing both molecular modeling and experimental techniques, and it led to the development of a high performance polymer project team involving the university, the materials producer and the materials user to insure efficient technology transfer.

PBI is unique as an available 400^{+}°C Tg (glass transition temperature) resin but lacks true thermoplastic processibility and has poor thermo-oxidative (TOS) stability. Blends with polyimides have been shown to have lower Tgs and to have improved moldability. At temperatures of 371°C (700°F), the only resins with sufficient thermo-oxidative stability appear to be polyimides (PI) containing the hexafluoroisopropylidene (6F) moiety such as DuPont's Avamid N™ and Ethyl Corporation's Eymyd™ . A third family of potential candidates containing this moiety which are characterized by processing ease are the Sixef™ polymers being developed by Hoechst Celanese. All of these latter materials, however, fail to meet specifications on the basis of processibility and/or mechanical properties at temperature, especially in compression. The state of the art would thus suggest that the optimum 400-700°F matrix resin would contain elements of PBI for high temperature mechanical properties and solvent stability and a polyimide for ease of processing; in particular, the use of perfluorinated polyimide technology for very high temperature thermo-oxidative stability.

1.2 Objectives

It was the mission of this Polymer Blends Program to translate the inventions and feasibility studies of the Improved Structural Polymer Alloy and Composites Program into useful and unique materials for aerospace. Specifically, the objectives of this program were to:

- Develop miscible PBI/PI blend systems meeting aerospace requirements for a tough, processible matrix and adhesive for use at 400 to 700°F.

- Develop a user relevant miscible polymer blend database for aromatic heterocyclic and mesogenic polymers.

- Advance the understanding of miscible polymer blends.

The key to this program was the recognition that its major focus was the development of a superior matrix material for aerospace within a three year timeframe. To meet this objective, materials must be supplied to the aerospace evaluators in sufficient quantities for comparative testing with other candidate resins. To provide materials in these quantities, the starting polymers or the raw materials and technology for making them must exist as of the start of this program.

1.3 Program Definition

The working methodology of the Polymer Blends Program was established by a team comprised of the prime contractor, program subcontractors, university advisors, representatives of interested government laboratories and participants of related government funded programs. This methodology included the definition of technical milestones, evaluation protocols and detailed material specifications.

1.3.1 Milestones

Five major tasks were identified to achieve program objectives, these were:

1. Definition of protocols for the identification and selection of program materials by February 1988.

2. The development and composite performance screening of three generations of candidate matrices as follows:

    i. First generation blend material, 85/15 PBI/Ultem™ to be available for evaluation by March 1988.

    ii. A blend of thermo-oxidatively improved PBI with an "available" polyimide (e.g. Ultem or a 6F product) to be available for evaluation by October 1988.

    iii. A blend of TOS-improved PBI with improved 6F containing copolymers such as 6F containing PBI and polyimide (PI) copolymers to be available for evaluation by July 1989.

In addition, new concepts for high temperature matrix resins were to be continuously explored with feasibility demonstrations provided as appropriate.

3. The optimization of composite fabrication and part shaping from PBI/PI blends.

4. An identified candidate for scale-up so as to provide sufficient quantities for aerospace evaluation under user relevant conditions by March 1989.

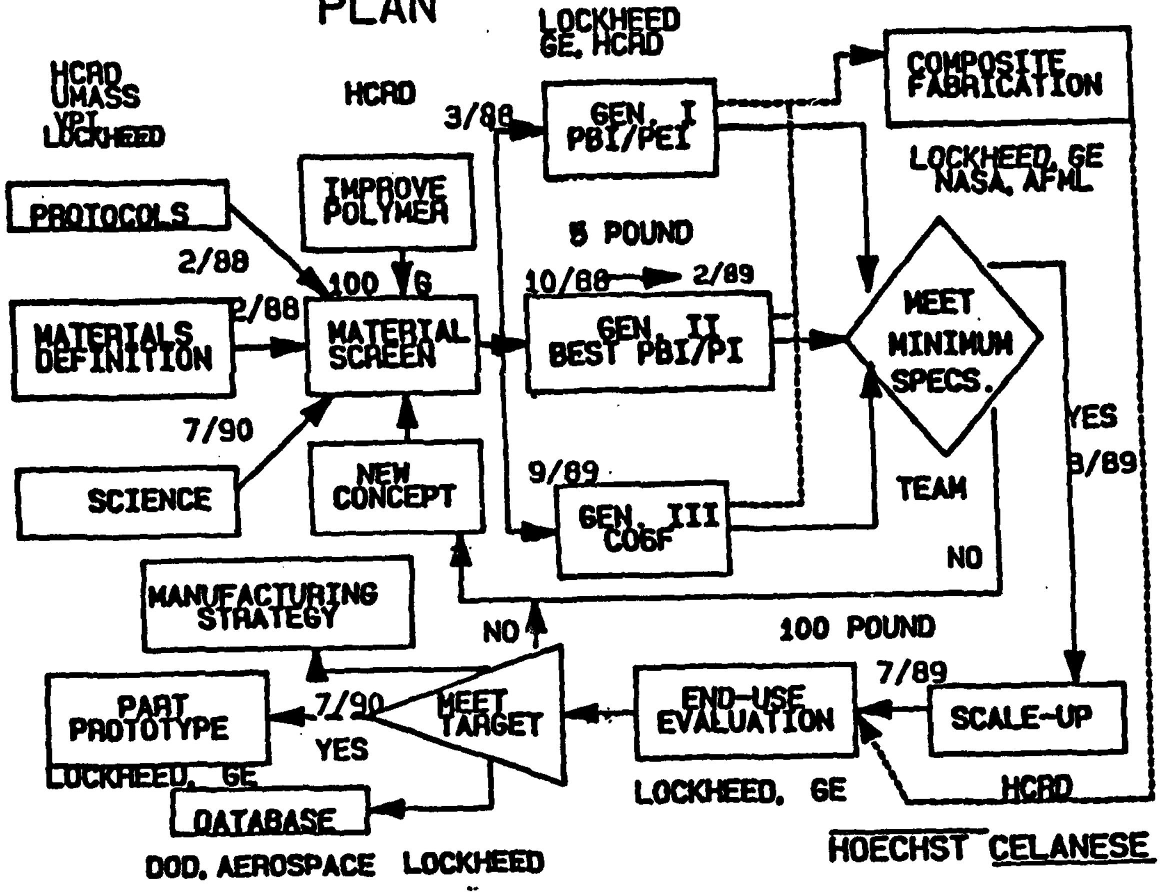
5. Aerospace end-user evaluation as the primary focus of the third year of the program.

Figure 1 schematically shows the overall plan for the High Performance Polymer Blends Program including the timing as listed above and the interactions of the multidisciplinary team.

2.0 POLYMER BLEND DEVELOPMENT

As indicated by the milestones, three generations of PBI/PI blends were evaluated by the project team as candidates for scale-up for user-relevant evaluations. Each generation represented resins of high potential utility and each advanced the program forward toward the use temperature objective. In addition, the sequential evaluation of each material focused understanding of state-of-the-art high temperature matrix resins and miscible polymer blends toward meeting the program objectives.

FIGURE 1



HIGH PERFORMANCE POLYMER BLENDS PLAN

2.1 PBI/Polyetherimide Blends: First Generation Matrix Candidate

An 85/15 (by weight) PBI/Ultem blend was chosen by the project team as the first generation candidate. This selection was based upon miscibility studies conducted under the Improved Structural Polymer Alloy and Composite Program; a result of which is the phase separation diagram for PBI and Ultem developed at UMASS and shown in Figure 2. This figure indicates that both a high temperature, composite matrix end-use regime and processing window exist for PBI levels in excess of 75%. The end-use regime was defined as those temperatures below the glass transition or softening temperature of the material; the processing window as those temperatures between Tg and the phase separation temperature. At an 85/15 blend ratio, the glass transition temperature is 400°C (752°F) and the processing window is 25°C. Blends of 85/15 PBI/Ultem were prepared by individually dissolving each component material in DMAc at the 20 percent solids level and then combining the individual dope solutions at the above specified weight percent levels. Portions of these dopes were precipitated in methanol to form a blended polymer powder. Residual DMAc was removed by Soxhlet extraction in methanol. The remaining portions were either cast into uniform, 1 mil films or spun into fiber by the dry spinning process. Ultem fibers were melt spun.

Initial powder, film and fiber characterizations were performed according to set protocols for Exploratory Materials. FTIR results (Figure 3) exhibited a significant imide carbonyl band absorbance

FIGURE 2

PBI/ULTEM SEPARATION DIAGRAM

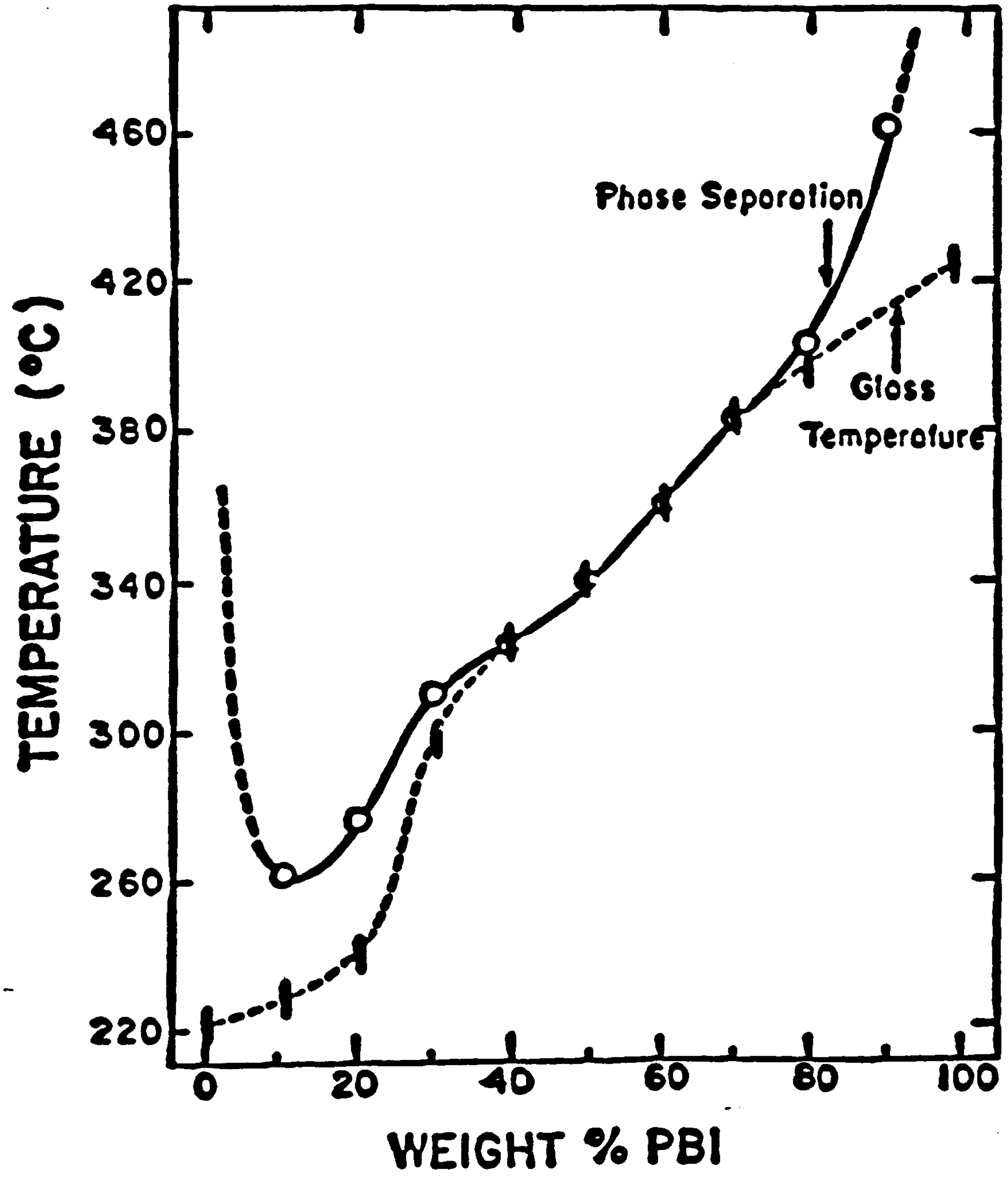
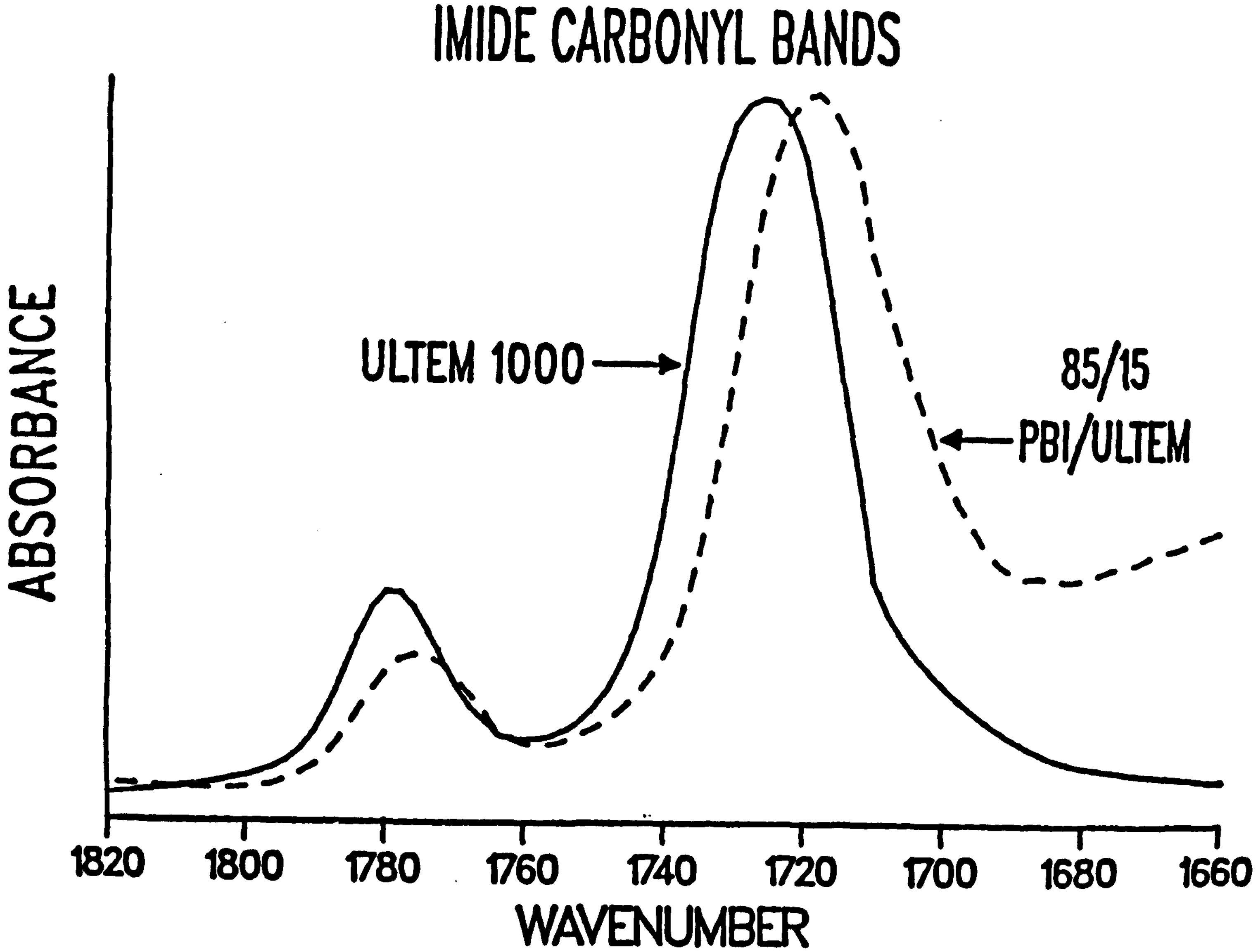


FIGURE 3


IMIDE CARBONYL BANDS
ABSORBANCE
ULTEM 1000
85/15
PBI/ULTEM
1820
1800
1780
1760
1740
1720
1700
1680
1660
WAVENUMBER

shift between the pure Ultem and its 85/15 blend with PBI thus indicating polymer interactions on the molecular level and hence miscibility.

DSC and DMTA results also confirmed miscibility. The DSC traces in Figure 4 show a single discontinuity in heat flow with a second heating midpoint temperature of 421°C (790°F). This figure also shows an increasing glass transition temperature with subsequent reheating. This effect was attributed to either additional crosslinking reactions or chain extensions within the blend. In either case, these reactions were later shown to increase viscosity and thus to inhibit neat resin molded bar consolidation. The DMTA result of Figure 5 shows a single loss tangent peak of 411°C (772°F). The slight difference between the DSC and DMTA results for Tg is due to the different measurement techniques involved.

2.1.1 Thermal Stability Evaluations

Long term isothermal, thermo-oxidative studies of neat PBI and the 85/15 PBI/Ultem blend were performed on fiber and/or film samples air aged at three temperatures: 260°C (500°F), 316°C (600°F) and 343°C (650°F) to 500 hours. Subsequent studies were also conducted on molded 85/15 PBI/Ultem neat resin tensile bars at 204°C (400°F) and 260°C (500°F).

Typical test results, shown in Figures 6 and 7, indicated that the blend may have utility as a 500°F material but suffered severe

FIGURE 4 DSC of 85/15 PBI/ULTEM

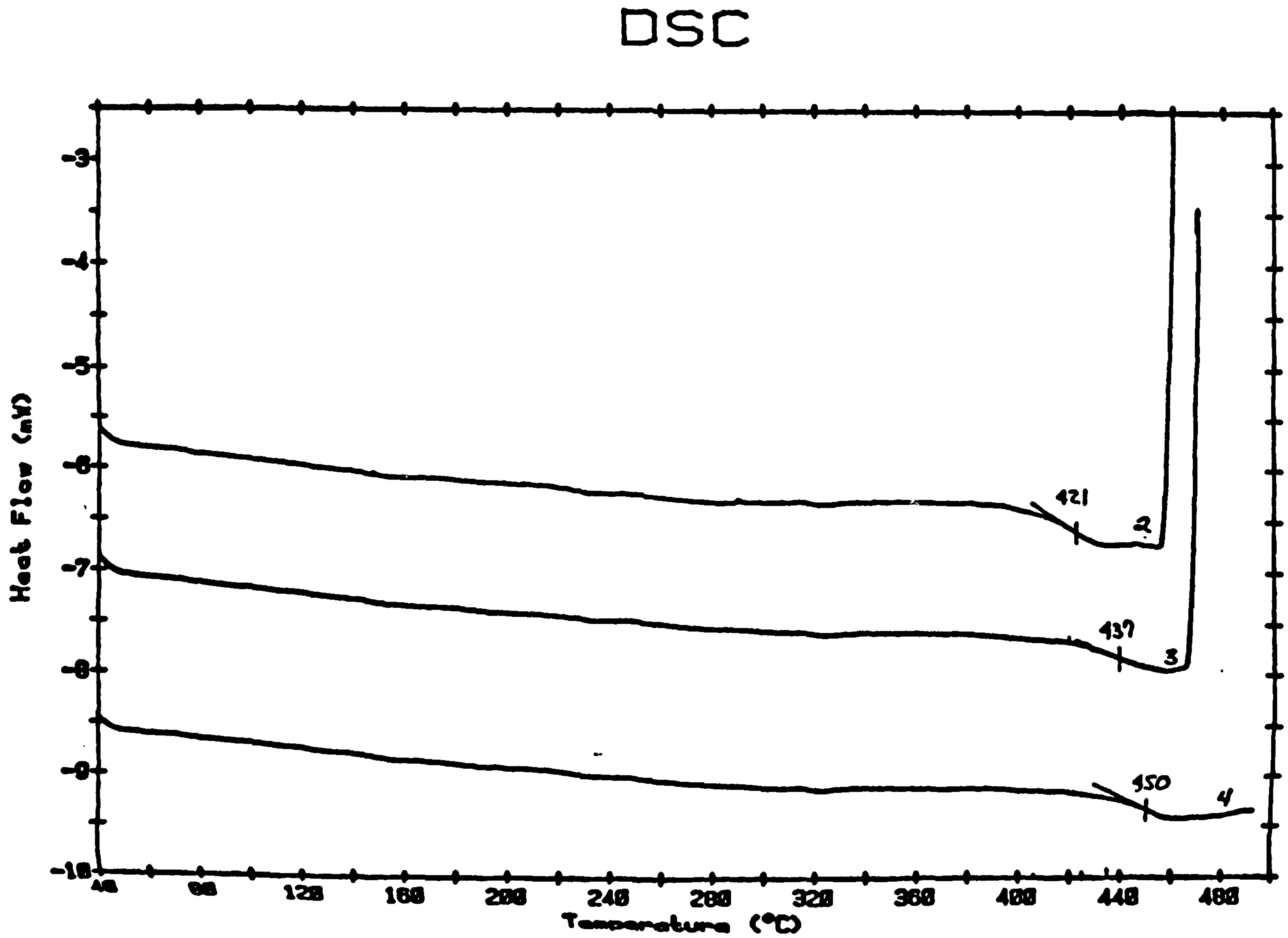


FIGURE 5 DMTA of 85/15 PBI/ULTEM

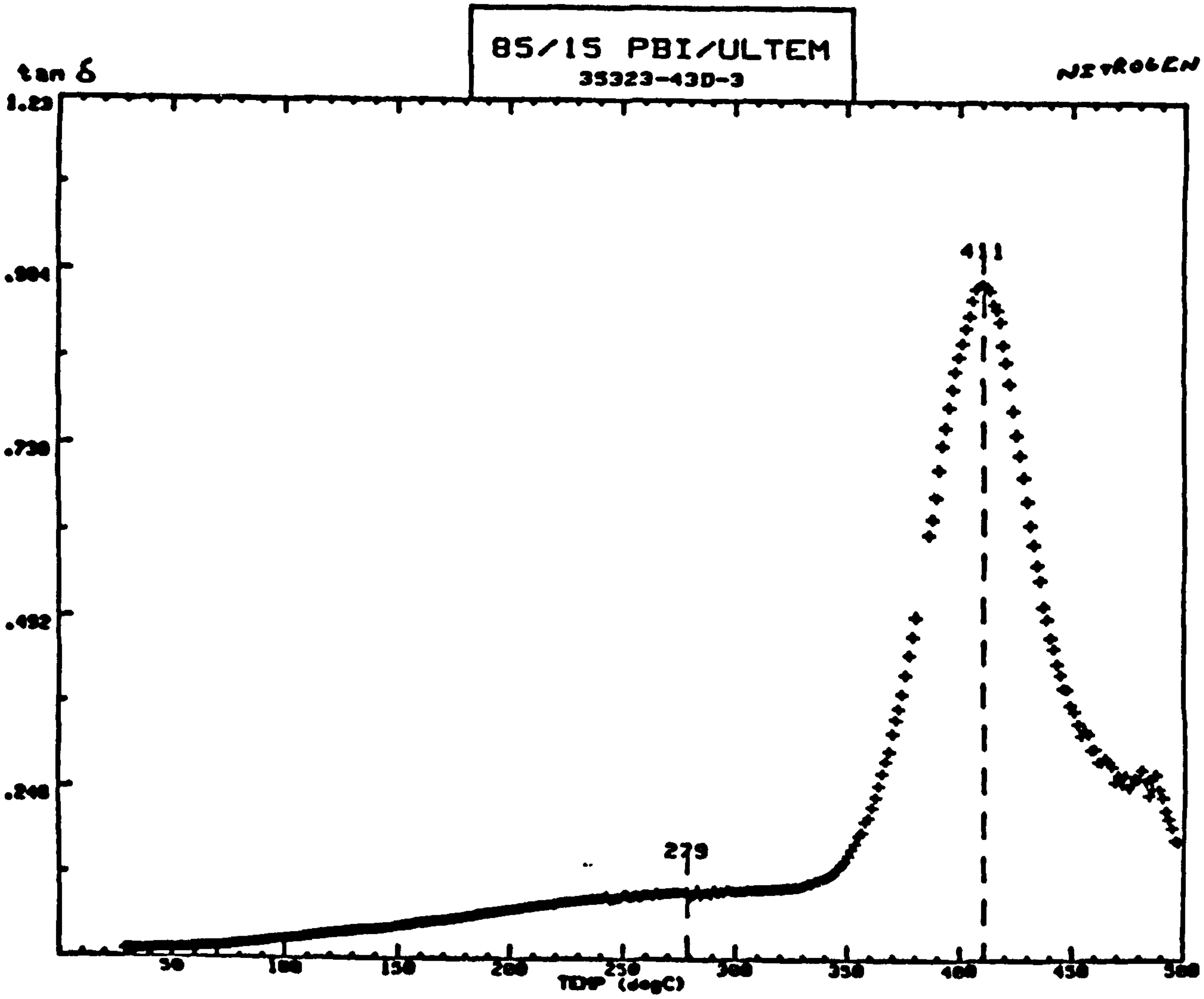


FIGURE 6 PBI/ULTEM 85/15 BLEND FIBERS

AGED IN AIR OVEN AT 500°F, 600°F and 650°F

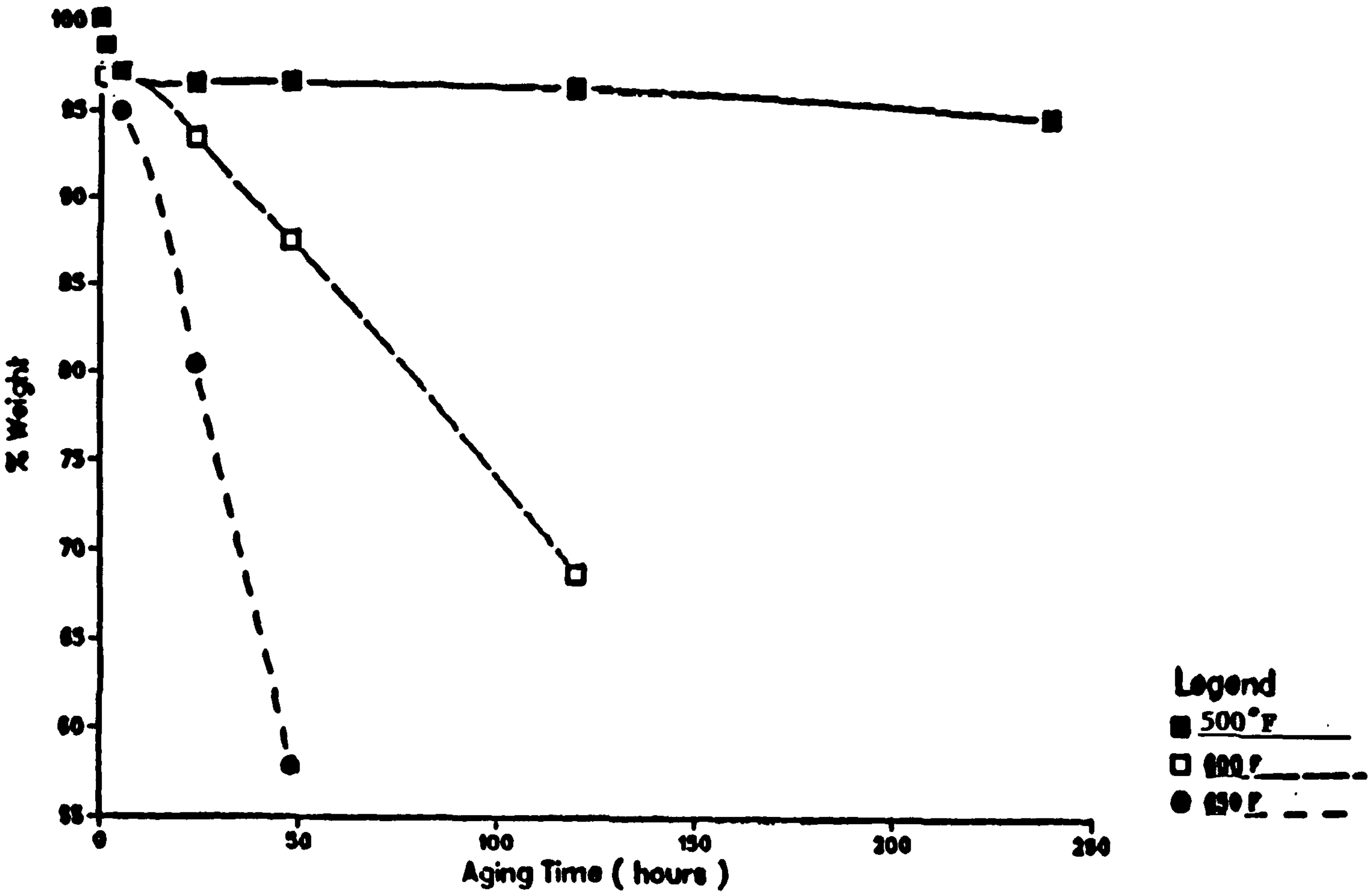
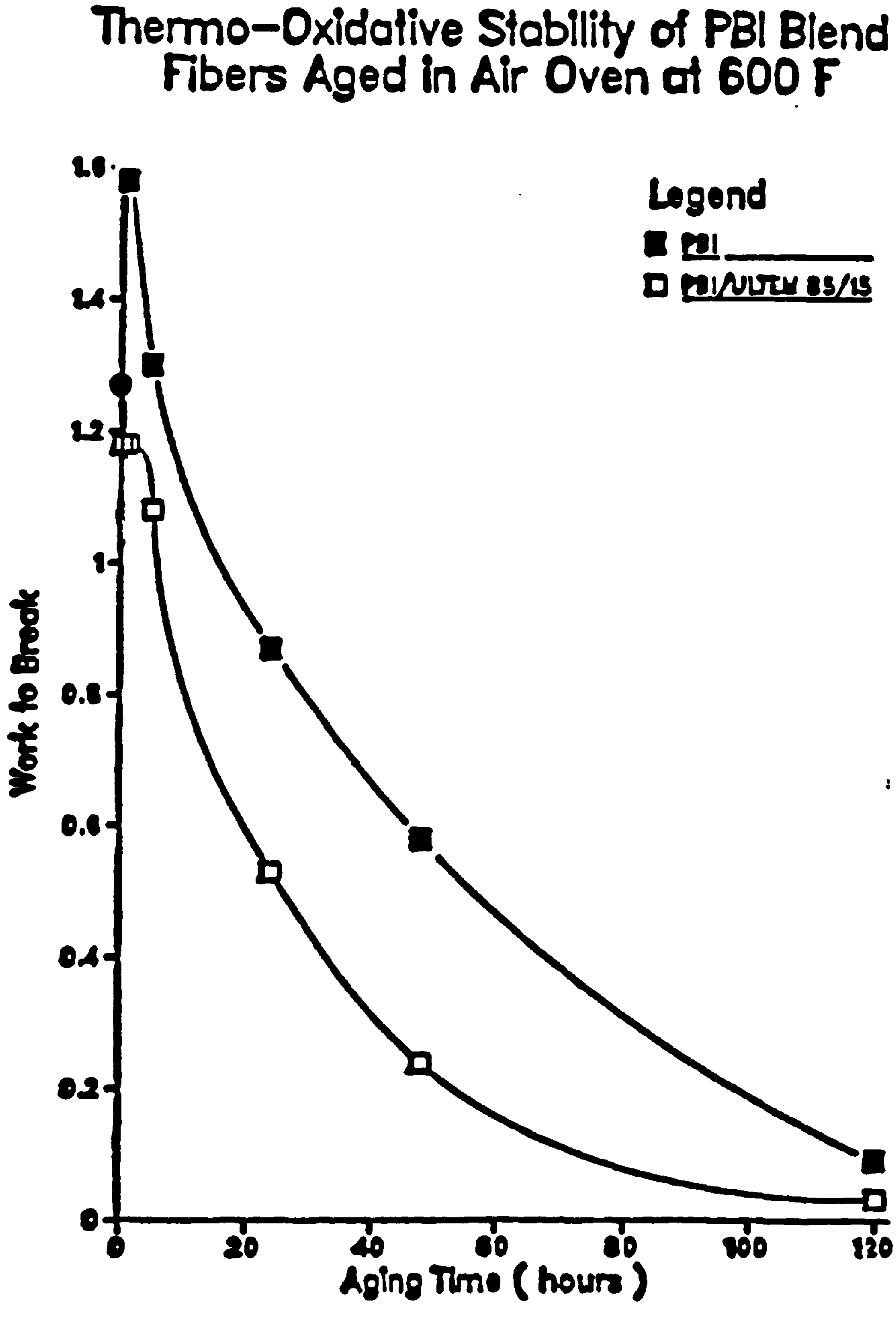
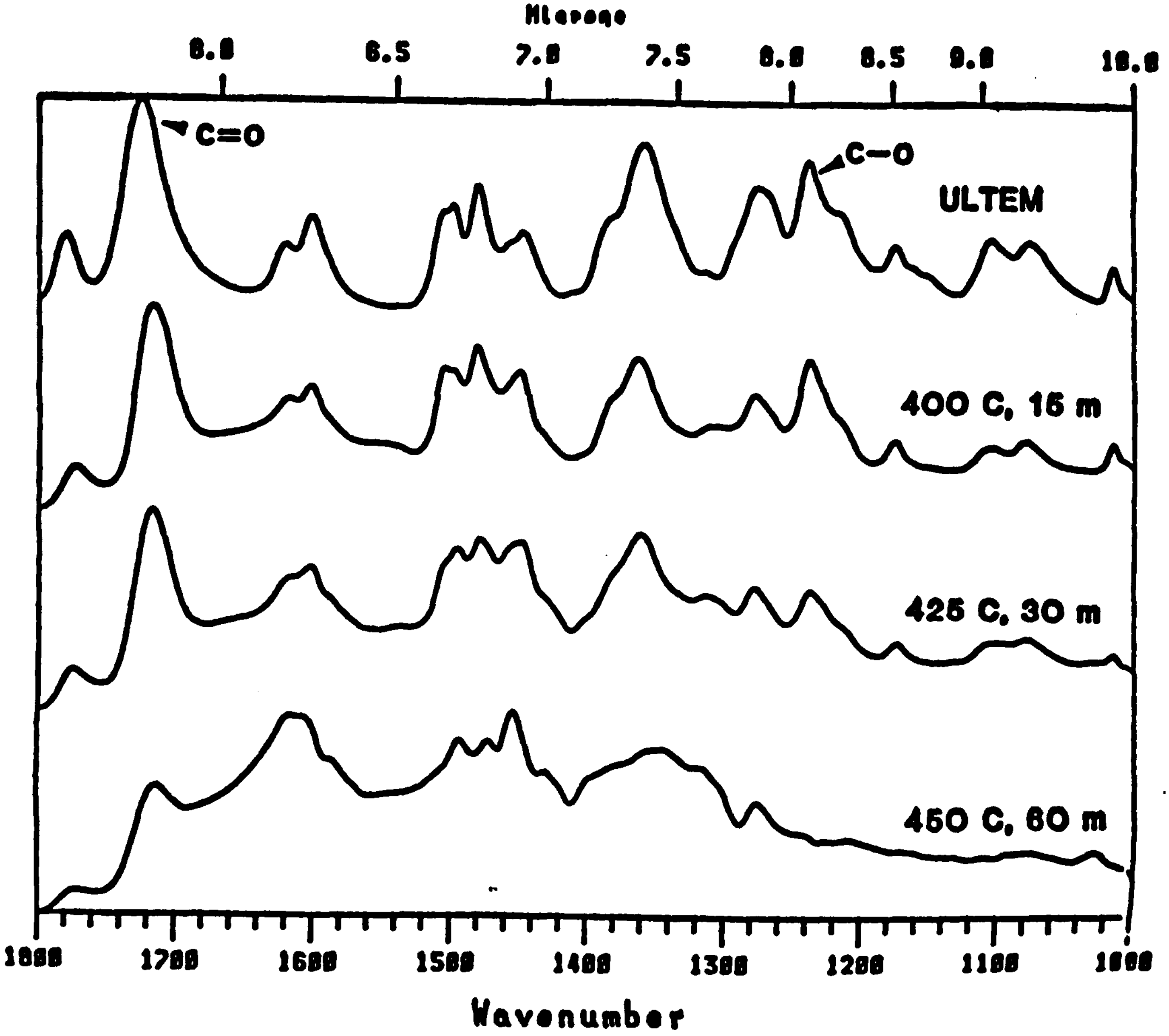


FIGURE 7



Thermo-Oxidative Stability of PBI Blend Fibers Aged in Air Oven at 600 F

FIGURE 8 FT-IR SUBSTRACTION SPECTRA 85/15 PBI/ULTEM - PBI



weight and mechanical property losses at the higher temperatures. The rate of weight loss for the blend was unexpectedly greater than the loss for neat PBI. The addition of the imide to PBI had been expected to improve upon the known poor TOS of PBI. The rate of weight loss indicated a negative interaction between the PBI and the polyimide which accelerated the degradation.

FT-IR was used to assess the chemistry of the blend under conditions that simulated neat resin molding. Blend fibers were heated to temperatures in the range from 400°C (752°F) to 450°C (842°F) for 15, 30 and 60 minutes, respectively and subjected to FT-IR. The FT-IR subtraction spectra of Figure 8 in which the unannealed PBI spectrum was subtracted from the spectra of annealed 85/15 fibers revealed the behavior of the polyetherimide. Normalization of the peak heights for the C-O ether stretch band at ca. 1240 cm^{-1} and the C=O imide carbonyl at ca. 1725 cm^{-1} to the constant out-of-plane PBI bending mode at 800 cm^{-1} showed that both the ether and imide bands decrease with temperature and time at temperature (Table 1). The ether band decreased more rapidly than the imide carbonyl with complete degradation at 450°C in 60 minutes. Gaseous products from this degradation were also shown to cause spherical voids in molded bars. From the data it was hypothesized that imidazole or aromatic amine in PBI degradation products catalyzed the decomposition of the Ultem and, in particular, attacked the ether linkage.

Table 1

NORMALIZED PEAK HEIGHTS RELATIVE TO 800CM^{-1}

CONDITIONS Temperature (°C)	 Time (Minutes)	Imide Carbonyl	Ether
400	15	100	100
425	30	88	51
425	60	76	21
450	30	57	10

The oxidative degradation of PBI and of the PBI/Ultem blend were investigated to provide insight into the blend degradation mechanism and to develop a rational action plan to overcome these problems. The oxidative degradation mechanism for PBI is shown in Figure 9 as proposed by Conley et. al. This mechanism was proposed based upon various gaseous products such as CO and CO_2 and on solution oxidation products. Carboxylic acid structures were postulated as intermediates in the thermal oxidation because they were isolated in the solution oxidation experiments.

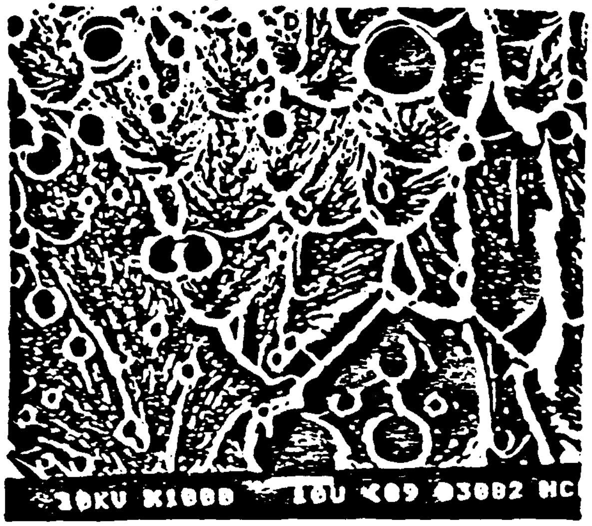
Two of the last steps in Conley's mechanism were substantiated under the current effort, thus providing evidence that PBI oxidative degradation proceeds through a radical mechanism in which abstraction of the hydrogen from the imidazole N-H forms species which further react and cause chain scission. These data were obtained from comparisons of FT-IR results from both thermally oxidized PBI and thermally oxidized carbon-13 labeled PBI. Figure 10 shows the position the labeled carbon in PBI and a comparison of the IR spectra for each. The nitrile band at 2226 cm^{-1} is consistent with the formation of carboxylic acids during oxidative degradation. Figure 11 shows a scheme in which a carbon-13 labeled nitrile reacts with carbon-12 acid to form an unlabeled nitrile and a labeled acid. The reaction sequence proceeds through an isoimide and an imide and results in products speculated in Conley's mechanism.

2.1.2 85/15 PBI/Ultem Neat Resin Molding Evaluations

Initial attempts to mold neat resin 85/15 from either fiber or powder yielded plaques with extensive void structure (Figure 12)

SEM OF MOLDED PANEL CROSS-SECTIONAL

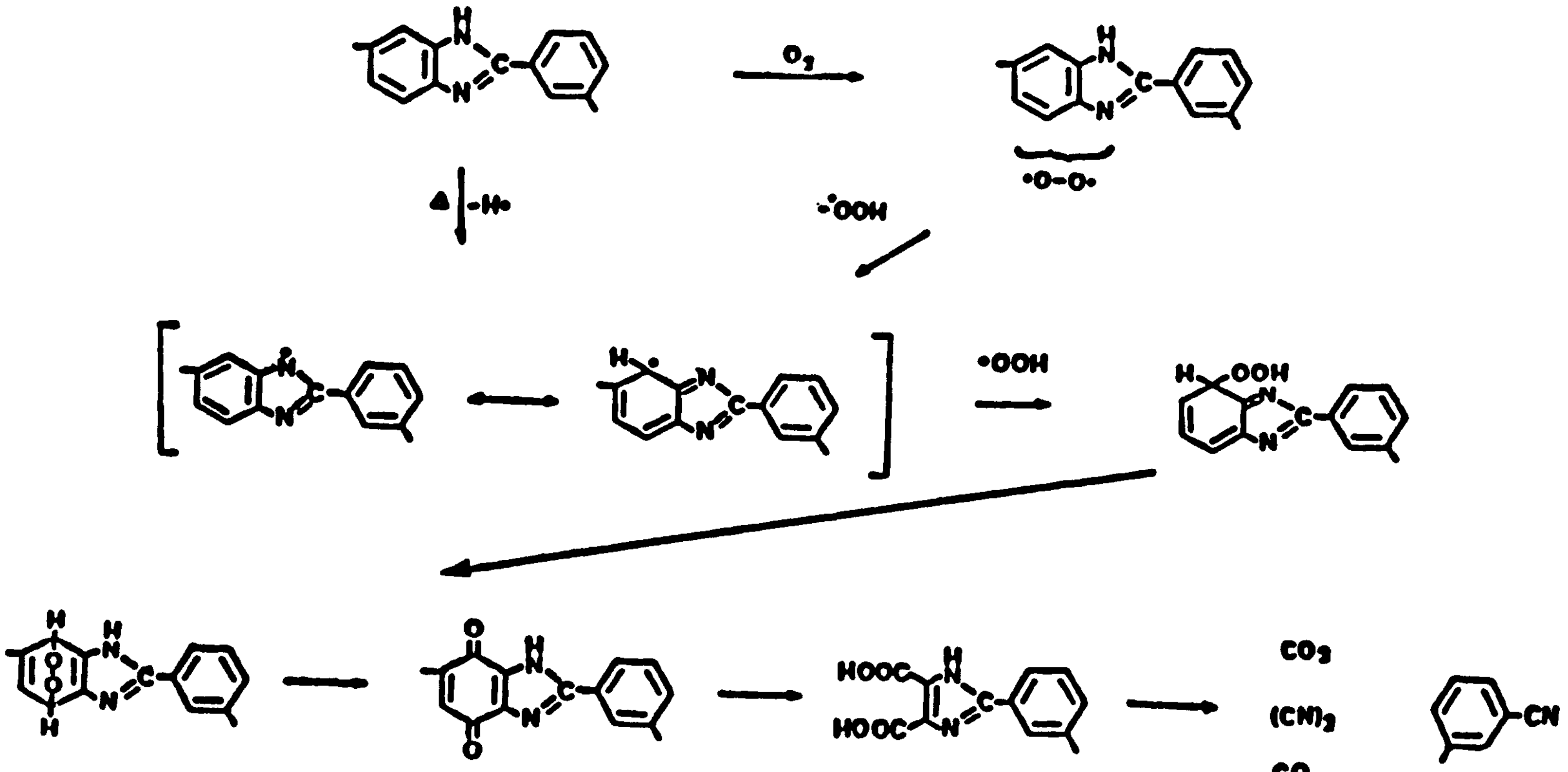
Figure 12.



OLD MOLDING CYCLE

FIGURE 9

PBI DEGRADATION



R. Conley, J. Kane, S. Ghosh, Technical Report AFML-TR-71-219, November, 1971.

FIGURE 10

OXIDATION OF PBI AT 350 C
FOR 24 h

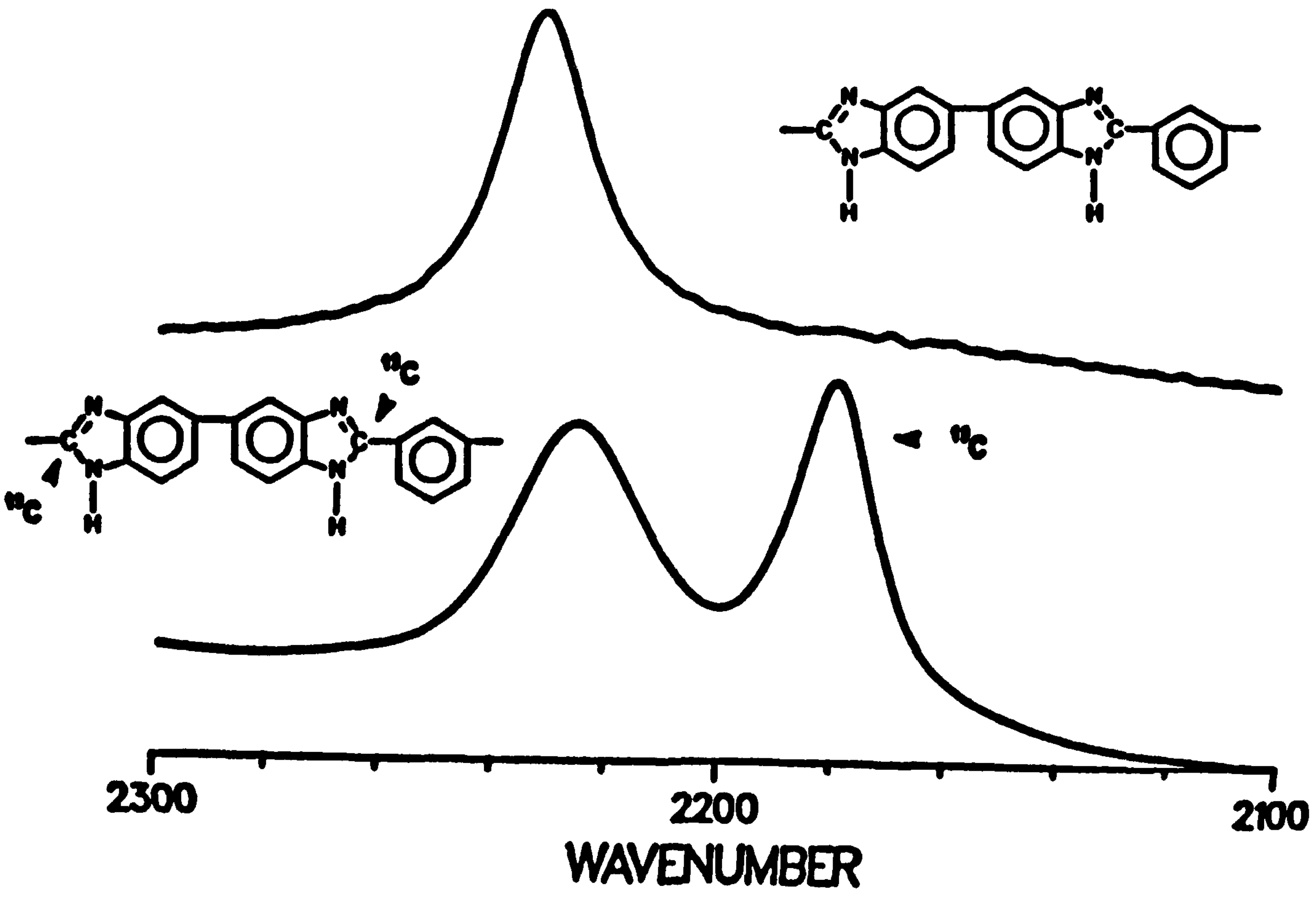
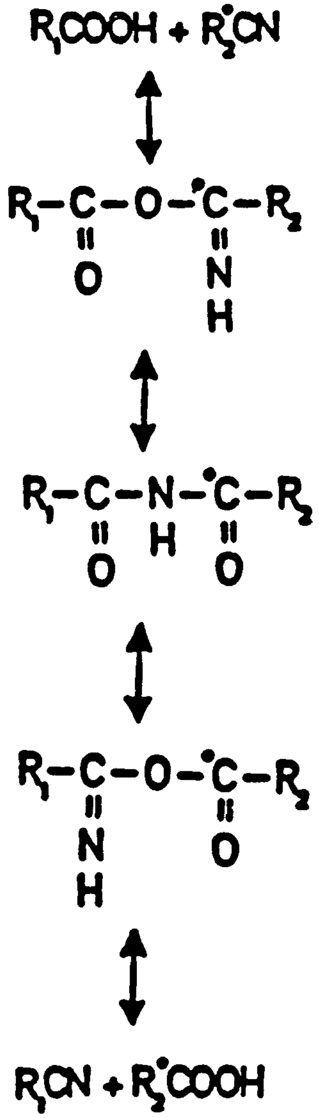


FIGURE 11

MECHANISM FOR LABELED CARBON SUBSTITUTION



and correspondingly low densities from off-gassing during blend degradation. The molding cycle consisted of a 30 minute hold at 460°C (860°F) and 500 psi. Reoptimization of the molding cycle resulted in fully consolidated plaques at or near the theoretical densities and with void volumes less than 1.5%. Both the old (initial) and new (reoptimized) molding cycles are shown in Figure 13. The newer cycle utilized a hold time of only three to 10 minutes at maximum temperature depending upon part thickness. The effect of this latter cycle on tensile properties is shown in Table 2 and on the surface properties of the molded part in Figure 14 (to be compared with Figure 12 above). FT-IR analyses (Figure 15) showed that molding by the new cycle induced a tendency toward phase separation as evidenced by the reverse shift in the spectrum toward the original wavenumber. However, additional FT-IR analyses confirmed the presence of the Ultem at the original 15% level after molding. This result was in direct contrast to those from the simulated molding at 450°C for 30 and 60 minutes (Table 1).

2.1.3 85/15 PBI/Ultem Composite Evaluations

Celion 3000 carbon fiber, unidirectional prepregs were produced by Hoechst Celanese by solvent impregnation of the 85/15 PBI/Ultem dope from DMAc. Solids content of the dope was 20% or 25%. In all cases, poor wetout of the prepreg occurred. The dried prepregs were molded into composites for tensile, flexural and short beam

FIGURE 13

MOLDING CYCLE FOR 85/15 PBI/ULTEM PEI BLENDS

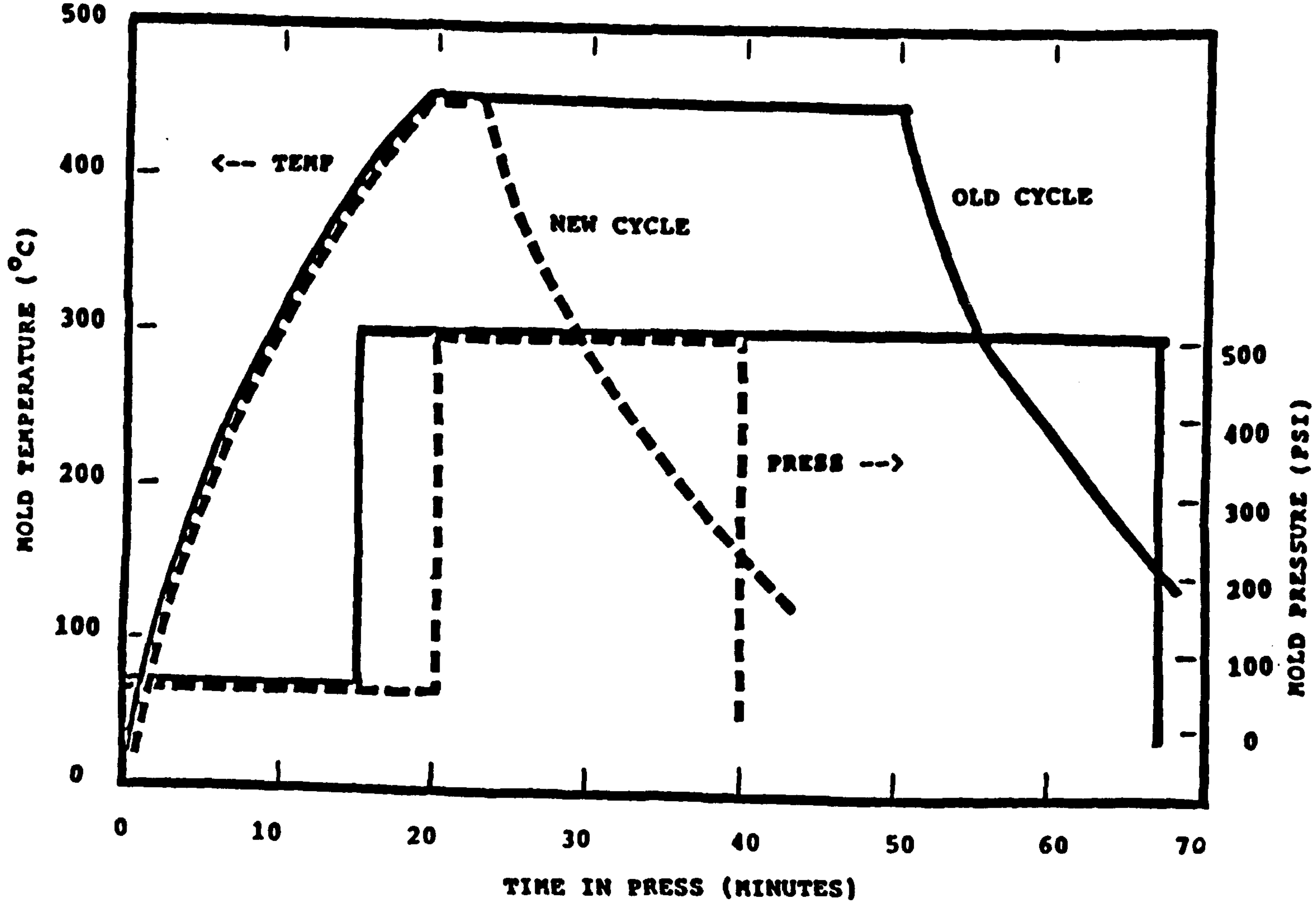


Table 2 Effect of Molding Time on the Mechanical Properties of Neat Resin 85/15 PBI/Ultem

Time at Temperature	30 Minutes	5 Minutes
Tensile Strength (ksi	17.4	25.5
Tensile Modulus (ksi)	564.	787.
Tensile Elongation (%)	3.8	3.8
Density (gm/cm^3)	1.059	1.291
Void Content (%)	19.2	1.5

FIGURE 14
SEM OF MOLDED PANEL CROSS-SECTION
(NEW MOLDING CYCLE)

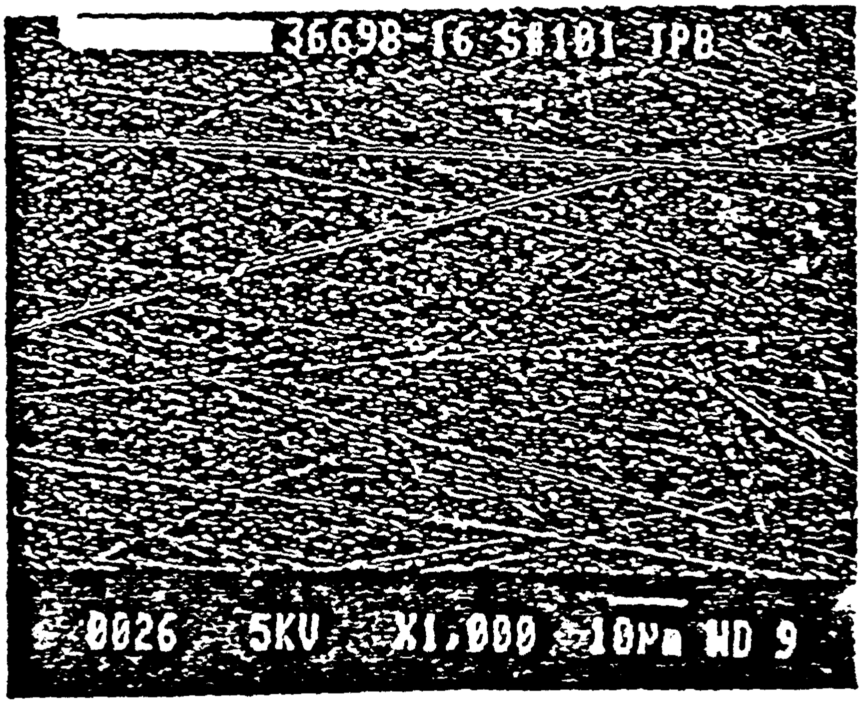
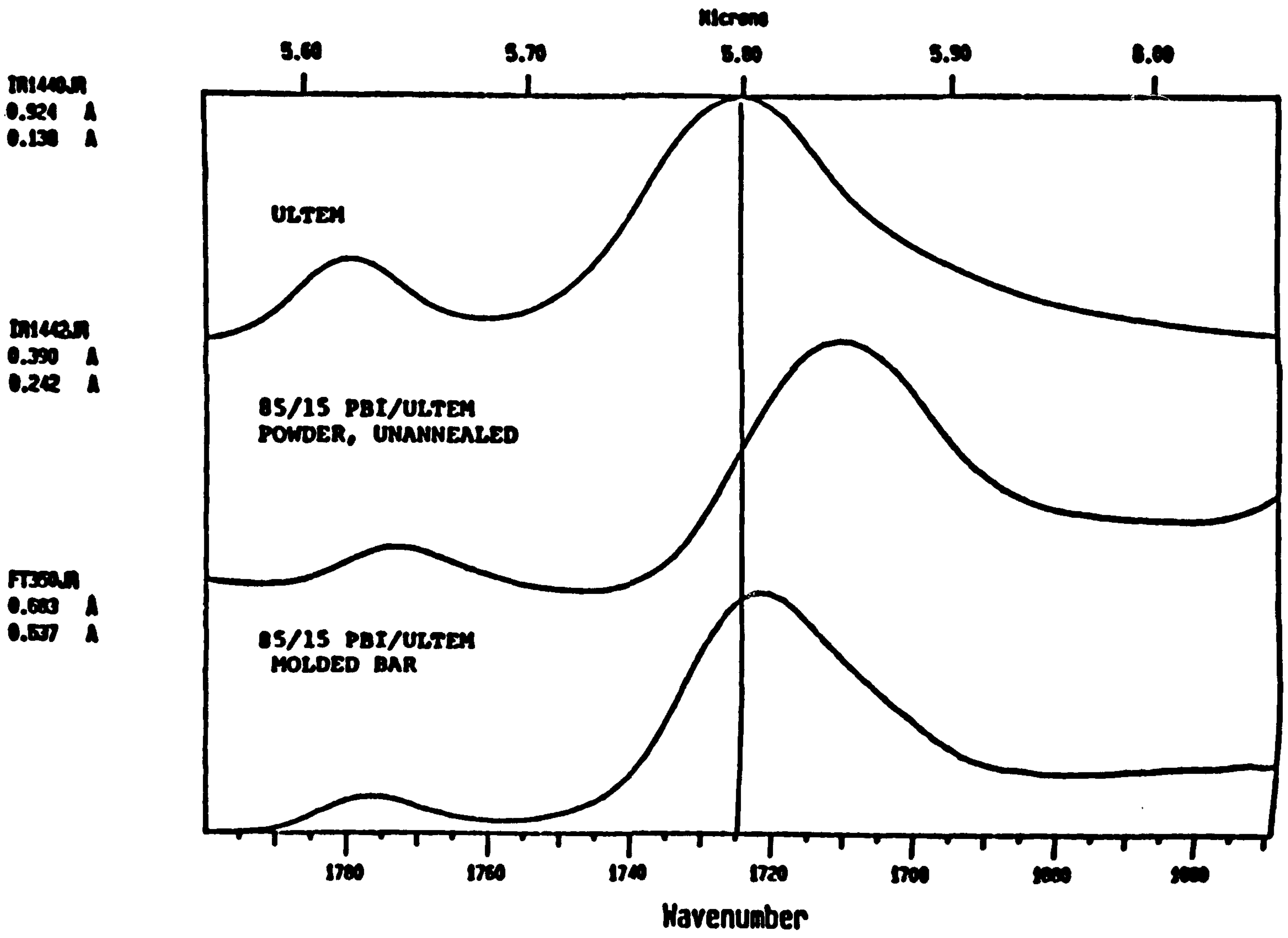


FIGURE 15

ULTEM CARBONYL BANDS



shear property determinations. Molding was done at 500 psi and 440°C for 30 to 60 minutes. Minimal resin flow during molding resulted in an alternating structure of pure polymer followed by a fiber-rich layer. This layered structure was due, at least in part, to high temperature crosslinking of the PBI. This process competed with and inhibited resin flow during consolidation. Bonding between layers was poor as evidenced by the short beam shear results (Table 3). Translation of fiber strength and modulus were 60 and 80 percent, respectively, based upon 3588 kpa (520 ksi) fiber strength and 253 mpa (34.1 msi) fiber modulus reported by the manufacturer. Void content as calculated from composite density was ca. 10-15 percent.

2.1.4 First Generation Summary

The miscibility of the neat 85/15 PBI/Ultem resin was confirmed by thermal analysis, FT-IR and microscopic techniques. While the system appeared to have utility below 500°F (260°C), thermo-oxidative studies at higher temperatures revealed an unexpected synergistic degradation of the blend most probably as the result of PBI degradation products attacking the ether linkage of the polyimide.

A neat resin molding cycle was developed which obtained near theoretical density i.e. low void volume and preserved the miscibility of the blend. Composite evaluations were hampered by poor wetout and resin impregnation. The latter was due, in part,

Table 3 Properties Of Molded 85/15 PBI/ULTEM Carbon Fiber Panels

		Prepreg			Composite	
Polymer Dope	No. Plies	Fiber Loading (Vol%)	DMAc Level (%)	Smpl. Size	Strength (ksi)	Modulus (msi)
Tensile Prop.						
25% Solids	6	61	0.4	5	186	15.8
20% Solids	7	55	0.7	5	168	16.0
Flexural Prop.						
20% Solids	6	39	0.7	6	55	11.8
Short Beam Shear						
20% Solids	6	39	0.7	12	3.5	

to crosslinking of the PBI during consolidation.

2.2 Improved PBI/"Best Available" Polyimide Blend: Second Generation Matrix Candidate

The second generation matrix candidates consisted of blends of an improved PBI with Ultem. Changes in PBI were directed toward obtaining increased thermo-oxidative stability, improved thermoplastic processibility and lower moisture regain.

2.2.1 End-Capped PBI (ecPBI)

PBI is simply the reaction product of a stoichiometric mixture of monomers reacted together in a two stage process with a short high temperature heating cycle. The glass transition temperature of the final product is higher than the polymerization temperature. Thus, the additional reactions of chain extension, crosslinking and/or ring closure occur at composite matrix molding temperatures which are above Tg and typically 100°C (or more) higher than the polymerization temperature. The Tg of PBI was shown to increase with temperatures above 400°C (752°F) most probably as the result of these reactions. Thus these reactions directly compete with thermoplastic flow behavior; i.e., the moldability of PBI.

End-capping of PBI with phenyl benzoate was shown to decrease or eliminate end group activity by converting reactive o-phenylene diamine groups into stable phenyl benzimidazole end groups.

Synthesis of the ecPBI followed the standard, two step PBI polymerization process with the phenyl benzoate added to the initial reaction mixture of tetraaminobiphenyl and diphenylisophthalate. The results from a series of polymers with 1/2 mol%, 1 m%, 2 m%, 4 m% and 6 m% phenyl benzoate are shown in Figure 16 and Table 4. The amount of end-capping controlled the final inherent viscosity (molecular weight) and the ultimate glass transition temperature of the PBI. In addition, end-capping restricted the increase in Tg with time at temperature as compared to the standard non-endcapped polymer. Compression molding of neat resin discs from the above series of polymers resulted in the selection of 2 mole percent phenyl benzoate end-capped PBI (ecPBI-2) for scale-up for blend evaluations. Molded discs at higher levels of end-capping were brittle, most probably as the result of lower molecular weight. These moldings also indicated that the ecPBI-2 had more thermoplastic flow behavior than conventional PBI. Isothermal aging of the ecPBI-2 at 316°C (600°F) showed no effect of the end-capping in mitigating the oxidative degradation of characteristics of PBI (Figure 17).

One hundred seventy (170) pounds of ecPBI-2 were synthesized to provide a consistent batch of polymer for blending with Generations II and III polyimides. Inherent viscosity of this material was 0.6 dl/gm and the glass transition temperature was 407°C (765°F). Calculated molecular weight was 31,000 with 100 repeat units in the polymer backbone.

FIGURE 16

GLASS TRANSITION TEMPERATURES VS 'INHERENT
VISCOSITIES OF END CAPPED PBIs

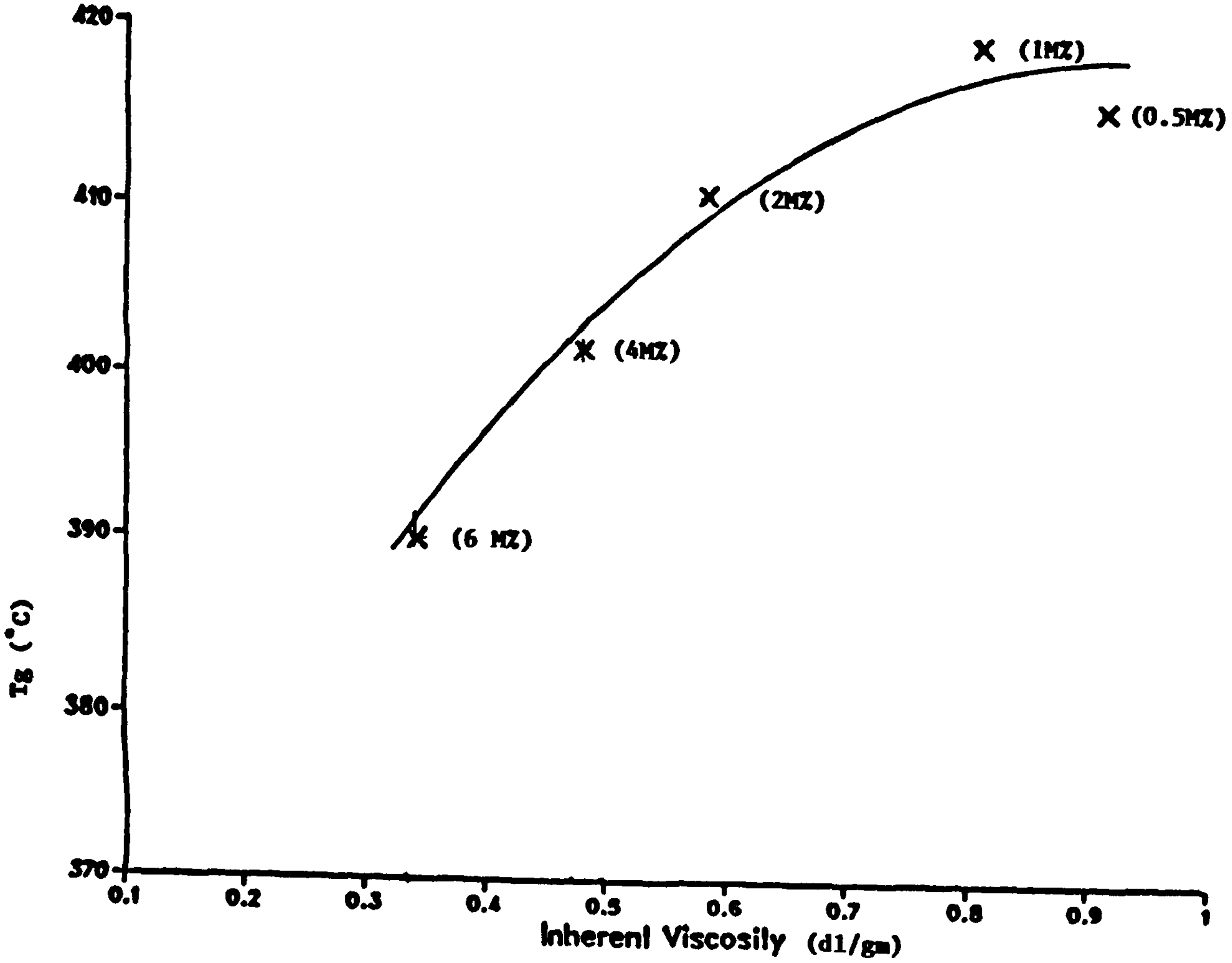


TABLE 4

Glass Transition Temperature Change And Inherent Viscosity Of Phenyl Benzoate End Capped PBI

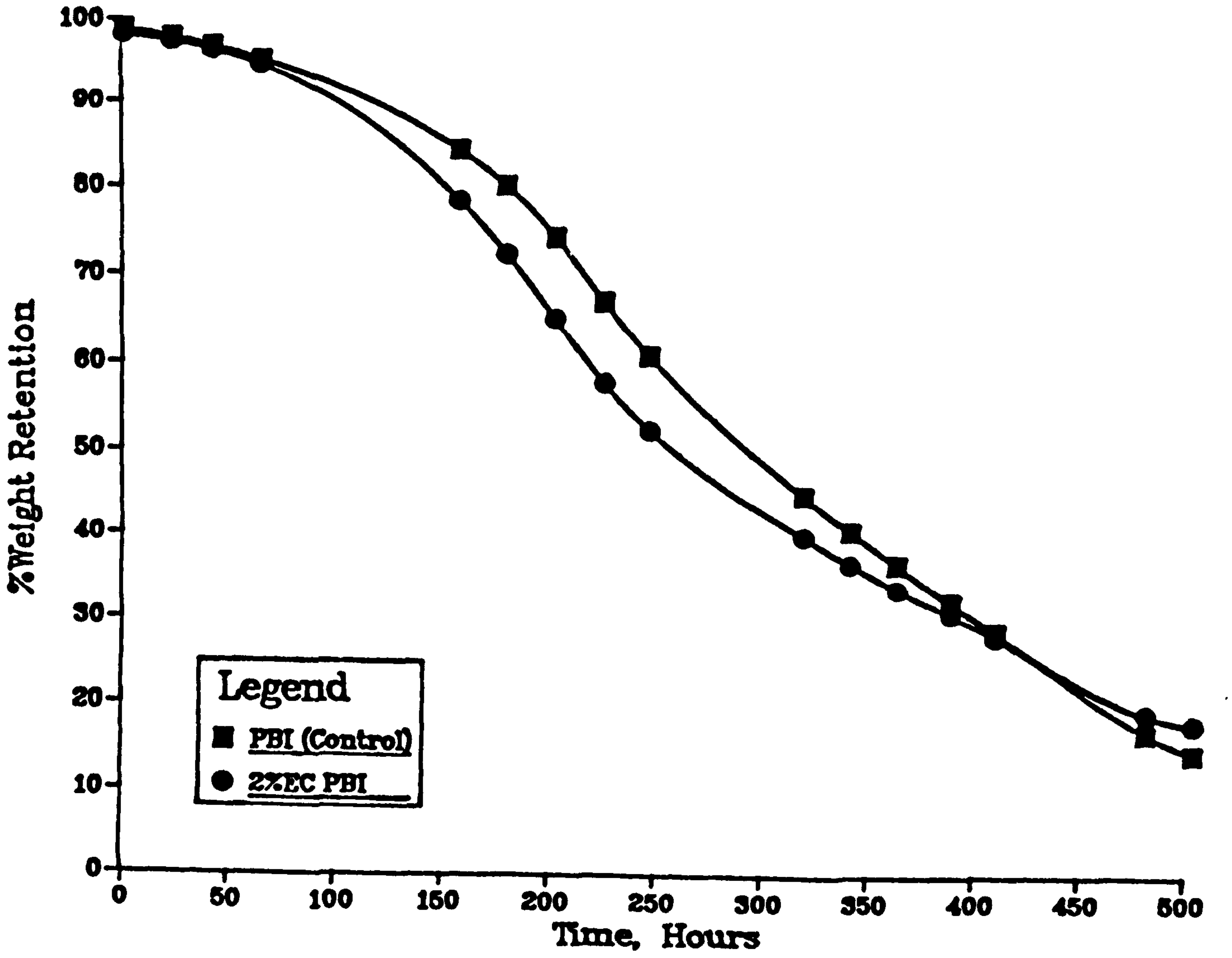
SAMPLE*	IV (dl/gm)	SECOND HEATING+ Tg (°C)	5 MIN. THIRD HEATING‡ Tg (°C)	ΔTg	30 MIN. THIRD HEATING‡ Tg (°C)	ΔTg
0.5% PB	0.91	409	417	8	415	6
1.0% PB	0.81	410	416	6	418	8
2.0% PB	0.58	403	408	5	410	7
4.0% PB	0.47	391	397	6	401	10
6.0% PB	0.34	381	388	7	390	9
0.0% PB PBI CONTROL	0.71	402	417	15	419	17

* Samples heated to 225°C and held for 5 minutes to remove moisture, cooled, reheated to 450°C (2nd heating) and held for 5 minutes or 30 minutes, cooled, and reheated to 500°C (3rd heating). Heating rates were 20°C/minute.

+ n=4
‡ n=2

FIGURE 17

Thermo–Oxidative Stability of 2% End Capped PBI Film Aged in Air at 600 F



2.2.2 Substituted PBI

To increase TOS, 6FPBIs were synthesized which contained the hexafluoroisopropylidene moiety in the backbone. Initially, a homopolymer 6FPBI, with 0.77 dl/gm IV, was formed by the substitution of 6F diacid for isophthalic acid (IA) in the polymerization with tetraaminobiphenyl (TAB). Subsequently a 50/50 copolymer of 6F and IA produced a material with 0.64 IV. Based upon these results, the remaining copolymers shown in the matrix of Figure 18 were also synthesized in glassware at the 35 gram scale. Representative results from TOS testing at 316°C (600°F), in air, of the 6FPBIs are shown in Figure 19. Both the 6F homopolymer and the 50/50 copolymer showed a distinct improvement in TOS over conventional PBI. However, the weight losses incurred were still unacceptable for the program at hand. Further development of the 6FPBI concept was suspended based upon these results and the inability to scale-up these materials to the tens and hundreds of kilos necessary for aerospace composite evaluations.

A third attempt to develop an improved PBI was through the substitution of the imidazole hydrogen by a phenyl group to produce N-phenyl PBI (Figure 20). Polymerization of this material proceeded from diphenyl isophthalate and N-phenyl TAB to achieve 100% substitution. The inherent viscosity and Tg of this material were 0.29 dl/gm and 295C, respectively. Moisture uptake was 1.7%; an order of magnitude lower than standard PBI. As shown in Figure 21, however, the thermo-oxidative stability of this polymer was

FIGURE 18

EXPERIMENTAL DESIGN -- 6FPBI
TAB + ACID RATIO 6F/IA,TA

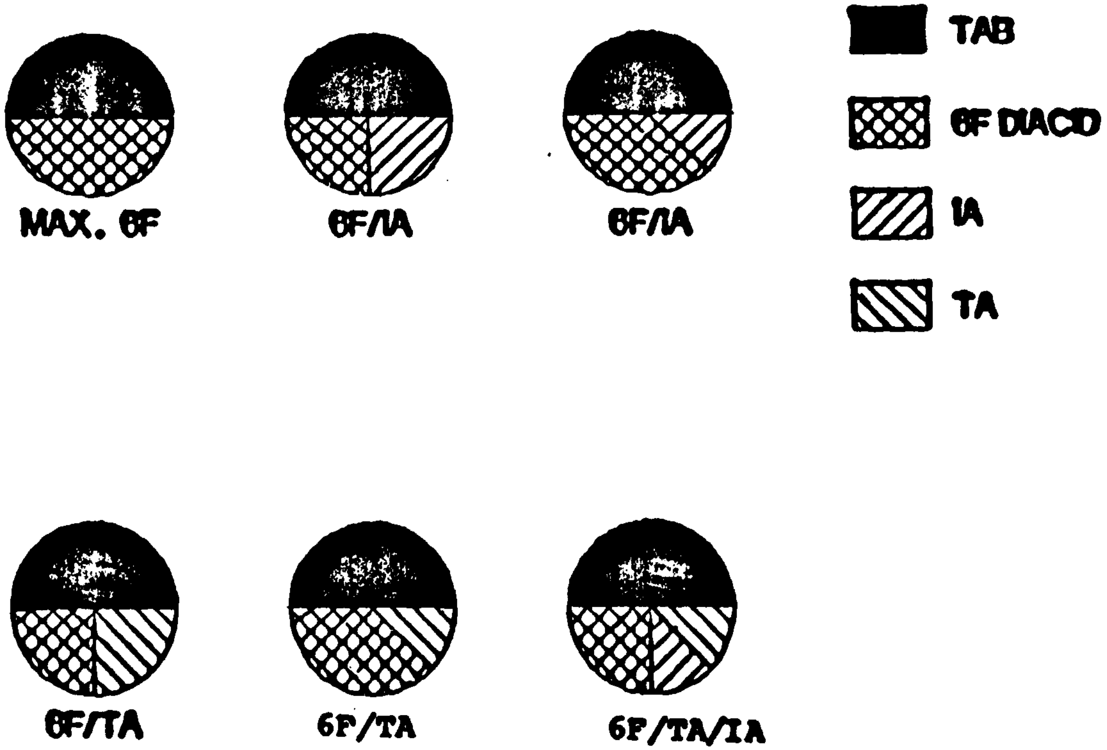


FIGURE 19

Thermo–Oxidative Stability of 6FPBI
Films Aged in Air Oven at 600 F

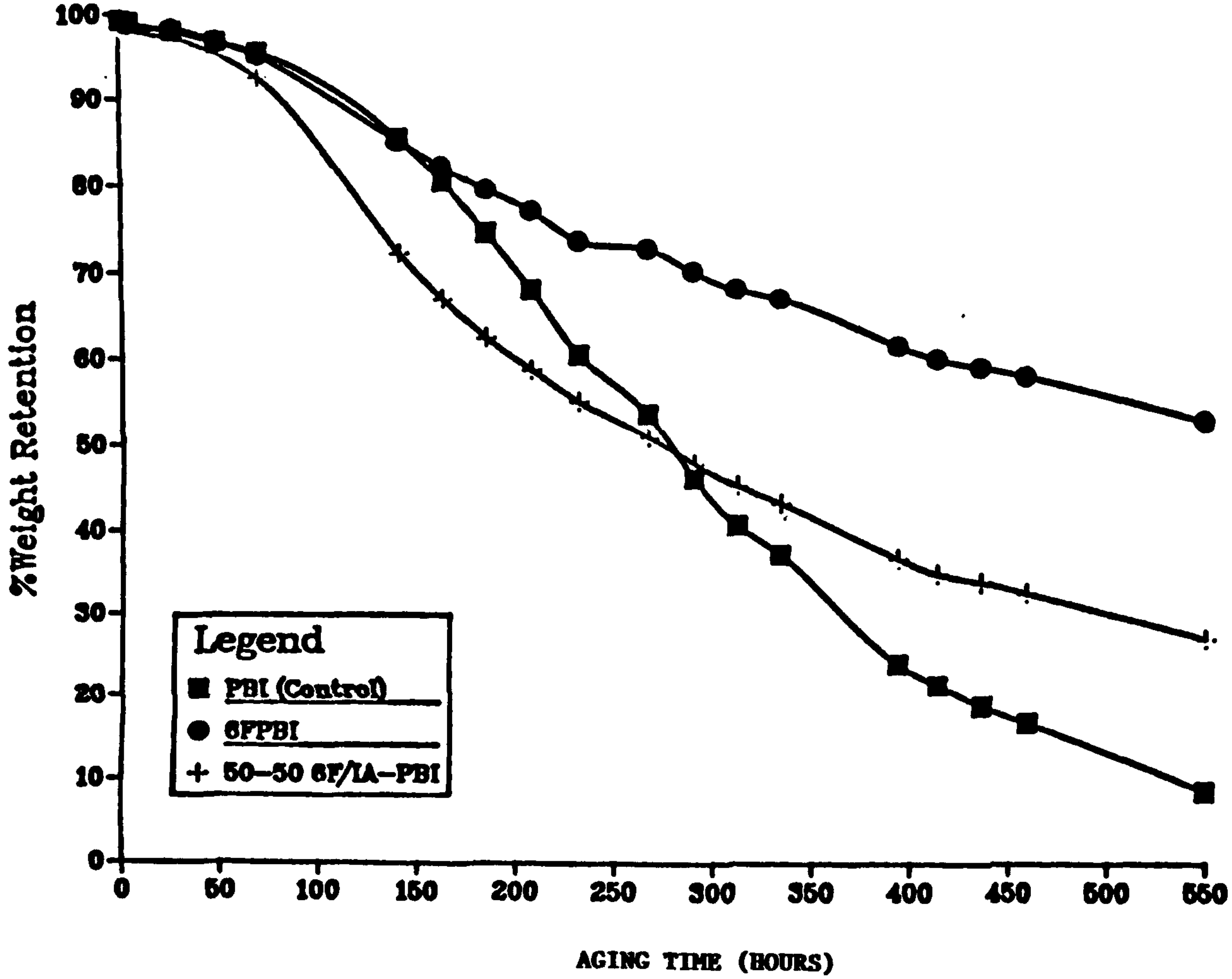


FIGURE 20 **N-PHENYL PBI**

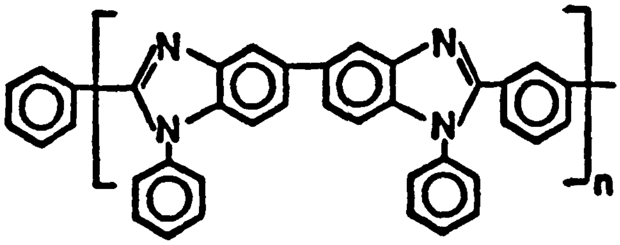
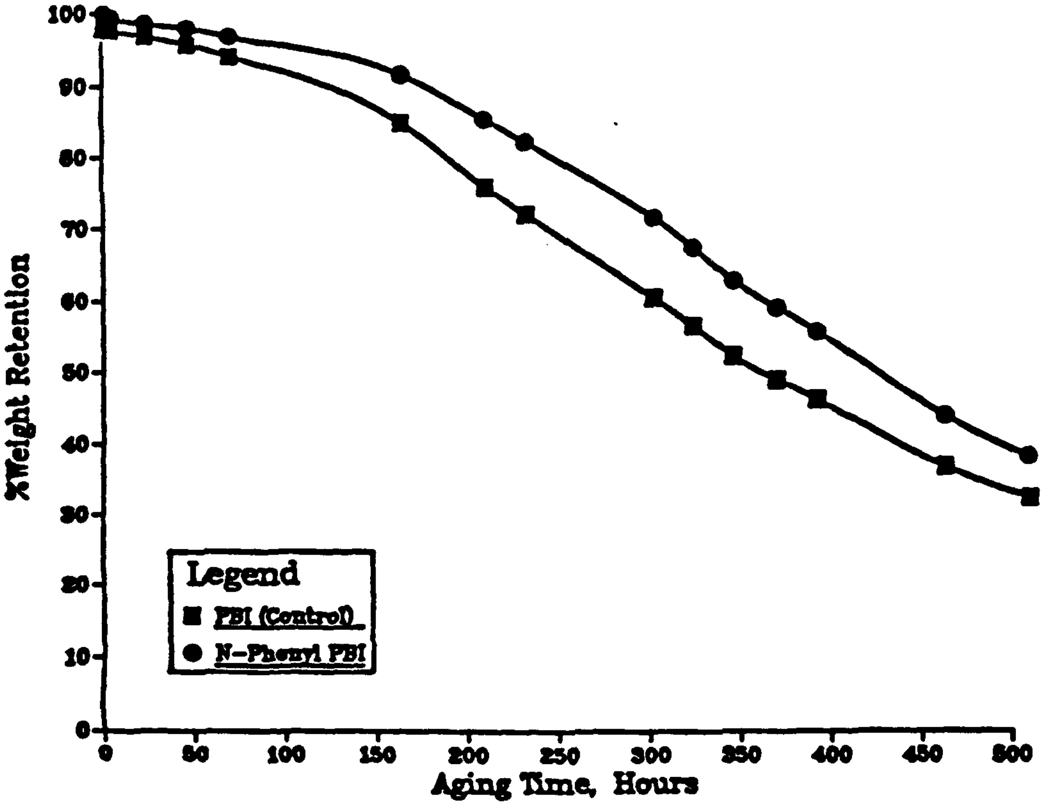


FIGURE 21

Thermo Oxidative Stability of N–Phenyl PBI Film Aged in Air Oven at 600 F



only marginally improved and still unacceptable for this program.

2.2.3 Phosphoric Acid Treated PBI

Improved thermo-oxidative stability of both ecPBI-2 and 85/15 ecPBI-2/Ultem blends was demonstrated by treating films of these materials with a 5% solution of phosphoric acid at 50°C (122°F) for 2 hours. Long term isothermal aging results (Figures 22 and 23) to 500 hours, in air, at 316°C (600°F) show a 3.5-4.0 fold increase in weight retention of the acid treated films.

Fourier Transform Infrared analysis and scanning electron microscope/energy dispersive X-ray (SEM/EDX) studies were used to better understand the stabilization mechanism by determining the extent of phosphorous incorporation and the nature of its bonding in films. FT-IR results indicated that the phosphoric acid protonated the imidazole ring and formed a phosphate salt (Figure 24). Figure 25 displays spectra of PBI and phosphoric acid treated PBI. The bands at 1068 and 952 cm^{-1} in the treated sample are indicative of ionic phosphate. The band at 1530 cm^{-1} in the PBI spectrum is related to the imidazole ring. Protonation of this ring shifts this band to 1566 cm^{-1}, however, it is not complete since the 1530 cm^{-1} band is still observed. FT-IR spectra of the surface and bulk portions of these films also concluded that phosphate level was higher at the surface. A similar result was also obtained for 85/15 ecPBI-2/-Ultem films.

FIGURE 22

Effects of Phosphoric Acid and Heat Treatment
on the TOS of End Capped PBI Films Aged in Air at 600 F

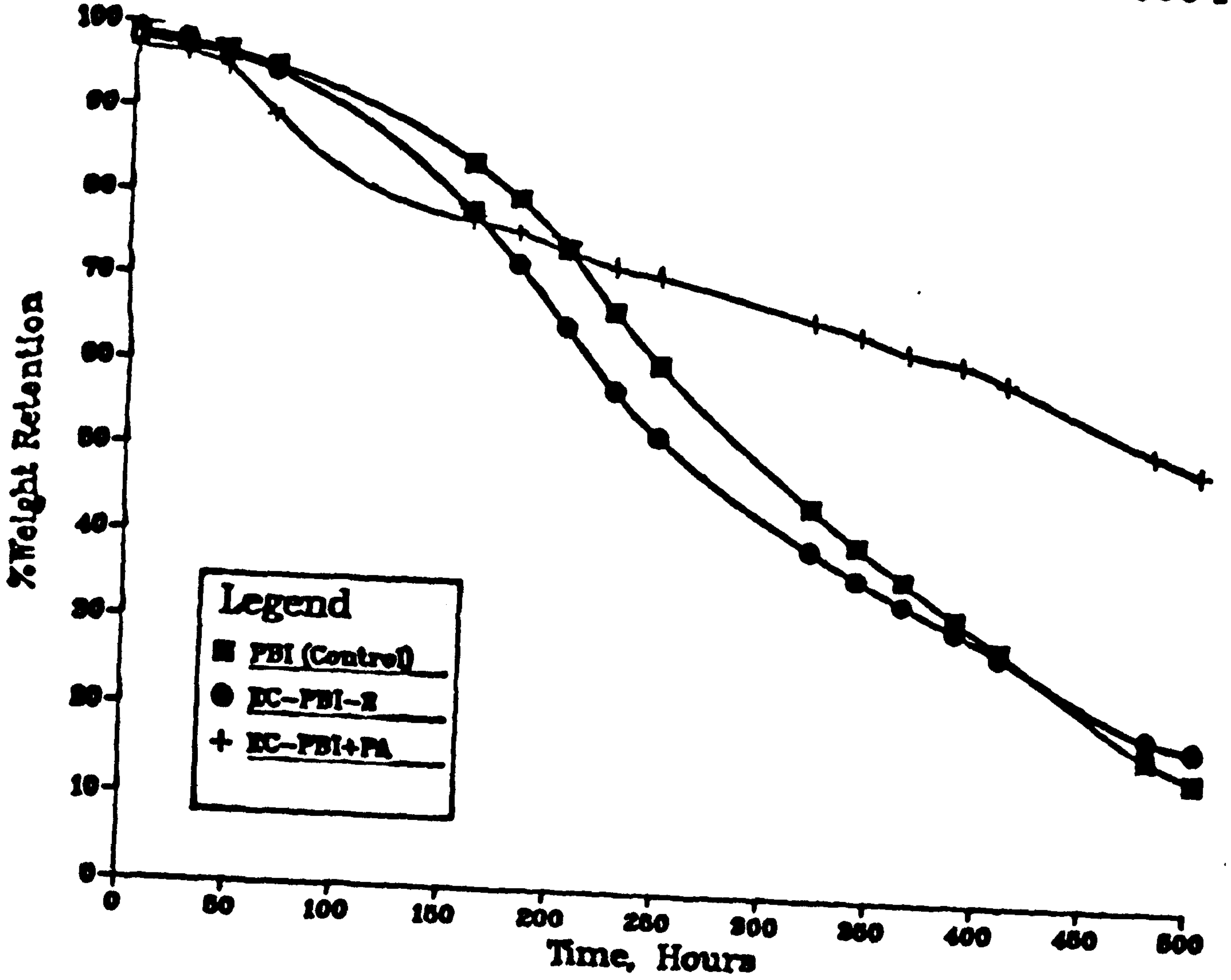
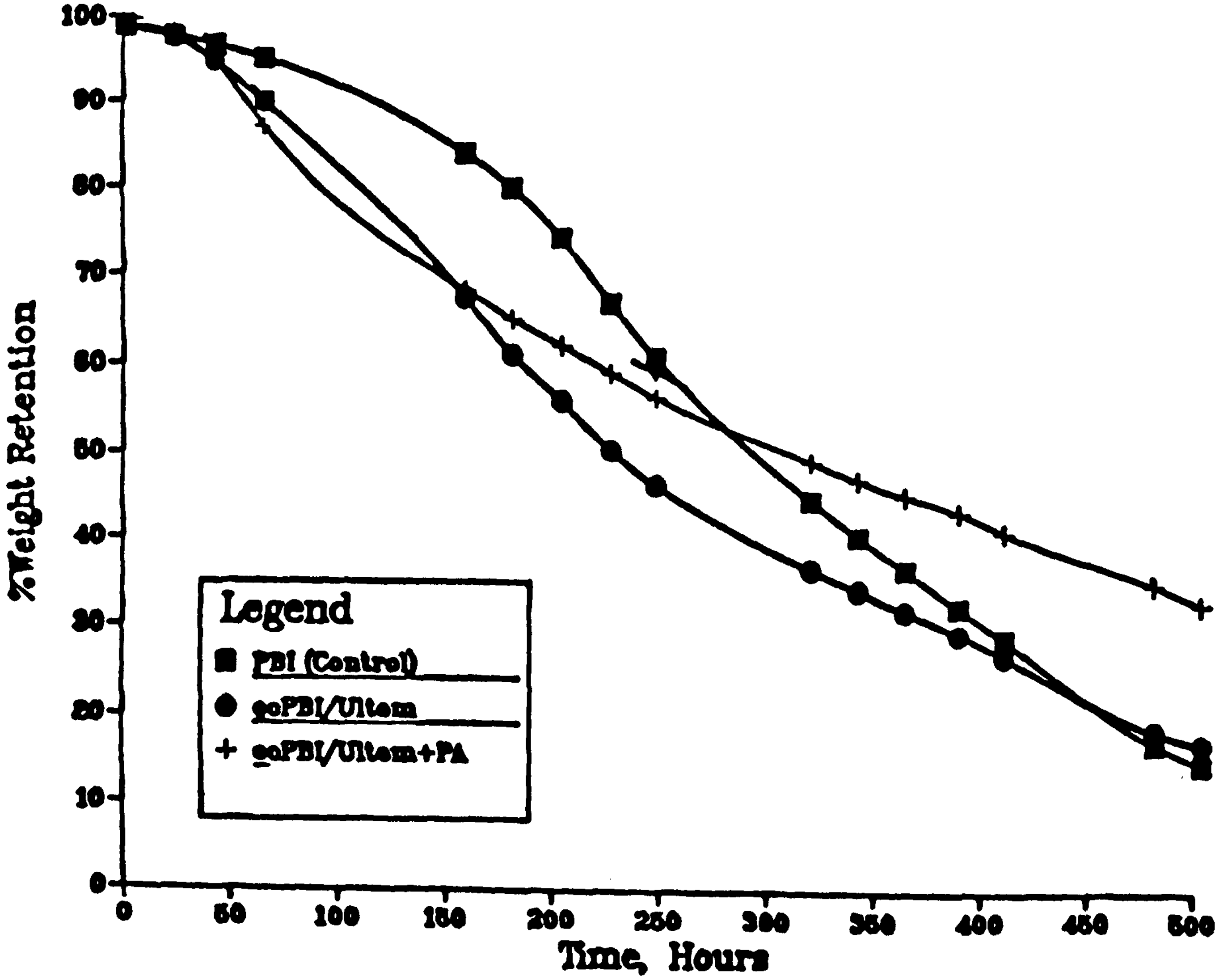


FIGURE 23



Effects of Phosphoric Acid and Heat Treatment on the TOS of 85/15 ecPBI/Ultem Blend Films Aged in Air at 600 F

FIGURE 24

Phosphoric Acid + PBI

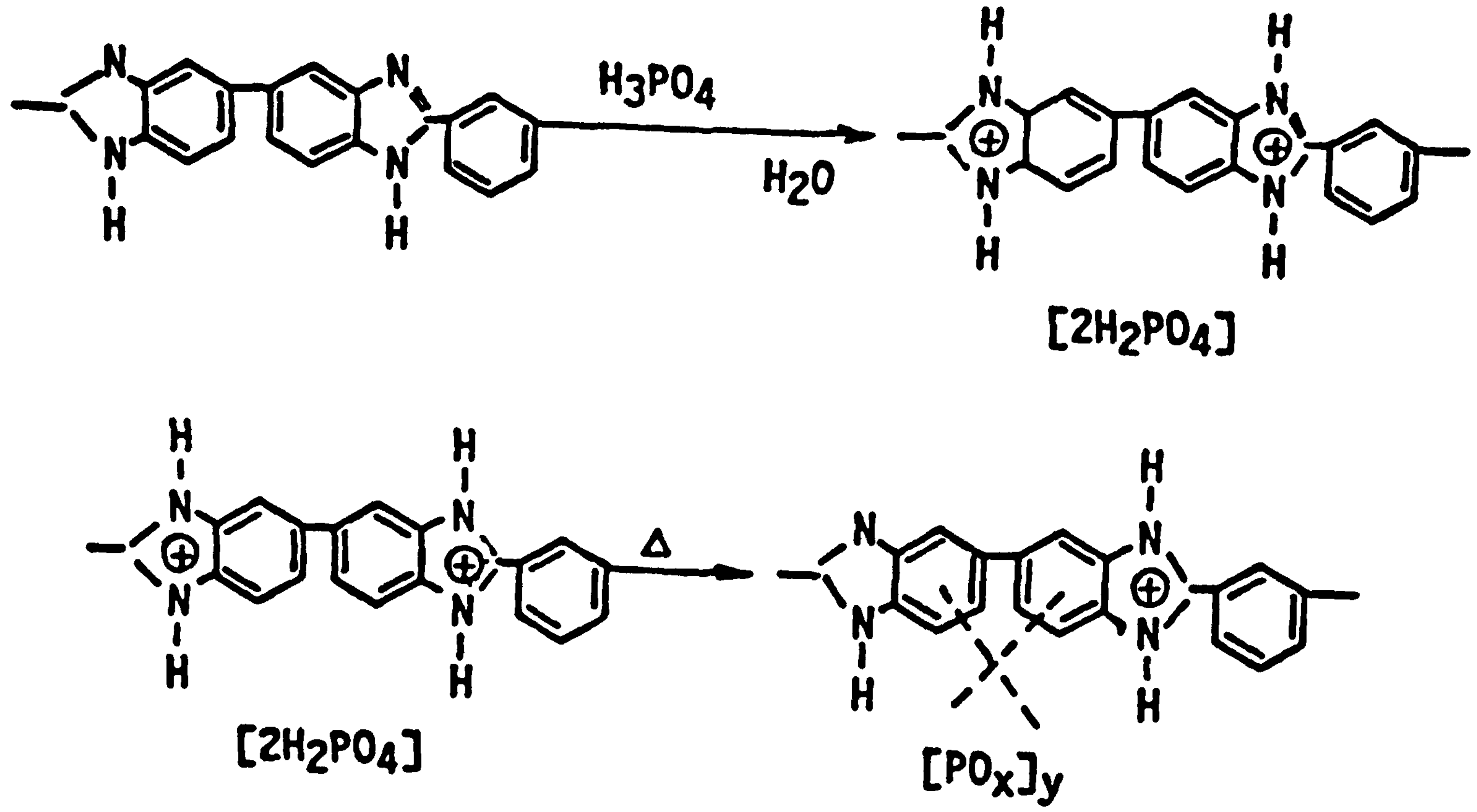
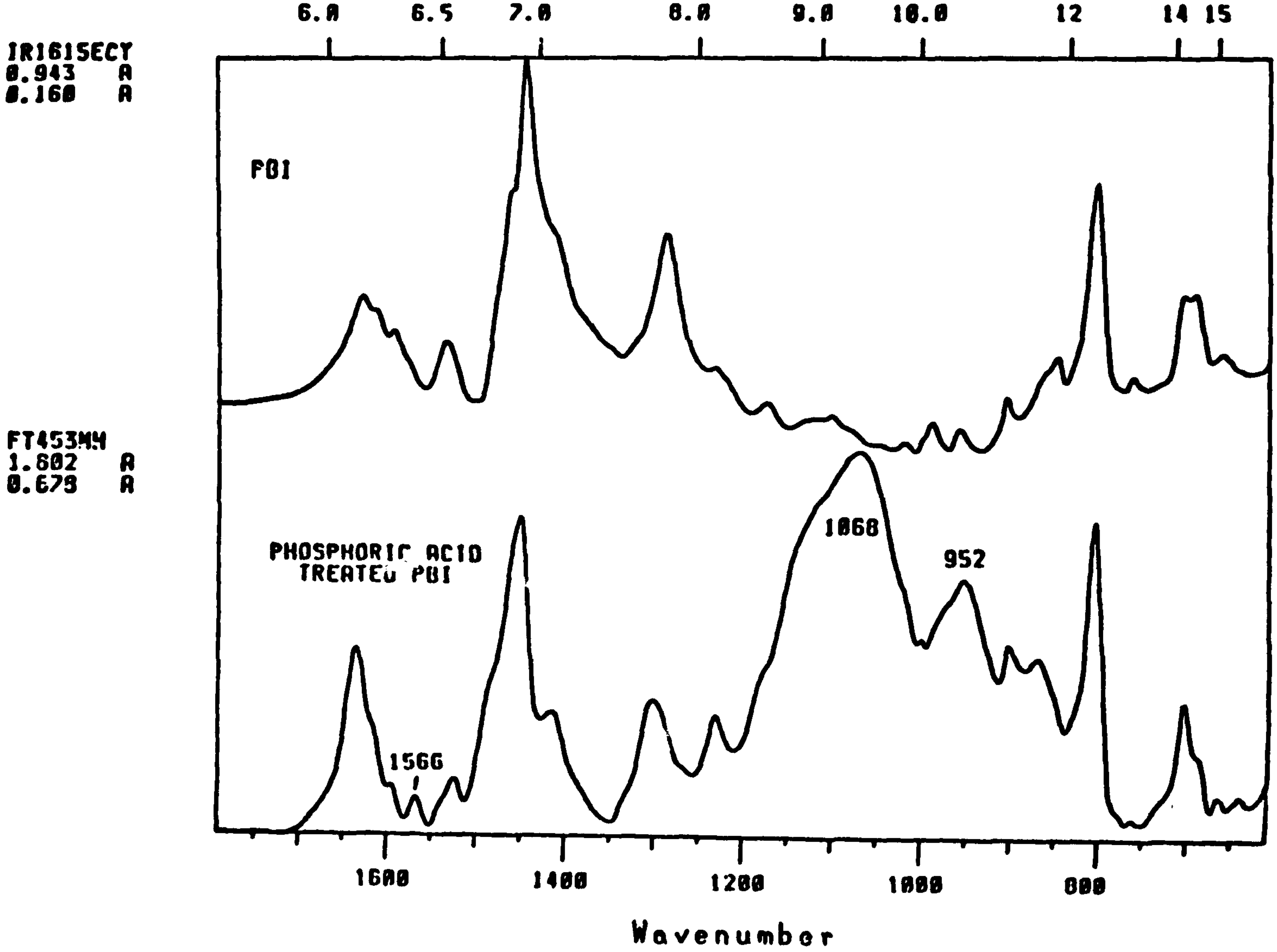


FIGURE 25

COMPARISON OF PBI AND ACID TREATED PBI



SEM/EDX studies of both treated and untreated molded PBI bars also confirmed that the diffusion of phosphoric acid is slow and mostly confined to the surface. Elemental mapping of phosphorous in cross sections of these specimens showed the penetration to be approximately 0.5-1.0, 2.0-4.0 and 6.0-10.0 microns for acid treatments of 2, 24 and 72 hours, respectively. Thus in molded bars, phosphoric acid treatment formed a barrier layer at the surface which inhibited oxidation. This layer shows up as the bright band at the surface of the PBI bar in Figure 26, i.e. between the epoxy mounting material and the PBI bulk.

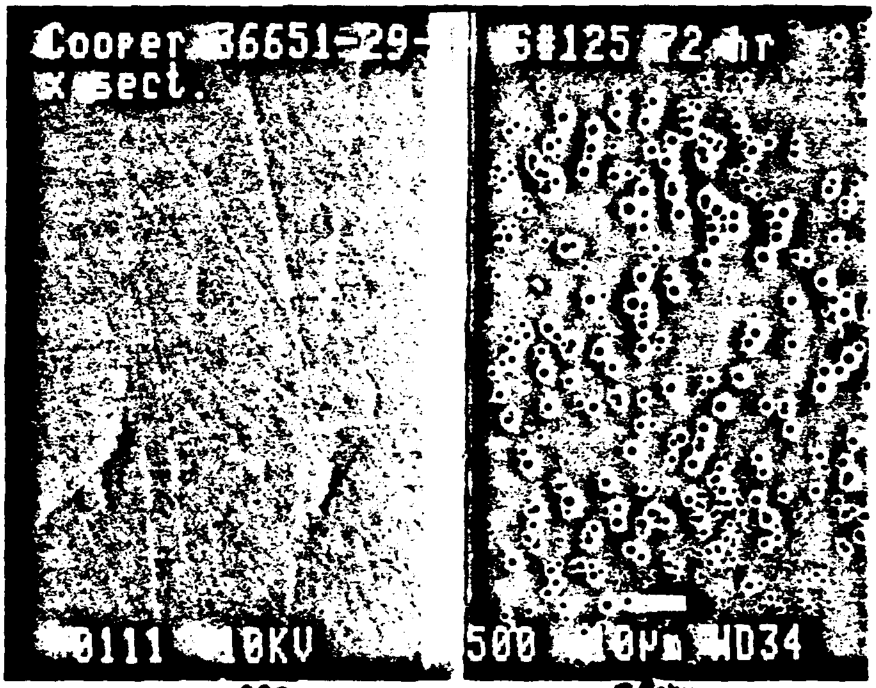
2.2.4 85/15 ecPBI-2/Ultem Neat Resin Evaluations

End-capped PBI (ecPBI-2) was dissolved in DMAc and solution blended with Ultem 1000 (in DMAc) at an 85/15 (by weight) ratio. The blended dope was filtered to remove insolubles, precipitated into water and washed extensively in boiling water to remove residual solvent. The blend was dried under vacuum at 150°C.

A comparison of the molded bar tensile properties of ecPBI-2/ Ultem and standard PBI/Ultem are shown in Table 5. Both sets of bars were fabricated using the new molding cycle of Figure 13. Molding temperatures and pressures were 435°C (815°F) and 500 psi, respectively. As expected, end-capping did not effect the mechanical properties of the blend.

Twenty seven Type V ASTM tensile specimens were molded from 85/15

FIGURE 26 Barrier Layer Formed After 72-Hours Phosphoric Acid Soak



PBI Epoxy

TABLE 5

Properties of 85/15 ecPBI/Ultem Tensile Bars

Time at Temperature	85/15 ecPBI-2/Ultem 10 Minutes	85/15 PBI/Ultem 5 Minutes
Tensile Str. (ksi)	23.0	25.5
Tensile Mod. (ksi)	775.	787.
Tensile Elo ng. (%)	3.4	3.8
Density (g/cm^3)	1.288	1.291

ecPB-2/Ultem blend polymer and sent to Lockheed and GE Aircraft Engines for room temperature, elevated temperature and hot/wet evaluations. The bars were machined from 125 mil panels molded for 3 minutes at 450°C (842°F) and 1000 psi. Results from the Lockheed evaluations are shown in Table 6, below, along with Hoechst Celanese results for a similar set of test specimens.

2.2.5 Second Generation Summary

End-capping of PBI with phenyl benzoate was found to prevent significant increases in polymer molecular weight due to end group reactivity during high temperature exposure. This result insured maximum thermoplasticity of PBI during molding. One hundred seventy pounds of 2% phenyl benzoate end-capped PBI were produced for use in Generation II and III blend trials.

Attempts to improve the thermo-oxidative stability of PBI by substitution of the 6F moiety into the PBI backbone or by substitution of the imidazole hydrogen by a phenyl group were only partially successful and thus not readily applicable to this program. Phosphoric acid treating of PBI (and ecPBI-2) resulted in 3.5-4.0 fold increase in weight retention after TOS testing at 316°C (600°F) in air. This phenomena was related to the formation of a thin oxidation barrier on the surface of the treated specimens. While of utility, such barriers can be easily breached during machining, drilling and other composite part fabrication steps and thus are of little practical value in this program

TABLE 6

MECHANICAL PROPERTIES OF 85/15 ecPBI/ULTEM MOLDED BARS

Test Conditions	n	Tensile Strength ksi	Tensile Strength kPa	Modulus Msi	Modulus MPa	% Weight Gain 20 Day Soak
Room Temp. Dry	5	20.2	139.6	0.9	6.2	
Room Temp. Wet	6	16.5	113.9	0.9	6.2	7.583
500°F	6	10.6	73.4	0.4	2.8	
HCC R.T., Dry		23.0	158.7	0.8	5.5	

without considerable additional development and evaluation. Such efforts were outside the scope of this program.

2.3 Improved PBI/ 6F Polyimide Blends: Third Generation Matrix Candidate

PBI has been shown to be miscible with certain polyimides containing the hexafluoroisopropylidene or 6F moiety shown in Figure 27. This moiety is known to impart ultrahigh temperature stability, oxidative resistance, processibility, moisture insensitivity and enhanced fracture toughness to resins.

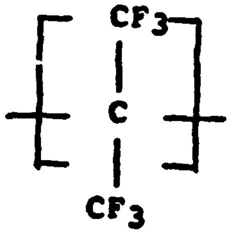
2.3.1 Polyimide Development, Evaluation and Selection

A series of nine copolymer polyimides (coPI) containing the 6F moiety were synthesized, at the 35 gram level, and evaluated for Tg, thermal and thermo-oxidative stability, solubility in DMAc and solvent sensitivity to common organic solvents both as neat resins and in blends with PBI. The statistical design for these coPIs is shown in Figure 28 and listed in Table 7. The dianhydride portion of each copolymer consisted or either 6F dianhydride (6FDA) or 6FDA and benzophenone tetracarboxylic dianhydride (BTDA). The diamine portions consisted of 4,4′ diaminodiphenylsulfone (DADPS) or DADPS diluted with either meta or para phenylene diamine.

The DSC glass transition temperatures of the above polymers are shown in Table 7 while their solubilities, at 20% solids, in DMAC

FIGURE 27

6F Moiety



$$-\left[C(CF_3)_2\right]-$$

FIGURE 28

EXPERIMENTAL DESIGN - 6FCOPI
DIANHY. - 6F, BTDA DIAMINE - m,p,PDA, DADPS

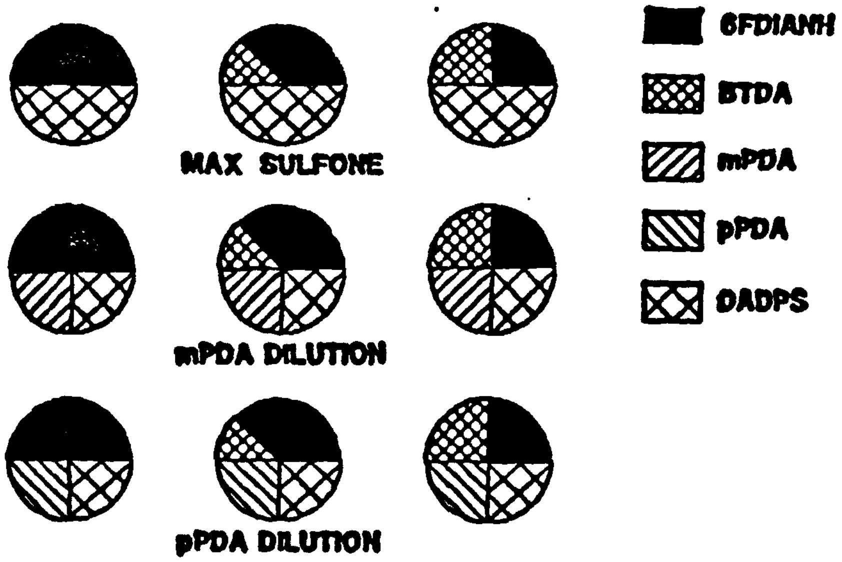


TABLE 7

Thermal Properties Of 6F Copolyimide Polymers

$Sixef^{TM}$PI	Dianhydride		Diamine			DSC* T_g
	6FDA	BTDA	DADPS	mPDA	pPDA	(°C)
1	100		100			274
2	75	25	100			333
3	50	50	100			335
4	100		50	50		332
5	75	25	50	50		321
6	50	50	50	50		314
7	100			50	50	346
8	75	25		50	50	351
9	50	50		50	50	351

* As Prepared

are listed in Table 8. Polymers 8 and 9 were insoluble and thus were unable to be solution blended with PBI. Solubility decreased as the 6F content decreased. The long term thermo-oxidative stabilities of these polymers in 50/50 and 75/25 PBI/6FcoPI blend films at 316°C (600°F) to 500 hours is presented in Figures 29 and 30. Of particular note, was the fact that the degradation of the blend was roughly proportional to the PBI content in the blend. Copolymers 2, 5 and 7 were selected for scale-up to the 100 gram level for additional characterizations.

Figure 31 shows the thermo-oxidative stability of 6FcopI-2, 6FcoPI-5 and 6FcoPI-7 films as compared to that of neat PBI and Kapton films at 316°C (600°F) to 500 hours. Also shown is the stability of a 6FDA and oxydianiline (ODA) copolymer. Except for 6FODA, the weight loss for each of the neat films was less than 5% with most of the (early) loss attributed to the evolution of moisture. None of the aged films exhibited evidence of thermal degradation; all of the samples maintained their yellowish transparent color without apparent brittleness.

Figure 32 compares the isothermal weight loss of these neat copolymers with their 50/50 and 25/75 PBI/6FcoPI blends. The blend ratios were chosen to increase the percentage of imide content in the blends to improve melt processibility and to help abate the TOS and moisture problems associated with PBI. Again, the degradation in the blends was proportional to the PBI content.

TABLE 8 COPOLYMER POLYIMIDE SOLUBILITY

SAMPLE NUMBER*	SOLUBILITY IN DMAc
1	Soluble at room temperature.
2	Required heating to 100°C.
3	Required heating to 100°C.
4	Soluble at room temperature.
5	Required heating to 100°C.
6	Required heating to 100°C.
7	Soluble at room temperature.
8	Formed gel at 15% solids and 150°C.
9	Formed gel at 15% solids and 150°C.

* See TABLE 7 for compositions

FIGURE 29

Thermo–Oxidative Stability of 50/50 PBI/6F–PI Blend Films Aged in Air Oven at 600 F

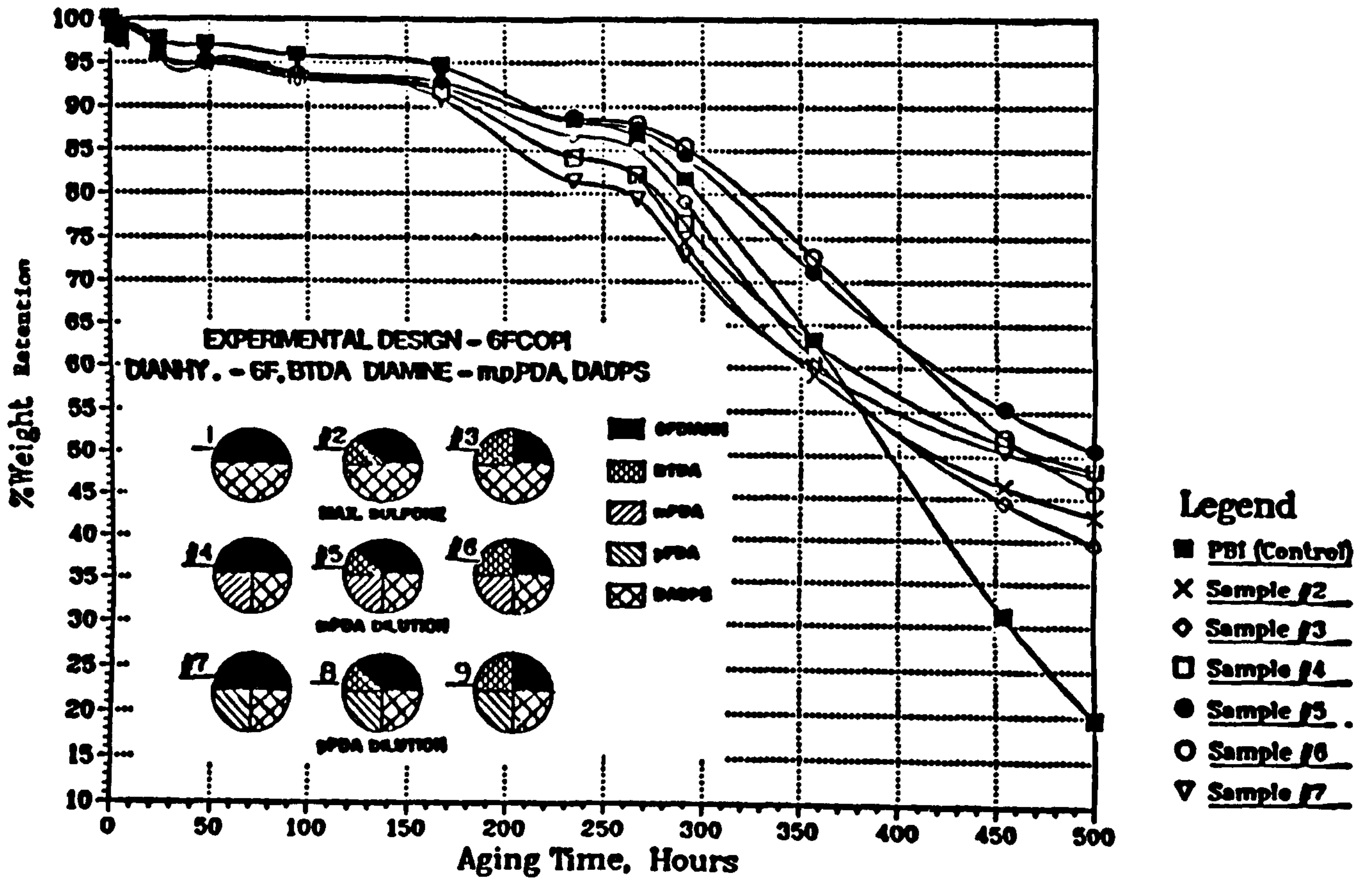


FIGURE 30

Thermo–Oxidative Stability of 75/25 PBI/6F–PI
Blend Films Aged in Air Oven at 600 F

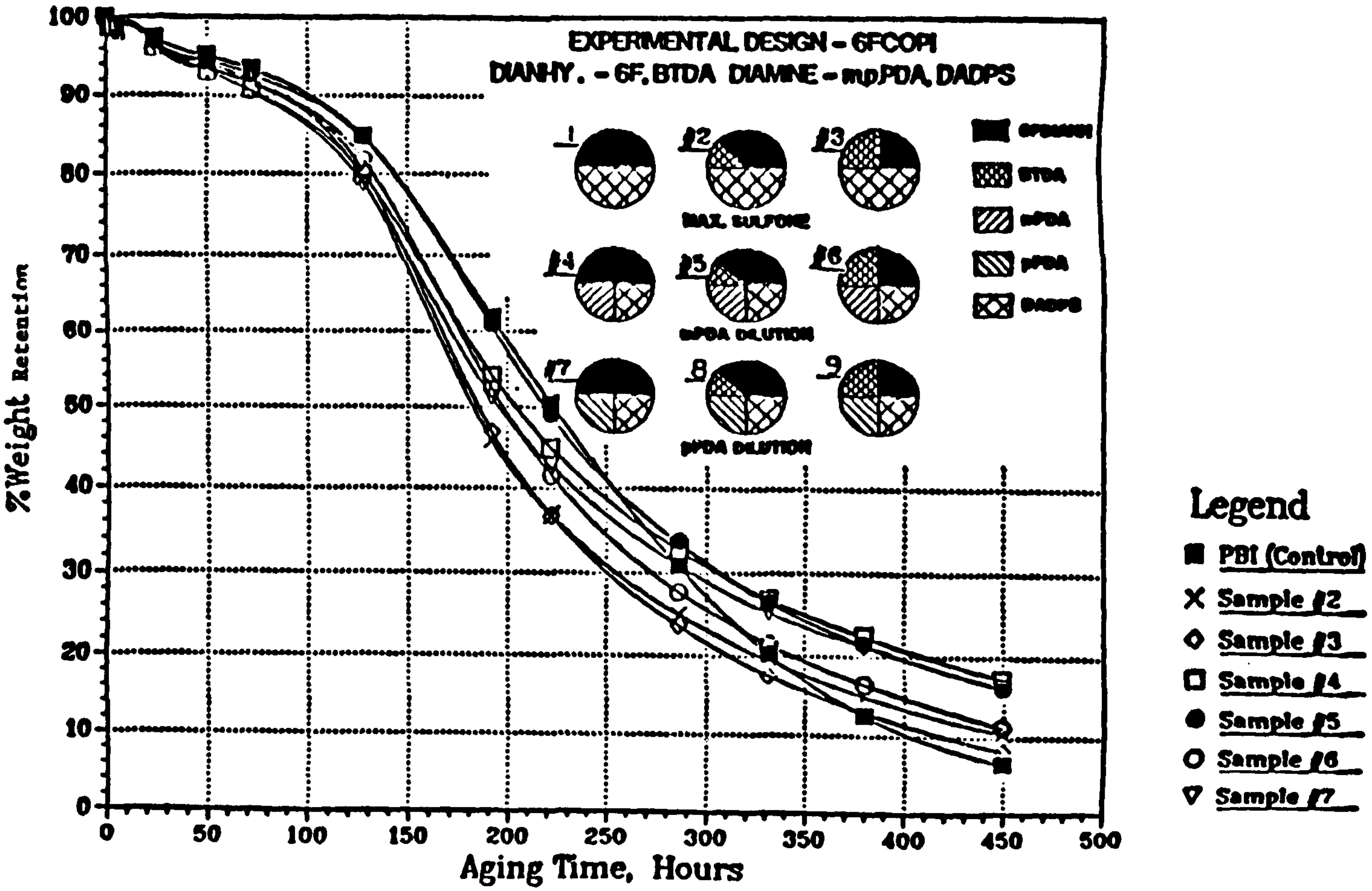


FIGURE 31

Thermo–Oxidative Stability of Neat 6F Copolymer Films Aged in Air Oven at 600 F

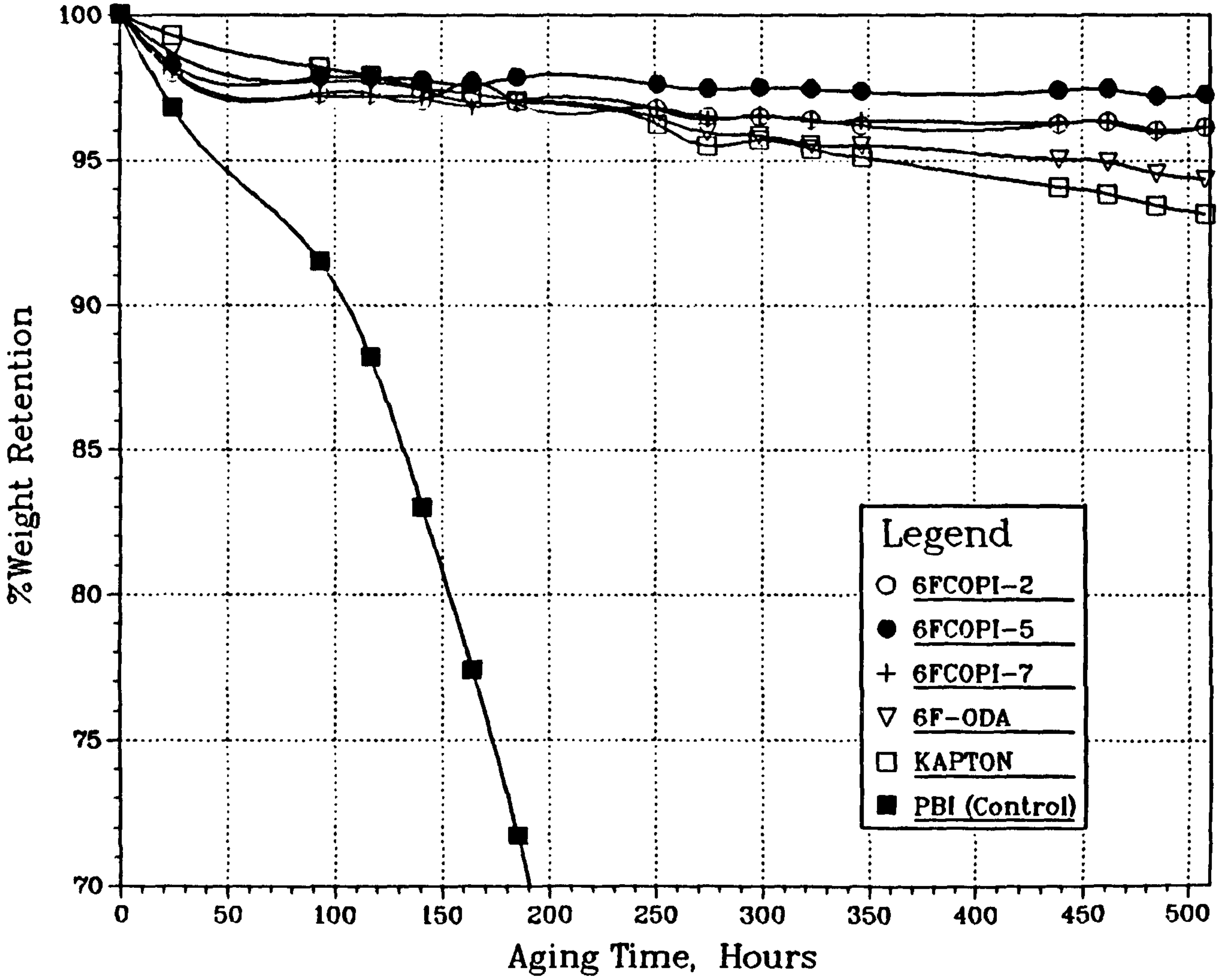
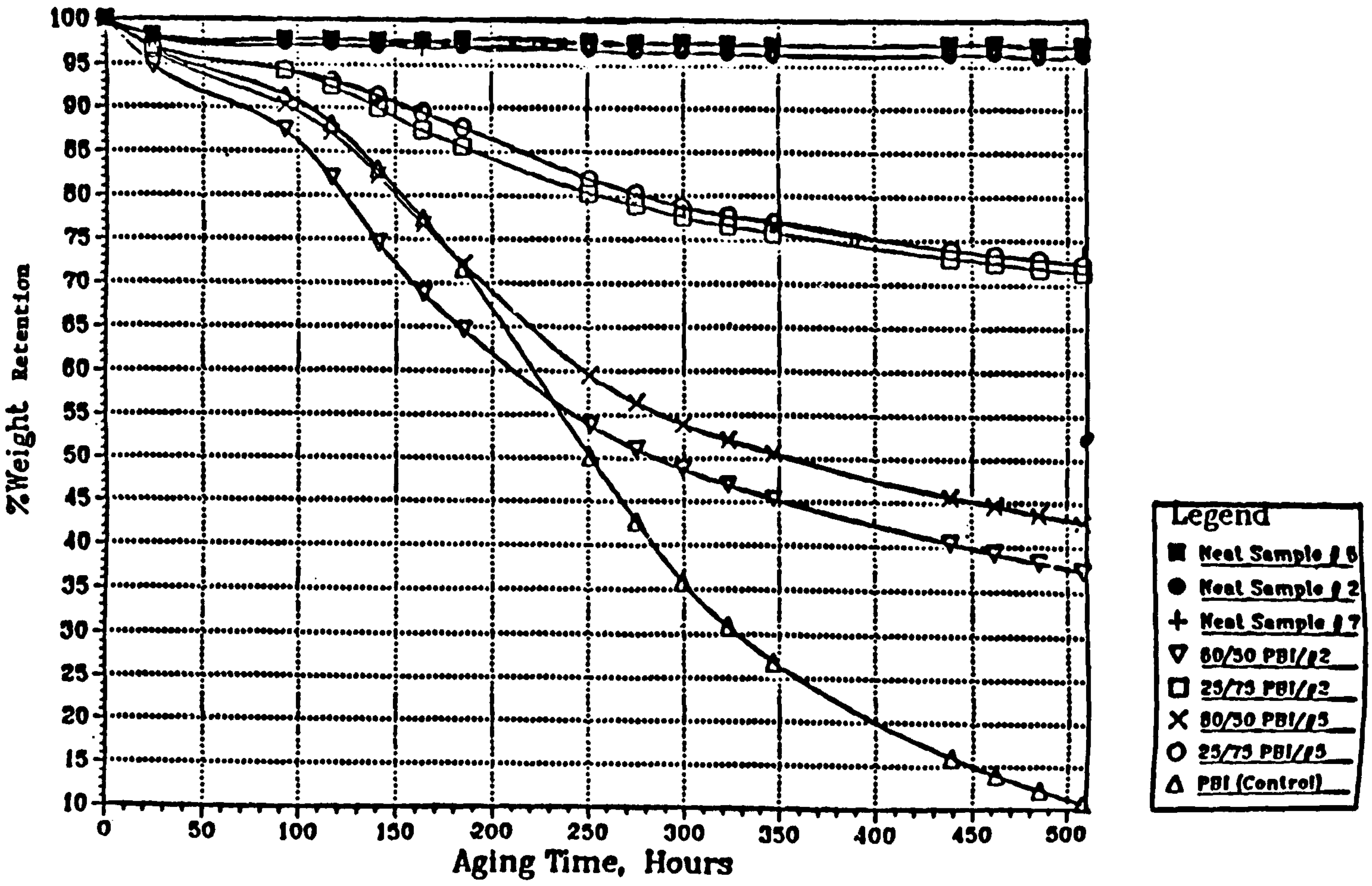


FIGURE 32

Thermo-Oxidative Stability of Neat 6F-PI Copolymer
Films and Their PBI Blends Aged in Air Oven at 600 F



The tensile properties and methylene chloride solvent resistance of compression molded, neat resin 6FcoPI and PBI/6FcoPI plaques are given in Table 9. The effect of blending with PBI to enhance tensile properties is clearly evident from this data. More importantly, the addition of PBI rendered the blends insoluble in methylene chloride despite phase separation upon molding.

6FcoPI-2 was chosen for additional scale-up and evaluation. Upon thermal treatment it appeared to have the largest processing window as judged by the Tgs of the phase separated products, was simpler to make (3 components versus 4 for coPI-5) and was slightly less expensive. Figure 33 gives the DSC trace of the phase separated 25/75 PBI/6FcoPI-2 blend and shows separation into PBI (Tg = 414°C) and 6FcoPI-2.

The 6FcoPI-2 copolymer was scaled up in several steps which included going from the 100 grams scale to ca. 1 kilogram and then to ca. 10 and finally 50 kilograms, respectively. Each of these polymers was evaluated for its neat resin thermal and mechanical properties, its blend properties with PBI and its matrix properties in carbon fiber composites. Except for the final polymer which was used by Lockheed for large composite part fabrication, the results of the interim 6FcoPI-2 evaluations were given in the Quarterly Reports. The properties of the final polymer are in Section 2.5, below. The composition of 6FcoPI-2 is 37.5 wt% 6FDA, 12.5% BTDA and 50% DADPS.

TABLE 9

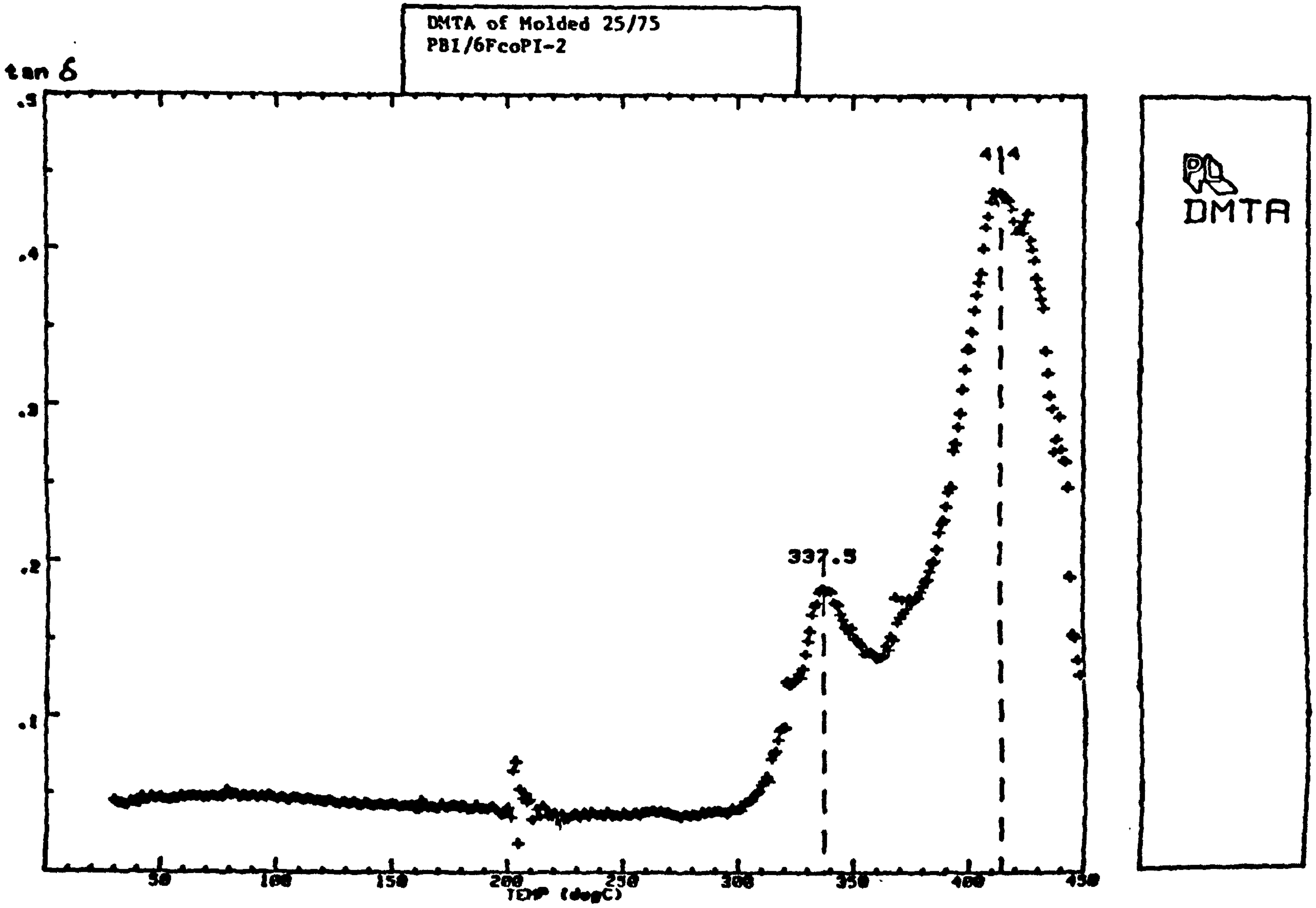
PROPERTIES OF COMPRESSION MOLDED 6F COPOLYMER POLYIMIDES AND BLENDS WITH PBI

SAMPLE	Tg (oC)	TENSILE PROPERTIES STRENGTH (KSI)	TENSILE PROPERTIES MODULUS (KSI)	TENSILE PROPERTIES ELONGATION (%)	SOLVENT SENSITIVITY IN CH_2CL_2
coPI-2	333	9.1	499	2.0	SWELL
coPI-5	321	12.5	450	3.6	SWELL
coPI-7	346	7.8	488	1.7	DISSOLVE
25/75 PBI/coPI-2	PS	14.5	583	3.3	INSOL.
50/50 PBI/coPI-2	PS	10.7	653	1.9	-
25/75 PBI/coPI-5	PS	16.1	549	3.9	INSOL.
50/50 PBI/coPI-5	PS	14.9	654	2.6	-

1. NEAT SAMPLES MOLDED AT CA. 375°C, 500-1000 PSI AND 10 MINUTES AT TEMP.
2. BLENDS MOLDED AT 410°C, 1000-3000 PSI AND 10-15 MINUTES AT TEMP.

PS - PHASE SEPARATION

FIGURE 33


DMTA of Molded 25/75
PBI/6FcoPI-2
tan δ
.5
.4
.3
.2
.1
50
100
150
200
250
300
350
400
450
TEMP (degC)
337.5
414
DMTA

Sections 2.3.2 through Section 2.4 of this report detail the development of the 6FcoPI-2 copolymer and its blend with PBI for use as a high temperature matrix resin throughout the scale-up period. This discussion highlights the technical issues which were resolved during this effort. As indicated, Section 2.5 discusses the development and evaluation of the polymer used for aerospace evaluations.

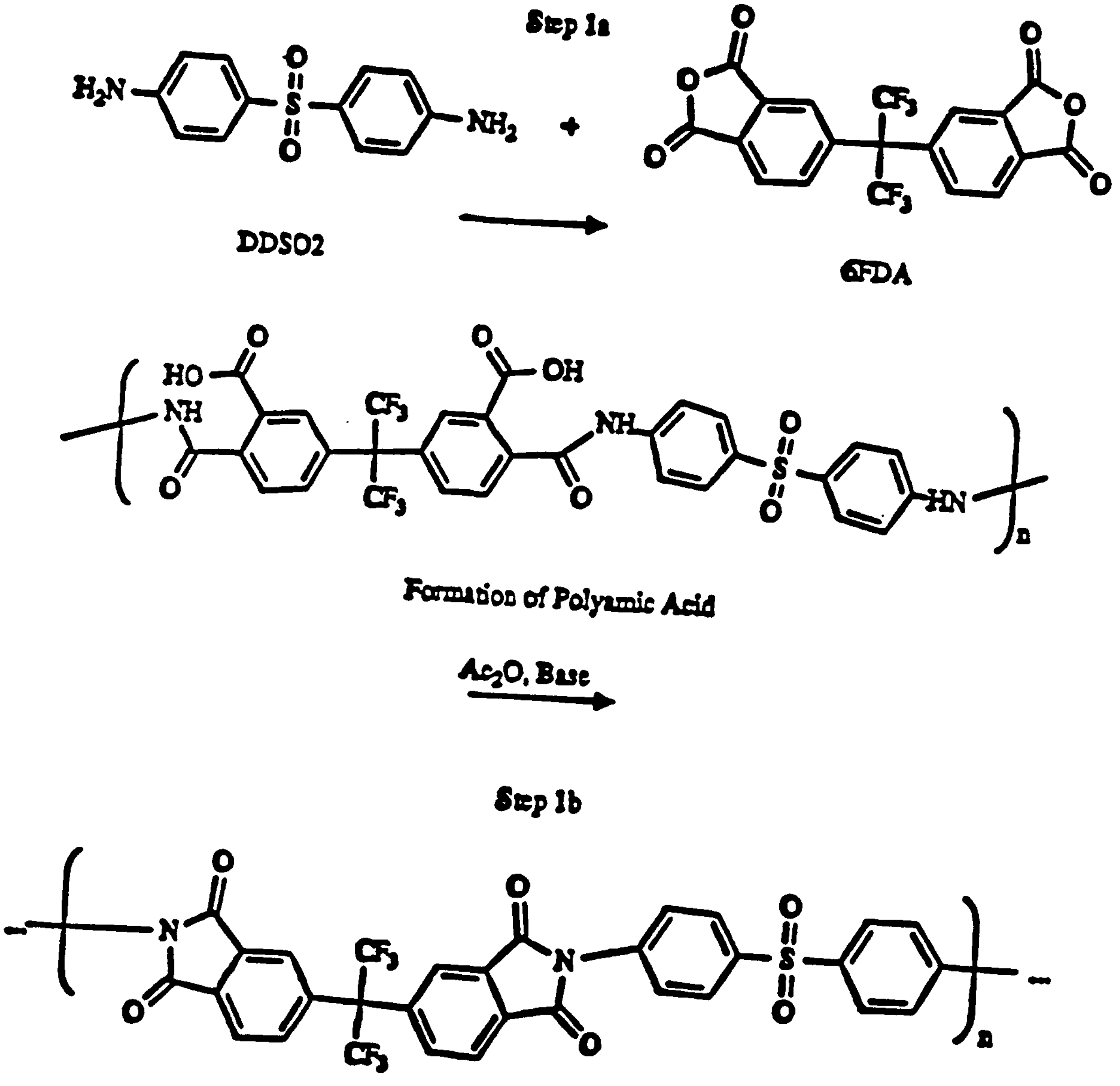
2.3.2 6FcoPI-2 Synthesis and Blending

The generalized synthesis scheme for 6FcoPI-2 is shown in Figure 34. A more complete description of this polymerization is given in Section 2.5, below, which describes the pilot plant synthesis of 100 pounds of polymer to facilitate large scale composite testing. Initial gram-scale polymerizations of this copolymer utilized beta-picoline at room temperature (1/2 beta-picoline and 4 acetic anhydride per imide group) for the imidization procedure. No isoimide was detected in this polymer.

Model compound studies subsequently showed that imidization with a strong base reduced or eliminated the potential for isoimide formation in these types of polymers. A synthesis of 6FcoPI-2 utilizing triethylamine as the strong base resulted in a polymer with an inherent viscosity of 0.45 dl/gm. However, precipitation and extensive washing (solvent removal) of the polymer in water reduced the IV to 0.15 dl/gm.

FIGURE 34

Preparation of Polyimides



Formation of Polyimide

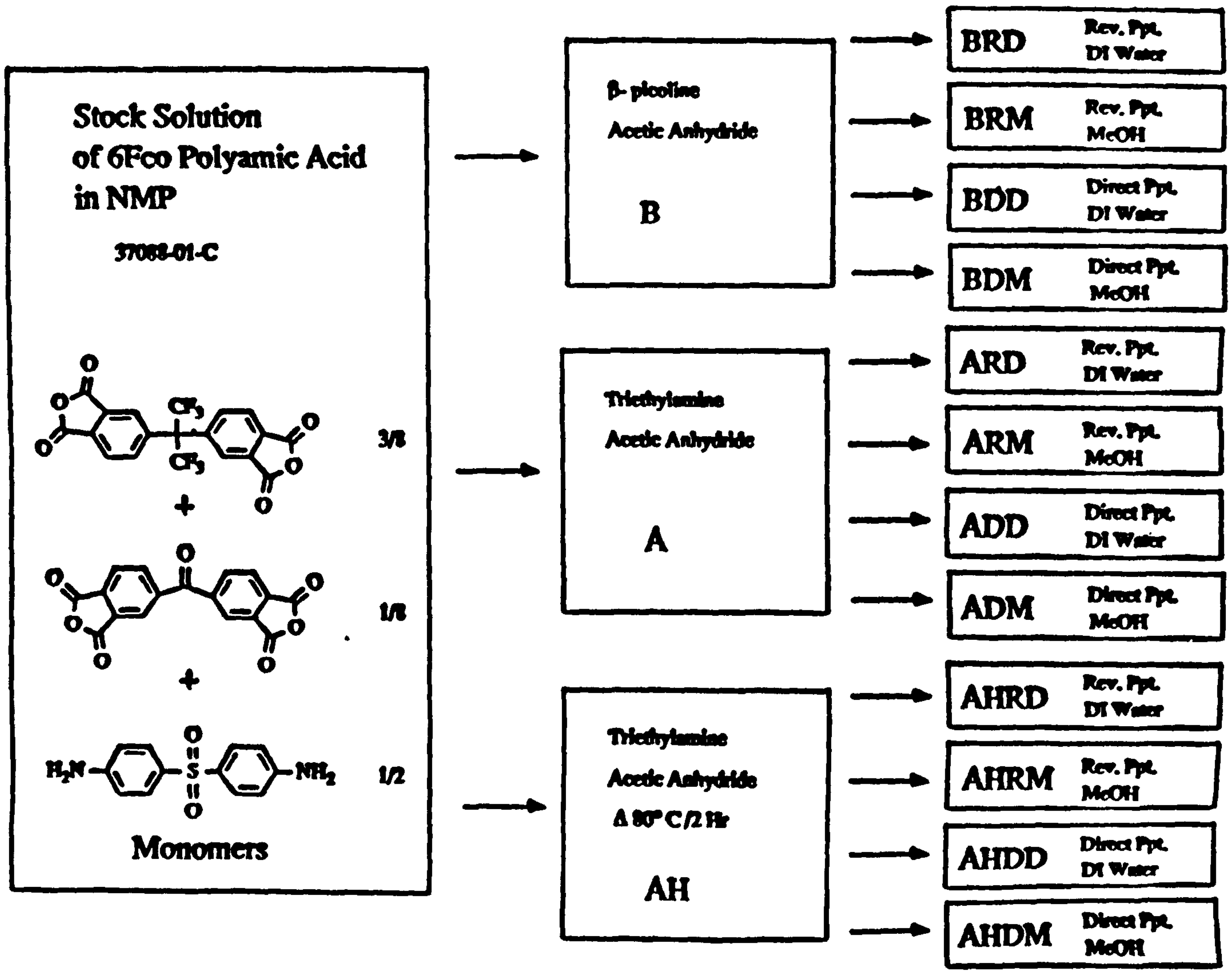
A systematic study was conducted to determine both the effects of triethylamine and beta-picoline on the imidization of 6FcoPI-2 and the effects of water versus methanol precipitation and washing on the resulting polymer molecular weight. A master batch of polyamic acid was prepared according to the generalized scheme of Figure 34 and divided into three portions. The first portion was imidized by the beta-picoline procedure and the remainder by triethylamine at room temperature (2.2 triethylamine and 1.1 acetic anhydride per imide group). One-half of this remainder was subsequently heated to 80°C (176°F) for 2 hours to insure completion of the reaction. The polymer dopes were precipitated in either water or methanol by either the direct (polymer into nonsolvent) or reverse (nonsolvent into polymer) precipitation method. Figure 35 shows the division of the amic acid and the subsequent processing and labeling of the 12 samples.

The 6FcoPI-2 dope made with beta picoline had a molecular weight (MW) of 55,000 (Sample B) while the material from triethylamine was slightly higher at 61,000 (Sample A). Heating of Sample A resulted in a 16% loss of molecular weight to 51,000 (Sample AH).

The polymers imidized with triethylamine and subsequently precipitated with either water or methanol retained only 1/6 to 1/3 of their initial molecular weight. The polymers imidized with beta-picoline and isolated with water lost about 1/2 of their initial MW while the polymer precipitated with methanol suffered little or no degradation. The latter thus became the preferred

FIGURE 35

SAMPLE PREPARATION FOR IMIDIZATION AND WASHING STUDY



method of polymer preparation.

Degradation of polymer molecular weight during isolation was shown to have occurred through ring opening and subsequent chain scission. This is illustrated in Figure 36. As shown, the imide structure was ring opened and then scissioned to form an amide and either carboxylic acid or methyl ester; or free amines and acids, respectively.

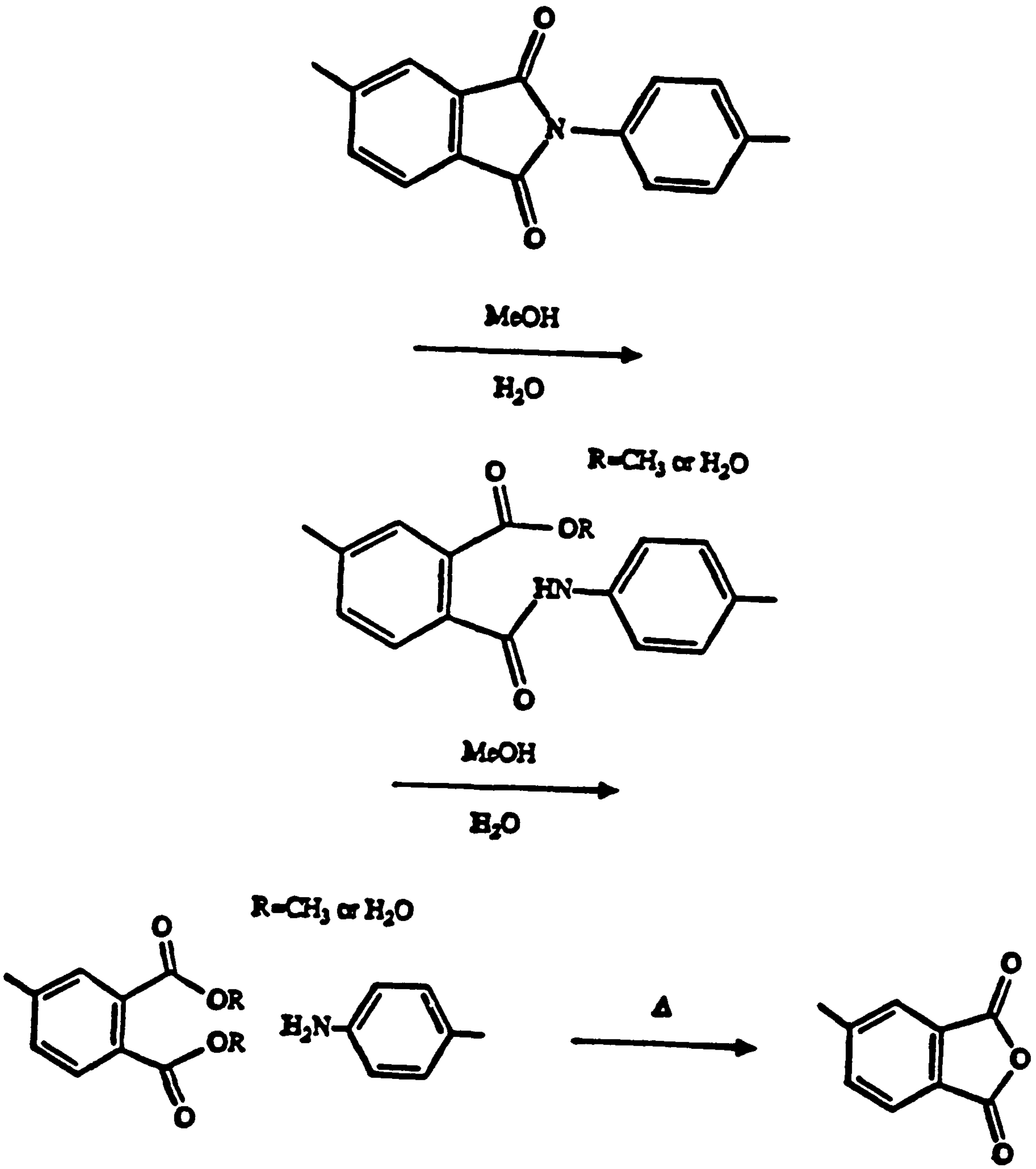
2.3.3 Improved PBI/6FcoPI-2 Blends

A series of ecPBI/6FcoPI-2 blends were prepared in order to optimize the blend ratio. Blends were prepared with ecPBI contents ranging from five weight percent to 30 wt% in increments of 5%. Prior efforts suggested making ecPBI the minor component to maximize thermo-oxidative stability. In each case, the blend Tg was maintained, according to the rule of mixtures for a miscible blend, above 333°C (631°F) i.e. the Tg of 6FcoPI-2.

Films cast from the six blends described above and from neat 6FcoPI-2 were immersed in methylene chloride or acetone, at room temperature, to determine their solvent resistance. The neat 6FcoPI-2 films disintegrated in both solvents without dissolving. All of the blend films, however, maintained their integrity with sharp (cut) edges. At twelve weeks, the 5/95 ecPBI/6FcoPI-2 film became weak and tore easily. Solvent testing on the remaining films was continued for approximately 1 1/2 years without notice-

FIGURE 36

ISOLATION PROBLEMS



able degradation of the samples. Thus the blending of a minor proportion of ecPBI with the 6F copolyimide was sufficient to render the latter stable in the organic solvents tested.

Figure 37 shows the results of isothermal aging at 316°C (600°F), in air, of the blend films and the PBI control. The thermo-oxidative stability of the neat 6FcoPI-2 was outstanding with >96% weight retention after 1000 hours. Two percent (2%) or one-half of this loss occurred in the first 40 hours due to loss of bound water or residual solvent. The stability of the ecPBI/6FcoPI-2 blends varied inversely with the PBI content.

2.3.4 10/90 ecPBI/6FcoPI-2 Blend Preparation

The blend of 10/90 ecPBI/6FcoPI-2 was chosen to be moved forward through the High Performance Polymer Blends Program. This blend combined good thermo-oxidative stability with solvent resistance and high glass transition temperature (343°C, 650°F).

The blends were prepared by solution blending the individual dopes (in DMAc) of each polymer. The effects of water and methanol during precipitation and washing on ring opening of the blend were investigated by FT-IR. A series of 10/90 dopes were precipitated and washed in methanol, water and/or hot water and then dried at 100°C (212°F) from two to 12 hours. This series of polymers is listed in Table 10. The 6FcoPI-2 was imidized with beta-picoline.

FIGURE 37

Thermo–Oxidative Stability of PBI and 6FCOPI–2
Blend Films Aged in Air Oven at 600 F

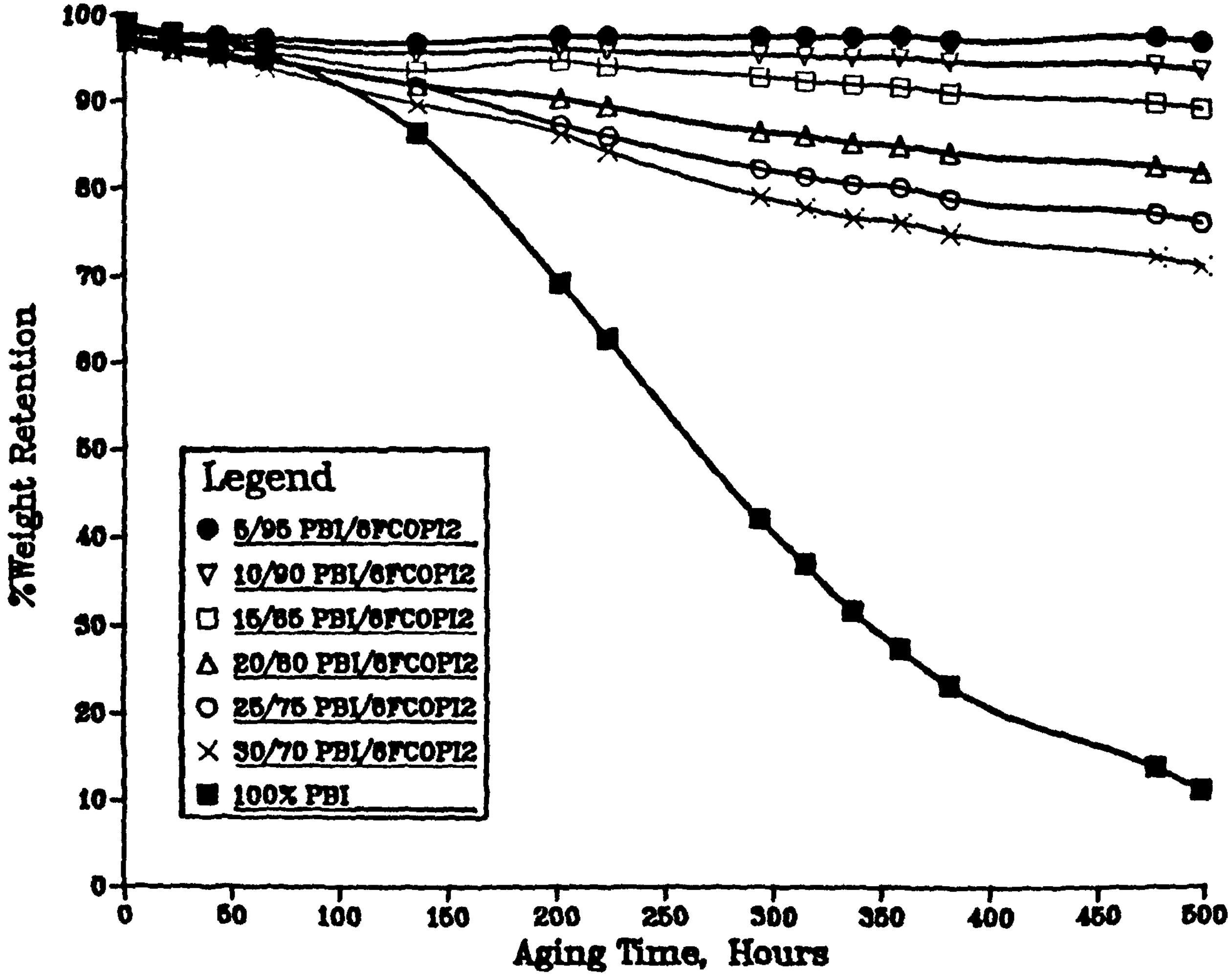


TABLE 10

RELATIVE RING OPENING AS A FUNCTION OF PRECIPITATION AND WASHING MEDIA IN 10/90 ECPBI/6FCOPI-2 POLYMER

SAMPLE	PRECIPITATION MEDIUM	WASHING MEDIUM	REL. RING OPENING A(1530)/A(1016)	DMAc (%)
10/90 Blend All Samples	Methanol	None	4.67	
	Methanol	Soxhlet MeOH	8.18	
*	Methanol	R.T. MeOH	9.54	<0.02
*	Methanol	MeOH, Dried 150°C Oven	5.64	
	Methanol	Boiling H_2O	3.70	0.46
	Methanol	Boiling MeOH	15.70	
	Water	None	0.95	
	Water	Soxhlet MeOH	2.21	
*	Water	R.T. MeOH	1.61	<0.02
	Water	Water, Dried 150°C Oven	2.16	
	Water	Boiling Water	1.70	
	Hot Water	None	0.93	

* Molded and fractured for morphology analyses. See below.

The relative amounts of ring opening as determined by FT-IR are also shown in Table 10 in terms of the ratio of the amide band at 1530 cm^{-1} to the invariant band representing the ring vibration of the para-substituted aromatics at 1016 cm^{-1}. On a statistical basis, PBI appeared to catalyze ring opening in the presence of water or methanol with methanol causing more extensive ring opening than water. Drying of the ring opened powders at temperatures below the normal imidization temperature caused ring closure (Sample 4 vs 3) with the evolution of methanol (or water).

2.3.4.1 10/90 ecPBI/6FcoPI-2 Neat Resin Molding Evaluations

For neat resin molding and property evaluations, the blend was precipitated and washed with methanol to form a molding powder. Initial sets of 10/90 ecPBI/6FcoPI-2 neat resin tensile, flexural and compression specimens were molded at HCRD for evaluations by Lockheed, GE and Hoechst Celanese. These sets consisted of 18 Type 1 tensile, 14 flexural and 18 compression samples, each. All specimens were matched-metal-die molded in a vacuum press at 375°C (707°F) and 1000 psi pressure with a 10 minute dwell at temperature. Individual specimens were cut and machined from four 8x8-inch tensile panels, one 8x8-inch flex panel and five 0.5x10 inch compression panels; and randomly assigned to the three laboratories.

Table 11 provides a summary of the mechanical property data obtained by Lockheed and HCRD. Good agreement exists between

Table 11

MOLDED 10/90 EC-PBI/CoPI-2 PROPERTIES

	HCRD DATA	LOCKHEED DATA		
	AMBIENT	AMBIENT	RTW (1)	HIGH-TEMP (2)
TENSILE STRENGTH (ksi)	12.0	11.7	3.0	1.2
TENSILE MODULUS (ksi)	544	629	444	168
ELONGATION	2.8	2.5	0.6	0.6
FLEXURAL STR. (ksi)	23.1	23.7	12.5	5.2
FLEXURAL MOD. (ksi)	571	564	579	261
COMPRESSIVE STR. (ksi)	28.4	26.9	(3)	(3)
COMPRESSIVE MOD. (ksi)	589	589	601	222

(1) Room Temperature Wet. Samples conditioned at 160oF and 95% RH for 14 days and tested at room temperature.
(2) Samples tested at 500 oF after 10 minute soak at temperature.
(3) Compressive strength taken at 10 percent strain. No values for hot-wet and high temperature testing calculated; stess-strain curves unavailable.

---

datasets obtained at ambient temperature. The Lockheed data shows a substantial loss in tensile strength of samples aged under room-temperature-wet (RTW) conditions, and a large loss in all mechanical properties for specimens tested at 260°C (500°F). Examination of these samples indicated that some specimens failed by brittle fracture. The RTW flex specimen failed by splitting and an examination of the fracture surface clearly showed void areas which could have been generated by gas evolution during molding (Figure 38). Catastrophic failure by swelling and blistering also occurred in the GE samples during an attempt to devolatilize the specimens by rapid heating to 287°C (549°F). Subsequent controlled experiments confirmed the development of voids during rapid heating most probably as the result of ring closure and the evolution of methanol (See Section 2.3.4 above). The results thus suggested the need for devolatilization to be incorporated into any composite molding cycle for the 10/90 blend.

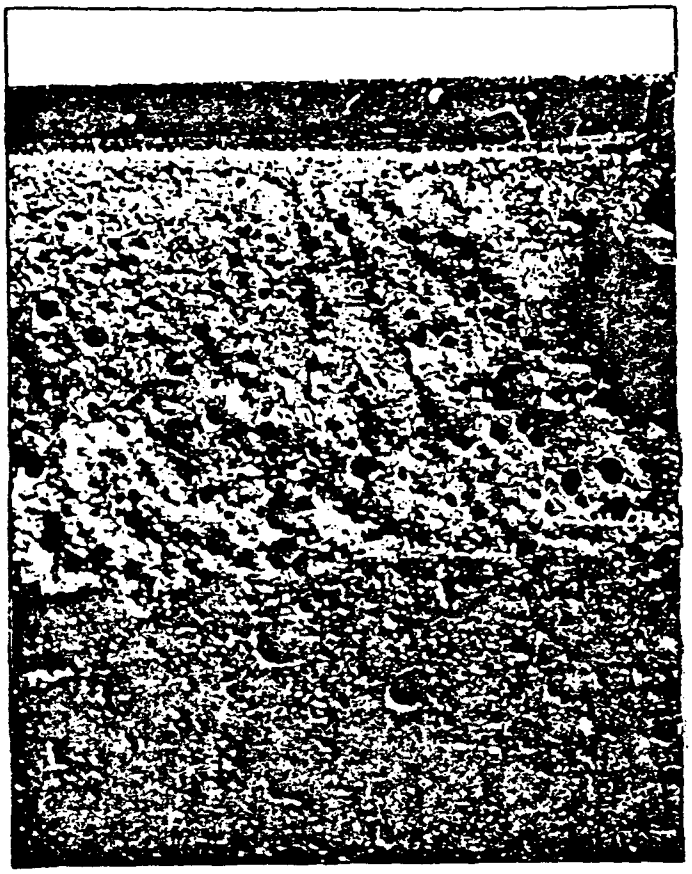
2.3.4.2 10/90 ecPBI/6FcoPI-2 Prepreg

Continuous prepregging of unsized, AS4, plain weave carbon fabric with 10/90 resin was successfully demonstrated at YLA, Corporation, Benicia, California. In all, a total of three prepregging operations were performed during the course of this development. In each, 24-inch AS4 fabric was fed vertically downward through a pair of nip rolls heated to ca. 60°C (140°F). A 10/90 resin solution in DMAC at 39-45 percent solids was fed into the nip on both sides of the fabric. Release paper coming over each roll sandwiched the wet prepreg and held it in place. The prepreg was then automatically rolled to remove entrapped air and wound onto a spool. The uniformly impregnated, undried prepregs were soft and tacky with good drape. Each of first two trials produced 50 linear feet (100 square feet) of material while the final trial resulted in 1350 linear feet of prepreg. The latter material was used by Lockheed for large part fabrication.

Twelve-inch wide unidirectional prepreg was fabricated on a second prepreg machine using a similar technique. Fifty four, 12000-filament spools of unsized AS4 carbon fiber were creeled to form a collated tow. This tow was then passed over a horizontal, heated

FIGURE 38

MAGNIFIED PORTION OF FAILED FLEX SPECIMEN



TYPICAL AREA 10X

nip roll at ca. 70°C (158°F) with resin applied to one side only. The prepreg was sandwiched between release paper, rolled and wound onto a spool. Although uniform wetting was not achieved, the unitapes had sufficient film strength for ease of handling and good tack and drape. Four hundred fifty linear feet of unidirectional prepreg were produced for aerospace evaluation during the third and final prepregging operation.

2.3.4.3 Composite Fabrication

Material from the second trial was divided between Lockheed and Hoechst Celanese and used to prototype composite fabrication techniques and to develop initial datasets. The prepreg was partially dried as single sheets in a vacuum press for 1 minute at 160°C (320°F). Eleven plies of prepreg were then molded in a matched-metal die using a 30 minute degassing cycle at 190°C (374°F) followed by 30 minutes at 500 psi and 380°C (716°F). Rapid cooling was employed at an average rate of 25°C/minute over the first 10 minutes.

Unidirectional flexural and tensile bars were also matched-metal die molded at 380°C (716°F). Pressure was applied for 10 minutes at either 200 or 500 psi. The prepreg was loaded into the mold without predrying and brought directly to temperature without a degassing cycle.

Microscopic examination of the fabric composites revealed the presence of microcracks in the resin rich areas. Similar results were also obtained by Lockheed from their laminate processing (Figure 39). In response, a two-pronged program was initiated to resolve the microcracking problem. This effort consisted of: 1) the synthesis and re-evaluation of 6FcoPI resin variants with particular emphasis on 6FcoPI-5, and 2) optimization of the composite molding cycle. The re-evaluation of the 6FcoPI variants is discussed in Appendix 1.

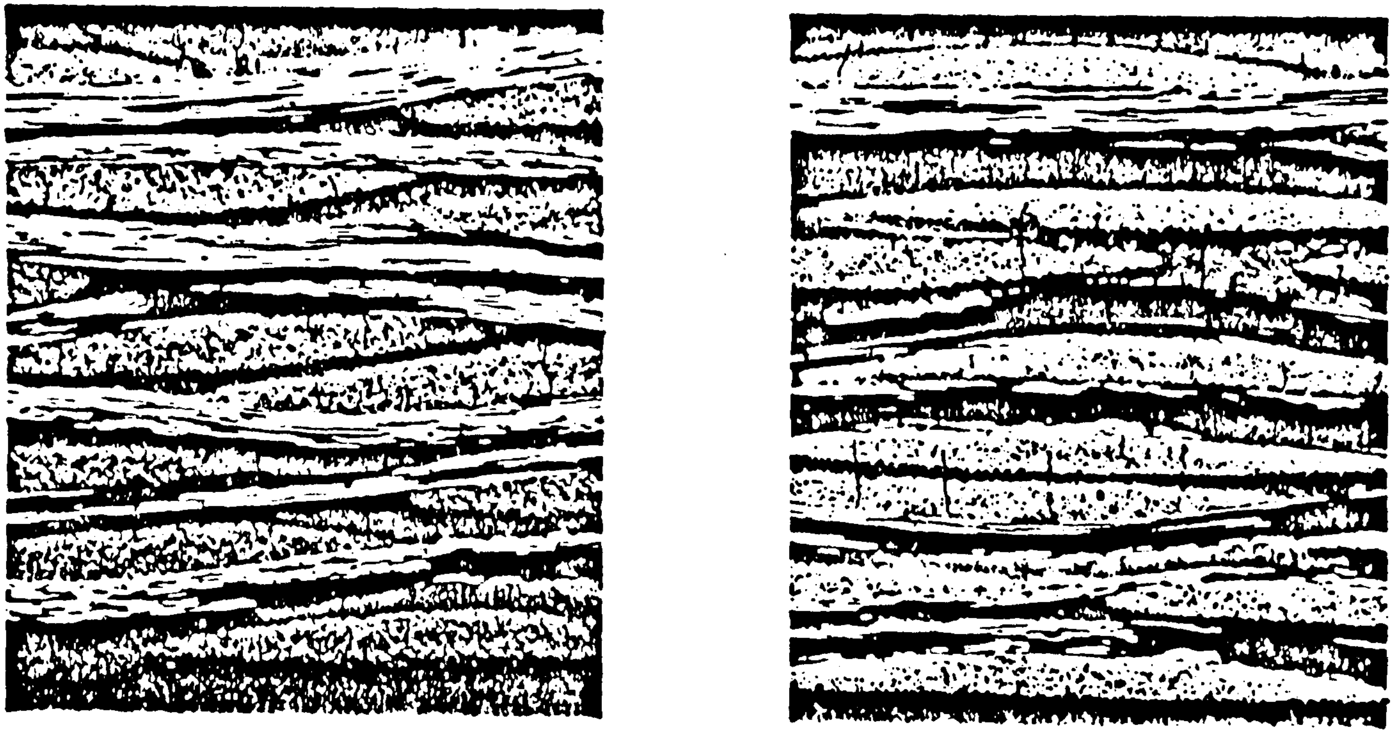
A priori, it was assumed that the microcracks originated from thermal stresses induced by rapid cooling of the mold. This assumption was subsequently confirmed when no microcracks were found in a 12-ply, 10/90 ecPBI/6FcoPI2 - AS4 fabric panel molded and allowed to cool naturally overnight at the molding pressure.

The molding cycle shown in Figure 40 was ultimately developed for use in this program at HCRD. As shown it employed a ramped heat-up to the molding temperature, a 15 minute hold at this temperature and 500 psi, and a slow cooling to below Tg at ca. 3°C/minute. Table 12 gives the average laminate properties from fabric prepreg for panels molded with this "long/slow cool" cycle. Also given for comparison are the properties of a panel fabricated using the same molding cycle but with rapid (21°C) cooling of the mold. The slow cooling permitted thermal accommodation within the panel such that no microcracks were formed.

2.4 Improved 6FcoPI-2 Polymer

FIGURE 39

PI/PBI POLYMER BLEND FABRIC LAMINATE
PREDRIED 18 MINUTES



50 x

50 x

FIGURE 40

HIGH PERFORMANCE POLYMER BLENDS

COMPOSITE MOLDING CYCLE

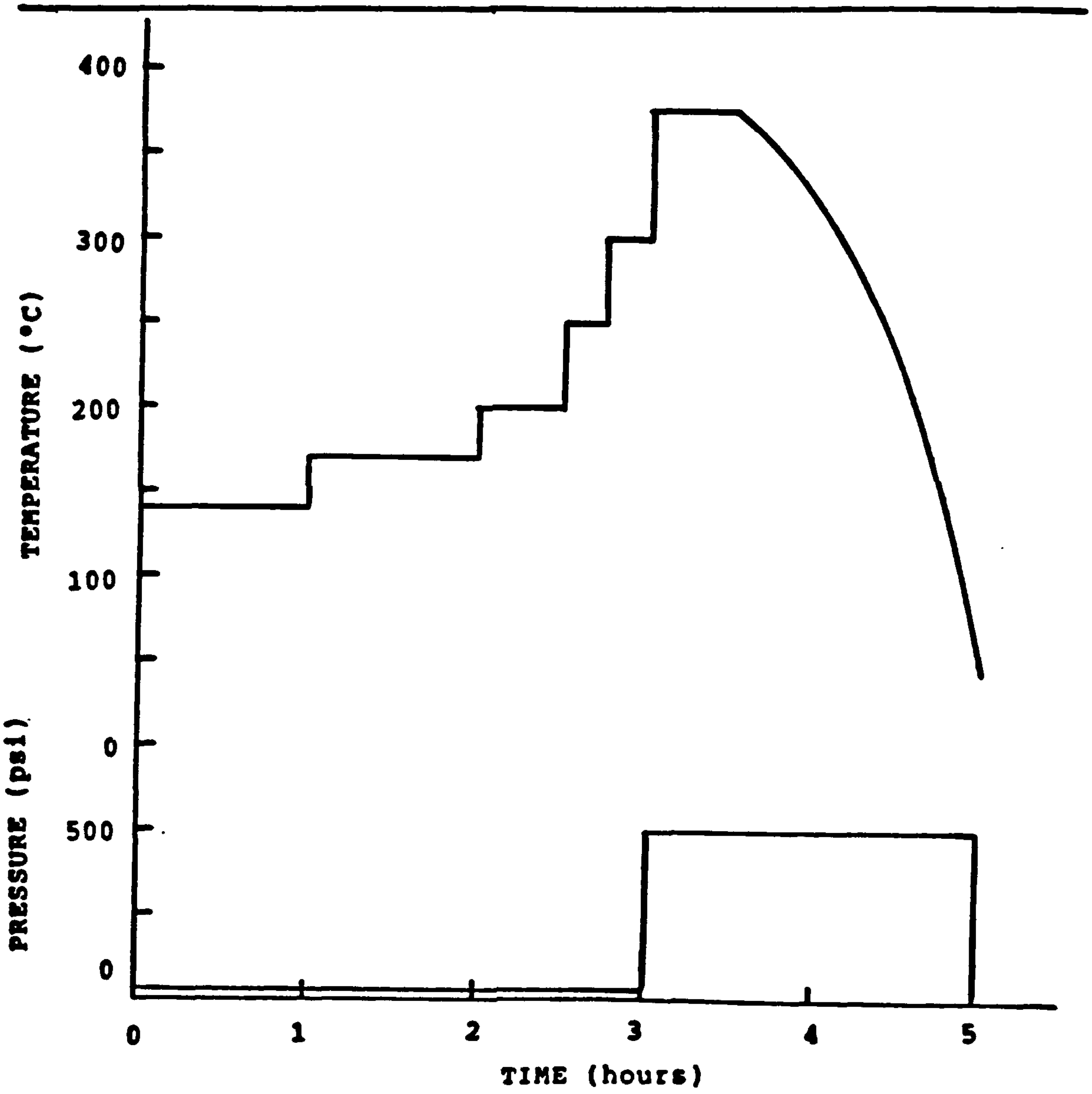


Table 12

Laminate Properties from Molding Optimization Trials

Cycle/Properties	Target Spec.	Long Cycle	Long/Slow Cool Cycle
Carbon Fiber Loading (%)	61±4	53.7	54.8
Density (gm/cc)	>1.540	1.5419	1.5465
Void Volume (%)	<3.0	4.3	4.4
Shear Str. psi	>6000	6680	6910
(KPa)	(>41.4)	(46.4)	(47.7)
Flex Str. (Ksi)	>75.0	64.9	82.5
(MPa)	(>518)	(448)	(569)
Flex Mod. msi	>8.0	5.5	6.5
(GPa)	(>55.2)	(38.0)	(44.9)
Matrix		Micro Cracked	No Microcracks

Differential scanning calorimetry (DSC) was used to evaluate the thermal stability of 6FcoPI-2 polymer. A powder sample of the copolymer was exposed to four cycles of heating. In each, the sample was heated from 100°C (212°F) to 450°C (842°F) at 20°C/minute and held isothermally before cooling. The isothermal hold times were 5, 10, 15 and 0 minutes for the four cycles, respectively. Thus the total accumulated residence time at maximum temperature was 30 minutes. The data indicated that Tg of the neat resin increased with time-at-temperature from a minimum of 332°C (630°F) to 362°C (684°F). This increase was attributed to insitu polymerization.

To prevent increases in molecular weight during composite molding which inhibit resin flow, 6FcoPI-2 was synthesized with a phthalic anhydride end-cap. Calculated molecular weights for these polymers were 25,000 and 50,000, respectively. The results (Table 13) indicated, however, that only a small suppression of the increase in Tg was obtained.

The effect of end-capping on the mechanical properties of the polymer were also investigated. These results are shown in Table 14. At the higher molecular weight, the resin properties are comparable to those without an end-cap. Thus it was concluded that end-capping did not adversely effect the polymer and that future syntheses of this resin would include the end-cap.

2.5 Final Polymer Scale-Up and Evaluation

TABLE 13

GLASS TRANSITION TEMPERATURE OF END-CAPPED 6FCOPI-2 VARIANTS AS A FUNCTION OF TEMPERATURE

TIME AT 450°C	0.5 IV CONTROL	HCRD 25K	HCRD 50K
0	332	335	329
5 MIN	345	335	340
15 MIN	354	341	347
30 MIN	362	347	354
Δ Tg (30 MIN-5 MIN)	17	12	14

TABLE 14

MECHANICAL PROPERTIES OF LABORATORY SCALE END-CAPPED 6FCOPI-2 POLYMERS

	50K MW ec6FCOPI-2
TENSILE STR. (ksi) (MPa)	10.6 (75.2)
TENSILE MOD. (ksi) (MPa)	481 (3319)
ELONGATION (%)	2.7
FLEXURAL STR. (ksi) (MPa)	19.5 (134.5)
FLEXURAL MOD. (ksi) (MPa)	519 (3581)
COMPRESSIVE STR. (ksi) (MPa)	27.5 (189.8)
COMPRESSIVE MOD. (ksi) (MPa)	548 (3781)
FRACTURE TOUGHNESS (psi-in$^{1/2}$)	922

One hundred pounds of phthalic anhydride end-capped 6F copolymer polyimide #2 (ec6FcoPI-2) were synthesized in the Hoechst Celanese Coventry Rhode Island Pilot Plant under the direction of the Hoechst Celanese Research Division (HCRD). This polymer was used to facilitate large composite part fabrication and evaluation by Lockheed (see Volume 2 of this final report). These composites were fabricated from AS-4 carbon fiber impregnated with a 10/90 blend (by weight) of end-capped PBI and end-capped 6F copolymer polyimide #2 (10/90 ecPBI/ec6FcoPI2) matrix resin.

2.5.1 Polyimide Synthesis

Polymerization of the ec6FcoPI-2 polymer was targeted for 75 gram-moles (103 pounds) with a polymer molecular weight of 50,000. Expected inherent viscosity of the polymer was 0.4 dl/gm. Before use, the 6FDA was dried at 200°C and the sulfone at 100°C over P_2O_5. The BTDA was slurred with tetrahydrofuran on a frit to dissolve less polar impurities and then dried at 150°C. The BTDA was then crushed and further dehydrated at 200°C.

Synthesis of the ec6FcoPI-2 was done in a 100 gallon, glass lined vessel at 30% solids. The amine was added to the reactor at the beginning of the reaction. The mixed dianhydrides were then incrementally added as a powder with each aliquot being allowed to dissolve before the next addition. The reaction temperature was maintained at ca. 20°C (68°F). The polyamic acid was stirred for 9 hours and allowed to reach equilibrium before the addition of the phthalic anhydride. The latter was added (with a slight excess) as a 2% solution in NMP, the common reaction solvent. Sufficient additional solvent was also added, at this time, to reduce the solids content of the reactants to 25% to improve both stirring and heat transfer from the batch. Immidization was initiated 24 hours after addition of the phthalic anhydride by adding beta picoline, mixing, and then slowly adding acetic anhydride to prevent local precipitation. Imidization of the amic acid proceeded with little exotherm. Final solids content of the batch was 17.5%.

Precipitation was done by slowly discharging small quantities of the 6F copolymer directly into methanol while using an air driven propeller to stir the mixture. Precipitation was completed in two hours. The slurry was then pumped into a 500 gallon glass lined vessel for subsequent washing in methanol. After three hours in the wash vessel the methanol was decanted with vacuum, after which, 2.5 drums (110 gallons) of fresh methanol were added and allowed to stir overnight. A total of four such washings were completed before filtering and vacuum drying. The polymer cake weighed 342 pounds (155.5 kg). The polymer was subsequently air dried to remove the bulk of the remaining solvent and then further dried at 150°C to yield 103 pounds (46.8 kg) of polymer in the form of a fine powder.

2.5.2 Neat Resin ec6FcoPI-2 and PBI Blend Polymer Characterizations

Characterizations of the neat ec6FcoPI-2 and its 10/90 blend with ecPBI (i.e. 10/90 ecPBI/ec6FcoPI-2) included: solution viscosity, glass transition temperature, inherent viscosity/molecular weight and mechanical properties from molded plaques.

Solution viscosities of the polymers, in dimethylacetamide, were measured over a range of solids contents from ca. 33% to 50%. These results indicated that a 45% solids dope of the 10/90 blend was readily amenable to prepregging with viscosities ranging from 1340 poise at 30°C to 50 poise at 90°C (Table 15).

Table 16 gives the DSC results for the glass transition temperatures (Tg) of the ec6FcoPI-2 and 10/90 blend polymers. As was done in previous testing, each powder sample was exposed to four cycles of heating from 100°C to 450°C at 20°C/minute. Each sample was held isothermally for 5, 10 and 15 minutes, respectively, such that the accumulated hold time at maximum temperature was 30 minutes. As before, the data showed an increasing Tg with time at temperature despite the end-capping of both the 6F and PBI polymers.

The inherent viscosity of the ec6FPBI-2 was 0.26 dl/gm with a corresponding molecular weight of 20,000. Proton Nuclear Magnetic Resonance (NMR) showed the polymer to be high in amine and anhydride end groups as well as methyl ester. A result consistent

Table 15

Dope Viscosity (poise)

Lab Screening Trials

ec6FCoPI-2

	Temperature°C		
Solids (%-DMAc)	30	60	90
35	10	4	2
40	42	12	5
45	215	42	16
50	1510	185	52

ecPBI/ec6FcoPI-2

	Temperature°C				18 Hour Heating	
Solids (%-DMAc)	30	60	90	110	90	110
33.6	20	7	5			
37.7	66	18	7			
41.6	224	48	18		36	
45.4	1020	158	42	30	87	35

Production Batch

45.4	1340	190	50		100	

Table 16

Change in Glass Transition Temperature
with Thermal Aging

Time @450^{o}C (min)	ec6FcoPI-2	ecPBI/ec6FcoPI-2
0		
5	347	347
15	356	357
30	361	363
ΔTg	14	16

with low IV. Compression molding of the neat resin, however, produced strong, tough plaques; and Gel Permeation Chromatography (GPC) and NMR confirmed an increase in IV to 0.40 dl/gm, an increase in molecular weight to 35,000 and an order of magnitude reduction in end groups and methyl ester content (Table 17). Thus it was hypothesized that the polymer underwent chain extension with the evolution of acetic acid or methanol etc. during the molding process.

Molding of the neat ec6FcoPI-2 and the neat 10/90 resins was done in a two-step cycle which permitted venting of the evolved gases. In both cases, the polymer was heated in an open mold and held at the molding temperature for 10 minutes before pressure was applied to consolidate the sample. The mechanical properties of these

TABLE 17

END GROUP ANALYSIS OF ec6FcoPI-2

Sample	Acetamide	Methyl Esters	Free Amine	Amide	NMP
Initial	106	405	20	270	2.6
Molded	60	49	24	24	nd

NMP is reported in weight %, whereas the other groups are reported in µeq/g.

polymers are shown in Table 18.

Thermo-oxidative stability studies were also done on the 10/90 resin. ASTM "mini" tensile bars were aged for up to 500 hours at 500 (260) and 600°F (260, 315°C). Weight loss and mechanical properties the as-molded and aged samples are listed in Table 19. As shown, the resin retained 95-98 percent of its weight and 75-88 percent of its tensile strength.

2.5.3 Composite Evaluations

Composite evaluations with prepreg from the third YLA prepregging trial were conducted at HCRD. The composites were matched-metal die molded from both the fabric and unidirectional prepreg with the long/slow cool cycle shown in Figure 40. All samples were made at 500 psi pressure. The mechanical and physical properties of these laminates are shown in Table 20. (GE target specifications for air craft engines from PMR-15 composites are shown in Table 12 for comparison).

3.0 Program Summary Conclusions and Recommendations

3.1 Summary

Three generations of PBI and polyimide blends have been evaluated for use as high temperature matrix resins for carbon fiber composites in aerospace applications. Miscible PBI/polyetherimide

TABLE 18

PHYSICAL PROPERTIES OF MOLDED RESINS

Description	EC-CoPI-2 Aug YLA
Tensile str., ksi	14.6
Tensile mod. ksi	445
Elongation, %	5.9
Work-to-break, in-lb	3.9
Sample Size	7
Flex strength, ksi	21.7
Flex modulus, ksi	543
Sample size	5
Compressive str. ksi	26.7
Compressive mod., ksi	554
Sample size	8

Description	10/90 EC-PBI/ EC-CoPI-2 Aug YLA
Tensile str., ksi	14.4
Tensile mod. ksi	507
Elongation, %	4.1
Work-to-break, in-lb	2.4
Sample Size	6
Flex strength, ksi	22.3
Flex modulus, ksi	574
Sample size	5
Compressive str. ksi	27.8
Compressive mod., ksi	550
Sample size	9

TABLE 19

THERMO-OXIDATIVE STABILITY OF 10/90 EC-PBI/EC-6FCoPI-2

	Sample Size	---- Tensile Properties ----		
		Strength (ksi)	Modulus (ksi)	Elong (%)
TOS @ 260 °C (500 °F)				
0 hours	8	15.3	500	4.5
504 hours	8	13.5	494	3.5
TOS @ 315 °C (600 °F)				
0 hours	8	14.8	495	4.4
504 hours	4	11.1	494	2.6

	-- Time at Temperature (hrs) --			
Weight Retention (%)	0	168	336	504
260 °C (500 °F)	100	98.9	98.7	98.6
315 °C (600 °F)	100	97.6	96.4	95.4

TABLE 20

PHYSICAL PROPERTIES OF MOLDED CARBON FIBER/BLEND COMPOSITES

	10/90 EC-PBI/EC-6FCoPI-2 on Hercules AS-4 CF	
	Fabric	Uni-tape
Tensile str., ksi	92.5	189
Tensile mod. msi	9.6	18.1
Elongation, %	1.1	1.0
Sample Size	5	6
Density, g/cc	1.56	1.59
Void fraction, %v	3.8	2.3
Fiber loading, %v	51	59
Flex strength, ksi	78.6	147
Flex modulus, msi	6.4	13.4
Sample size	6	3
Short-beam shear, psi	6500	11240
Sample size	8	6
Density, g/cc	1.56	1.54
Void fraction, %v	3.8	4.7
Fiber loading, %v	51	56
Compressive str. ksi	60.5	154
Compressive mod., msi	15.6	14.8
Sample size	5	5

(Ultem) blends were shown to be potentially feasible for such applications to 500°F (260°C). In particular, the blend of 85/15PBI/Ultem was shown to be thermally and thermo-oxidatively stable with useful mechanical and physical properties to this temperature. To enable property testing, a neat resin molding cycle was developed to produce plaques with less than 2% void volume. Phthalic anhydride end-capping of the PBI was shown to significantly reduce crosslinking as measured by the change in Tg after high temperature exposure. This reduction in end-group chemistry provided for maximum thermoplasticity of the blend during molding.

As indicated above, PBI/polyetherimide blends required that PBI be the major component to maintain a high glass transition temperature and a correspondingly high service temperature. Above 500°F, however, such blends were subject to synergistic degradation most probably catalyzed by PBI degradation products attacking the ether linkage of the polyimide. Thermo-oxidative stability studies indicated that at 600°F (316°C) and above, the weight loss of the blend was approximately proportional to its PBI content. Attempts to mitigate this effect by incorporating the hexafluoroisopropylidiene (6F) moiety into the PBI backbone or by substitution of the imidazole hydrogen by a phenyl group to produce N-phenyl PBI were unsuccessful. Phosphoric acid treatment of 85/15 molded blend samples was shown to provide a four-fold increase in weight retention in TOS testing at 600°F. However since this effect was due to a surface oxidation barrier of only 1-10 microns in thickness, it was not considered to be feasible for further investigation within this program.

A series of nine copolymer polyimides containing the hexafluoroisopropylidiene moiety (6F) were synthesized and evaluated as neat resins and in blends with PBI. From these, the copolyimide, 6FcoPI-2, containing 37.5 wt% 6FDA, 12.5% BTDA and 50% DADPS was selected for scale-up and extensive composite evaluations in PBI blends.

To improve the thermo-oxidative stability of the PBI/polyimide blends at temperatures in excess of 600°F, 6FcoPI-2 was evaluated as the major component of the blend. Initially 50/50 and 25/75 ecPBI/6FcoPI-2 were evaluated. TOS results again indicated that weight loss at high temperatures was approximately equal to the PBI content of the blend. Additional tests did show, however, that the PBI insolubilized the 6FcoPI-2 to the common organic solvents of methylene chloride and acetone. Further results showed that the blend: 10/90 ecPBI/6FcoPI-2 was insoluble in these same solvents. The glass transition temperature of this latter blend was 353°C (667°F). This blend of 10/90 ecPBI/6FcoPI-2 was chosen to be moved forward through this program for aerospace evaluations.

Optimization of the polyimide synthesis included end-capping of the 6FcoPI-2 polymer and imidization with a strong base. In the former, phthalic anhydride end-capping was shown to have only a small effect on end-group chemistry during high temperature exposure such as in neat resin or composite molding. However, the end-cap did not appear to effect resin properties and was incorporated into the final polymer synthesis. Imidization with the strong base, however, led to the discovery of substantial ring opening and chain scission during polymer precipitation or washing with water. Some ring opening was also observed in polymer imidized with beta-picoline and precipitated and washed in methanol. However, ring closure was found to occur during neat resin molding with the evolution of methanol.

The 6FcoPI-2 and subsequently the end-capped polymer were scaled-up in steps from gram quantities to 50 kilograms. With each step, the neat resin and its 10/90 blend with ecPBI were fully characterized for thermal stability, thermo-oxidative stability, physical and mechanical properties. To facilitate these measurements a two step matched-metal-die molding cycle was developed. The first step in this cycle provided for venting of the evolved gases at the molding temperature prior to the application of pressure.

Prepregging of the neat resin onto plain weave AS-4 carbon fabric and onto AS-4 unidirectional tape was successfully demonstrated by YLA, Incorporated, Benicia, California. Three prepregging trials produced a total of 1450 linear feet (442 meters) of fabric and over 450 feet (137 meters) of unidirectional prepregs.

Composite laminate fabrication was demonstrated by both Lockheed (See Volume 2 of this report) and Hoechst Celanese. Initial laminates from fabric prepreg contained microcracks in resin rich areas due to residual stresses. An optimized molding cycle was demonstrated by HCRD which included a ramped heat-up to the molding temperature and a long slow cooling of the mold at less that 3°F/minute which prevented microcracking. Composite properties were demonstrated which either approached or exceeded GE Aircraft Engines specifications for PMR-15 composites.

During the course of this development 6FcoPI-5 was prepared with tensile properties nearly equivalent to those of 6FcoPI-2 but with significantly higher fracture toughness (see Appendix A). Remaining program resources, however, prevented the scale-up of this copolyimide to the kilogram level and beyond.

3.2 Conclusions

The High Performance Polymer Blend Program has demonstrated that an integrated, multisector, multidisciplinary team can translate new science into an aerospace part demonstration within three years. This is obviously not equivalent to either the definition of a manufacturing process nor the qualification of a part. These results do represent an in-depth and relevant evaluation of PBI/PI blends as high performance matrix materials for aerospace use in a highly efficient manner, taking about one-half the time historically associated with such evaluations. Over the course of the program more than 13 neat polyimide resins (nine developed specifically for blend matrix use) were screened for thermomechanical and thermo-oxidative performance both neat and in blends with PBI. Of these, two candidates were chosen for scale-up to the several kilogram range and evaluated as both neat resin and carbon reinforced test specimens from room temperature to 700°F for up to 1000 hours. One material, the 10/90 blend of end-capped PBI with end-capped 6FcoPI2 was scaled to 50 kilograms and ultimately used by Lockheed to produce a demonstration part (TR-1 avionics access door with three 1-inch hat sections, See Volume 2). Specific conclusions from this program are:

- 85/15 end-capped PBI/Ultem blend is a viable 500°F matrix candidate.
- 10/90 end-capped PBI/6FcoPI2 blend is a viable 600°F matrix candidate.
- All PBI/PI systems exhibit miscibility which:
  - exhibit improved processibility over neat PBI
  - are thermoformable
  - have improved mechanical performance, especially in compression
  - have improved solvent resistance (as compared to thermoplastic PI)
- Miscibility is metastable however phase separation does not appear to be detrimental
- PBI/PI blends exhibit negative thermo-oxidative synergy which is mitigated by choice of a high TOS polyimide.

  - 6FcoPI2 shows ca. 5% weight loss after 1000 hours at 600°F
  - degradation reactions are exacerbated by miscibility (similar to homogeneous reaction)
  - phosphoric acid surface treatment improves stability by four fold

- PBI/PI blends can be solution prepregged onto carbon fabric and tow and then thermally formed into parts

- 6FcoPI2 resin can be synthesized in large quantities suitable for meaningful aerospace part fabrication and evaluation

3.3 Recommendations

The High Performance Blend Program had a series of integrated, yet diverse objectives. These might usefully be categorized under the headings of Research, Development, Fabrication and Organization. Recommendations will be made for each.

3.3.1 Research

Blending, as a means for tailoring the performance of polymer matrices is a viable approach and should be continued. The problems associated with the optimization of new polymer backbones (i.e., imide copolymers) should be pursued, recognizing the importance of technical performance and business attractiveness.

The blending criteria developed within this PBI/PI program should be extended to blends of other aromatic, heterocyclic polymers with long term oxidative stability superior to that of PBI.

3.3.2 Development

The design of polyimides for long term, high temperature thermo-oxidatively stable matrix applications should be pursued, with emphasis on para linkages and the fluorinated isopropylidene moiety. The difficulties of predicting polymer matrix processibility and performance based upon laboratory testing of small, glassware produced samples must be addressed.

3.3.3 Fabrication

Future programs aimed at composite applications should continue to specify that it is fabricated part cost/performance rather than material properties that define material utility.

3.3.4 Organization

The integrated team composed of industrial, university and government scientists has proven an effective and efficient approach to the rapid translation of science into useful technology and should become the paradigm for the organization of large, highly focused materials development programs.

Appendix 1. **Synthesis and Re-evaluation of 6F Copolymer Polyimide Resin Variants**

A1.0 Re-Evaluation of Resin Variants

A two-pronged program was initiated to resolve the problem of microcracking which occurred in resin rich areas of carbon fiber composites fabricated from prepreg with 10/90 ecPBI/6FcoPI-2 matrix resin. This effort consisted of: 1) the synthesis and re-evaluation of 6FcoPI resin variants with particular emphasis on 6FcoPI-5, and 2) optimization of the composite molding cycle. (See Section 2.3.4.3).

A1.1 Synthesis and Evaluation of Copolymer Polyimide Resin Variants

Figure 28 shows the original copolymer polyimide resin matrix which was investigated early in this program. From these original investigations, resin #2 or 6FcoPI-2 was selected for scale-up to the tens of pounds for prepreg and composite evaluations. Polyimide #5 was judged to be equivalent to 6FcoPI-2 but was bypassed because it did not demonstrate a clear advantage while containing a fourth monomer.

A1.1.1 6FcoPI-5 and End-Capped 6FcoPI-5

A new batch of copolyimide #5 (37.5% 6FDA, 12.5% BTDA, 25%DADPS and 25% mPDA) was prepared using a procedure similar to the one described below for end-capped 6FcoPI-5; and the mechanical properties of the neat resin were evaluated from molded test specimens. As before, the 6FcoPI-5 polymer was nearly equivalent to coPI-2 in tension, flex and compression. The fracture toughness of the former, however, was found to be 40% higher than that of the latter thus indicating that 6FcoPI-5 may have a lower propensity to microcrack.

An end-capped 6FcoPI-5 polymer was then prepared on the 400-gram scale in glassware using a procedure nearly identical to the one described for ec6FcoPI-2 in Section 2.5.1, above. Polymerization was done at 35% solids. The calculated molecular weight of the polymer was ca. 50,000 based upon 90 repeat units with phthalic anhydride end groups. In this case, the polyamic acid was stirred for 24 hours and allowed to reach equilibrium before the addition of the phthalic anhydride.

Immidization was initiated 24 hours after addition of the end-capping agent by adding 3-piccoline, mixing well and then adding acetic anhydride dropwise to the batch to prevent local precipitation. The batch was diluted to 15% solids (3 poise viscosity) before direct precipitation into methanol. The polymer had an inherent viscosity of 0.44 dl/gm.

To form blends with PBI, the precipitated polymer was resolutioned in dimethylacetamide (DMAc) and solution blended with dopes of end-capped PBI. These blends were then precipitated and washed in methanol. Table 21 compares the mechanical properties of neat ec6FcoPI-5 with those of ec6FcoPI-2 as determined from compression molded samples of the neat resins. Table 22 compares the properties of the 10/90 ecPBI/ec6FcoPI-5 blend with those of the 10/90 ecPBI/ec6FcoPI-2 system.

A1.1.2 Polymers Containing Pyromellitic Dianhydride

A series of polymers were synthesized substituting pyromellitic dianhydride (PMDA) for benzophenonetetracarboxylic dianhydride (BTDA) in the polymer matrix of Figure 28. The substitution of PMDA for BTDA was aimed at increasing the glass transition temperature (Tg), reducing the solubility of the polymer in common organic solvents and at possibly improving the fracture toughness of the neat resin. Other benefits might have included: increased melt flow and long term high temperature thermo-oxidative stability through the total elimination of PBI as a blend component.

Three mol-scale batches of polymer were synthesized with PMDA. These included one each of end-capped: 6FcoPI-2A, 6FcoPI-3A and 6FcoPI-5A where the "A" represents polymers with the dianhydride substitution. Polymer films of ec6FcoPI-2A were cast directly from the NMP dope, vacuum dried at 120°C and then washed free of NMP with water. These films, however, readily degraded in acetone or

TABLE 21

EC6FCOPI-5 VERSUS EC6FCOPI-2: NEAT RESIN PROPERTIES

	ec6FcoPI-2	ec6FcoPI-5
TENSILE STRENGTH (KSI) (MPA)	10.6 (73.1)	13.7 (94.5)
TENSILE MODULUS (KSI) (MPa)	481 (3319)	495 (3416)
TENSILE ELONGATION (%)	2.7	3.5
FLEXURAL STRENGTH (KSI) (MPa)	19.5 (134.5)	20.2 (139.4)
FLEXURAL MODULUS (KSI) (MPa)	519 (3581)	557 (3843)
COMPRESSIVE STR. (KSI) (MPa)	27.5 (189.8)	28.7 (198.0)
COMPRESSIVE MOD. (KSI) (MPa)	548 (3781)	610 (4209)
FACTURE TOUGHNESS (PSI-IN$^{1/2}$) (MPa-m$^{1/2}$)	922 (1.01)	1538 (1.69)

TABLE 22

A COMPARISON OF MECHANICAL PROPERTIES BETWEEN NEAT 10/90 ECPBI/EC6FCOPI-5 AND 10/90 ECPBI/6FCOPI-2 BLENDS

	10/90 e[illegible]BI/6FcoPI-2		10/90 ecPBI/ec6FcoPI-5	
TENSILE STR. (ksi) (MPa)	1[illegible]	(102.8)	16.2	(111.8)
TENSILE MOD. (ksi) (MPa)	487	(3360)	508	(3503)
ELONGATION (%)	4.8		4.6	
FLEXURAL STR. (ksi) (MPa)	22.7	(156.6)	23.8	(164.2)
FLEXURAL MOD. (ksi) (MPa)	566	(3905)	584	(4030)
COMPRESSIVE STR. (ksi) (MPa)	27.1	(187.0)	29.6	(204.2)
COMPRESSIVE MOD. (ksi) (MPa)	553	(3816)	598	(4126)
FRACTURE TOUGHNESS (PSI-IN$^{1/2}$) (MPa-m$^{1/2}$)			1320	(1.45)

methylene chloride and thus exhibited solvent susceptibility equivalent to that of neat 6FcoPI-2. The Tg of this polymer was 377°C (711°F); a value approximately 20°C higher than the Tg of 6F#2. To decrease the solubility of ec6FcoPI-2A, the PMDA content was increased from 12.5% to 25% of the total monomer thus leading to ec6FcoPI-3A (Figure 28 with PMDA substituted for BTDA). The polyamic acid preparation was routine but precipitation occurred after only one equivalent of acetic anhydride was added during imidization. The remainder of the acetic anhydride was added to the slurry and the mixture was then washed in copious quantities of methanol. As expected, it was insoluble and thus not useable. The glass transition temperature of this polymer was 390°C (734°F).

The preparation of ec6FcoPI-5A was routine through imidization, however, the dope appeared to be slightly gelled several hours after the acetic anhydride addition. The dope was, at this point, diluted with additional NMP, allowed to react for 24 hours and then precipitated in methanol. The cause of the slight gelation is unknown but could have resulted from: the high solids level, the large excess of acetic anhydride employed, or the polymer composition itself. As expected the Tg of this polymer was 362°C (684°F) or about 10°C and 30°C higher than that of 6FcoPI-2 and 6FcoPI-5, respectively.

Table 23 lists the above polymer variants, their glass transition temperatures, inherent viscosities, molecular weights and solvent resistance characteristics. Table 24 gives the neat resin flexural

TABLE 23

PROPERTIES OF THE LABORATORY-SCALE END CAPPED 6F POLYMER VARIANTS

VARIANT ec6FcoPI-	IV (dl/gm)	Mw (1000)	Mn (1000)	Tg* (OC)	SOLVENT** --RESISTANCE-- Acetone	Methylene Chloride
2	0.43	56	37	353	Softens	Softens
2A	0.56	57	34	377	Softens	Softens
3A	Insol.	--	--	402	-----	-----
5	0.38	34	25	330	Soluble	Softens
5A	0.36	272	29	362	Softens	Softens

* Glass transition temperature after 30 minutes at 4500C.

** 1-mil film sample immersed in solvent. Solvent resistance determined after 12 hours soak time.

TABLE 24

MECHANICAL PROPERTIES OF 6F POLYMER VARIANTS

	ec6FcoPI-2A	ec6FcoPI-3A	ec6FcoPI-5A	10/90 ecPBI/6FcoPI-5A
TENSILE STR. (ksi) (MPa)	13.5 (93.5)	4.9 (33.8)	4.2 (29.0)	14.8 (102.1)
TENSILE MOD. (ksi) (MPa)	440 (3036)	155 (1070)	187 (1090)	497 (3429)
ELONGATION (%)	4.8	4.8	2.6	3.8
FLEXURAL STR. (ksi) (MPa)	18.0 (124.2)	—	19.1 (131.8)	24.3 (167.7)
FLEXURAL MOD. (ksi) (MPa)	507 (3498)	—	547 (3774)	602 (4154)

and tensile properties of these variants and the properties of 10/90 blends of end-capped PBI with ec6FcoPI-5A.

Collectively, the data of Tables 21-24 indicate that coPI-5 type polymers may provide an advantage over coPI-2 polymers in composites. The neat resin and blend tensile properties of the former are equal to or slightly higher than those of coPI-2 with significantly higher fracture toughness. The glass transition temperature of coPI-5 is lower than that of coPI-2, however, and thus dictates a lower working temperature. Other than Tg, no clear advantage was found for polymers with PMDA.

A1.2 Review and Risk Analysis

A program review and risk assessment was performed by members of the HCRD Project Team to determine the 6F copolymer of choice for scale-up to the 100 pound level for the final composite evaluations. The two copolymers under consideration were ec6FcoPI-2 and ec6FcoPI-5. The assessment considered the remaining limited program resources, program milestone requirements and overall experience in the synthesis of each polymer. The limited resources dictated only one scale-up to the 100 pound level.

The copolymer, ec6FcoPI-5 was re-evaluated in this program as a route to the elimination of microcracking in composites. Neat resin evaluations of this polymer and of its 10/90 blend with end-capped PBI showed this resin to have mechanical properties equivalent to or slightly greater than those of ec6FcoPI-2 or of the 10/90 ecPBI/6FcoPI-2 blend, respectively. Of particular note was the increased fracture toughness. However, ec6FcoPI-5 was made in quantities of only ca. 400 grams and thus the large scale synthesis behavior of the polymer was unknown. In addition, the 10/90 ecPBI/ec6FcoPI-5 resin in dimethylacetamide exhibited significantly poorer phase stability than the corresponding dope of ec6FcoPI-2. Phase stability of at least 2 weeks was needed to accommodate the time required for dope preparation, shipping and prepregging.

Finally, it was judged that the microcracking problem could be solved through optimization of the molding cycle and principally through the elimination of residual stress by slow cooling. Thus, it was concluded that the final resin scale-up to the 100 pound level should be with ec6FcoPI-2.

HIGH PERFORMANCE POLYMER BLENDS

DARPA/AFOSR/HOECHST-CELANESE
CONTRACT F49620-88-C-0014

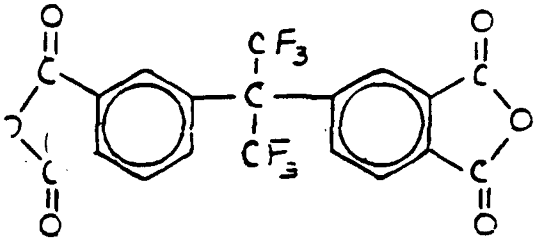
LOCKHEED AERONAUTICAL SYSTEMS COMPANY
SUBCONTRACT NO. LASC-88-HCC01

FINAL REPORT
VOLUME 2

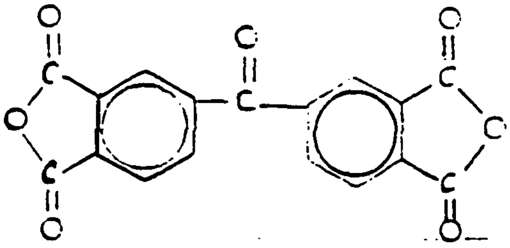
MAY 1991

ABSTRACT

As part of a resin development program at Hoechst-Celanese Research Corporation, with the objective of developing a processable composite material matrix resin for service in the temperature range of 400°F to 700°F, a polyimide blend was selected from a group of nine candidate resin blends. The blend selected consisted of the polymeric product of 50% monomeric anhydrides 6FDA (I) and BTDA (II) in 2:1 ratio, and 4, 4 diaminodiphenylsulfone III.



I



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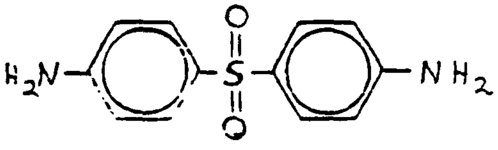

III

An endcapped version of this polyimide was blended with endcapped polybenzimidazole (PBI) to form the polymer blend 10/90 ecPBI/COPI used in this work.

The blend was processed into a dimethyacetamide (DMAc) dope suitable for solution prepregging. Prepreg was fabricated by YLA, Inc. Prepreg fiber materials consisted of unsized AS4 plain weave

A demonstration part, a simulated TR-1 3-hat stiffened avionics access door, with dimensions about 14" x 25", was fabricated using the fabric prepreg material. The part consisted of a curved face sheet coconsolidated with three hat stiffeners.

FOREWORD

This is the final report for Lockheed Subcontract LASC-88-HCC01 to Hoechst-Celanese Contract F49620-88-C-0014, "High Performance Polymer Blends", sponsored by the Defense Advanced Research Projects Agency (DARPA) and monitored by the Air Force Office of Scientific Research (AFOSR). The work covered in this report was completed in April 1991, and represents progress on this subcontract from the program kickoff meeting in November 1987 to the present time.

Materials development tasks were performed by the Hoechst-Celanese Research Division, Summit, New Jersey, and end user large part fabrication development and testing were performed by the Lockheed Aeronautical Systems Company, Burbank, California and the General Electric Aircraft Engine Company, Evandale, Ohio. The Lockheed Subcontract Program Manager has been Dr. Robert Boschan. Support in the laminate evaluation effort was provided by Dr. Margaret Talbott[1] and Mr. Jay Shukla[2] and supervision of layup and autoclave fabrication was provided by Ms. Cindy Vehling. Assistance in fabrication of laminates via the Therm-X process was provided by Mr. Ken Fouts of Dow/United Technologies, Wallingford, Connecticut.

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HIGH PERFORMANCE POLYMER BLENDS
DARPA/AFOSR CONTRACT F49620-88-C-0014
LOCKHEED SUBCONTRACT LASC-88-HCC01

1.0 INTRODUCTION

1.1 Background

A polymeric matrix resin is needed for advanced aerospace, fiber reinforced composite and adhesive applications which is readily processible to large parts while meeting thermo-oxidative and thermomechanical requirements at temperatures above 400°F. To 400°F, thermal stability and processibility are not major issues with either thermoplastic or thermoset materials (e.g., polyimides, PEEK, etc.) being generally capable of meeting performance requirements. The feasibility of applying miscible polymer blend technology to the definition and development of materials with a balance of properties and processibility for demanding DOD end-use applications has been demonstrated.

Under the DARPA/AFOSR "Improved Structural Polymer Alloy and Composite Program" (1984-1987) it was concluded that miscible blends are a viable way to modify and tailor resin properties offering cost, flexibility and time savings advantages when compared to new chemistry. In particular, polybenzimidazole (PBI) was found to be miscible with a range of polyimides, including the thermoplastic polyimides, thereby potentially leading to a viable, new class of high temperature, thermoformable resins for 371°C (700°F) applications. The Polymer Alloy and Composite Program also established a framework to systematically identify and verify miscible polymer pairs, utilizing both molecular modeling and experimental techniques; and, it lead to the development of a high performance polymer project team involving the university, the materials producer and the materials user to insure efficient technology transfer.

PBI is unique as an available 400+°C Tg (glass transition temperature) resin but lacks true thermoplastic processibility and has poor thermo-oxidative (TOS) stability, in addition to a high moisture regain (10-15%). Blends with polyimides have been shown to have lower Tg's and to have improved moldability, and considerably lower moisture regain if the polyimide is the major blend component. At temperatures of 371°C (700°F), the only resins with sufficient thermo-oxidative stability appear to be polyimides (PI) containing the hexafluoroisopylidene (6F) moiety such as DuPont's Avamid N and Ethyl Corporation's Eymyd. A third family of potential candidates containing this moiety which are characterized by processing ease are the Sixef™ polymers being developed by Hoechst-Celanese. All of these latter materials, however, fail to meet specifications on the basis of processibility and/or mechanical properties at temperature, especially in compression, and have unacceptable solubility in common solvents such as acetone and methylene chloride. The state of the art would thus suggest that the optimum 400-700°F matrix resin would contain elements of PBI for high temperature mechanical properties and solvent stability and a polyimide for ease of processing; in particular, the use of perfluorinated polyimide technology for very high temperature thermo-oxidative stability.

1.2 Objectives

It is the mission of the current Polymer Blends Program to translate the inventions and feasibility studies of the Improved Structural Polymer Alloy and Composites Program into useful and unique materials for aerospace. Specifically, the objectives of this program are to:

- Develop miscible PBI/PI blend systems meeting aerospace requirements for a tough, processible matrix and adhesive for use at 400 to 700°F.
- Develop a user relevant miscible polymer blend database for aromatic heterocyclic and mesogenic polymers.
- Advance the understanding of miscible polymer blends.

The key to this program is the recognition that its major focus is the development of a superior matrix material for aerospace within a three year timeframe. To meet this objective, materials must be supplied to the aerospace evaluators in sufficient quantities for comparative testing with other candidate resins. To provide materials in these quantities, the starting polymers or the raw materials and technology for making them must exist today.

1.3 Approach

The program approach is three-pronged with simultaneous investigations of the underlying blend science, blend scale-up through composite fabrication and focused research into areas of anticipated resin deficiency.

1.3.1 Blend Development and Fabrication

This portion of the program seeks to develop the capabilities to scale-up blend production to match evaluation needs and to prepare carbon fiber reinforced prepreg and composites with (blend) PBI/PI matrices. At present the prepreg methods of choice are the intermingled or hybrid yarn approach and solvent impregnation. The dimethylacetamide (DMAc) solvent impregnated plain weave fabric and unidirectional tow were evaluated at Lockheed.

1.3.2 Anticipatory Studies

Anticipatory studies are aimed at improving the performance of blend component polymers, in key areas, prior to performance data generated on composite specimens fabricated from these polymer blends. Targets of these studies are improvements in the thermo-oxidative stability (TOS) PBI and PBI/PI blends, reduction in moisture regain of PBI and the insolubilization of Sixef polyimides.

2.0 TECHNICAL PROGRESS

For blending with endcapped polybenzimidazole (PBI), a number of blends, shown in Figure 1, were proposed by Hoechst-Celanese Corporation. Of these nine originally proposed blends, a downselect process resulted in the selection of two polyimide blends, No. 2 and No. 5, for blending with endcapped PBI in a 10/90 ECPBI/ec6FCOPI polymer blend.

Table 1 shows typical neat resin mechanical properties for 6FCOPI-2 and 6FCOPI-5. Mechanical properties for these two polyimide blends are, as expected, quite comparable. Endcapping of these polymers to provide better molecular weight control, uniformity and processability does not seriously compromise neat resin properties as shown in Table 2. Blends of the polyimides EC (Endcapped) 6FCOPI-2 and EC6FCOPI-5 with 10% PBI significantly improved solvent resistance without seriously compromising mechanical properties. Neat resin mechanical properties of 10/90 ec PBI 6FCOPI-2 and 10/90 ecPBI6FCOPI-5 are shown in Table 3. The 6FCOPI-2, a three monomer system, was selected for scale-up over 6FCOPI-5, a four monomer system. Additional discussion relevant to the choice of the 10/90 ec PBI6FCOPI-2 blend for scale-up is found in the Tenth Quarter Interim Report on this program, January 1991. Reinforcing fiber materials used for impregnation by the 10/90 PBI/PI polymer dope included both unsized AS4 6K tow and custom woven unsized plain weave (0°,90°) fabric.

Figure 1

EXPERIMENTAL DESIGN – 6FCOPI
DIANHY. – 6F, BTDA DIAMINE – m,p,PDA, DADPS

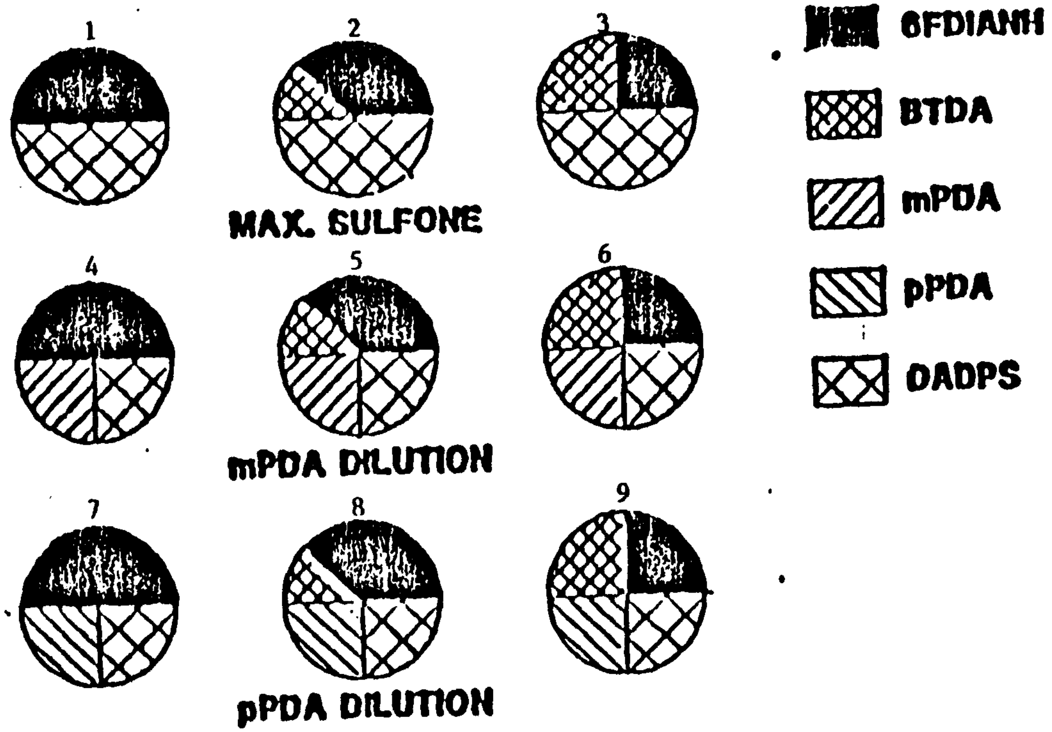


Table 1. 6FCOPI-5 VERSUS 6FCOPI-2: NEAT RESIN PROPERTIES

	6FcoPI-2	6FcoPI-5
TENSILE STRENGTH (KSI) (MPA)	14.1 (97.3)	14.7 (101.4)
TENSILE MODULUS (KSI) (MPa)	487 (3360)	494 (3409)
TENSILE ELONGATION (%)	4.4	3.9
FLEXURAL STRENGTH (KSI) (MPa)	22.2 (153.2)	19.2 (132.5)
FLEXURAL MODULUS (KSI) (MPa)	555 (3830)	546 (3767)
COMPRESSIVE STR. (KSI) (MPa)	26.6 (183.5)	28.2 (194.6)
COMPRESSIVE MOD. (KSI) (MPa)	538 (3712)	522 (3602)
FACTURE TOUGHNESS (PSI-IN$^{1/2}$) (MPa-m$^{1/2}$)	1073 (1.18)	1511 (1.66)

Table 2. EC6FCOPI-5 VERSUS EC6FCOPI-2: NEAT RESIN PROPERTIES

	ec6FcoPI-2	ec6FcoPI-5
TENSILE STRENGTH (KSI) (MPA)	10.6 (73.1)	13.7 (94.5)
TENSILE MODULUS (KSI) (MPa)	481 (3319)	495 (3416)
TENSILE ELONGATION (%)	2.7	3.5
FLEXURAL STRENGTH (KSI) (MPa)	19.5 (134.5)	20.2 (139.4)
FLEXURAL MODULUS (KSI) (MPa)	519 (3581)	557 (3843)
COMPRESSIVE STR. (KSI) (MPa)	27.5 (189.8)	28.7 (198.0)
COMPRESSIVE MOD. (KSI) (MPa)	548 (3781)	610 (4209)
FACTURE TOUGHNESS (PSI-IN$^{1/2}$) (MPa-m$^{1/2}$)	922 (1.01)	1538 (1.69)

Table 3. A COMPARISON OF MECHANICAL PROPERTIES BETWEEN NEAT 10/90 ECPBI/EC6FCOPI-5 AND 10/90 ECPBI/6FCOPI-2 BLENDS

	10/90 ecPBI/6FcoPI-2		10/90 ecPBI/ec6FcoPI-5	
TENSILE STR. (ksi) (MPa)	14.9	(102.8)	16.2	(111.8)
TENSILE MOD. (ksi) (MPa)	487	(3360)	508	(3503)
ELONGATION (%)	4.8		4.6	
FLEXURAL STR. (ksi) (MPa)	22.7	(156.6)	23.8	(164.2)
FLEXURAL MOD. (ksi) (MPa)	566	(3905)	584	(4030)
COMPRESSIVE STR. (ksi) (MPa)	27.1	(187.0)	29.6	(204.2)
COMPRESSIVE MOD. (ksi) (MPa)	553	(3816)	598	(4126)
FRACTURE TOUGHNESS (PSI-IN$^{1/2}$) (MPa-m$^{1/2}$)			1320	(1.45)

weave (0°,90°) fabric.

Subsequent to resin scale-up at Hoechst-Celanese Corporation, resin dope was provided to YLA, Inc. for solvent impregnation. Fabrication of prepreg at YLA yielded approximately 1300 linear feet of 12" wide unitape, 400 linear feet of 24" wide fabric prepreg, and 33 linear feet of neat resin film. The inventory of prepreg is shown in Table 4.

2.1 Processing Study

2.1.1 Solvent Removal

The solvent process used to make the polymer blend prepreg resulted in a material containing about 20-25% dimethylacetamide (DMAc). Some solvent is needed during laminate consolidation to enable the resin to flow sufficiently, but such a large amount would cause uneven resin distribution in the final product, in addition to serious problems with voids and delaminations due to gas evolution. Therefore, the first laminate was made in an autoclave with three hold periods at low temperatures to dry the prepreg. The resulting laminate was very poor and contained several large resin-starved areas on the surfaces. It was therefore decided to dry the prepreg before it was laid up and consolidated, in the hope that pre-autoclave drying would allow better control of solvent content. Solvent removal curves for removal of solvent at vacuum were run at 400°F and 450°F, however at these temperatures the solvent vanishes so rapidly that there is a lack of control. Thus, a solvent removal curve at 300°F was run.

Two pieces were cut from roll 1 of graphite fabric prepreg and dried under vacuum at 300°F. They were weighed every fifteen minutes, and the drying proceeded until the weight stopped changing. The resulting solvent removal curve is shown in Figure 2. It is clear that most of the solvent was gone in the first

TABLE 4

INVENTORY OF ECPBI/6F COPI-2 DMAC PREPREG

YLA REFERENCE	ROLL NO.	DESCRIPTION	QTY-LIN.FT.
FB570	1	Sixe F/PBI Unitape	98
FB570	2	Sixe F/PBI Unitape	109
FB570	3	Sixe F/PBI Unitape	100
FB570	4	Sixe F/PBI Unitape	100
FB570	5	Sixe F/PBI Unitape	100
FB570	6	Sixe F/PBI Unitape	100
FB570	7	Sixe F/PBI Unitape	100
FB570	8	Sixe F/PBI Unitape	100
FB570	9	Sixe F/PBI Unitape	100
FB570	10	Sixe F/PBI Unitape	100
FB570	11	Sixe F/PBI Unitape	100
FB570	12	Sixe F/PBI Unitape	100
FB570	13	Sixe F/PBI Unitape	100
FB569	1	Sixe F/PBI Fabric Prepreg	49
FB569	2	Sixe F/PBI Fabric Prepreg	50
FB569	3	Sixe F/PBI Fabric Prepreg	56
FB569	4	Sixe F/PBI Fabric Prepreg	50
FB569	5	Sixe F/PBI Fabric Prepreg	50
FB569	6	Sixe F/PBI Fabric Prepreg	50
FB569	7	Sixe F/PBI Fabric Prepreg	55
FB569	8	Sixe F/PBI Fabric Prepreg	55
FB569	11	Sixe F/PBI Film	33

fifteen minutes, but solvent removal proceeded until at least 90 minutes. With the use of the experimentally obtained curve in Figure 2, it was estimated that residual solvent contents of approximately 4% and 2% could be obtained after drying in vacuum at 12 and 18 minutes, respectively. The assumption was made that solvent removal times for both fabric prepreg and unidirectional tow prepreg were about the same at 300°F.

2.1.2 Initial Laminate Fabrication

Initial laminate studies consisted of fabrication of four 8" x 8", 8-ply laminates, two from fabric prepreg and two from unidirectional prepreg. Several differences in the behavior of the two prepregs were noted. The woven fabric was much less tacky, much easier to handle and a great deal better in appearance. The unitape was very tacky indeed; it was almost impossible to handle unless it was refrigerated before the plies were cut from the roll. Drying made it much easier to handle. The 8" x 8" plies were dried in a stack in the small laboratory vacuum oven between sheets of porous Armalon. Fiberglass was used as a separator in one attempt at drying, but the glass fibers stuck to the prepreg. Each ply was weighed before and after drying and a "traveler" or smaller piece was dried in the middle of each stack. After the plies were dried, the volatile content of the traveler was measured by drying for two hours under vacuum at 300°F. The weight changes and the traveler volatile content for each set of plies are recorded in Tables 5-6. The solvent contents of the two rolls of prepreg were not very uniform, thus the usefulness of the traveler as a gauge of final solvent content is limited, however the data obtained is certainly indicative of the solvent removal behavior.

The four laminates were laid up and consolidated in an autoclave as follows:

> Under atmospheric pressure, raise the temperature to 500°F and hold for two hours.

Figure 2
Solvent Removal Curve
300 deg F, Full Vacuum

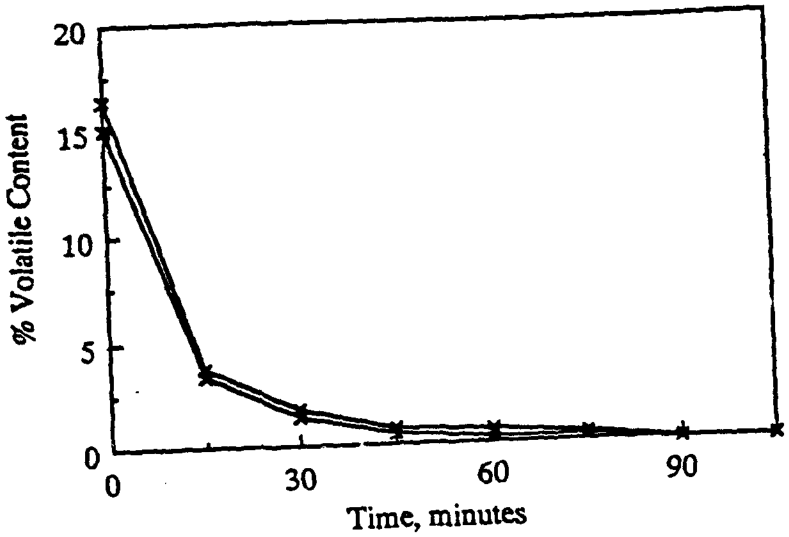


Table 5

Weight Lost by Plies During Drying

Ply Number	% Weight Lost Panel 12W	Panel 18W	Panel 12U	Panel 18U
1	19.0	21.2	27.9	31.1
2	19.2	22.9	32.5	20.7
3	14.5	22.7	30.5	33.3
4	17.8	22.1	29.4	27.7
5	16.0	20.3	25.0	32.5
6	13.2	20.9	22.6	30.0
7	14.5	20.0	17.2	17.2
8	15.3	18.9	28.2	17.3
traveler	17.6	24.4	31.4	30.8

Table 6

Final Volatiles Content of Travelers

Panel Designation	Traveler % Volatiles
12W	6.6
18W	4.3
12U	5.8
18U	3.2

Explanation of Panel Designations: The number 12 or 18 is the number of minutes for which the plies and traveler were dried in the vacuum oven before the panel was laid up and consolidated. W signifies woven fabric prepreg, and U indicates unidirectional tape.

Increase pressure to 200 psi.
Increase temperature to 725°F and hold for 15 minutes.
Increase temperature to 750°F and hold for 15 minutes.
Cool under pressure and remove from the autoclave.

The cycle is shown graphically in Figure 3. The resulting consolidated laminates had significant resin-starved areas on their surfaces. They were C-scanned and found to be of less than perfect quality. The panels made from woven fabric prepreg were less defective than those made from unitape, while the plies dried for 18 minutes gave better laminates than those dried for 12 minutes. Photomicrographs were made from sections cut from "good" and "bad" areas of panels 18U and 18W as indicated by C-scan. Both showed large voids and poor consolidation, as well as many small cracks in the z-direction. While both contained a number of large voids, the bad area also showed poor consolidation with some sizable areas with no fibers between plies. Further, the plies were wrinkled. However, the unitape panel showed none of the cracks in the z-direction.

Figures 4 and 5 are black and white photocopies of the color ultrasonic C-scans of laminates 12U and 18W. Even with the greater per ply thickness of the fabric, it is clear that the transmission of sonic energy through the fabric laminate 18W is significantly better than that of the unitape laminate 12W, indicating fewer void areas in the 18W laminate. Thus, the 18 minute drying cycle at 300°F was adopted for subsequent laminate fabrication.

Rheometric studies conducted on the resin in the prepreg show a minimum viscosity of about 2×10^8 poise, and this minimum viscosity prevails over a wide temperature range of 390°C to 470°C (735°F to 880°F). This high viscosity is undoubtedly responsible for the observed difficulty in laminate consolidation, since resin flow at this high viscosity is exceedingly slow. Fortunately, the DMAc solvent prepregging procedure provided very good fiber

Figure 3
Autoclave Cycle

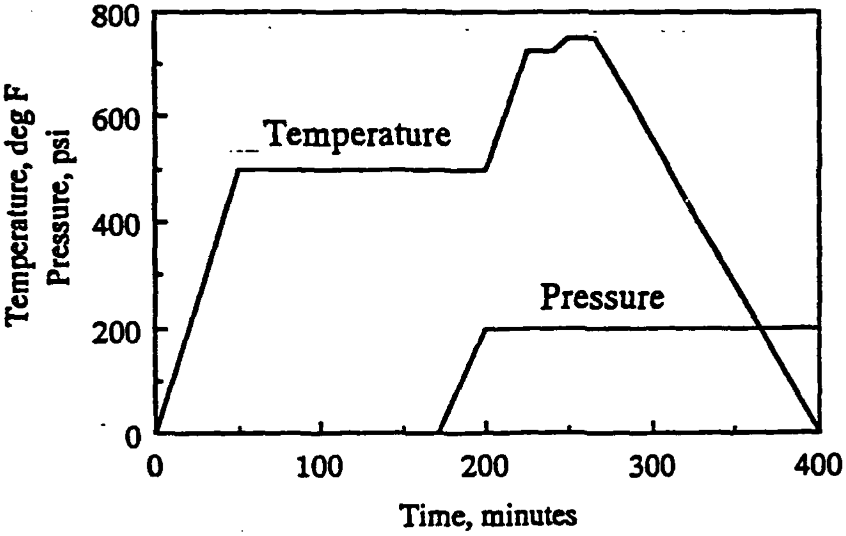


FIGURE 4. ULTRASONIC C-SCAN - LAMINATE 12U

LAMINATE CONTAINING 8 PLIES OF UNITAPE PLIES WERE DRIED 12 MINUTES

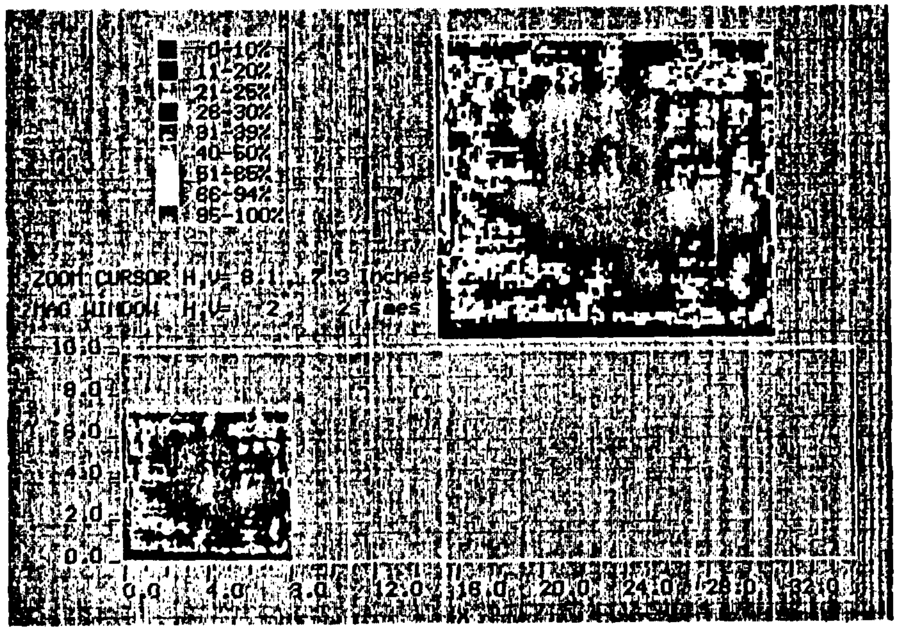
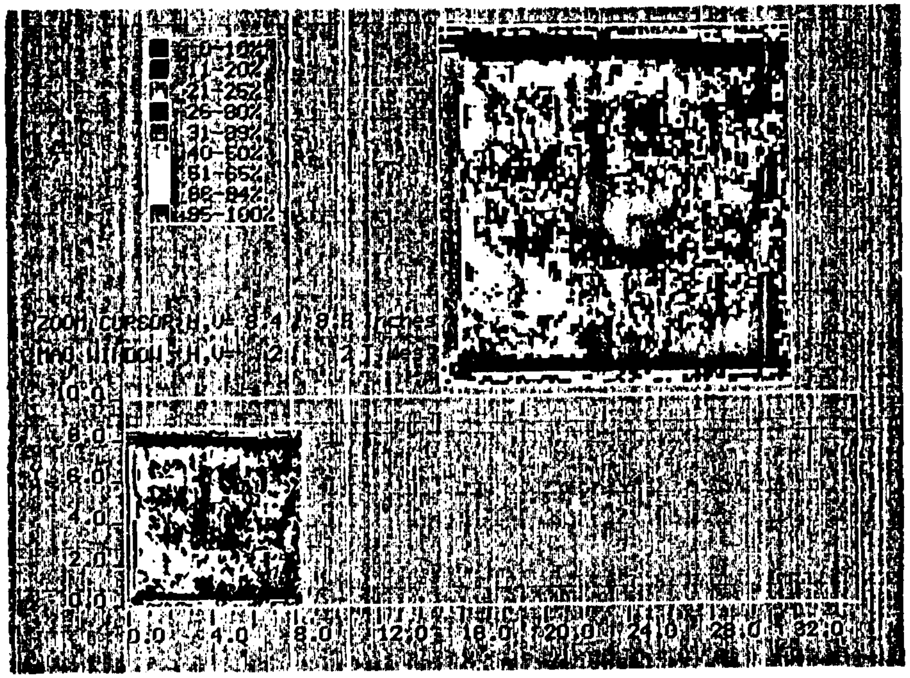


FIGURE 5. ULTRASONIC C-SCAN - LAMINATE 18W

LAMINATE CONTAINING 8 PLIES OF FABRIC PLIES WERE DRIED 18 MINUTES



wetting, however consolidation to a monolithic composite structure was difficult due to the high resin viscosity and limited flow.

2.2 Laminate Fabrication - Autoclave Processing

A number of panels of various sizes and thicknesses were fabricated from the fabric and unitape prepregs made from the 10/90 ECPBI/COPI #2 resin dope, using the established solvent drying and laminate processing cycles. Table 7 shows the panels fabricated by autoclave processing at Lockheed.

Ultrasonic C-scans of these laminates showed that they were not of overall acceptable quality. This was verified by microscopic examination which, in all cases, showed well consolidated areas along with scattered voids, delaminations, and microcracks.

Figure 6 is a photomicrograph of Panel OJZ675, a 16-ply unidirectional AS4/PBI/COPI laminate. A "good" area was chosen and photomicrographs perpendicular and parallel to the fibers were taken. The pictures show areas which are very well consolidated along with voidy areas.

Figures 7 and 8 are photomicrographs of 8-ply and 16-ply (0°,90°) woven fabric reinforced panels. As before, the photomicrographs show very well consolidated areas along with some voids. In Figure 9, two more areas of the 16 ply (0°,90°) woven fabric laminate are shown, however a few microcracks are evident. It is noteworthy that the microcracks do not appear in the 0° plies.

Figure 10 shows a photomicrograph of OJZ676, a quasiisotropic, $(45^\circ,0^\circ,-45^\circ,90^\circ)_{2S}$ 16-ply panel. The well consolidated areas are evident, however microcracks are considerably more prevalent in this panel. As before, microcracks do not appear in the 0° plies.

TABLE 7 - LOCKHEED AUTOCLAVE PROCESSING

PANELS FABRICATED FROM 10/90 ECPBI/COPI #2 DMAC PREPREGS (1)

PANEL #	PROCESS	ORIENTATION	NO. PLIES	SIZE (IN.)
OAZ631	AC/VB	0,90 FABRIC (2)	8	12 X 12
OCZ251	AC/VB	(0°)8 (3)	8	8 X 8
OCZ252	AC/VB	(0°)8	8	8 X 8
OCZ255	AC/VB	0,90 FABRIC	8	8 X 8
OCZ256	AC/VB	0,90 FABRIC	8	8 X 8
OJZ673	AC/VB	0,90 FABRIC	8	24 X 24
OJZ674	AC/VB	0,90 FABRIC	16	24 X 24
OJZ675	AC/VB	(0°)16	16	12 X 24
OJZ676	AC/VB	(45,0,-45,90)2S	16	12 X 24
ODZ348	AC/VB	0,90 FABRIC	8	24 X 24
ODZ349	AC/VB	0,90 FABRIC	8	24 X 24

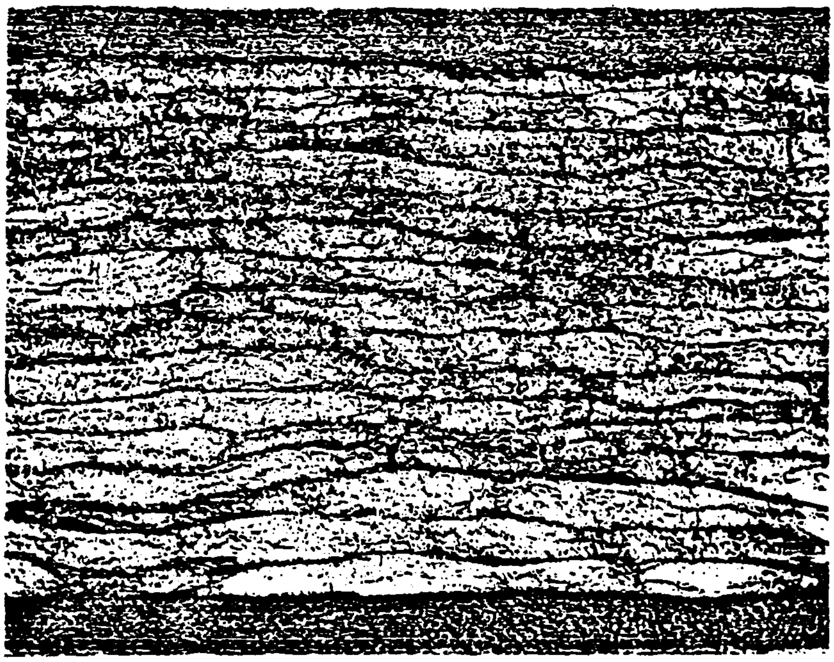
(1) PREPREGGING FROM DMAC POLYMER BLEND DOPE WAS PERFORMED BY YLA, INC.

(2) UNSIZED PLAIN WEAVE AS4 FABRIC WAS CUSTOM WOVEN BY KETEMA, INC.

(3) UNSIZED AS4 3000 GRAPHITE TOW WAS OBTAINED FROM HERCULES, INC.

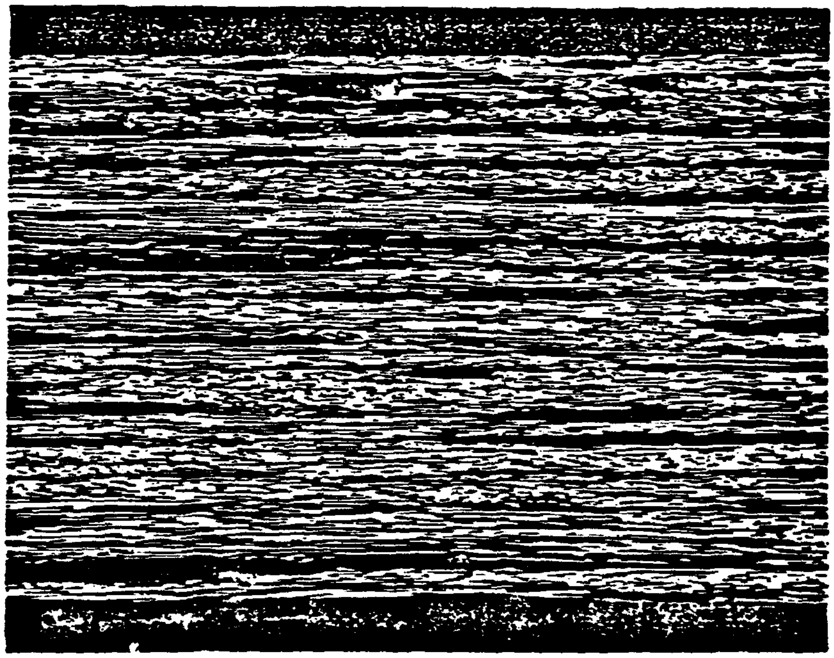
PI/PBI TEST PANEL NO. 0JZ675

FIGURE 6. UNIDIRECTIONAL 16-PLY AS4/PBI/COPI LAMINATE



⊥ TO FIBERS

25X

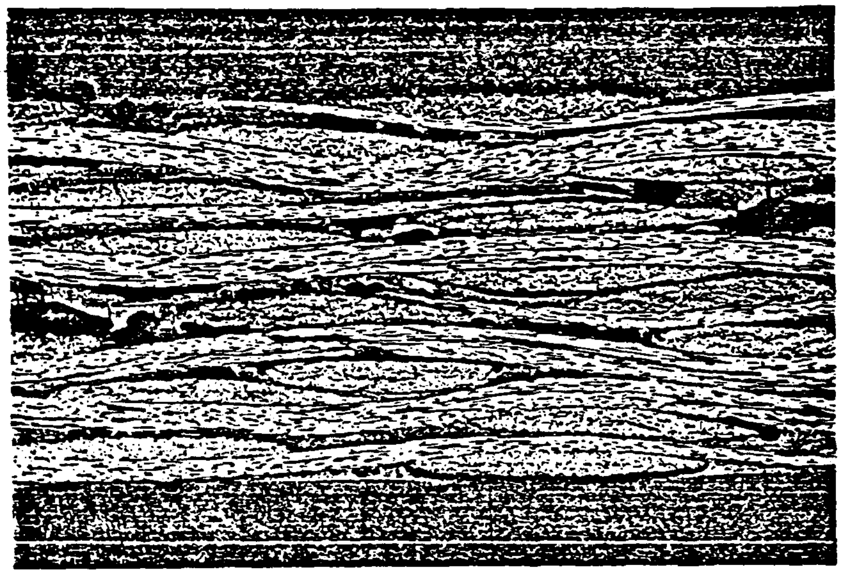


|| TO FIBERS

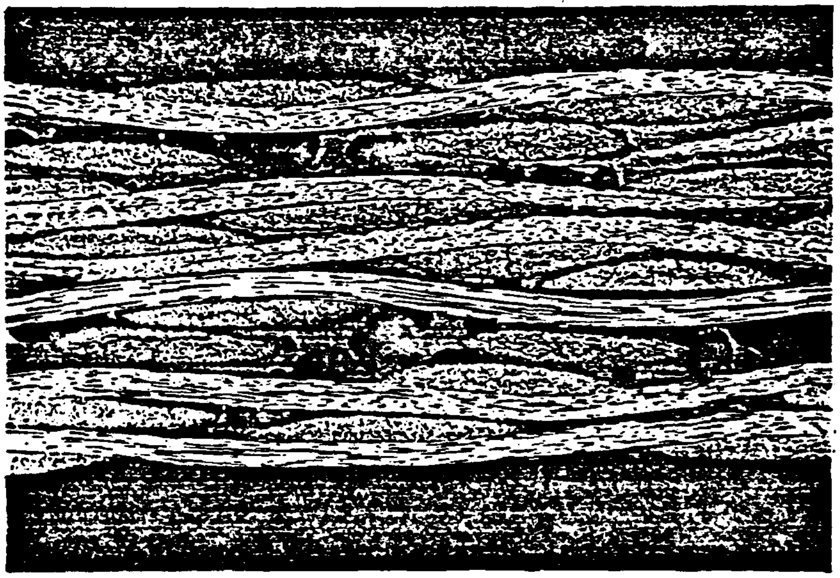
25X

FIGURE 7. PHOTOMICROGRAPH OF PANEL NO. OJZ673

AS4/PBI/PI 8-PLY WOVEN FABRIC (0, 90 WEAVE)

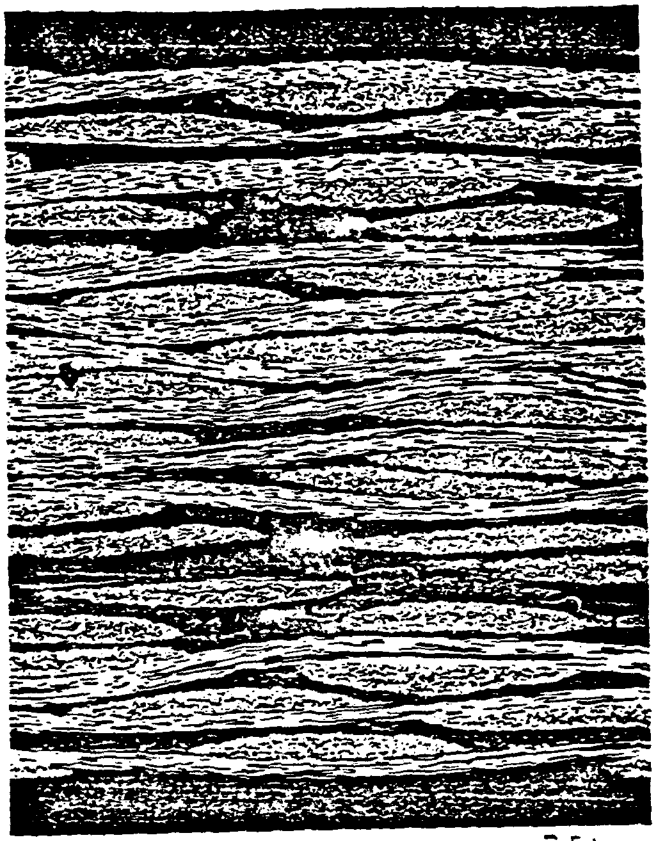


25X

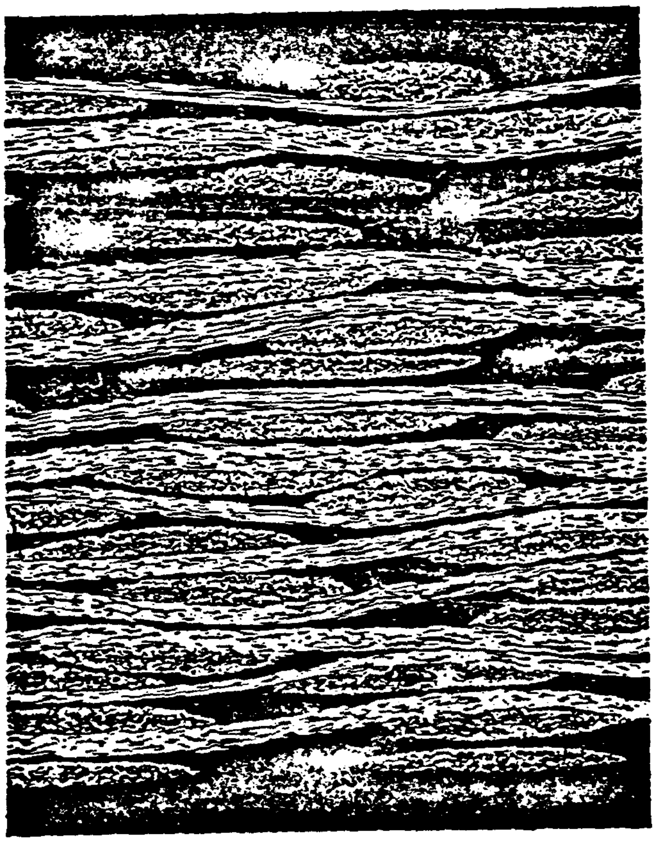


25X

FIGURE 8. PHOTOMICROGRAPH OF PANEL NO. OJZ674 AS4/PBI/PI 16-PLY WOVEN FABRIC (0, 90 WEAVE)

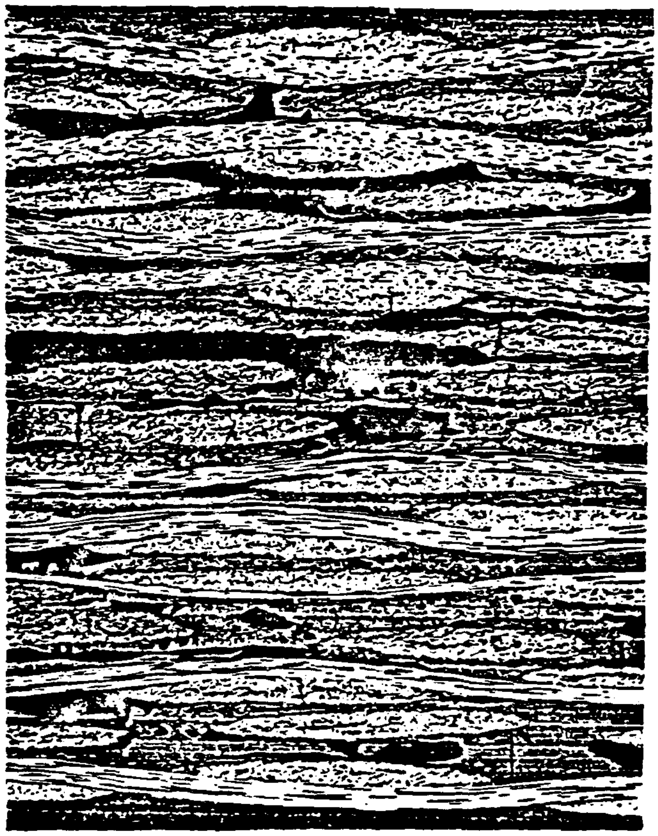


25X

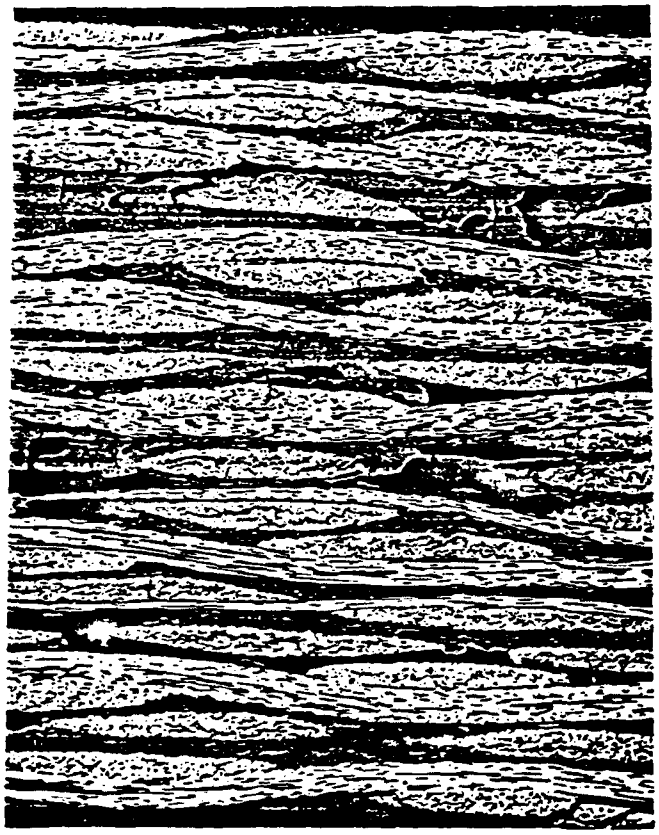


25X

FIGURE 9. AS4/PBI/PI 16-PLY WOVEN FABRIC (0, 90 WEAVE) #OJZ674



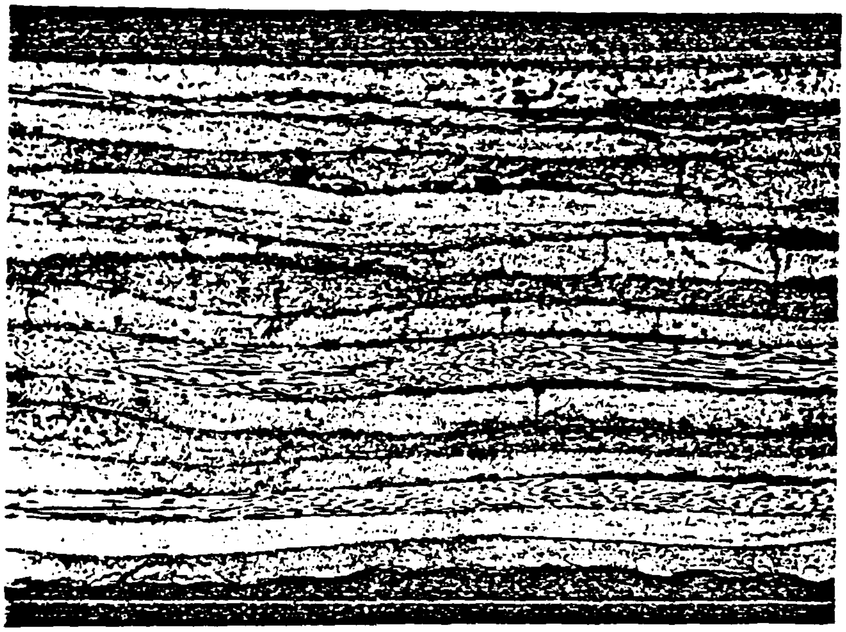
25X



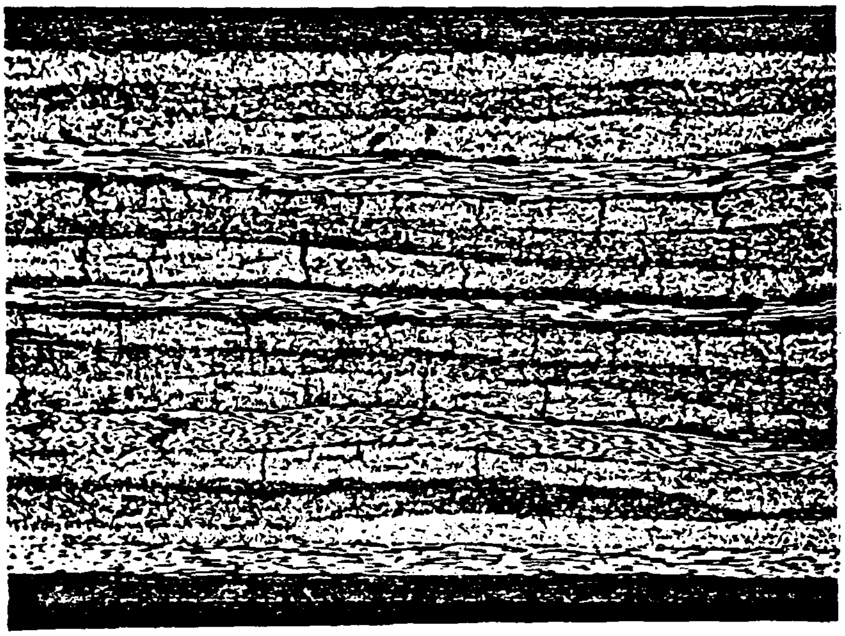
25X

FIGURE 10. AS4/PBI/PI QUASIISOTROPIC

(45°, 0°, -45°, 90°)$_{2S}$ 16-PLY PANEL #0JZ676



25X



25X

2.3 Laminate Fabrication - THERM-X Processing

Fabrication of PBI/PI blend laminates via the THERM-X is a proprietary laminate fabrication process of Dow/United Technologies. The laboratories of Dow/United Technologies are currently in Wallingford, Connecticut. Their processing equipment was recently relocated from their former facility in San Jose, California. The THERM-X process makes use of a polysiloxane polymer which undergoes a reversible phase change from solid to liquid upon application of pressure. By use of this polymer as a means of pressure application, a very high pressure (up to 3000 psi) can be safely applied. If the pressurizing system leaks, reversion of the liquid polymer to the solid state occurs, thus eliminating the hazard due to a high pressure leak.

Fabrication of four 17"x20" PBI/PI panels were attempted. These included a 16 ply unidirectional laminate, a 16 ply quasiisotropic laminate, a 32 ply (0,90) fabric laminate, and a 32 ply quasiisotropic laminate. These laminates are summarized in Table 8.

Prepreg materials were cut and kitted and supplied to Dow/United Technologies in kits prepared for fabrication of two 17"x20" laminates per run. The plies from the kits were stacked and bagged by Dow/United Technologies personnel for processing in their equipment. The processing cycle is shown in Table 9.

The 32 ply quasiisotropic and 0,90 fabric laminate were examined by ultrasonic c-scan and microscopic cross section. As previously observed in the autoclave processed laminates, the presence of voids and delaminations due to inadequate resin flow made sonic transmission very difficult. C-scans of these two panels are shown in Figure 11. The quasiisotropic panel was virtually opaque to the sonic energy, while the fabric laminate had poor transmission in the center with some good areas in the perimeter of the panel.

TABLE 8

PANELS FABRICATED FROM 10/90 ECPBI/COPI #2 DMAC PREPREGS (1)

PANEL #	PROCESS	ORIENTATION	NO. PLIES	SIZE (IN.)
UNI - 1	THERM-X	(0°)16 (2)	16	17 X 20
F - 1	THERM-X	0,90 FABRIC (3)	32	17 X 20
QI - 1	THERM-X	(45,0,-45,90)2S	16	17 X 20
QI - 2	THERM-X	(45,0,-45,90)4S	32	17 X 20

(1) PREPREGGING FROM DMAC POLYMER BLEND DOPE WAS PERFORMED BY YLA , INC.

(2) UNSIZED AS4 3000 GRAPHITE TOW WAS OBTAINED FROM HERCULES, INC.

(3) UNSIZED PLAIN WEAVE AS4 FABRIC WAS CUSTOM WOVEN BY KETEMA, INC.

The structural flaws, including voids and delaminations, are clearly seen in the photomicrographs of the 32 ply quasiitropic and fabric panels shown in Figure 12. These photographs show areas of excellent resin consolidation along with a number of obvious flaws. It is interesting that the THERM-X processed panels show far fewer microcracks than the autoclave processed panels. The high magnification photographs shown in Figure 13 demonstrate very good fiber wetting from the solution prepreg process. The resin solution has penetrated well into the fiber bundles to provide thorough uniform resin distribution in the prepreg. Since the voids generally appear between the fiber bundles, it seems apparent that these observed flaws are due to inadequate resin flow during processing and consolidation. In the quasiitropic laminate, the 0° plies appear to be most vulnerable toward voids and delaminations.

3.0 Fabrication of Demonstration Part

To demonstrate the fabrication of a more complex structure, a demonstration part was fabricated from the PBI/PI Polymer Blend fabric prepreg. The part chosen for this demonstration is a simulated TR-1 3-hat stiffened avionics access door, with dimensions about 14"x25". The part consists of a curved 16 ply quasiisotropic face sheet coconsolidated with three hat stiffeners. The face sheet and hats were formed separately, and they were coconsolidated, with the hat sections filled with plaster to prevent collapse. The manufacturing process is summarized in Table 10. Successful fabrication of this complex part demonstrates that the PBI/PI resin system is amenable to conventional composite fabrication procedures. A top view and front view of the door are shown in Figures 15 and 16.

Table 9. CURE CYCLE FOR 10/90 PBI POLYIMIDE LAMINATES

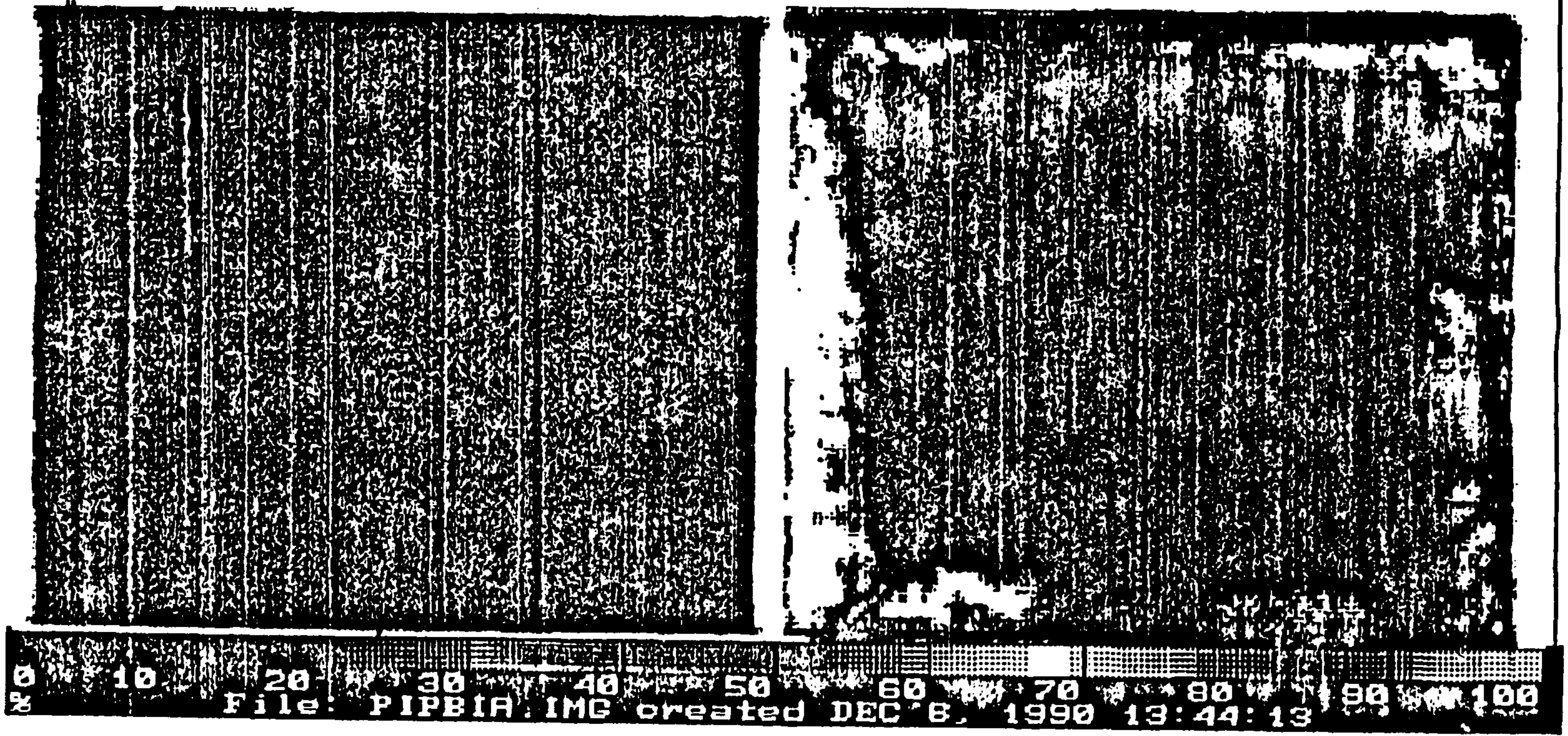
THERM-X PROCESS

1. Apply Vacuum
2. Heat to 500 F rapidly and hold 2 hours under vacuum to vent residual DMAC
3. Apply 1500 psi pressure
4. Heat to 725 F and hold 15 minutes
5. Heat to 750 F and hold 15 minutes
6. Release vacuum and cool under pressure
7. Release pressure
8. Remove part

Figure 11. Ultrasonic C-Scan

THERM-X Processed Quasiitropic and o°, 90° Fabric PBI/PI Laminates

32 Plies



Quasiitropic
Defects Cause Poor Sound Transmission

Fabric
Some Good Areas Around Perimeter

```
*************************************************************************
*                     DATA ACQUISITION PARAMETERS                       *
*************************************************************************

                    Horizontal     Vertical
                    ----------     --------
Axes..............  X              Y             Mode............  CSCAN
Viewport..........  42.4960        33.6750       Min.............  1
Offset............  0.0000         0.0000        Max.............  254
Spotsize..........  0.1200         0.1200        Origin..........  Lower Left
Increment.........  0.0830         0.0750        Split...........  1
Hyst..............  2              2             Active..........  0
                                                 Hires...........  1
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*************************************************************************
*                       PLOT CHARACTERISTICS
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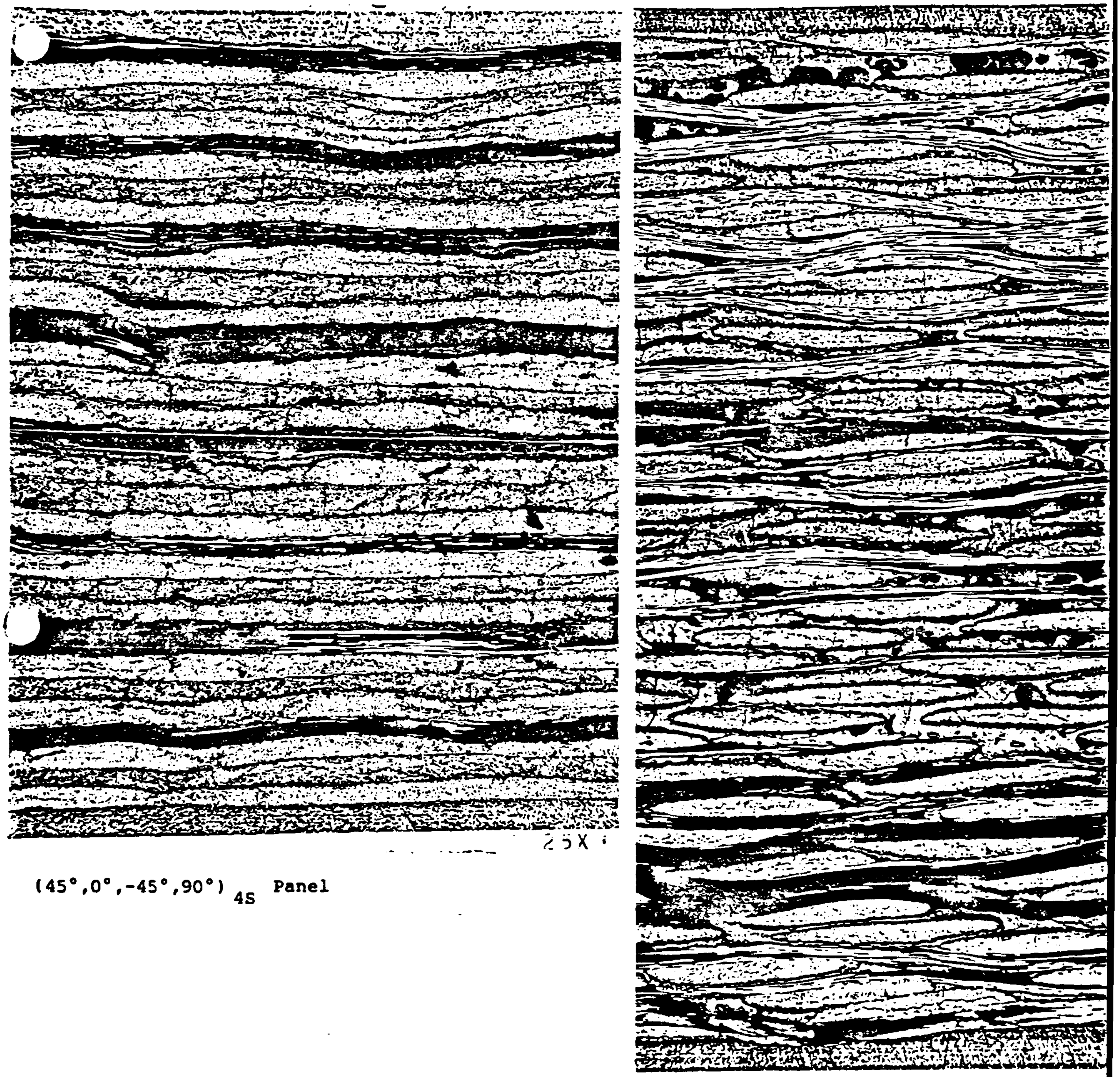
Figure 12 Photomicrographs of THERM-X Processed 32 Ply PBI/PI Fabric and Quasiitropic Laminates Low Magnification

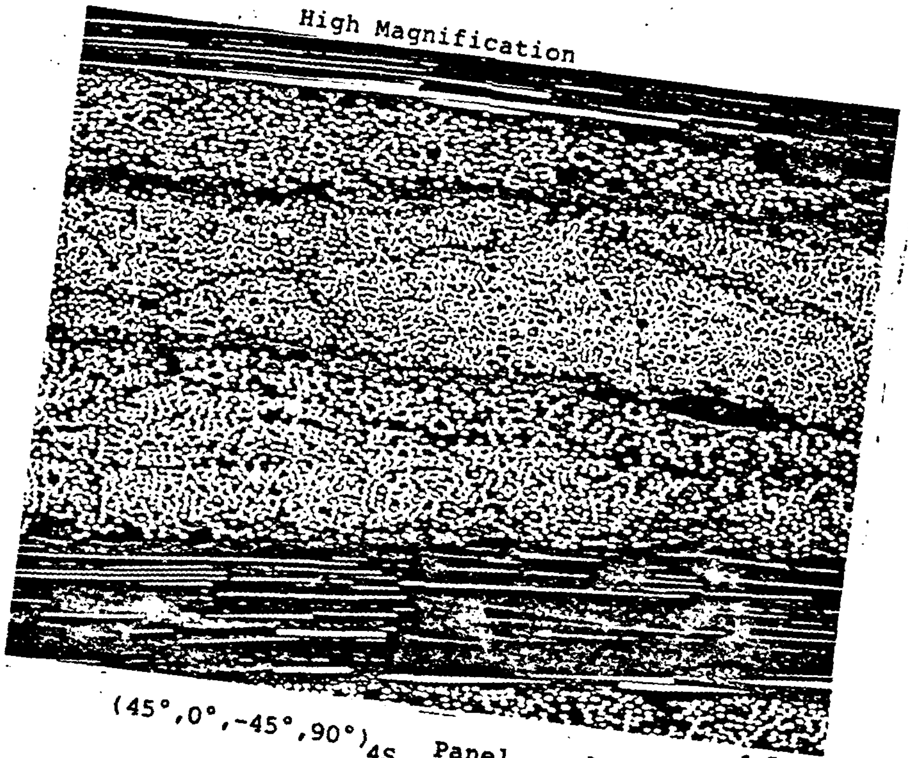


(45°,0°,-45°,90°)$_{4S}$ Panel

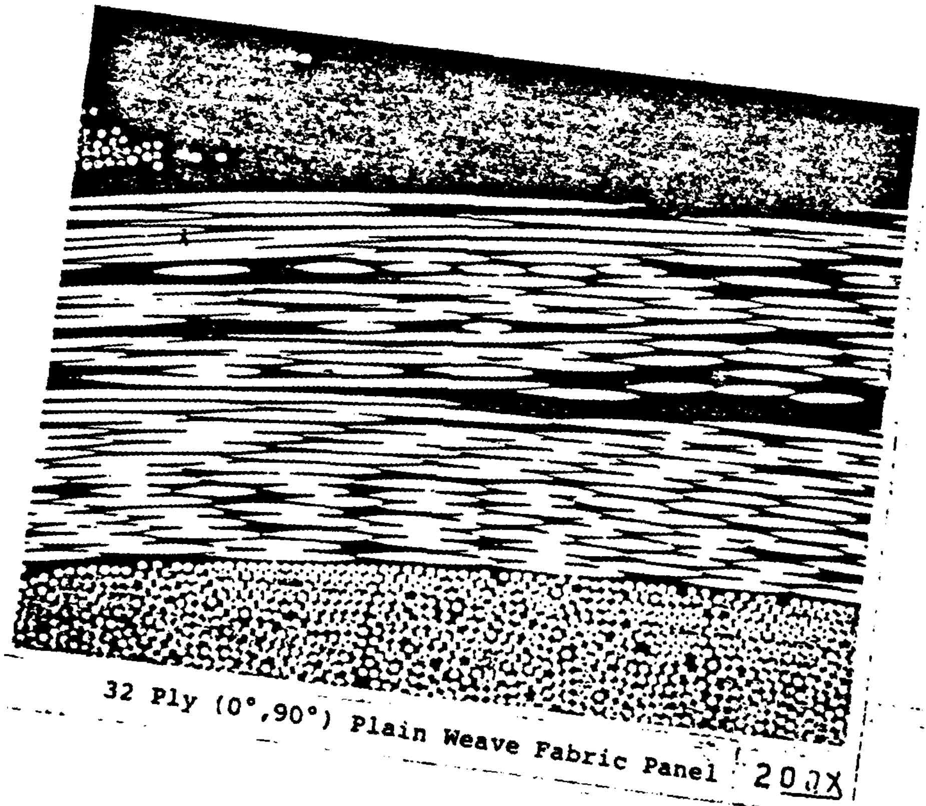
32 Ply (0°,90°) Fabric Panel

Figure 13 Photomicrographs of THERM-X Processed 32 Ply PBI/PI Quasiitropic and Fabric Laminates

High Magnification



(45°,0°,-45°,90°)$_{4S}$ Panel 100X



32 Ply (0°,90°) Plain Weave Fabric Panel 200X

Table 10 MANUFACTURING PROCESS FOR PBI/PI THREE HAT DOOR

1. Obtain PBI/PI plain weave prepreg material and cut kits for a 16 ply quasiisotropic skin and an 8 ply quasiisotropic hat section.

2. a. Load skin material kit in rack, placing Armalon separator plies between each material ply.

   b. Enclose rack inside of sheet aluminum bag.

   c. With rack under vacuum, run devolatilization cycle, 300 degrees F for 15 minutes.

   d. Stack prepreg fabric skin plies as follows: (45/135)(90/0) 4s

   e. Bag per attached bagging scheme to contoured tool. See Figure 4
   f. Cure in autoclave as follows:
      Heat to 500 degrees F at 10 degrees F/minute
      Apply vacuum-500 degrees F for 1 hour
      Apply 200 psi pressure
      Heat at 10 degrees/minute to 725 degrees F
      Hold 30 minutes
      heat to 750 degrees F and hold 30 minutes
      Cool at 2 degrees/minute and remove

   g. Unbag and trim part as required.

3. a. Lay up and bag one ply of the hat section kit on the hat tool. Note: Tool has three hats.

   b. Run devolatilization cycle, 300 degrees F for 15 minutes. This cycle also preforms the ply to the hat shape.

   c. Repeat a and b for all 8 plies. Note: 2 plies were devolatilized together with armalon separator in between.

   d. Trim the preformed hat plies into three separate hat pieces.

   e. Stack preformed hat plies as per layup sheet.

   f. Bag on the hat tool.

   g Cure in autoclave as per 2f.

   h. Unbag and trim hat sections as required.

4. a. Prepare faying surfaces of skin and hat sections by scrubbing with scotchbrite and bon ami to obtain a water break surface.

   b. Obtain plaster mandrels to fill hollow area between hat and skin.

Table 10 (con't)

c. Assemble skin, hats and mandrels on the contoured tool.

d. Bag assembly using preformed aluminum bag.

e. Cure in autoclave as per 2f.

f. Unbag part, remove plaster mandrels, and clean off plaster dust and debris

g. Trim part as required

Figure 14
PBI/PI THREE HAT DOOR

BAGGING SCHEME FOR 16-PLY QI SKIN

$[(45/135)(90/0)]_{4S}$

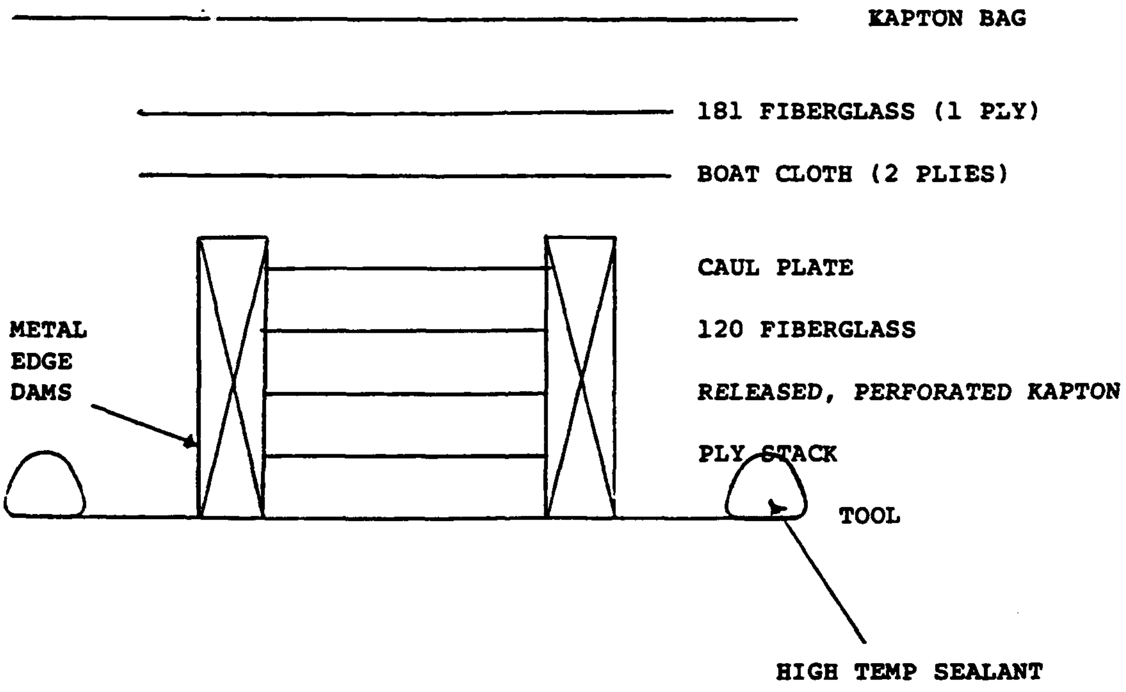


Figure 15 THREE HAT DOOR
TOP VIEW

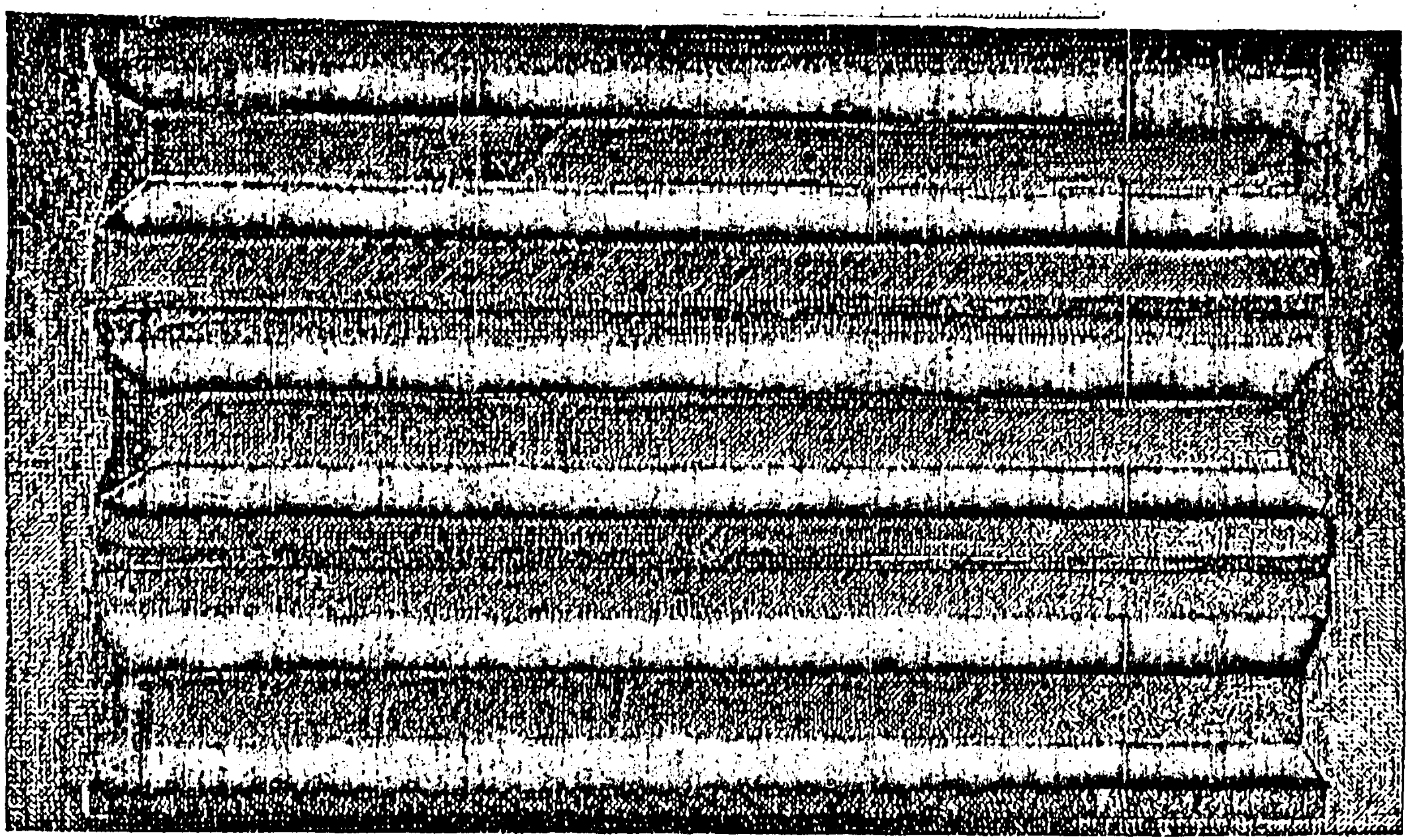
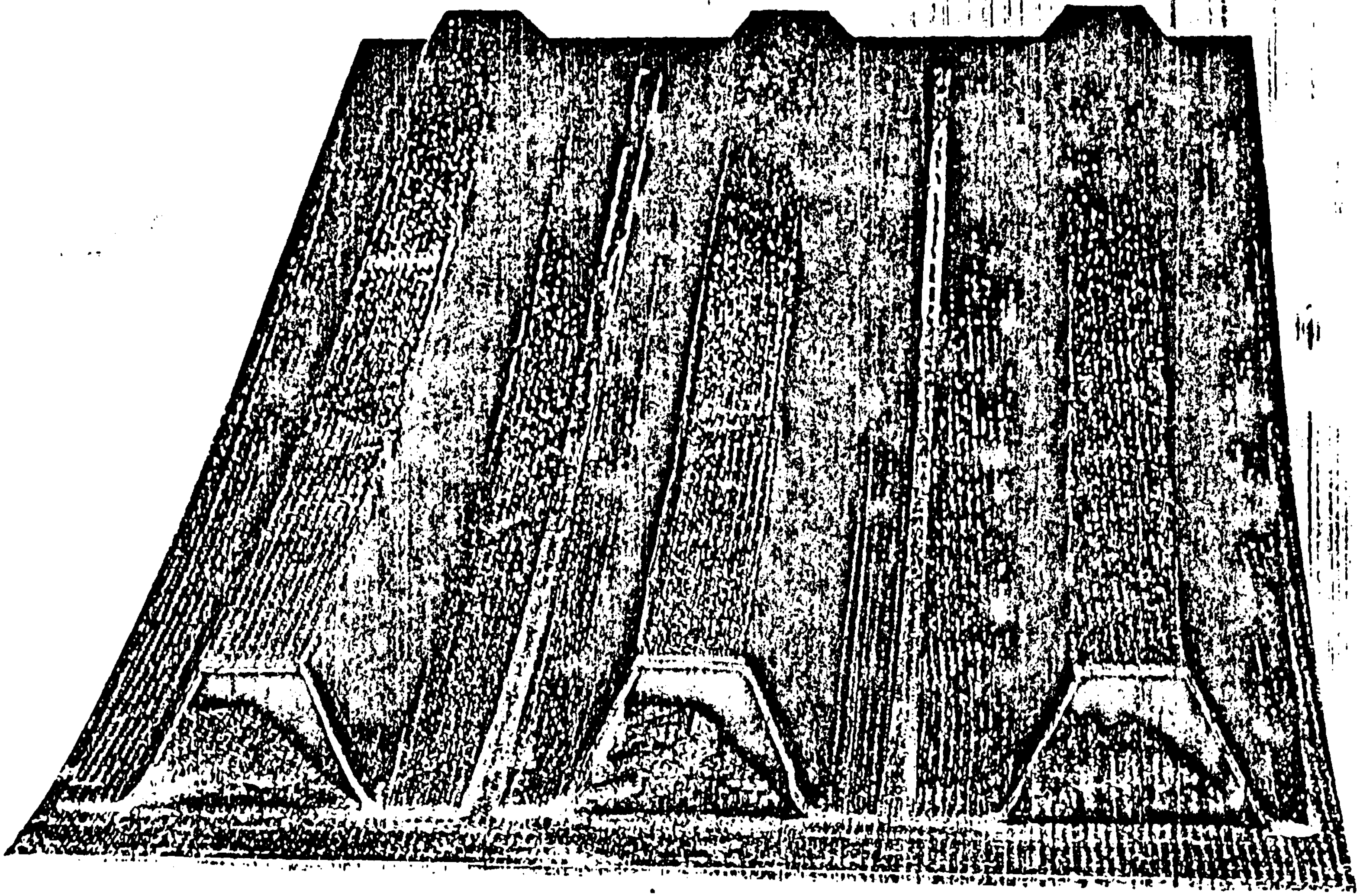


Figure 16 THREE HAT DOOR
FRONT VIEW



4.0 Summary and Conclusions

This program has demonstrated the feasibility of the development process of a PBI/copolyimide blend starting form the laboratory research and development polymer resin screening stage to fabrication of a complex aircraft part. The time period allotted for this highly ambitious program was approximately 3-4 years.

In this period of time, an evaluation of the blend fabrication parameters, including physical, analytical, rheological and mechanical characteristics of the various polymer blends was made, and fabrication of excellent quality prepreg on unsized fabric and tow was achieved. The final polymer blend in the program, the 10/90 ECPBI COPI-2, proved to be readily amenable to pilot plant scale-up production of large quantities of high quality prepreg fabric and tow. Mechanical properties, particularly compressive strength and stiffness, of the final resin blend were attractive.

Small panels were fabricated by high pressure processing in a press. Panels up to 16 plies were fabricated from both fabric and tape prepregs by conventional autoclave processing panel 16 and 32 ply panels were made by the THERM-X process. The panels included fabric, unidirectional, and quasiisotropic layups. Because of the high melt viscosity of the matrix resin polymer blend, high quality consolidation to a true monolithic structure was not achieved, and the resulting panels had flaws including voids and delaminations, as shown by ultrasonic C-scans and microscopic analysis of sections of the panels. However, microscopic inspection did indeed reveal the high quality of the prepregging process, and excellent wetting of the filaments in the fiber bundles. Additionally, C-scan and microscopic section analysis did indeed show areas in the panels where acceptable consolidation did occur, even though the overall panel quality was not acceptable.

As a final test of the applicability of the ECPBI/6FCOPI-2 matrix resin toward production of aircraft composite hardware, a demonstration part, consisting of a simulated TR-1 3-hat stiffened avionics access door, with dimensions 14"x25" with three 1 inch hat sections, was fabricated using AS4 plain weave prepreg fabric. The part consisted of a curved 16-ply quasiisotropic face sheet coconsolidated with three 8-ply QI hat stiffeners. The part appeared to be well consolidated and had an excellent outward appearance. The part was submitted to the prime contractor, Hoechst-Celanese Research Corporation, as a deliverable hardware item for the Lockheed Aeronautical Systems Company Subcontract No. LASC-88-HCC01.

Although very substantial progress was made during the terms of this contract on resin development, prepreg formulation and panel and part fabrication, the very high viscosity of the matrix polymer blend is a serious deterrent in the fabrication of acceptably well consolidated parts by conventional autoclave fabrication. Perhaps higher quality thick section parts could be made at higher pressures such as those used in the THERM-X process, but this is not immediately evident from the few THERM-X panels that were made.

Some improvements in processability were made at Celanese through improved molecular weight control, and it was shown that mechanical properites were not seriously compromised by endcapping the various segments of the polymer blend to control molecular weight. If further work is undertaken in PBI/PI blends, it is apparent that additional experiments in molecular weight control by endcapping should be an integral portion of the effort toward providing aircraft hardware for extended elevated temperature service under high mechanical loads.