NASA Contractor Report 4485

P-106

Advanced Composite Structural Concepts and Materials Technologies for Primary Aircraft Structures

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K. S. Y. Lau, A. L. Landis,
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CONTRACT NAS1-18888
FEBRUARY 1993

(NASA-CR-4485) ADVANCED COMPOSITE STRUCTURAL CONCEPTS AND MATERIALS TECHNOLOGIES FOR PRIMARY AIRCRAFT STRUCTURES: ADVANCED MATERIAL CONCEPTS Final Technical Report, Jun. 1989 - Jun. 1992 (Lockheed Aeronautical Systems Co.) 106 p

N95-29027

Unclas

H1/05 0051428

Date for general release February 28, 1995

NASA

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Prepared for
Langley Research Center
under Contract NAS1-18888

National Aeronautics and
Space Administration
Office of Management
Scientific and Technical
Information Program
1993

FOREWORD

This final technical report covers the work performed under Phase 1, Evaluation and Initial Development, Task 3, Advanced Material Concepts, of NASA Contract NAS1-18888 entitled, "Advanced Composite Structural Concepts and Materials Technologies for Primary Aircraft Structures," between June 1989 and June 1992. This contract is administered under the management direction of Dr. John G. Davis, and under the technical direction of Dr. Randall C. Davis, STPO, NASA Langley Research Center, Hampton, Virginia 23665.

Lockheed Aeronautical Systems Company (LASC) is the prime contractor. Mr. Anthony C. Jackson is the LASC Program Manager, directing all the contract activities. This task has been performed by Lockheed Missiles and Space Company, Inc. (LMSC) under an Inter-Company Work Transfer, under the technical leadership of Dr. Kreisler S. Y. Lau.

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SUMMARY

Development of lightweight polymer composite structural components for future aerospace vehicles is important for our civil, military, and space transport systems, particularly in supersonic transport. Materials technologies must satisfy the requirements of cost-effectiveness and durability, while maintaining high toughness and tensile modulus at temperatures, and achieving environmental and high-energy radiation resistance.

To achieve acceptable performance and long-term durability at elevated temperatures (350° to 600°F) for high-speed transport systems, further improvements of the high-performance matrix materials will be necessary to achieve very long-term (60,000-120,000 service hours) retention of mechanical properties and damage tolerance.

Polyimides are potentially suitable because of their demonstrated ultrahigh temperature tolerance and well-established chemistry. The more difficult processing problems inherent in thermoplastic polyimides are generally improved by their corresponding thermosetting analogs, the bismaleimides, which have their own attending shortcomings.

Thermoplastic polyimides and other polyheterocycles which possess high tensile modulus, high strength, and inherent toughness, are needed for future high-speed technologies, but are difficult to produce as cost-effective single-component resin systems. Multicomponent polymer resins via judicious blending of two or more selected polymers are expected to satisfy engineering design requirements, and be cost-effective to produce.

Our studies emphasize isoimide modification as a complementary technique to semi-interpenetrating polymer networks (SIPNs) to achieve greater processibility and better curing dynamics, and possibly enhanced thermomechanical properties in composites. A key result is the demonstration of enhanced processibility of isoimide-modified linear and thermosetting polyimide systems.

Results from our studies in isoimide modification of polyimides, copolymer formation, and semi-interpenetrating polymer networks (SIPNs), including the effect of end-capping on the processing rheology, will be discussed in the context of their relevance to processible high-performance composite matrix resins and structural adhesives.

The isoimide modification technique was specifically applied to NASA-Langley's high-performance materials, poly(BTDA-DAB)imide and poly(imide-sulfone), which lack processibility. Poly(BTDA-BDAF)imide and poly(PMDA-BDAF)imide derived from the

commercial EYMYD polyamic acid lacquers require harsh conditions to process into void-free laminates due to volatiles evolution. These polyamic acids were converted to the corresponding polyisoimides which are soluble in THF and more processible. Other emerging candidate polymers include Upilex, OPDA-based polyimides, and NASA Langley's LARC-CPI. Isoimide modification of these materials are also possible.

Many linear polyimides, previously unprocessible, can now be used in the isoimide form. The wider range of component miscibility permits increased tailorability of materials properties. The final cured product has the composition that would be obtained if it were possible to start with the imide forms of the components.

The demand for higher speed and better durability of the transport systems requires development of high-performance polymer materials suitable for bonding composite structural components fabricated from these high-performance materials. These technologies are important to future aerospace vehicles for our civil, military, and space transport systems, particularly in the supersonic realm.

Although polyimides possess excellent adhesive strengths and high- temperature stability, their inherently high melt viscosities (10^5 poise or higher) necessitate harsh bonding conditions, requiring high temperatures of up to 750°F, and high pressures of 200 to 1000 psi. SIPN approaches were applied at NASA to achieve more gentle processing conditions for these polyimide adhesives. SIPNs derived from both poly(BTDA-DAB)imide and poly(BTDA-3,3'-DDS)imide were shown to be still excellent adhesives, compared to the parent polymers, but need only bonding conditions of less than 500°F and 50 - 100 psi.

We examined the isoimide modifications of oligomeric and polymeric imides. The most successful SIPN system was prepared from poly(BTDA-APB)isoimide and the commercial Thermid IP-600 isoimide oligomers, which are structurally related.

The superior solubility of these isoimide materials in low-boiling solvents permits facile impregnation of tow and fabric for composite and adhesive applications. A comparison of the processing requirements for linear polyimides, SIPN polyimide blends, and SIPN polyisoimide blends demonstrates the improvement of processing by the SIPN and isoimide SIPN techniques.

Preliminary structural adhesive bonding studies were conducted with a number of substrates. The substrates included aluminum, aluminum-iron-cerium alloy CZ42, 1020 cold-rolled steel, and a silicon carbide whisker-reinforced metal matrix composite. Respectable adhesive strengths were obtained.

1.0 INTRODUCTION

The use of graphite-epoxy for conventional medium primary and secondary structures has been demonstrated to save weight compared to conventional metal structures and to meet all the strength, stiffness, and durability requirements of transport aircraft in commercial airline service. This is also true for military transport aircraft. However, the full potential of these composite materials has not yet been realized, primarily because cost savings have not been demonstrated in conjunction with efficient structural concepts.

The Advanced Composite Technology (ACT) Program was initiated to provide creative research on new and innovative structural concepts, in particular concepts for wing and fuselage primary structures, to achieve this potential for future transcentury aircraft. The new structural concepts are to take advantage of improved organic matrix materials and new and emerging fabrication techniques. The validated structures technology being developed under the ACT program is necessary to provide the confidence essential for the use of composite materials for future primary aircraft structures.

The Lockheed contract consists of two phases. Phase I, Evaluation and Initial Development, was initiated in May, 1989 and ran through June, 1992. Phase II, Development and Verification of Technology, was initiated in October, 1991 and is scheduled to run through April, 1995. The total program extends over 72 months.

Phase I consisted of five tasks: Task 1, Design/Manufacturing Concept Assessment; Task 2, Structural Response and Failure Analysis; Task 3, Advanced Material Concepts; Task 4, Assessment Review; and Task 5, Composite Transport Wing Technology Development.

Phase II consists of four tasks: Task 1, Advanced Resin Systems for Textile Technology; Task 2, Preform Development and Processing; Task 3, Design, Analysis, Fabrication and Test; and Task 4, Low-Cost Fabrication Development.

Phase I has been completed and Final Reports are published for Tasks 1, 2, and 3. Task 4 was an assessment of Phase I results and the plans for Phase II. Tasks 4 and 5 has no Final Report. The results were published in papers presented at the First and Second NASA-ACT Conferences.

This report covers the work performed in Phase I, Task 3.

Throughout this program, technical information gathered during the performance of the contract is being disseminated throughout the aircraft industry and to the Government. This information is being distributed through monthly reports and final task reports. Oral reviews have been conducted to acquaint the aircraft industry and government with progress on the program.

Use of commercial products or names of manufacturers in this report does not constitute official endorsement of such products or manufacturers, either expressed or implied by the National Aeronautics and Space Adminstration.

1.1 BACKGROUND

The state-of-the-art polymer composites technology serving subsonic transport systems is based on the well-established graphite/epoxy composites. Graphite/epoxy composites are suitable from a practical standpoint, since the usefulness of a polymer depends on its processibility and the cost of raw materials and processing. Epoxies are processible to different forms. They also have an extensive processing window at moderate temperatures, and an optimal solution or melt viscosity during processing. Solvent-free processing is most desirable. To facilitate composite manufacture, good fiber wetting and repeatable thermoformability are also key issues of concern. Graphite/epoxy composites essentially address most of the requirements except repeatable thermoformability.

Although graphite/epoxy composites are currently used in composites technology because of their easy processibility and low cost of raw materials and processing, their performance at temperatures beyond 200°F, particularly in a high-humidity environment, is generally inadequate. A representative state-of-the-art graphite/epoxy composite material, Hercules' AS4/3501-6, shows a 50% decrease of mechanical properties at 250°F. Other available epoxies that are modified with elastomeric or thermoplastic tougheners do not demonstrate better hot/wet performance.

The emerging high-temperature toughened epoxies, such as those from Shell Chemical Company, appear to have good hot/wet properties at temperatures to 250°F. This class of new epoxies may be adequate for subsonic aerodynamics provided that the damage tolerance and failure strain requirements are met.

The August 91 NASA-sponsored Seattle meeting on materials technologies concluded that more work is needed to develop and produce better polymer composites for high-speed civil transport (HSCT) supersonic aircraft technology to improve mechanical strength (toughness, modulus, and strength), thermo-oxidative stability (up to 600°F), and retention of strength after thermal cycling, environmental and thermooxidative wear and tear over 60,000-120,000 hours.

Optimizing processibility, mechanical strength, and damage tolerance for structural matrices can be achieved by thermoplastic/thermoset blending, as exemplified by toughened epoxies, BMIs, PMR, and semi-interpenetrating polymer network (SIPN) blends, in which improved failure strain and damage tolerance of thermosets are provided from thermoplastic components.

Supersonic aircraft demands sustained performance at 400°F. The long-term durability (60,000-120,000 hours) issue translates to requiring performance at 600°F. This may eliminate epoxy formulations in favor of high-performance polyimide- or BMI-based composites, which better retain useful properties even after exposure to the stresses of temperature, atmosphere, chemical, mechanical, electrical, and irradiation over time [1]. The imide function allows isoimide modification to improve polymer processibility [2-5].

Candidate HSCT polymers include Langley's LARC-TPI, LARC-ITPI, LARC-CPI, and the toughened PMR-type SIPN systems, such as RP-46. LARC-ITPI is an emerging cost-effective thermoplastic polyimide for HSCT applications [6-8]. Lockheed's on-going polyisoimide development complements NASA's direction. Other potential candidates are DuPont's Avimid-N, K-III, and K-IIIB; Ethyl's EYMYD L20N; NASA-Lewis' PMR-II-30 and newer variations (PMR-II-50, VCAP 75, AFR 700B, and EMTL-8-T); OPDA-based polyimides (Oxychem); and Upilex polyimides (Ube Industries).

Durability relates to quantification of microcracking, mechanical strength, ultimate strength, and the temperature for 100% property retention. Thermal cycling testing should bracket ambient-to-600°F, and include such variables as number of cycles, dT/dt, humidity, P, and perhaps dP/dt.

1.2 TECHNICAL RELEVANCE OF POLYIMIDES

Advanced composites suitable for HSCT are concerned with such key attributes of high-performance polymer materials as a high level of fracture toughness, high modulus and strength, especially in compression, and environmental durability. State-of-the-art technologies indicate that high-performance polymers meeting the high-temperature requirement are mostly polyimides. Polyimides can be used over a broad range of temperatures, even to beyond 700°F for a brief time. Isothermal weight loss studies over a 200-hour span at 700°F in air indicated that polyimides fare significantly better than other processible nitrogen-containing polyheterocyclic polymers.

Polyimides have a well-defined chemistry and a vast literature data base to allow many possibilities for structural modification. Many polyimide systems have demonstrated usefulness as structural matrices and adhesives. Although polyimides are generally difficult to process, they are amenable to isoimide modification for the enhancement of processibility. Processibility and cost-effectiveness determine their ultimate usefulness.

Bismaleimides (BMIs) are baseline imide-type materials to serve the future HSCT needs. The BMI technology emphasizes mimicking the easy processing of epoxies in imide-tpye materials. Since BMIs are thermosets, the attending generic problems of microcracking, brittleness, and thermo-oxidation must be addressed. BMI-toughening studies address the microcracking problem. Recent NASA and Lockheed/Rohr work on SIPN polymer blending offers a fruitful technique in property enhancements for BMIs and the related PMR resins [9-11].

There is a demonstrated commercial availability of a variety of high-performance polyimides and their constitutive monomers. Using these available monomers, NASA developed such thermoplastic polyimides as LARC-TPI, LARC-ITPI, LARC-CPI, and LARC-PIS. Other high-temperature resistant polyimide systems include Ube's Upilex polyimides, Ethyl's EYMYD resins, and OPDA-based polyimides. DuPont's thermoplastic NR 150-B2 (Avimid N prepregs) has the highest long-term thermo-oxidative staibility. The semicrystalline nature of LARC-CPI and Upilex permits molecular orientation to achieve modulus enhancement to about 1.4 million psi.

It is possible to modify these existing polyimide systems to produce multicomponent blend materials to fit the needs of viscosity, solubility, and flow. The technique of isoimidization also contributes to improve solubility and melt viscosity of polyimides and imide- containing thermoplastics and thermosets, such as poly(imide-sulfones), poly(ether-imides), poly(ether-ketone-imides), and other imide-heterocycle hybrids.

Polymer blending provides an avenue to tailor make polymers with balanced thermomechanical properties. In principle, it allows virtually unlimited permutations. A definable pathway to advance current composites technology to address the temperature, environmental, and durability issues of high-speed transport systems is at hand.

1.3 COMPREHENSIVE COMPOSITES DEVELOPMENT PROGRAM

NASA scientists have been evaluating several types of polymers for their potential as high-performance materials for advanced composites. These polymer types are toughened thermosets, notably the thermoplastically toughened PMR-based SIPNs, amorphous and semicrystalline thermoplastic polyimides [12-14].

Hergenrother suggested that a composite materials development program should consist of the following elements [1]:

- Polymer screening and selection;
- Polymer optimization to obtain the best overall combination of properties;
- Polymer scale-up;
- Prepreg development;
- Composites fabrication development to ensure quality composites;
- Thermomechanical testing, including fatigue and creep;
- Thermal cycling, quantification of microcracking;
- Correleation of microcracks and maximum temperature for 100% property retention;
- Degradative mechanisms;
- Time/temperature/stress/humidity testing;
- Real time versus accelerated aging.

Culmination of this composite materials development program is prototype fabrication and final verification of mechanical properties.

A key element in the materials development program is materials scale-up. The selection of a synthesis methodology is directed toward a straightforward and high-yield process. Procedures requiring too many steps and isolation of intermediates are deemed nonexpedient and labor-intensive. This philosophy underscores any materials development program, since cost-effectiveness is essential to fabrication and manufacture of large primary structures.

2.0 MATERIALS DEVELOPMENT FOR HIGH-SPEED RESEARCH

The strongest attributes of polyimides are their capacity to retain useful mechanical properties even after long-term exposure to temperature variations, the atmosphere, chemicals, mechanical and electrical stress, and irradiation [1]. The key issues for their ultimate utility, however, are processibility and cost-effectiveness.

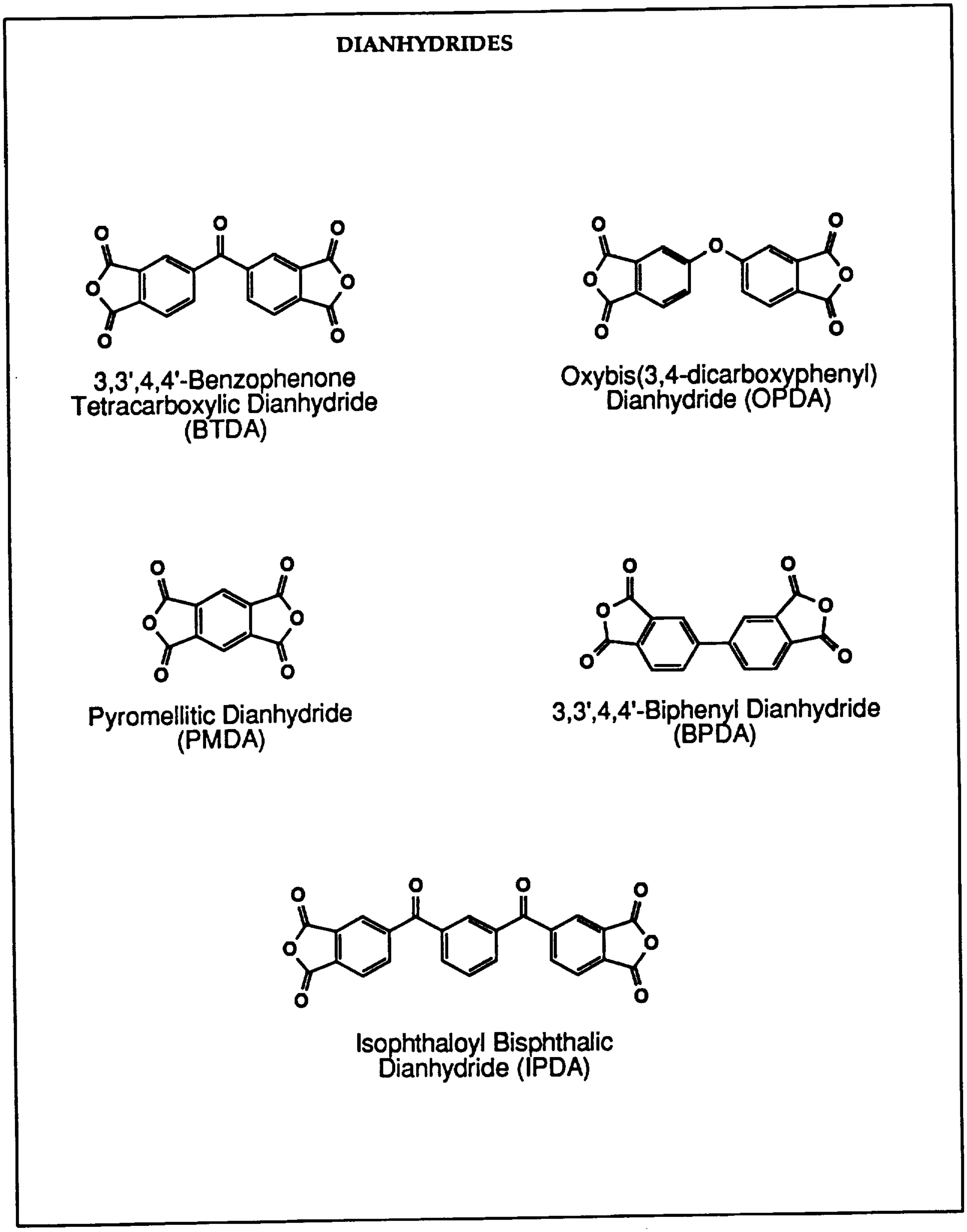
The supply of monomers allows permutations of these monomers to generate new polymers and copolymers. A glossary of these materials is presented in **Figure 1.** Using these available monomers, NASA developed such thermoplastic polyimides as LARC-TPI, LARC-ITPI, LARC-CPI, and LARC-PIS. Other high-temperature resistant polyimide systems include Ube's Upilex polyimides, Ethyl's EYMYD resins, and OPDA-based polyimides. For long-term thermo-oxidative stability, DuPont's thermoplastic NR 150-B2, used in the Avimid N prepregs, is a front runner. The semicrystalline nature of LARC-CPI and Upilex permits molecular orientation to achieve modulus enhancement to about 1.4 million psi.

The reliable source of monomers and practical purification techniques for polyimides makes it possible to modify these polyimides chemically to produce hybrid-imide materials to fit the needs of viscosity, solubility, and flow. Specifically, isoimidization provides a means to improve solubility and melt viscosity of polyimides. As will be discussed later, isoimide modification and polymer blending are two key technologies in the improvement of processibility of materials.

2.1 POLYMER BLENDING

The supersonic polymer materials have higher aromatic character and are more rigid and less amenable to RTM processing. Different types of polymer blending techniques, such as thermoplastic polymer alloying, semi-interpenetrating polymer networks (SIPNs), and fully interpenetrating polymer networks (FIPNs), can tailor make resin formulations to match the processing requirements by using existing polymers to provide new compositions.

Polymer alloying is exemplified by the Karasz-MacKnight approach of blending two or more thermoplastic polymers, such as polybenzimidazole (PBI) and polyimide. Several toughened PMR-type resins are examples of recent developments in SIPN systems [9, 10].



DIANHYDRIDES

3,3',4,4'-Benzophenone Tetracarboxylic Dianhydride (BTDA)

Oxybis(3,4-dicarboxyphenyl) Dianhydride (OPDA)

Pyromellitic Dianhydride (PMDA)

3,3',4,4'-Biphenyl Dianhydride (BPDA)

Isophthaloyl Bisphthalic Dianhydride (IPDA)

Figure 1a. **Glossary of Aromatic Dianhydrides for Polyimide and Polyisoimide Synthesis**

DIAMINES

$H_2N\text{-}AR\text{-}NH_2$

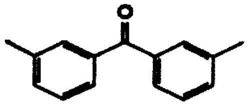
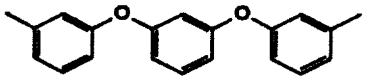
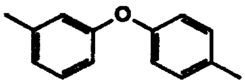
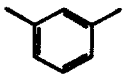
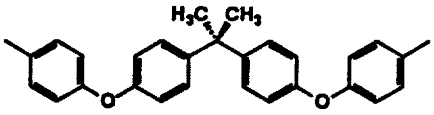
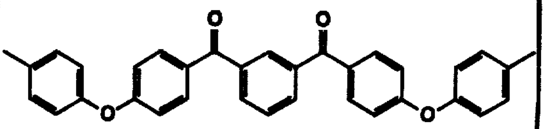
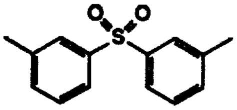
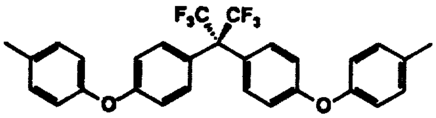
Name	Acronym	Ar
3,3'-Diaminobenzophenone	DAB	
1,3-Bis(3-aminophenoxy)-benzene	APB	
3,4'-Oxydianiline	3,4'-ODA	
1,3-Diaminobenzene (*meta*-Phenylenediamine)	MPDA	
2,2-Bis[4-(4-aminophenoxy)-phenyl]propane	BAPP	
1,3'-Bis[4-(4-aminophenoxy)-benzoyl]benzene	1,3'-BABB	
3,3'-Diaminodiphenylsulfone	3,3'-DDS	
2,2-Bis[4-(4-aminophenoxy)-phenyl]hexafluoropropane	BDAF	

Figure 1b. Glossary of Aromatic Diamines for Polyimide and Polyisoimide Synthesis

Lockheed's work in SIPN blending of thermoplastic polyisoimides with acetylene-terminated isoimide thermosetting oligomers also demonstrates better melt impregnation and resin consolidation to void-free laminates [2-5]. These multicomponent blend systems are practical modifications of the interpenetrating polymer network (IPN) concept [15].

Figure 2 illustrates the deleterious effect of porosity on matrix-sensitive laminate strengths. It is imperative to develop polymers that have an optimal flow characteristic (are processible) at the melt temperature to ensure complete fiber wetting and eventually produce void- free panels after consolidation.

Toughened PMR-type SIPNs demonstrated improvement in composites compressive and shear strengths, as exemplied by results from NR150-B2/PMR-15 (**Figure 3**), and recent Lockheed/Rohr results on polyimides/polyisoimides and PMR-II (**Table 1**).

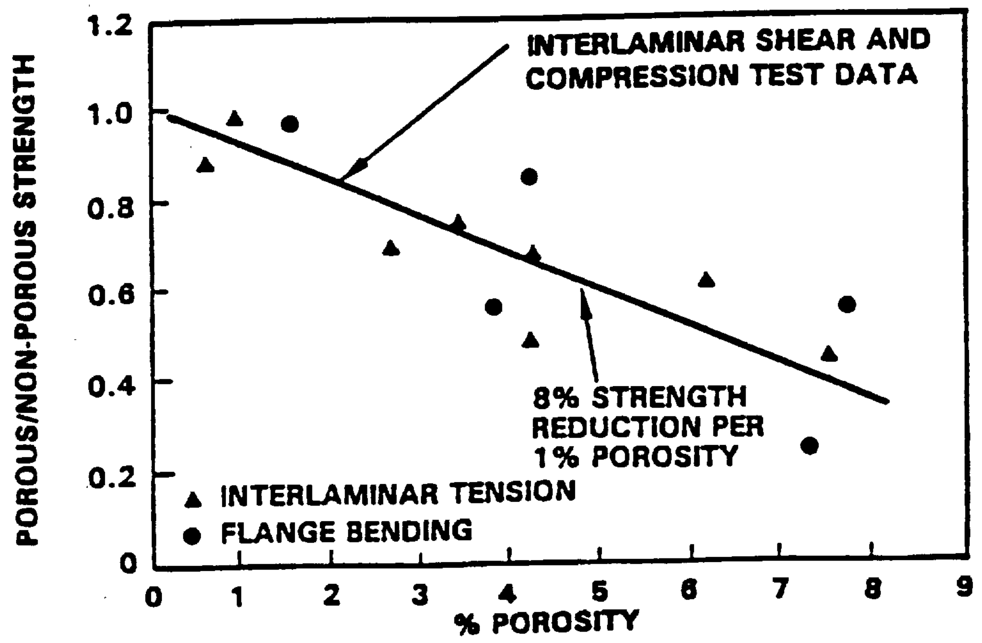


Figure 2. Matrix-Sensitive Strength Properties versus Percent Porosity (Data available from Rohr Industries)

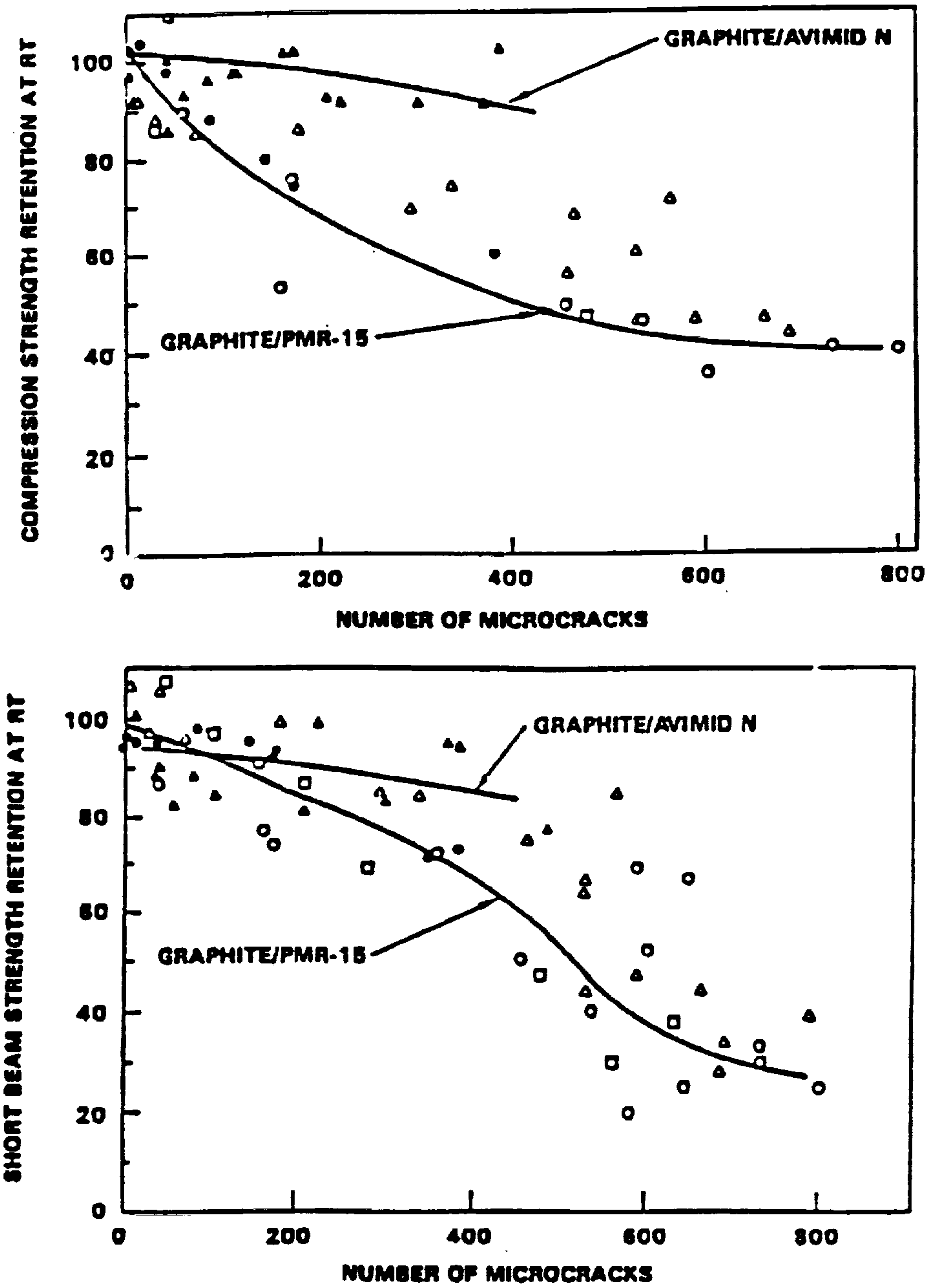


Figure 3. Compressive Strength and Shear Strength Retention versus Number of Microcracks Showing NR 150- B2/carbon fiber Composite is Superior to PMR-15/Carbon Fiber Composite.

Neat resin fracture toughness (G_{1C}) on polymer blends have confirmed that incorporation of a thermoplastic component (TP) increases the toughness of the blends, sometimes dramatically. Laminates fabricated from some of the blends were thermal cycled from 0 to 450°F for 2,000 cycles. Transverse microcrack counts (TVM/in), also shown in **Table 1**, show that blending by TP will improve the microcracking resistance of thermosetting polyimides [9].

Recent polymer studies emphasize the molecular weight control aspects. This approach provides a control on melt "processing window" and viscosity over time and temperature cycling. Melt stability due to a controlled molecular weight indirectly improves control on cure process parameters and, thus, reliability and quality.

The blending of a reactive oligomer (maleimide or acetylene-terminated) and an 8,000-15,000 molecular weight thermoplastic component, terminated with a reactive end-capper, produces a fully interpenetrating polymer network (FIPN). FIPNs represent a special example of topological isomerism in macromolecules. The reaction between pairs of end-groups among these long and short components provide permanent entanglements. Synergistic enhancement of tensile strengths was demonstrated with FIPNs of polyurethanes and polyacrylates [15].

The recent blending study at NASA of a BMI with an acetylene-terminated polyimide probably resulted in an FIPN. In this system, the acetylene-terminated imide oligomer undergoes chain extension to achieve higher molecular weight and also cross-linking to interlock with the BMI network. The 1:1 FIPN formed from BMI Compimide with bisbenzocyclobutene-imide has high weight retention under isothermal aging in air at 650°F over a 200-hour span [16].

Table 1. Fracture Toughness and Transverse Microcrack of Polymer Blends

TS1 PMR-II	TS2 IP-600	TP1 Matrimid	TP2 LA-100	G_{1C}(J/m^2)	TVM/in* (2,000 cycles)
100%	--	--	--	476	231
75%	--	25%	--	1932	54
75%	--	--	25%	1610	--
--	75%	25%	--	1080	192

* TVM/in for PMR-15 (various sources) ranges 250-300 after 2,000 cycles.

Other examples of FIPN networks are those studied by Stenzenberger and coworkers, who blended maleimide-terminated prepolymers with prepolymers having vinyl or benzocyclobutene end-groups. FIPN blending results in toughening the thermoset systems, as indicated by an enhancement of G_{1C} fracture energy [17].

Lockheed developed a thermoplastic-modified BMI composite matrix with excellent optimization of thermal stability, processibility, damage tolerance, and mechanical properties [11]. The material consists of Ciba-Geigy Matrimid 5292 BMI formulated with Matrimid 5218 thermoplastic polyimide. The Matrimid 5218 thermoplastic is dispersed as a finely divided second phase. The interphase, however, consists of a concentration gradient and does not have a definable interface between the thermoset and the thermoplastic domains. This allows the thermoplastic additive to act as a crack stopper, without the tendency to generate crack propagation pathways as with a sharp phase boundary. The interphasal consistency of this system is an SIPN between the thermosetting BMI and the thermoplastic polyimide.

This material can be processed at 350°F at 200 psi. The prepreg has excellent tack and drape. A free standing postcure at 400-450°F yields excellent mechanical properties. Particularly notable is the substantially higher compression strength-after-impact of 37.6 ksi compared with 22 ksi for the state-of-the-art materials. This matrix, with a wet Tg of 550°F, appears to be capable of long-term service at temperatures of 400-500°F, and is an potential candidate for long-term service even on supersonic aircraft.

2.2 ISOIMIDE MODIFICATION

Earlier SIPN work at NASA-Langley emphasized polyimides and polyamic acids. The imide moiety in the polymer chain generally makes the polymer insoluble. Only in very special cases are the linear polyimides soluble enough to be useful for the SIPNs. The alternative procedure is to use the more soluble amic acid precursor of the polyimide. This severely limits the expediency of fabricating thick composites because of volatile evolution during cure. High pressures are generally required to minimize void content in the consolidated composites.

The use of the more processible isoimide form of the linear polyimide and reactive oligomeric components alleviates the solubility and the volatiles problems. The structural asymmetry of the isoimide function generally contributes to higher solubility and lower melt viscosity than the imide form. In a model study with N-substituted phthaloisoimides, a dramatic decrease in the melting point of the isoimide form from that of the imide was observed. Also, the solubility of the isoimide form in a number of common solvents, in which the imide form is sparingly soluble, is greatly increased [18]. Isoimide modification in polyimide synthesis was used previously [19].

The isoimide converts to the imide during cure, without evolution of volatiles. The well-defined and reproducible chemical synthesis of polyamic acid, polyisoimide, and polyimide provides easy quality control (**Figure 4**). The isoimide modification technique improves the melt and solution processibility of poly(imide-sulfones), poly(ether-imides), poly(ether-ketone-imides), and other imide-heterocycle hybrids. Previously unprocessible linear polyimides can now be blended. Complete miscibility was achieved over a wider variation of the ratio of the thermoplastic and thermoset components.

An illustrative example is the comparison between LARC-TPI polyimide and its isoimide analog (**Table 2**). Scale-up potential of this technology was previously demonstrated by Lockheed researchers and National Starch and Chemicals Corporation. National Starch has a commercial line of isoimide polymer products.

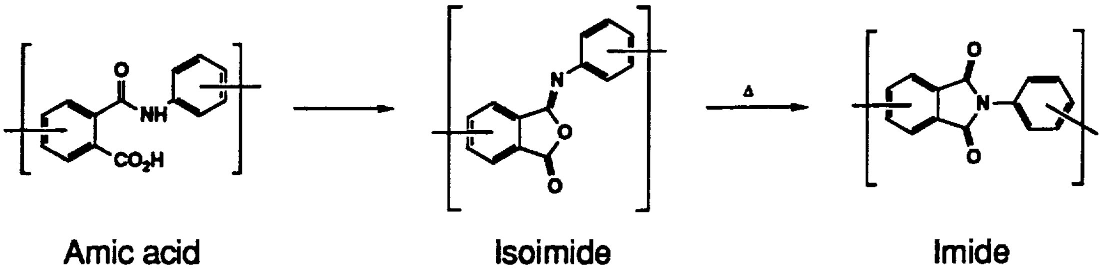


Figure 4. **Chemistry of Isoimide Modification**

Table 2. Comparison of Processibility Between LARC-TPI and its Isoimide Analog

Poly(BTDA-DAB)Imide (LARC-TPI)	Poly(BTDA-DAB)Isoimide (Isoimide Analog)
o Insoluble (DMAC)	o Soluble (DMAC, amides)
o Processed by powder methods	o Facile film-forming
o Prepregged from amic acid	o Potential for volatile-free prepregging
o High melt viscosity	o Lower melt viscosity and processing temperature
o Volatiles during processing	o Easy isoimide to imide conversion without volatiles

3.0 RESULTS AND DISCUSSION

Polymer composites suitable for high-speed transport must possess high thermal and thermo-oxidative stability, and high levels of fracture toughness, compressive modulus and strength. The major concern is long-term durability to withstand the environment and thermomechanical cycling. Most candidate polymer materials suitable for supersonic technology are polyimide-type materials, enhancement of processibility can be achieved by isoimide modification. Chemical modification of imide polymers is an established viable approach to property tailoring. Certain polyimides show semi-crystalline morphology and enhanceable anisotropic strength and modulus through orientation.

The technical goals specific to Task 3 (Advanced Materials) of the NASA ACT program entail the development of existing and more advanced materials that exhibit the greatest potential for property and/or process improvements, through chemical modification and blending.

Task 3 emphasizes the isoimidization of various polyamic acids, the characteristization of polyisoimides and their conversion to the polyimides. Polyisoimides were used in SIPN systems which are each formed by blending a thermoplastic polyisoimide with a thermosetting acetylene-terminated isoimide oligomer. The results have demonstrated that isoimide modification enhances processibility of polyimides.

3.1 POLYMER CANDIDATES FOR HSR

The most thermally-stable polyimides are those containing the hexa-fluoroalkylidene (6F) links. These include Ethyl's EYMYD resins, DuPont's NR150-B2, NASA's PMR-II, and TRW's AFR-700B resins. Noted for its long-term thermo-oxidative stability is DuPont's thermoplastic NR 150-B2, used in the Avimid N prepregs. Recent synthetic efforts resulted in various 6F-containing polymer types, including poly(thioether-ketones) [20], poly(ester-ethers) [21], polyacrylates [22], poly(imidine-esters) [23], poly(amide-imides) [24], polyimides and polybenzoxazoles [25, 26], and poly(phthalonitriles) [27]. The latter four types are particularly relevant to high-temperature usage. Although the cost issue limits their utility in large-scale composites fabrication, they are suited for the small-volume electronic and photonic applications.

A series of high-performance polyimides was selected for the evaluation of isoimide modification as a means of processibility enhancement. These polyimides are potential matrix resin and adhesive candidates for advanced composites. Their constitutive monomers are commercially available. Using these available monomers, such thermoplastic polyimides as poly(BTDA-DAB)imide [NASA's LARC-TPI], poly(IPDA-MPDA)imide [LARC-ITPI], poly(BTDA-1,3'-BABB)imide [LARC-CPI], and poly(BTDA-3,3'-DDS)imide [poly(imide-sulfone)] were synthesized previously at NASA. Except LARC-CPI, the other three polymers are now commercially available in experimental quantities. Other high-temperature resistant polyimide systems include Ethyl's BDAF-based polyimides (available as the polyamic acid lacquers L20N and L30N), Ube Industries' 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA)-based Upilex polyimides and Oxychem's oxybis(3,4-dicarboxyphenyl) dianyhydride (OPDA)-based polyimides. The semicrystalline nature of LARC-CPI and Upilex permits molecular orientation to achieve tensile modulus enhancement [13].

3.2 SYNTHESIS AND CHARACTERIZATION OF POLYISOIMIDES

In our laboratories, the isoimide form of all these polyimides have been synthesized from their respective polyamic acids. We synthesized a series of BTDA-based copolyisoimides comprising different ratios of the diamines APB and 3,4'-ODA. To compare with the EYMYD polyimides, we also synthesized a series of BDAF-based copolyisoimides from BDAF and different ratios of the dianhydrides BTDA and PMDA. The processibility (viscosity, solubility, and flow) of the polyisoimides is significantly better than their imide counterparts. Selection of 3,4'-ODA and BDAF is based on their contribution to thermo-oxidative stability of the rersulting polymers.

Compared to epoxies, the higher strength, better long-term environmental resistance and durability, and higher toughness of polyimides warrant considerations for their potential utility in providing better creep and fatigue resistance, and improving the mechanical properties (especially in hot/wet strengths) of current composites technologies. A cursory investigation revealed that good retention of hot/wet laminate properties at 177°C (350°F) was exhibited by polyimides and copolyimides which resulted from processing of poly(IPDA-MPDA)isoimide (i.e., LARC-ITPI isoimide), poly(BTDA-DAB)isoimide (i.e., LARC-TPI isoimide), copolymers derived from poly(BTDA-APB)isoimide (LA-100) and poly(BTDA-DAB)isoimide, and copolymers derived from LA-100 and poly(BTDA-3,4'-ODA)isoimide.

3.2.1 Synthetic Technique of Isoimidization

The general synthetic technique for the preparation of various polyisoimides of different molecular weights entails (1) the formation of the polyamic acid precursor by the reaction of stoichiometric amounts of acid anhydride, the diamine, and the end-capping agent phthalic anhydride (PA), in an appropriate solvent, such as tetrahydrofuran (THF), N,N-dimethylacetamide (DMAC), and N-methylpyrrolidinone (NMP); (2) cyclodehydration of the polyamic acid with a stoichiometric quantity of N,N'-dicyclohexylcarbodiimide (DCC) to yield the polyisoimide and the insoluble by-product, N, N'-dicyclohexylurea, (DCU), which can be removed by filtration; and (3) precipitation of the polyisoimide from the reaction solution with isopropyl alcohol, or acetone.

Fine-tuning of the reaction parameters to achieve a reproducible procedure resulted in higher yields and better quality of isoimides. Earlier, the cyclodehydration of the polyamic acid with DCC was carried at 25°C for the various combinations of dianhydrides and diamines. Lowering the temperature during the cyclodehyration step to 0-5°C suppressed the gellation tendency of the reaction mixture. A specially-designed thermostatted reaction vessel was used in performing the synthesis.

While poly(BTDA-APB)isoimide (LA-100) is unique in its high solubility in THF, the other polyisoimides are better solubilized in DMAC or NMP, the latter being safer, more economical, and more convenient to use in large-scale productions.

3.2.2 Acetone as Solvent for Precipitation

More recently, the use of acetone during the polymer isolation step offers a major significant improvement in minimizing solvent occlusion. The acetone work-up procedure precipitates the polymer in a finely-divided powder form. Solvent occlusion, which can become a technical problem in larger-scale synthesis, as indicated in many earlier runs using isopropyl alcohol as the solvent for precipitation, is minimized to less than 2 %. The solid-state instability of poly(BTDA-DAB)isoimide observed previously in samples obtained from isopropyl alcohol isolation has been ascertained to be the result of ineffective solvent removal. A Soxhlet extraction with ether is required to remove occluded NMP solvent. This additional purification step would add considerable cost to large-scale syntheses.

Experiments of the same reaction, of varying scales and under identical conditions, using acetone as the solvent for precipitation, consistently produced poly(BTDA-DAB)isoimide as a fine powder. All end products were characterized by consistent FTIR, thermal analytical, and rheological measurements.

In most recent experiments, good quality powders of polyisoimides derived from various combinations of dianhydrides and diamines, were obtained. **Figure 5** shows an exemplary synthesis of poly(IPDA-MPDA)isoimide.

From the scale-up safety standpoint, replacement of acetone with the higher homolog, methyl ethyl ketone, was deemed necessary. As described later, methyl ethyl ketone is a suitable replacement.

3.2.3 Effect of Molecular Weight Control

Molecular weight control imparts melt stability to the polymer systems. In addition, rheological data suggest a wider processing window and reduced viscosity, relative to the polymer without their molecular weights controlled by end-capping. In the polyisoimides studied, virtually identical Tg's were obtained for DP 10 and DP 50 samples as compared to higher molecular weight samples. Related research data from NASA also showed that polymers end-capped at MW 15,000 suffer no loss in tensile modulus when compared to polymers of higher molecular weights. Tensile strength, however, becomes invariant only when a threshold value (about M_w 65,000, measured in NMP) is attained [28].

Timing for the addition of the end-capping agent, i.e., phthalic anhydride (PA), either at the beginning of polymer synthesis or at a 2-hour to 24-hour delay, did not have any effect on the molecular weight distribution of the resulted polymer.

3.2.4 Molecular Weight Measurements of Polyisoimides

Ambiguous results in molecular weight determination were often obtained in NMP solvent. Molecular weight values are relative values calibrated against commercial polystyrene standards. Gel permeation chromatographic measurements of these polyisoimides produce molecular weight values in THF solvent in the expected range. Those values obtained in NMP solvent are several times or an order of magnitude larger. Solvent coordinative interaction is accountable for this anomaly. Addition of lithium salts (bromide) tends to break up this coordination effect. To facilitate molecular weight measurements, we calibrated this solvent effect.

Six (6) different molecular weight ranges of poly(BTDA-APB)isoimide (LA-100) were prepared: DPs = 1, 5, 10, 15, 25, and 50. The new calibration curves eventually obtained from this study are used for molecular weight determination in NMP solvent. The analytical results are summarized below in **Table 3**.

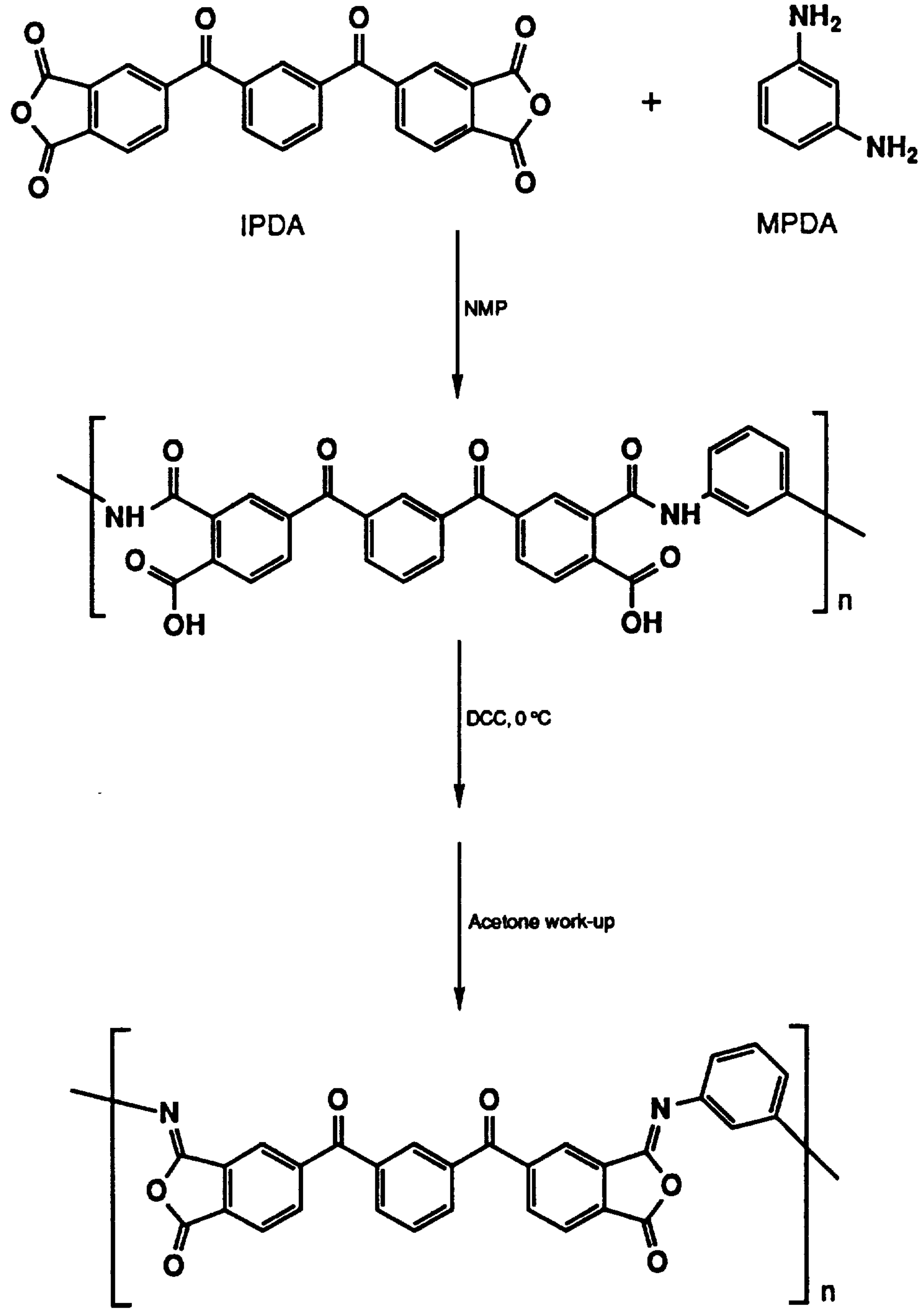


Figure 5. An Exemplary Synthesis of Poly(IPDA-MPDA)isoimide

Table 3. GPC Calibration for Molecular Weight Analysis in THF and NMP (Results Based on Poly(BTDA-APB)isoimide)

Degree of Polymerization (DP)	Theoretical Molecular Weight	Mn		Mw		Mz	
		THF	NMP	THF	NMP	THF	NMP
0	552	---	---	---	---	---	---
1	1058	1035	2160	3150	5020	22100	32000
5	3082	2860	5450	10400	15100	22500	35900
10	5612	4070	7540	16200	22650	29300	53400
15	8142	5050	8730	21800	30700	39800	61200
25	13202	6090	12200	33500	47400	61900	93000
50	25852	6140	12600	46000	63900	86500	120000

3.2.5 FTIR Characterization

The characteristic infrared absorptions of polyisoimides are the carbonyl band at 1790-1841 cm^{-1} and the imine band at 1680-1730 cm^{-1}, both intense. The characteristic broad band at 900-950 cm^{-1} is attributable to the lactone ring with an exocyclic double bond. A typical FTIR spectrum of polyisoimides is shown in **Figure 6**. The isoimide-to-imide conversion can be routinely monitored by the disappearance of these bands with the concomitant growth of the characteristic imide absorptions at 1776-1795 (asymmetric), 1707-1730 (symmetric), and at 1380 cm^{-1}. **Figure 7** shows comparative FTIR spectra of poly(BTDA-APB)isoimide before and after thermal isoimide-to-imide conversion. Comparable polyimides give similar infrared measurements [29]. The other characteristic imide absorptions at 1130 cm^{-1} and 710 cm^{-1} are generally shadowed by stronger bands at 1100-1180 cm^{-1} and at 670-700 cm^{-1} respectively, assignable to the isoimide. The amic acid absorption at 1535 cm^{-1} is conspicuously absent from both the isoimide and the imide spectra. Conversely, its presence indicates incomplete isoimidization.

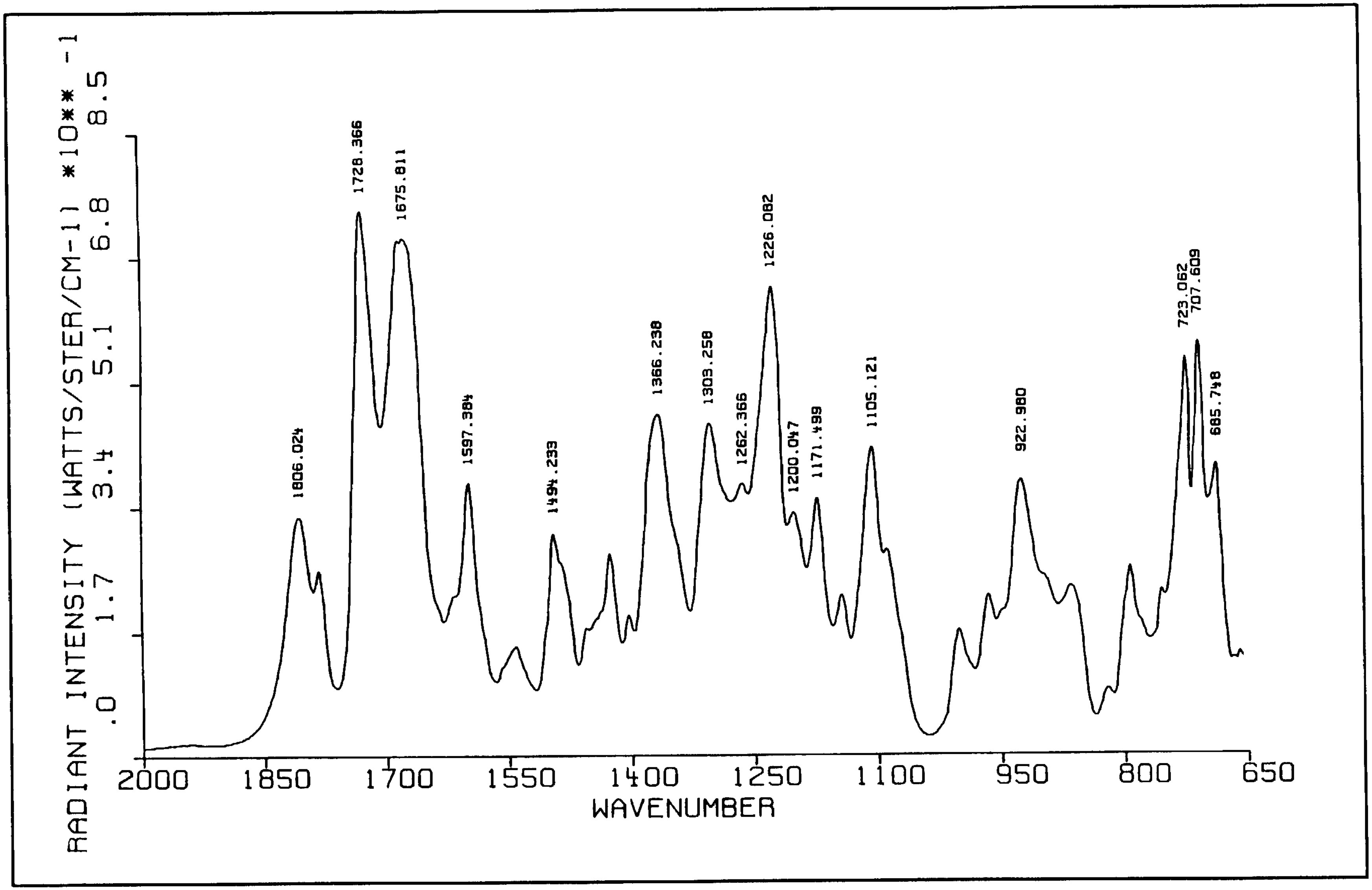


Figure 6. A Typical FTIR Spectrum of Polyisoimides, as exemplified by Poly(IPDA-MPDA)isoimide

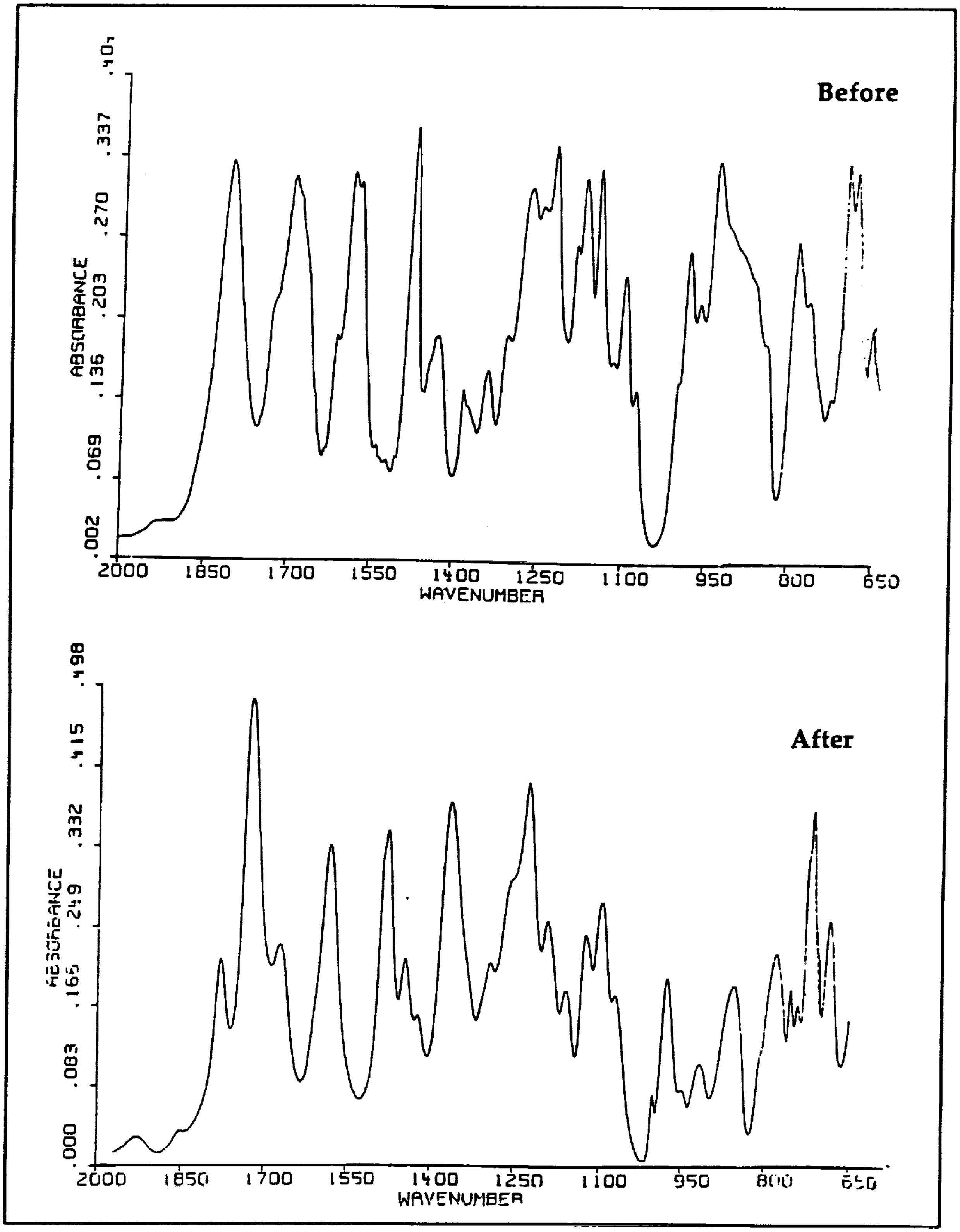


Figure 7. Comparative FTIR Spectra of Poly(BTDA-APB)isoimide Before and After Thermal Isoimide-to-Imide Conversion

3.2.6 Thermal Analysis

All thermochemical behavior and glass transition temperatures (Tg's) of the polyisoimides were obtained by differential scanning calorimetry (DSC). DSC specimens after the temperature ramp were cooled down slowly to ambient and rescanned to 400°C to capture the Tg's of the corresponding polyimides. Thermo-oxidative stability of the materials is ascertained qualitatively by their resistance to degradation in air under thermogravimetric analytical conditions. Table 4 summarizes some physical and thermal characterization results.

Table 4. **Physical and Thermal Characterization of Polyimide Materials**

TRIVIAL NAME	POLYMER CONSTITUENT		PHYSICAL & THERMAL EVALUATION				
	Dianhydride	Diamine	soluble in	ease of synth	Tg in °C	η^*, poise (Tmin)	wt loss§ T(onset)
Polyisoimide LARC-ITPI	IPDA	MPDA	DMAC NMP	1	259	1780 (250)	548
Polyisoimide O-10	BTDA	3,4'-ODA	DMAC NMP	2	254	2880 (243)	547
Copolyisoimide O-31	BTDA	3,4'-ODA (3) APB (1)	DMAC NMP	1	233	7720 (220)	548
Copolyisoimide O-11	BTDA	3,4'-ODA (1) APB (1)	DMAC NMP	1	217	59000 (218)	560
Copolyisoimide O-13	BTDA	3,4'-ODA (1) APB (3)	DMAC NMP	1	208	19100 (212)	590
Polyisoimide LA-100	BTDA	APB	THF, NMP DMAC	1	191	7020 (236)	570
Polyisoimide LARC-TPI	BTDA	DAB	DMAC NMP	1	260	1076 (243)	540
Polyisoimide B-10	BTDA	BAPP	DMAC NMP	2	236	41600 (213)	563
OPDA-based Polyisoimides	OPDA	4,4'-ODA	NMP	2	270	– –	570
Polyisoimide LARC-CPI	BTDA	1,3'-BABB	NMP	3	222	● 36200 ● (223)	—
Poly(isoimide-sulfone)	BTDA	3,3'-DDS	NMP	4	273	47200 (241)	545

§ measured in air
● DP=25; other polymers are DP=50

3.3 RHEOLOGICAL ANALYSIS

3.3.1 Rheological Response of Polyisoimides and Polyimides

Figure 8 shows the rheological response of poly(BTDA-DAB)isoimide in comparison with its corresponding imide (LARC-TPI) as a function of temperature. This rheological profile is characteristic of this class of polymers.

At temperatures below 190°C (region a) before the specimen softens, there is poor adhesion between the sample and the parallel plate fixture, leading to a significant amount of slippage at the solid boundaries. Therefore, the results are not meaningful in this region. As the polyisoimide is heated to over 190°C (region b), the softening of polyisoimide improves adhesion to the fixtures and wall slip diminishes. The measured dynamic viscosity decreases as the polymer softens or melts more with increasing temperature. Concurrently, the isoimide undergoes a thermally-induced chemical conversion to the corresponding imide isomer at these temperatures (region c), causing an increase in η^*. These two competing mechanisms result in a minimum in the viscosity profile (hmin) to occur at some intermediate temperature (T_{min}), about 243°C for poly(BTDA-DAB)isoimide, above which the effects of the chemical conversion begin to dominate (region d). Further increase in temperature completes the isoimide-to-imide conversion (region e).

Upon a second temperature scan of the imidized polymer, the viscosity minimum disappears (see **Figure 8**). Instead, the polymer exhibits high-performance properties, showing high dynamic storage modulus ($G' > 10^9$ dyn/cm^2) at low temperatures and a Tg of 260°C.

Figure 9 illustrates similar behavior of poly(IPDA-MPDA)isoimide and its polyimide (LARC-ITPI). The rheological data demonstrate the main advantage of the isoimide route to polyimide: The resin is rendered more processible at low temperatures (near the viscosity minimum) but retains the high Tg needed under use conditions.

The rheological profile obtained for the isoimide-to-imide conversion can be used to determine processing conditions. The viscosity minimum, η_{min}, results from a competition between melting of polyisoimide (lower η^* with increasing temperature) and conversion to polyimide (higher η^* with increasing temperature).

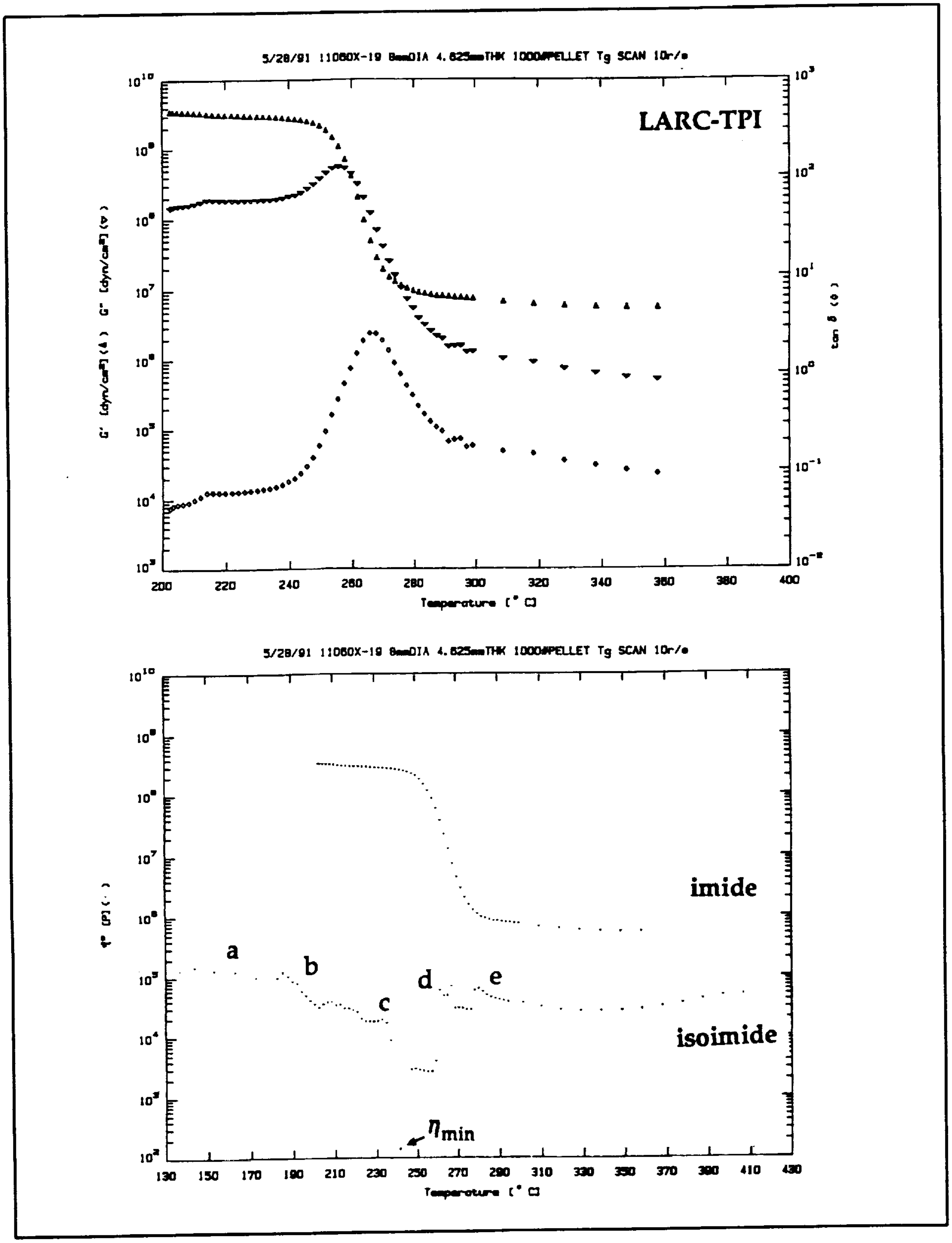


Figure 8. Rheometric Comparison of LARC-TPI and Its Isoimide Analog, Poly(BTDA-DAB)isoimide

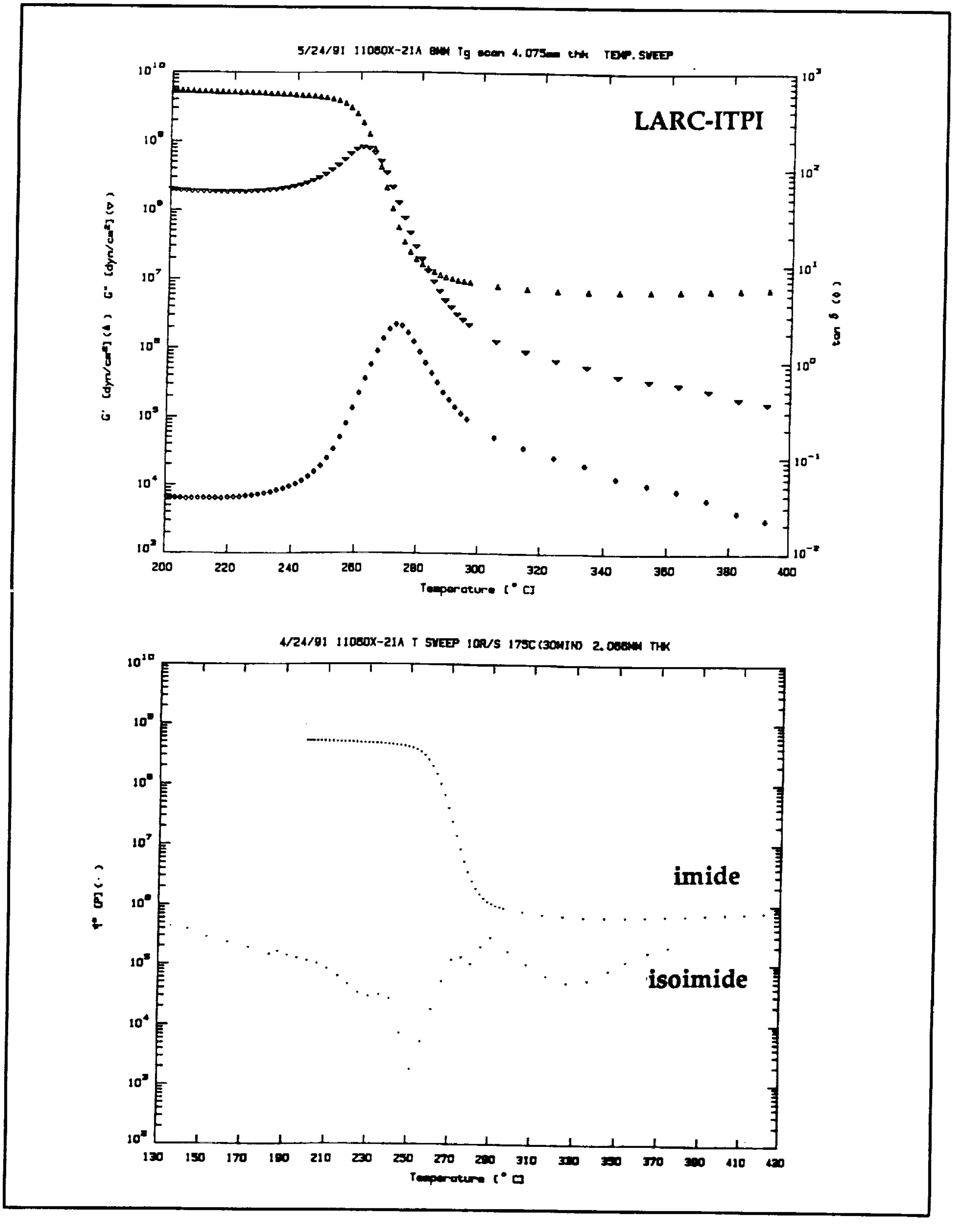


Figure 9. Rheometric Comparison of LARC-ITPI and Its Isoimide Analog, Poly(IPDA-MPDA)isoimide

Although the viscosity minimum, η_{min}, is not a fundamental quantity and is dependent on the measurement procedures, it can be used as an empirical tool to rank the processibility of polyisoimides, as the scanning rates chosen (an average of 1.6°C/min and 3.5°C/min for the 2°C and 5°C increments, respectively) are comparable to those in actual processing. As illustrated in **Figure 10**, both the 2° and 5°C increment scans from 190° to 300°C yield essentially identical results within the experimental uncertainty in determining T_{min}.

The value of η_{min}, however, can be determined more accurately from the 2°C increment scan since 5°C is sometimes too large of an increment to catch the minimum in the profile especially when the drop in the dynamic viscosity is very sharp as in the case of poly(BTDA-DAB)isoimide. T_{min} defines the processing window for prepregging and/or consolidation if these materials are to be used as resin matrix for composites. The rheological data demonstrate the main advantage of the isoimide route to polyimide: the resin is rendered more processible at low temperatures (near the viscosity minimum) but retains the high Tg needed under use conditions.

Ideally, the rheological profile most practical for processing is one with a low value of η_{min} and a wide window near T_{min} with the low viscosity. The rheological profile of poly(BTDA-DAB)isoimide with a sharp drop in the viscosity (thus, a relatively narrow processing window) **(Figure 10)**, contrasts the profile of poly(BTDA-APB)isoimide, that is characterized by a wider "valley" around T_{min} but a higher value of η_{min} **(Figure 11)**.

In these experiments, the observed rheological profile is a function of the temperature scanning rate, the melting rate of polyisoimide, and the reaction kinetics of the isoimide-to-imide conversion. Nonetheless, the use of the rheological characterization procedures developed here to rank processibility can be justified since our method for probing a chemical transition is analogous to the widely accepted measurements of the glass transition temperature (Tg) using differential scanning calorimetry (DSC) for probing a physical transition. In both cases, the parameters of interest (T_{min}, η_{min}, and Tg) are scan-rate dependent, but a judicious selection of scanning parameters allows us to utilize the measured quantities in a meaningful (albeit empirical) manner to rank materials and their usefulness in applications. Furthermore, as in the case of Tg measurements, T_{min} and η_{min} have been found to be relatively insensitive to small variations in scan rate **(Figure 10)**, thereby demonstrating the robustness of the characterization procedures for these polymers.

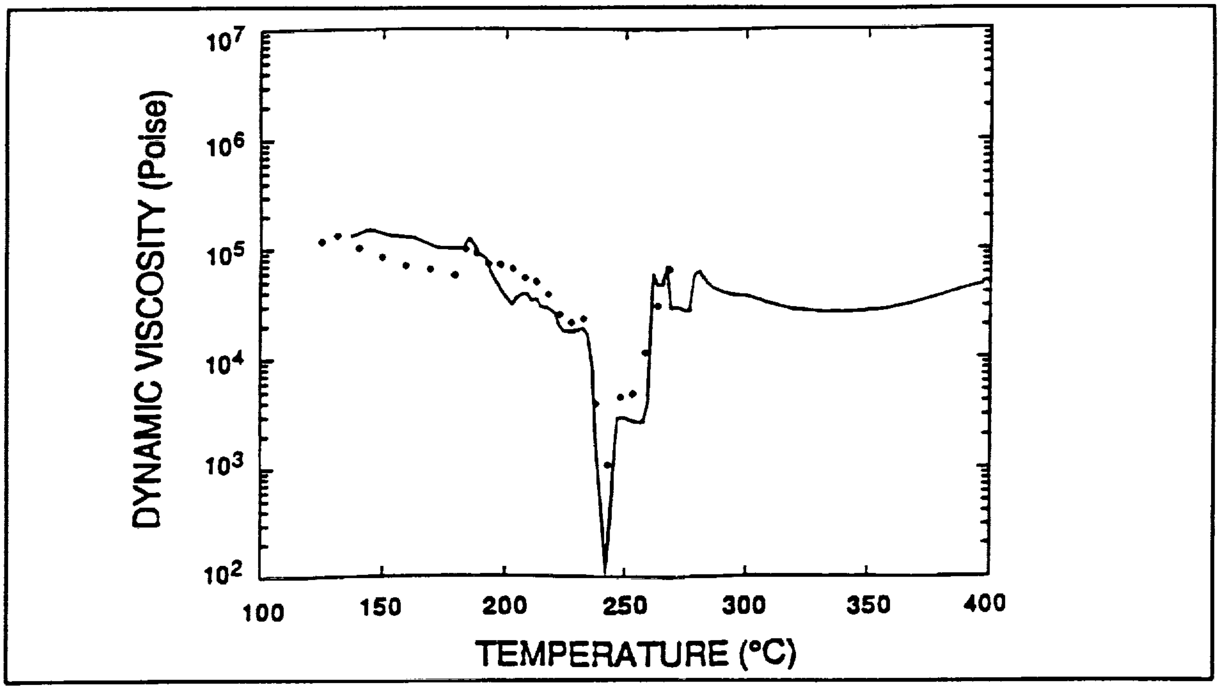


Figure 10. Dynamic Viscosity of Poly(BTDA-DAB)isoimide as a Function of Temperature at Two Different Scan Rates: solid line, 2°C per increment; diamonds, 5°C per increment.

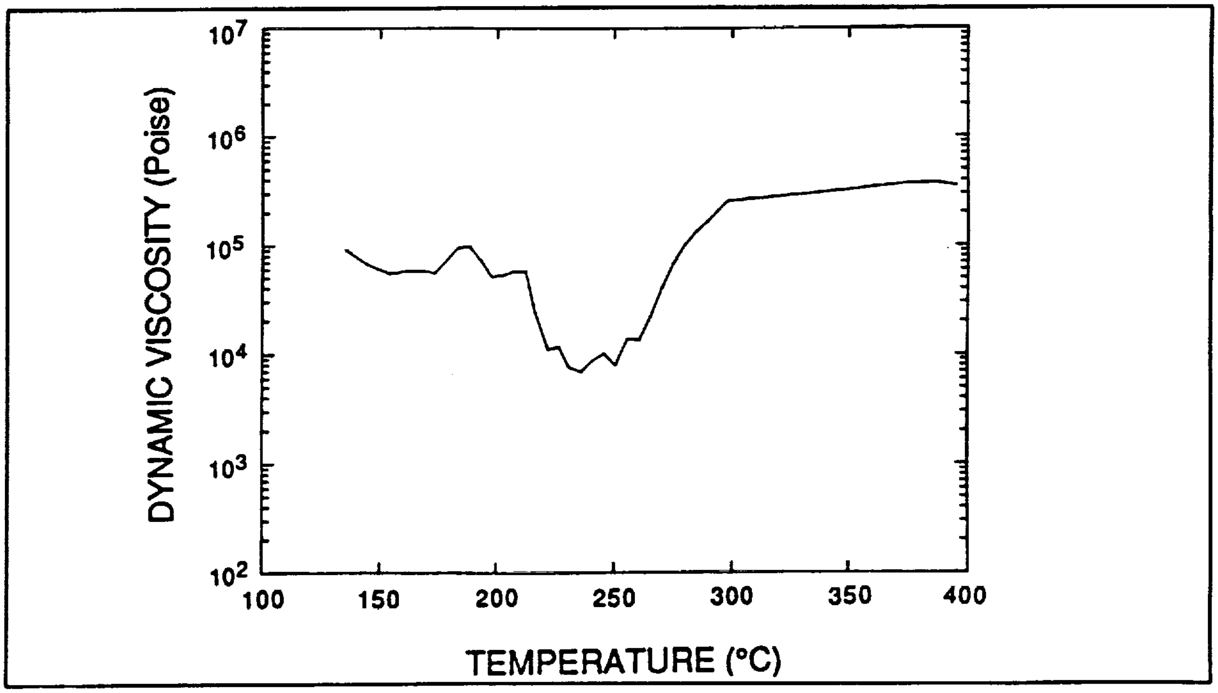


Figure 11. Dynamic Viscosity as a Function of Temperature During Conversion of Poly(BTDA-APB)isoimide to its Corresponding Polyimide.

We speculate that such insensitivity of the profile to scan rate is because both rates chosen in this study are fast compared to the conversion reaction at temperatures below T_{min} as indicated by very limited kinetic data obtained in our laboratory using FTIR to monitor the disappearance of the isoimide peaks. Consequently, regions b and c of **Figure 8** reflects mostly the melting of polyisoimide. As in the case of Tg measurements, one does not need a detailed knowledge of the kinetics of the transition to make use of the rate-dependent physical measurements made in the vicinity of the transition. Moreover, a quantitative measure of the detailed reaction kinetics of such complex systems is beyond the scope of our current work.

Because of the large variations (several orders of magnitude) in the rheological functions during the isoimide-imide conversion, dynamic shear is the most appropriate characterization method for assessing the rheology of these materials. However, due to the high modulus of the polyimides, transducer compliance could be a problem especially for the relatively large sample size of 25 mm in diameter. Thus, to obtain an accurate temperature dependence behavior for the polyimide, the pellet size has to be reduced to 8 to 5 mm in diameter. On the other hand, such small samples often do not provide a large enough stress signal near hmin; a larger sample is then needed if accurate values near the minimum viscosity during the conversion is desired. After completion of the conversion to polyimide (region e in **Figure 8**), the transducer compliance could again be a problem for the high modulus material, rendering large errors in the η^* measurements in that region. Finally, the slight normal force (less than 100 g), which has been applied to the pellet initially to enhance adhesion to the parallel plates fixture as the polyisoimide softens, may also affect the accuracy of the measured dynamic viscosity values. Nonetheless, with consistent sample loading and measurement procedures, we found that the reproducibility of data is usually less than 30% variations in η_{min} and $\pm 3^{\circ}C$ for T_{min}. These variations arise from the complexity of the dynamics and the difficulties in obtaining meaningful rheological measurements for these materials; but they are acceptable for our purposes.

3.3.2 Correlation with Molecular Weight

The value of the viscosity minimum exhibited by polyisoimides upon increasing temperature was found to depend on the polymer molecular weight. For the same polymer backbone structure, the lower molecular weight polyisoimide generally shows a lower value for the minimum than its higher molecular weight analog (**Table 5**).

Table 5. Correlation of Rheological Minima of Melt Viscosity with Molecular Weight of Polyisoimides

EXPERIMENT REFERENCE NUMBER	DATE REFERENCE NUMBER	POLYMER CONSTITUENT			RHEOLOGICAL CHARACTERIZATION			
		Dianhydride	Diamine	DP	Radius	Gap Dimension	Temp(Tmin) of min. η^*	Viscosity (η^*) x 10^{-4}
16538-22	900805	BTDA	BAPP	50	12.50	2.070	213	4.16
16548-08B	901217	BTDA	BAPP	10	12.50	2.325	235	1.65
16552-43	901018	PMDA	APB	50	12.50	2.058	257	8.10
15383-37	900807	PMDA	APB	10	12.50	1.990	171	6.19
16538-47B	901212	BTDA	3,3'-DDS	50	12.50	1.905	241	4.72
16548-02B	901017	BTDA	3,3'-DDS	10	12.50	2.055	218	2.76
11059-5	910906	BPDA	APB	50	12.50	1.980	196, 376	2.92, 0.012
11059-9	910909	BPDA	APB	10	12.50	2.296	208	0.440
11059-3	910906	OPDA	APB	50	12.50	2.075	197	0.451
11059-7	910909	OPDA	APB	10	12.50	2.263	194	0.0323

Viscosity (η^*) in Units of Poise

3.3.3 Correlation with Chemical Structures

Similar to the variation of Tg values with chemical structures, the more rigid structures tend to impart higher melt viscosities to the polyisoimides. Within a series of polyisoimides based on a common diamine (e.g., APB), melt viscosity increases in the order of increasing rigidity of the dianhydride, OPDA < BTDA < BPDA < PMDA **(Table 6)**.

Similarly, in the series of polyisoimides based on the dianhydride BTDA, e.g., APB < 3,3'DDS < MPDA, or 3,4'-ODA < 3,3'DDS < MPDA, melt viscosity increases in the order of increasing rigidity in the diamine **(Table 7)**.

It is interesting to note that the apparent added flexibility in the extended chain length and an extra oxy-linkage in APB, as compared to 3,4'-ODA, does not result in a lower value for the minimum melt viscosity of the polymer poly(BTDA-APB)isoimide. This result is consistent with a similar observation that the apparent flexibility in the extended chain length and oxy-linkages in the diamine components of poly(BTDA-1,3'-BABB)isoimide and poly(BTDA-BAPP)isoimide does not result in lower melt viscosities. The high melt viscosities are probably due to the increase in molecular weight within the same DP value, and molecular orientation in solution.

3.3.4 Correlation with Dielectric Spectroscopic Analysis

Figure 12a shows correlation results between rheometric and dielectric spectroscopic analyses of poly(BTDA-DAB)isoimide and imide (LARC-TPI). Similar results were obtained for poly(IPDA-MPDA)isoimide and imide (LARC-ITPI) **(Figure 12b)**. These techniques are complementary to each other. Both techniques indicated that the polyisoimides have a processing window between 200° and 260°C. In the case of LARC-TPI, both methods identified the polyimide Tg at 260°C.

The conventional equations governing dielectric measurements are given below:

$$\varepsilon' = \varepsilon_u + \frac{\varepsilon_r - \varepsilon_u}{1 + (\omega\tau)^2} \qquad (1)$$

$$\varepsilon'' = \frac{\sigma}{\omega\varepsilon_o} + \frac{(\varepsilon_r - \varepsilon_u)\,\omega\tau}{1 + (\omega\tau)^2} \qquad (2)$$

Table 6. **Correlation of Rheological Melt Viscosities of Polyisoimides with Structural Variation of Dianhydrides (Viscosity in Units of Poise)**

POLYISOIMIDE SERIES BASED ON DIAMINE APB	OPDA		BTDA		BPDA		PMDA	
	η^*	Tmin	η^*	Tmin	η^*	Tmin	η^*	Tmin
	4510	197	7020	236	29200	196	81000	257

Table 7. Correlation of Rheological Melt Viscosities of Polyisoimides with Structural Variation of Diamines (Viscosity in Units of Poise)

POLYISOIMIDE SERIES BASED ON DIANHYDRIDE BTDA	APB		3,4'-ODA		3,3'-DDS		MPDA	
	η^*	Tmin	η^*	Tmin	η^*	Tmin	η^*	Tmin
	7020	236	2880	243	47200	241	73000	234

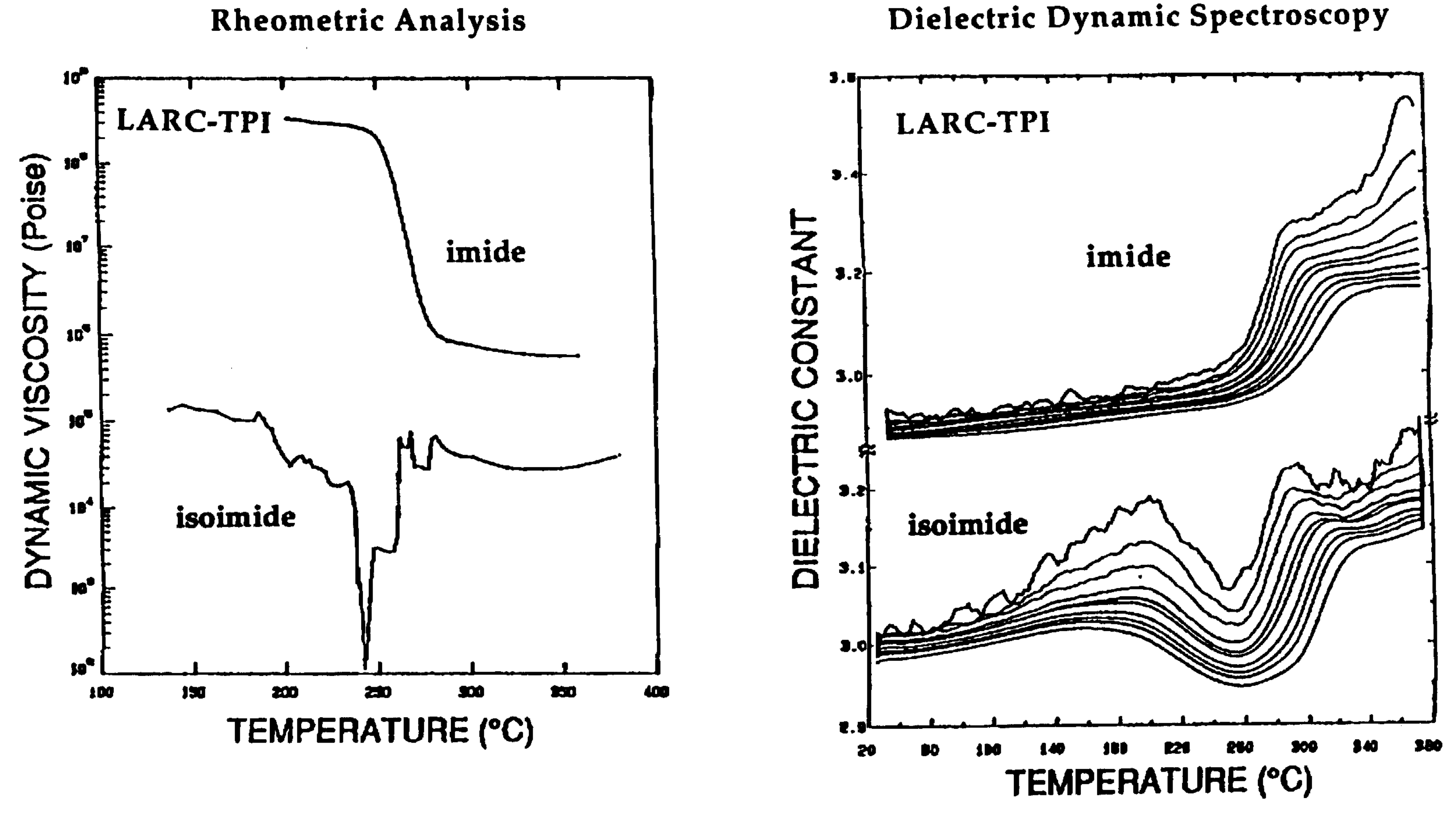
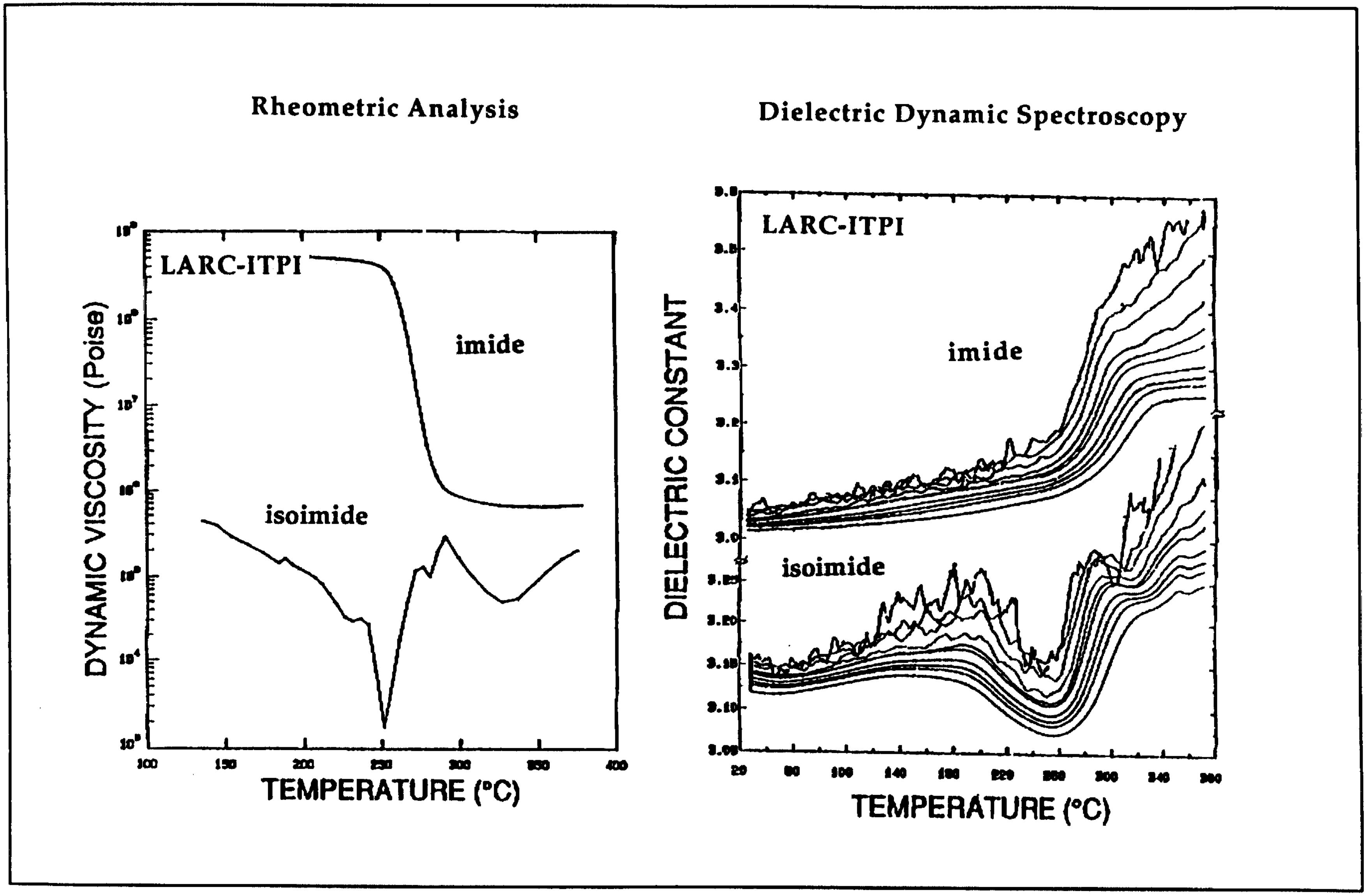


Figure 12a. Rheometric Analysis and Dielectric Dynamic Spectroscopy are Complementary Techniques for Polyisoimide-to-Polyimide Thermal Conversion (The BTDA-DAB System)


Rheometric Analysis

Dielectric Dynamic Spectroscopy

Figure 12b. **Rheometric Analysis and Dielectric Dynamic Spectroscopy are Complementary Techniques for Polyisoimide-to-Polyimide Thermal Conversion (The IPDA-MPDA System)**

where:

ε' = permittivity
ε'' = loss factor
σ = ionic conductivity
ε_u = unrelaxed permittivity
ε_r = relaxed permittivity
ω = angular frequency ($\omega = 2\pi f$)
τ = dielectric relaxation time
ε_o = permittivity of free space
($\varepsilon_o = 8.854 \times 10^{-12}$ farads/meter)

Quantitative correlations of ε' (permittivity) and ε'' (loss factor) to viscosity have been carried out via their dependence on ionic conductivity σ. Such correlations are valid for thermoset resins, such as the amine-curable tetraglycidyl ether epoxy system, in which the molecular size of the components are small enough to permit large contribution from the ionic conductivity of the materials **[30, 31]**. In our polymer systems, the molecular size of the DP 50 polymers renders σ necessarily negligible. The behavior of both ε' and ε'' is determined by the dipolar mobility alone. Equation (2) becomes (3).

$$\varepsilon'' = \frac{(\varepsilon_r - \varepsilon_u)\,\omega\tau}{1 + (\omega\tau)^2} \qquad (3)$$

It follows that cure monitoring, in this case, the isoimide-to-imide conversion, can be done by measuring either capacitive loss or resistive loss, since dipolar mobility is the major contributing factor to both.

3.3.5 Effects of Temperature History on Processibility

In composite manufacturing, processing conditions used in one step (e.g., prepregging) often have a significant impact on the processibility in subsequent steps (e.g., consolidation) and on product properties. For any reactive systems such as isoimide polymers and blends, the temperature history seen by the materials plays a particularly important role in their processibility. In a series of experiment on poly(MPDA-IPDA)isoimide, we included a lengthy isothermal hold at various temperature below T_{min} in order to study the effects of temperature history on the rheological profile. **Figure 13a** shows the profile of a control experiment using the established temperature scan procedure with no isothermal hold. This polymer exhibits a T_{min} of about 252°C. **Figures 13b-d** illustrate the rheological profiles as a function of temperature with an added temperature hold of 60 min at 200°, 240°, and 250°C. As expected, the higher the isothermal preconditioning temperature, the bigger the impact on the value of η_{min} and thus processibility. Interestingly, whereas η_{min} increases by up to an order of magnitude, T_{min} remains relatively constant. This trend supports our hypothesis that the profile prior to T_{min} reflects the melting of polyisoimide. As some isoimide functionalities are converted to imide during the isothermal preconditioning, the relative values of η_{min} within one polymer system reflect the portion of isoimide remaining. From a practical standpoint, our rheological data suggest that the processing window defined empirically by T_{min} is fairly insensitive to the temperature history seen by the material.

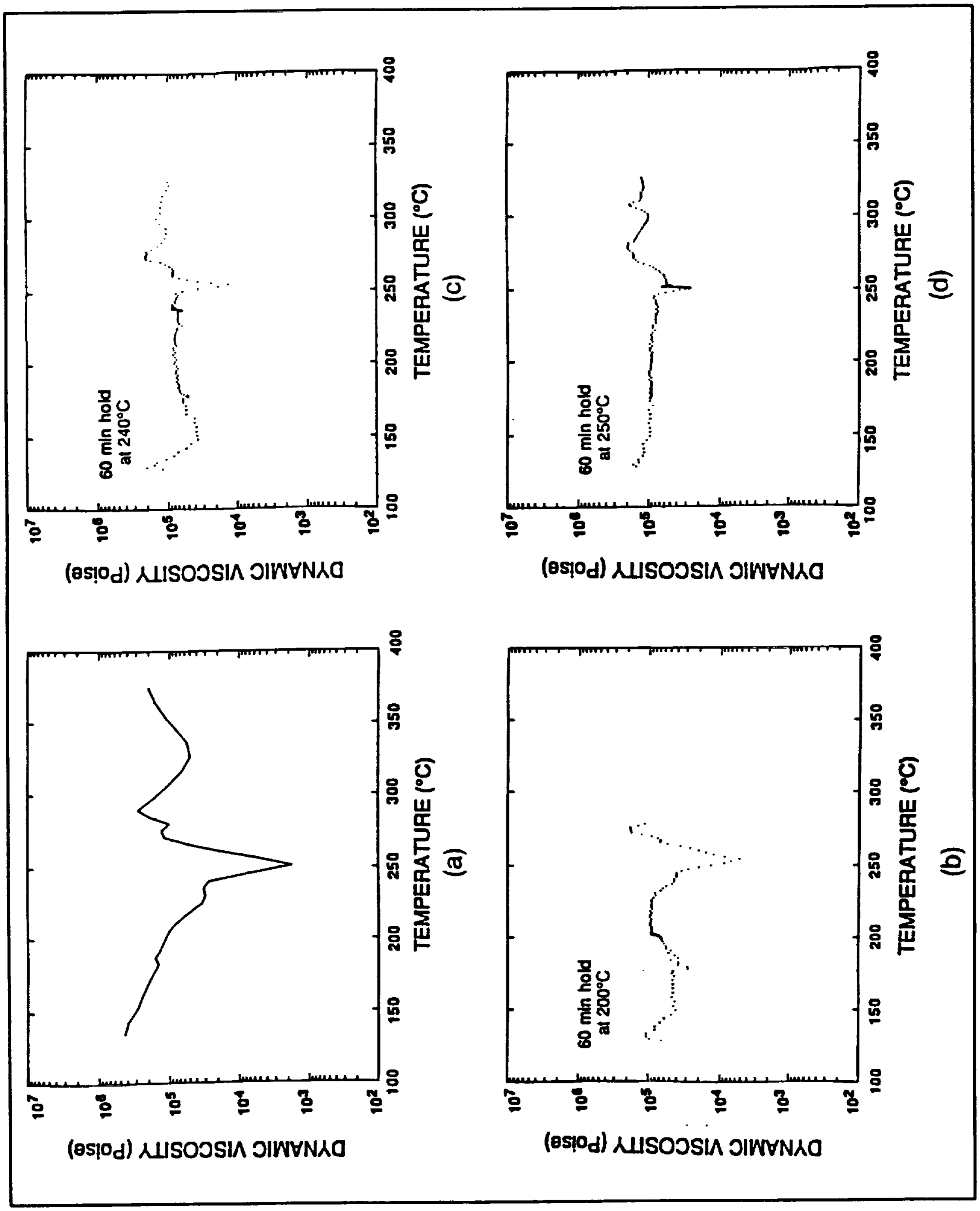


Figure 13. Dynamic Viscosity as a Function of Temperature During Conversion of Poly(IPDA-MPDA)isoimide to its Corresponding Polyimide, with (a) no isothermal hold, (b) an isothermal hold of 60 minutes at 200°C, (c) an isothermal hold of 60 minutes at 240°C, and (d) an isothermal hold of 60 minutes at 250°C.

3.4 ISOIMIDE ANALOGS OF HIGH-PERFORMANCE POLYIMIDES

3.4.1 Poly(BTDA-DAB)isoimide

Enhancement of processibility of LARC-TPI polyimide was demonstrated by the isoimide modification technique [2]. Preliminary laminate data on LARC-TPI isoimide also afforded encouraging composite properties, especially in hot/wet retention of strengths.

Poly(BTDA-DAB)isoimide is an excellent film former. At DP=50, the films (in thicknesses of 1-mil, 2-mil, and 5-mil) are easily creasable and do not break at the crease line. This polymer dissolves easily in NMP and the solution can be spin-coated onto electronic and photonic devices. Curing of this coating to polyimide does not generate volatiles.

The rheological profile of DP 50 poly(BTDA-DAB)isoimide is excellent. The observed dynamic melt viscosity, η^*, of 1,076 poise at T_{min} of 243°C is about an order of magnitude lower than most other polyisoimides. It is interesting to compare this value with the correlation series discussed in **3.3.3**. Extending the series of polyisoimides based on the dianhydride BTDA, generates the correlation orders of DAB < APB < 3,3'DDS < MPDA, and DAB < 3,4'-ODA < 3,3'DDS < MPDA. Melt viscosity increases in the order of increasing rigidity in the diamine **(Table 8)**.

However, the apparent added flexibility in the extended chain length and an extra oxy-linkage in APB, as compared to 3,4'-ODA and DAB, does not result in a lower value for the minimum melt viscosity of the polymer poly(BTDA-APB)isoimide. The high melt viscosities are probably due to the increase in molecular weight within the same DP value.

3.4.2 Poly(IPDA-MPDA)isoimide

The thermoplastic polyimide poly(BTDA-DAB)imide (i.e., LARC-TPI), has demonstrated excellent composites and adhesive properties, despite its poor processing characteristics. LARC-TPI is expensive, due mainly to the cost of the diamino component, 3,3'-diaminobenzophenone, which is also deemed toxicologically unsafe. Poly(IPDA-MPDA)imide (i.e., LARC-ITPI) and LARC-TPI are isomeric. LARC-ITPI duplicates LARC-TPI in glass transition temperature and thermo-mechanical properties **[6-8] (Table 9)**, but the cost is substantially lower. While LARC-TPI is priced at $150 per pound, LARC-ITPI can be produced on a production scale (1,000-lb lots) at a conservative estimate of $20 per pound. The cost of the prepreg is estimated to be less than $75 per pound.

Enhancement of processibility of LARC-TPI polyimide was demonstrated by the isoimide modification technique. Preliminary laminate data on LARC-TPI isoimide also afforded encouraging composite properties, especially in hot/wet retention of strengths. We initiated the study on LARC-ITPI isoimide.

The corresponding isoimide analog, poly(IPDA-MPDA)isoimide, was synthesized from isophthaloyl bisphthalic dianhydride (IPDA) and m-phenylenediamine (MPDA), and end-capped with phthalic anhydride at DP 50. A powder form is easily produced using the acetone work-up procedure [2]. We have recently transferred the synthetic technique to a pilot-plant-scale (10-15 kg) production. Poly(IPDA-MPDA)amic acid is commercially available from Imitec, Inc. (Schenectady, NY).

An interesting observation was the DSC endotherm at 258°C during the scan of a cured and annealed specimen (**Figure 14**). This endotherm was also detected on a different DSC instrument at 259°C. It is tentatively attributed to the material's crystalline behavior, pending results from a WAXS analysis.

The rheological profile of this DP 50 poly(IPDA-MPDA)isoimide is also excellent. The observed dynamic melt viscosity, η^*, of 1,780 poise at T_{min} of 250°C is comparable to that of poly(BTDA-DAB)isoimide.

Both poly(BTDA-DAB) isoimide and poly(IPDA-MPDA)isoimide give comparable dielectric spectroscopic responses, indicating a processing window between 200 and 260°C and Tg's at about 260°C.

Table 8. Correlation of Rheological Melt Viscosities of Polyisoimides with Structural Variation of Polymers (Viscosity in Units of Poise)

POLYISOIMIDE SERIES BASED ON DIANHYDRIDE BTDA	DAB		3,4'-ODA		APB		3,3'-DDS		MPDA	
	η^*	Tmin	η^*	Tmin	η^*	Tmin	η^*	Tmin	η^*	Tmin
	1076	243	2880	243	7020	236	47200	241	73000	234

Table 9. Thermomechanical Property Comparison Between LARC-TPI and LARC-ITPI (Reference 8)

POLYMER	Tg (°C)	temp (°)C	NEAT RESIN PROPERTIES				COMPOSITES PROPERTIES	
			yield strength (KSI)	tensile strength (KSI)	tan modulus (KSI)	% elongation	flex strength (KSI)	flex modulus (MSI)
LARC-TPI	260	25	15	20	465	7.2	242	15
		200	8.4	8.9	380	109	160	14
LARC-ITPI	259	25	14	19	540	4.9	220	14
		200	7.3	8.4	380	13	130	13

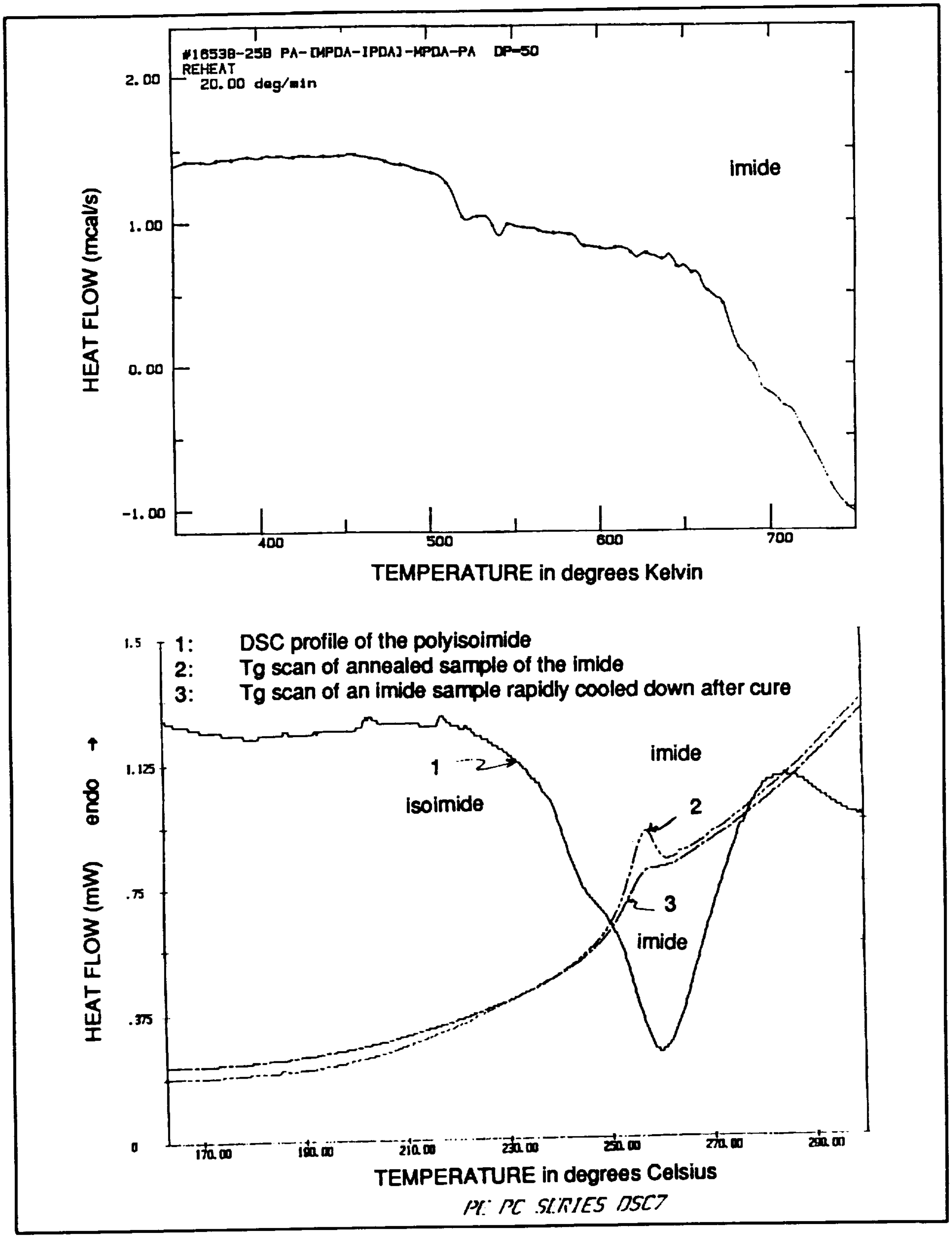


Figure 14. DSC Analysis of Poly(IPDA-MPDA)isoimide and imide (in collaboration with Allco Chemical Corporation, Galena, Kansas)

3.4.3 Poly(isoimide-sulfone)

Poly(imide-sulfone) has an impressive elastic modulus. It also has an inherent, higher Tg compared to its nonsulfone analog, i.e., LARC-TPI. The low flow limitation of the imide form necessitates processing of this material via solution prepregging of the amic acid. The only practical way to process this imide material is via powder prepregging techniques.

Isoimide modification of poly(imide-sulfone) was carried out, with the expectation that it can enhance the processibility of the material by improving flow, fiber wetting, and circumventing the volatiles issue in amic acid processing. Thus, poly(BTDA-3,3'-DDS) isoimide, i.e., poly(isoimide-sulfone), was synthesized from BTDA and 3,3'-diaminodiphenylsulfone (3,3'-DDS), end-capped with phthalic anhydride at DP =50 and DP=10.

Poly(isoimide-sulfone) has a melt viscosity, η^*, of 47,200 poise at T_{min} of 241°C for the DP=50 material **(Table 8)**. The corresponding DP=10 material still possesses a high melt viscosity of 27,600 poise at T_{min} of 218°C **(Table 5, Section 3.3.1)**. Further improvement of processing characteristics is deemed necessary. We surmise that such improvements could result either from copolymers of poly(BTDA-3,3'-DDS)isoimide and poly(BTDA-APB)isoimide (LA-100), or from SIPNs with acetylene-terminated oligomers.

3.4.4 Polyisoimides Based on 3,4'-Oxydianiline (3,4'-ODA)

Preliminary small laminate data indicating good retention of hot/wet properties at 177°C (350°F) were shown by copolymers derived from poly(BTDA-APB)isoimide (LA-100) and poly(BTDA-3,4'-ODA)isoimide. Phthalic anhydride-end-capped poly(BTDA-3,4'-ODA)isoimide was routinely synthesized. Several copolyisoimides based on BTDA, APB, and 3,4'-ODA, were also synthesized using mixtures of different proportions of the diamines. **Table 10** and **Figure 15** summarize some structure-property correlation data for this series of copolyisoimides.

The Tg correlation **(Figure 15)** suggests that the introduction of the more flexible component APB into poly(BTDA-3,4'-ODA)isoimide results in lowering the Tg of the imide after cure. The relationship between polymer structure and melt viscosity appears to be more complicated, the melt viscosity of the 1:1 copolymer (Copolyisoimide O-11) having a higher value than those of the 1:3 and the 3:1 copolymer, or the homopolymers **(Figure 15)**.

Table 10. **Imide Glass Transition Temperatures, Melt Viscosities, and Thermal Stability Data of Copolyisoimides Derived From Dianhydride BTDA and Diamine Mixturee of APB and 3,4'-ODA**

TRIVIAL NAME	POLYMER CONSTITUENT		PHYSICAL & THERMAL DATA				
	Dianhydride	Diamine	soluble in	Tg† (°C)	η^*_{min} (poise)	T_{min} (°C)	wt loss§ T(onset)
Polyisoimide O-10	BTDA	3,4'-ODA	DMAC NMP	254	2,880	243	547
Copolyisoimide O-31	BTDA	3,4'-ODA (3) APB (1)	DMAC NMP	233	7,720	220	548
Copolyisoimide O-11	BTDA	3,4'-ODA (1) APB (1)	DMAC NMP	217	59,000	218	560
Copolyisoimide O-13	BTDA	3,4'-ODA (1) APB (3)	DMAC NMP	208	19,100	212	590
Polyisoimide LA-100	BTDA	APB	THF, NMP DMAC	191	7,020	236	570

§ measured in air
† Tg refers to that of the imide (cured)

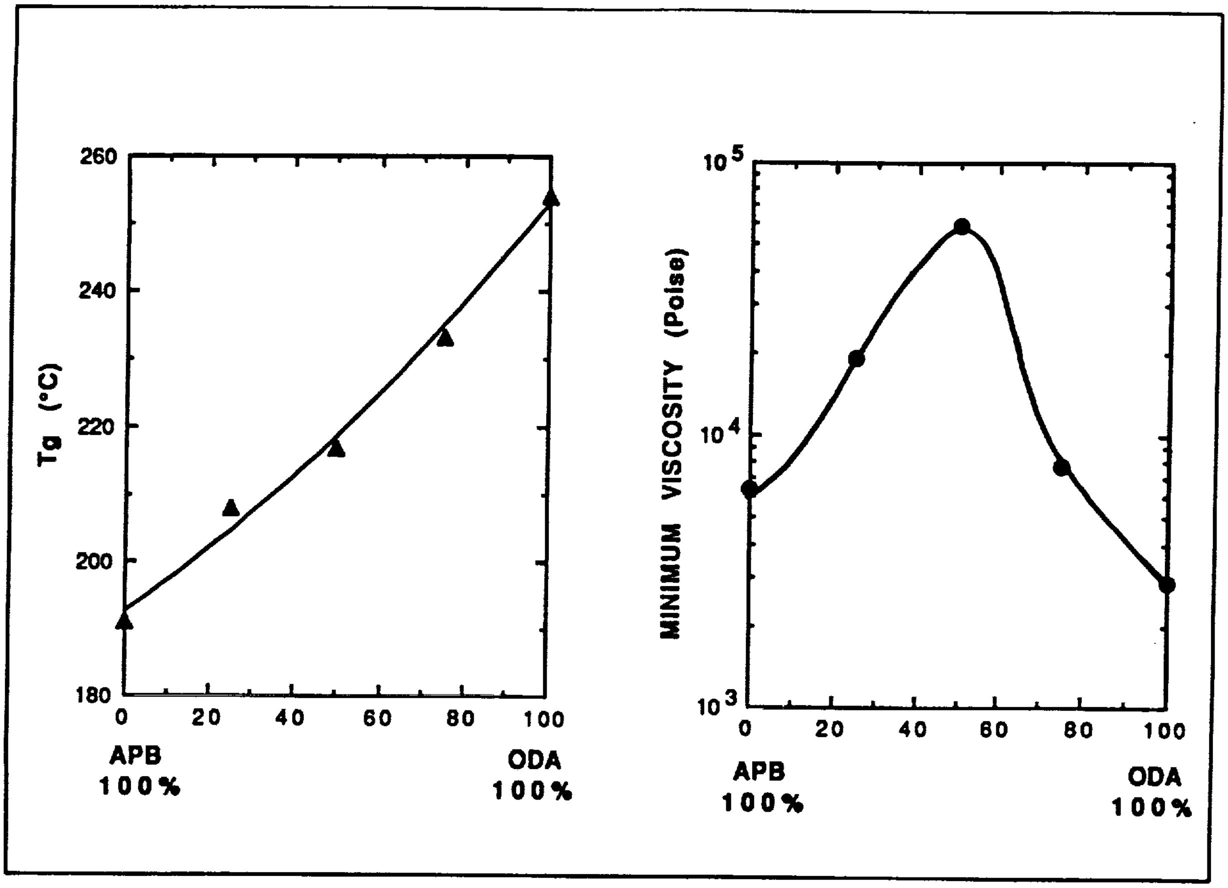


Figure 15. **Structure-Property Correlation of Copolyisoimides Derived From Dianhydride BTDA and Diamine Mixtures of APB and 3,4'-ODA (Tg Refers to the Imide; Melt Viscosity Refers to the Isoimide)**

3.4.5 Polyisoimides Based on 2,2-Bis[4-(4-Aminophenoxy)phenyl]hexa-fluoropropane (BDAF)

The Ethyl EYMYD polyamic acid resins L-20N and L-30N cure to yield poly(BTDA-BDAF)imide and poly(PMDA-BDAF)imide, respectively, which show excellent thermal and thermo-oxidative stability to be potential matrix resin materials. Recently, composites of high mechanical strength were prepared. The consolidation procedure requires high temperatures and pressures because of the generation of volatiles during processing. We evaluated the applicability of isoimide modification to this interesting class of polyimides.

The key diamine BDAF required for this study is not commercially available. We synthesized BDAF diamine from the commercially available 2,2-bis(4-hydroxyphenyl)-hexafluoropropane (Bisphenol AF), via a nucleophilic aromatic substitution reaction between Bisphenol AF and 1-chloro-4-nitrobenzene, followed by catalytic hydrogenation of the intermediate.

The corresponding polyisoimide, poly(BTDA-BDAF)isoimide, was synthesized from BTDA and BDAF, and end-capped with phthalic anhydride at DP 50. Similar to poly(BTDA-DAB)isoimide and poly(IPDA-MPDA)isoimide, poly(BTDA-BDAF)isoimide is also an excellent film-former. Similar to poly(BTDA-APB)isoimide, it is easily soluble in tetrahydrofuran.

Table 11 and **Figure 16** summarizes some structure-property correlation data for the BDAF-based series of copolyisoimides. The dianhydride component of these polyisoimides comprises different molar ratios of the dianhydrides BTDA and the more rigid PMDA. The Tg correlation **(Figure 16)** suggests that the introduction of the more rigid dianhydride PMDA into poly(BTDA-BDAF)isoimide raises the Tg of the final polyimide after cure. This is consistent with Ethyl's data that EYMYD L30N polyimide (based on the PMDA dianhydride) has a higher Tg than EYMYD L20N polyimide.

Compared to the Tg value obtained from curing of poly(PMDA-BDAF)isoimide, the previously reported Tg (over 400°C) of EYMYD L30N polyimide is much higher. This is probably the result of a different processing history which included a PMR-type processing and possible graphitization of the cured specimen in the TRW procedure [32].

The relationship between polymer structure and melt viscosity appears to be similar to the copolymers of poly(BTDA-APB)isoimide and poly(BTDA-3,4'-ODA)isoimide, discussed in the previous section. The melt viscosity of the 1:1 copolymer having a higher value than those of the 70:30 and the 30:70 copolymer, or the homopolymers. The range of variation, however, is not as large as the copolymer series of poly(BTDA-APB)isoimide and poly(BTDA-3,4'-ODA)isoimide.

3.4.6 Polyisoimides Based on 2,2-Bis[4-(4-Aminophenoxy)phenyl]propane (BAPP)

The cost issue in durable polymer materials for future high-speed aircraft applications may be addressed with still another new, low-cost diamine monomer, 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP). This new monomer structurally resembles its fluoro analog BDAF, used in the EYMYD resins, but costs much less. In light of the excellent thermomechanical properties shown by laminates made from the EYMYD resins, the BAPP-based polymers, namely, poly(BTDA-BAPP)imide, poly(PMDA-BAPP)imide, and their respective isoimide analogs, are potential candidates for applications as matrix resins.

Table 11. **Glass Transition Temperatures, Melt Viscosities, and Thermal Stability Data of Copolyisoimides Derived From Diamine BDAF and Dianydride Mixtures of BTDA and PMDA**

TRIVIAL NAME	POLYMER CONSTITUENT		PHYSICAL & THERMAL DATA				
	Dianhydride	Diamine	soluble in	Tg† (°C)	η^*_{min} (poise)	T_{min} (°C)	wt loss§ T(onset)
EYMYD L20N Isoimide	BTDA	BDAF	DMAC NMP	249	19,700	198	547
Copolyisoimide BF-7030	BTDA (70) PMDA (30)	BDAF	DMAC NMP	256	39,400	227	530
Copolyisoimide BF-5050	BTDA (50) PMDA (50)	BDAF	DMAC NMP	265	52,000	217	550
Copolyisoimide BF-3070	BTDA (30) PMDA (70)	BDAF	DMAC NMP	272	30,600	218	548
EYMYD L30N Isoimide	PMDA	BDAF	NMP DMAC	290	22,100	210	535

§ measured in air
† Tg refers to the imide form (cured)

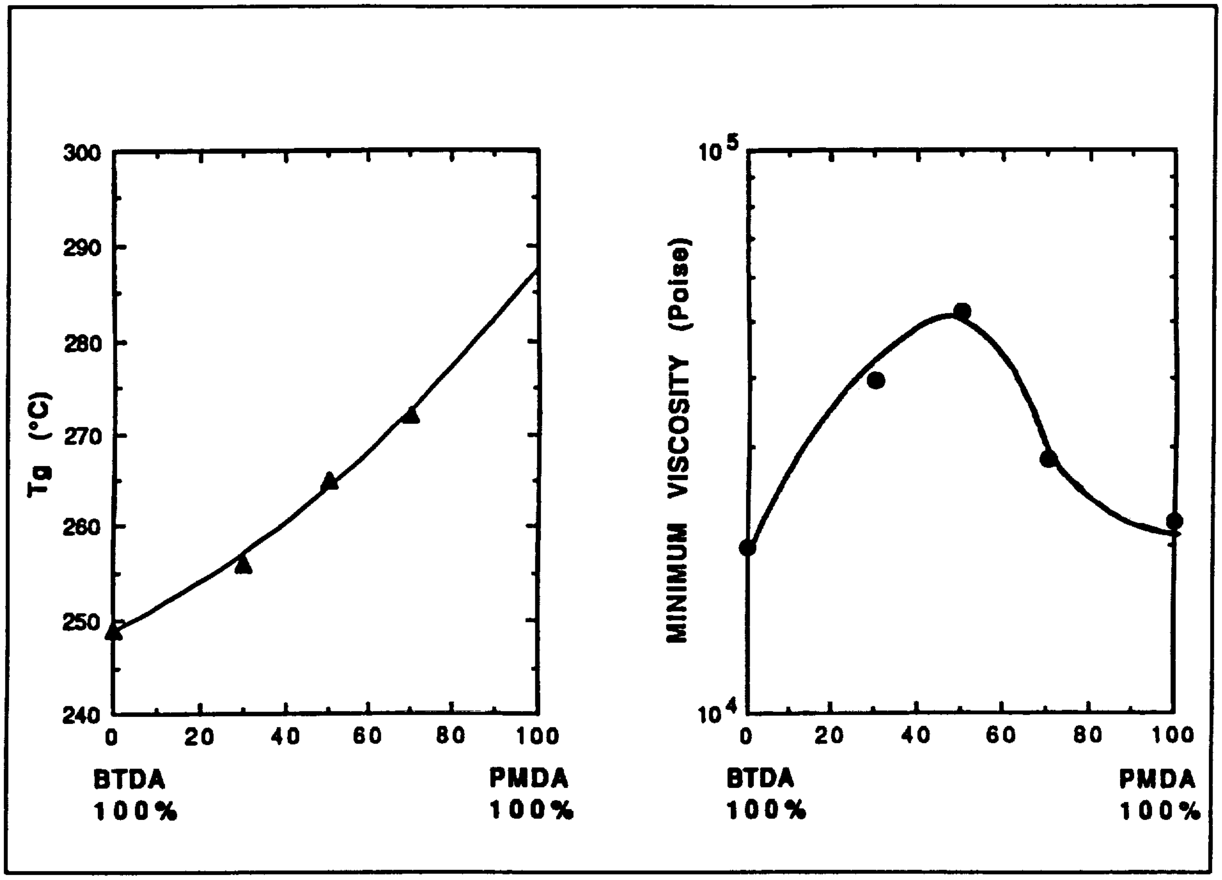


Figure 16.Structure-Property Correlation of Copolyisoimides Derived From Diamine BDAF and Dianhydride Mixtures of BTDA and PMDA (Tg Refers to the Imide; Melt Viscosity Refers to the Isoimide)

BAPP can be prepared from commodity chemicals Bisphenol A and p-chloronitrobenzene via a well-established procedure of base-catalyzed nucleophilic aromatic substitution and catalytic hydrogenation, which is amenable to scale-up.

3.4.7 Other Potential HSR Candidates

The above polymers are potentially affordable and processible. Affordability is defined as under $100 per pound of prepreg. Their mechanical properties will still require substantiation. Extrapolations from known mechanical properties of such structurally-related polyimides as LARC-TPI and poly(BTDA-BDAF)imide suggest that LARC-ITPI and poly(BTDA-BAPP)imide would have similar mechanical properties. Some other emerging candidate polymers, which also warrant evaluation for HSR applications, include Upilex (Ube Industries), OPDA-based polyimides (Oxychem), and LARC-CPI (NASA Langley).

3.5 POLYISOIMIDES AS STRUCTURAL ADHESIVES

Polyimides are effective, thermally stable bonding agents for substrates such as titanium, aluminum alloys, steel alloys, metal matrix composites, and polymer/carbon fiber composites with good tolerance toward elevated temperatures and humidity. Polyimide adhesives retain a high level of their room-temperature adhesive strengths even at service temperatures of 204 to 316°C (400 to 600 °F).

3.5.1 Polyimide Adhesives via Polyamic Acids

In comparison to epoxy adhesives, polyimide adhesives require much higher processing temperatures (up to 399°C or 750°F) and pressures (200 to 1000 psi) to effect good structural bonding. The higher molecular weight linear polyimides have high melt viscosities (10^5 poise or higher) and the consequently problems with low flow. To resolve the low flow restrictions common among polyimides, they are sometimes processed in their more soluble polyamic acid forms to effect acceptable impregnation of resin on the carrier (scrim). This is followed by thermal conversion to imide. This conversion is accompanied by evolution of water. As water is evolved during adhesive processing, it creates voids in the adhesive bond, thus resulting in weakness in the structural adhesive bond. High pressures are generally required to avoid excessive void formation.

The polyimide LARC-TPI, i.e., poly(BTDA-DAB)imide, I [33-35], and the LARC poly(imide-sulfone), i.e., poly(BTDA-3,3'-DDS)imide, II [36], were evaluated at NASA-Langley as structural adhesives (**Figure 17**).

Both of these polyimides proved to be excellent, durable adhesives for titanium substrates. LARC-TPI, for example, showed a titanium /titanium lap-shear strength of 6,180 psi at 25°C, 3,700 psi at 232°C (450°F) after 1,000 hours at 232°C (450°F), and 3,600 psi at 232°C (450°F) after 37,000 hours at 232°C (450°F). Poly(imide-sulfone) showed a titanium/titanium lap shear strength of 3,560 psi at 232°C (450°F) after 5,000 hours aging at 232°C (450°F). The bonding process for polyimide adhesives such as LARC-TPI and poly(imide-sulfone) requires bonding temperatures in excess of 343°C (650°F) and bonding pressures of at least 200 psi or as high as 1,000 psi.

These bonding conditions can be tempered [37, 38] by the utilization of SIPN adhesives for bonding. The thermosetting components of these adhesives were prepared by end-capping lower molecular weight analogs of the poly(imide-sulfone) and LARC-TPI polymers with 3-aminophenylacetylene to provide terminal functional acetylene groups. Blending these ethynyl-end-capped oligomers with the linear polyimides give polyimide blends which cure to yield semi-interpenetrating polyimide networks [39]. This blending approach resulted in tempering the cure requirements so that adherend specimens could be bonded at 275°C (527°F) and at pressures as low as 50 psi.

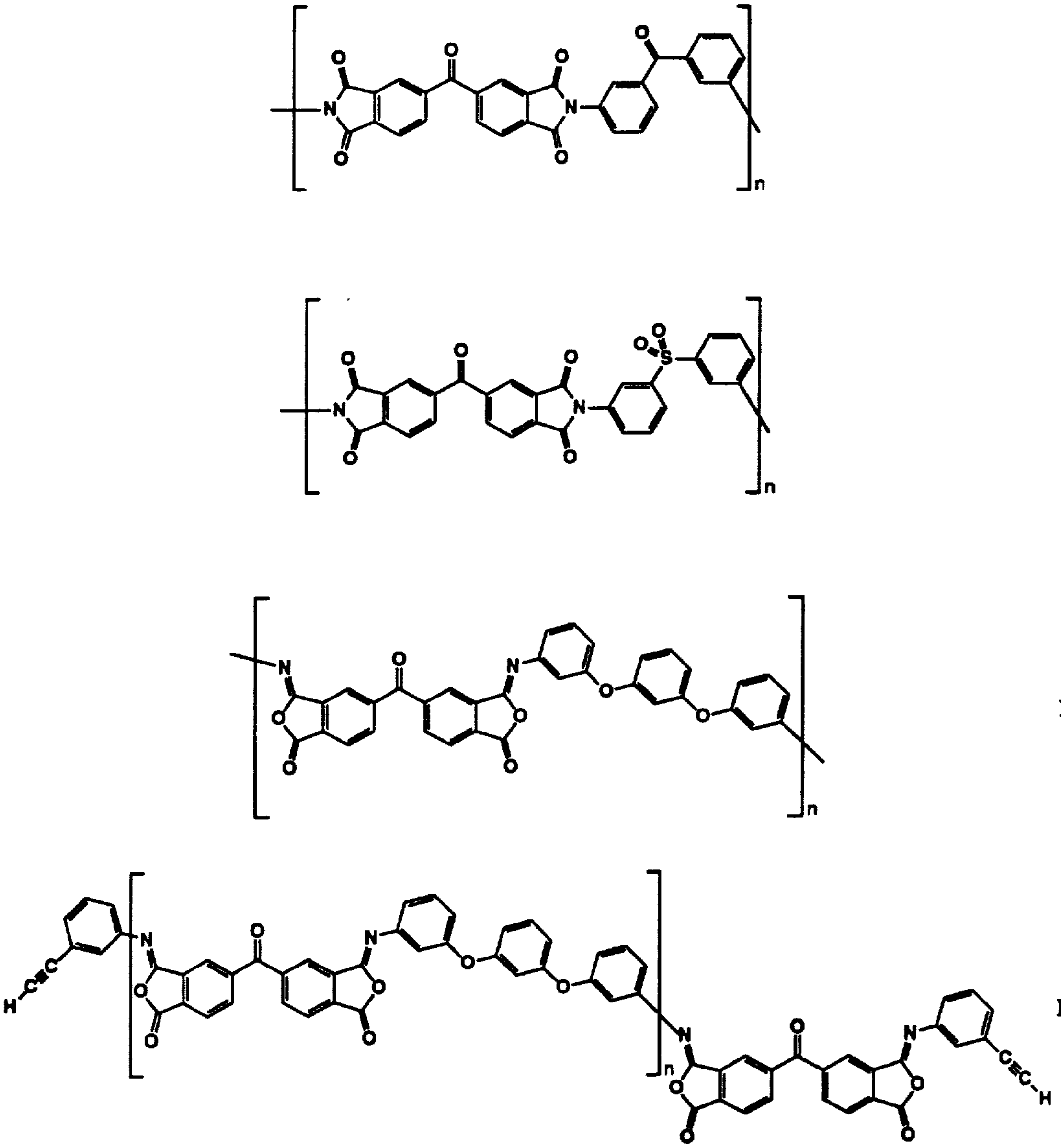
3.5.2 Isoimide Blends as Adhesives

Isoimide SIPNs analogous to the NASA-Langley systems were formulated from poly(BTDA-APB)isoimide, i.e., LA-100, III, and commercially available Thermid IP-600 isoimide oligomers, IV (**Figure 17**). Isoimides generally have excellent solubility in low boiling solvents such as acetone and tetrahydrofuran, lower melting temperatures and melt viscosity as compared to the imide form (**Section 3.4**).

The superior solubility of the isoimide oligomers and polymers permits facile impregnation of tow and fabric for composite and adhesive applications. This is a key benefit to conventional prepregging equipment. After solvent impregnation of fabric, imidization will occur during thermal processing with no accompanying evolution of volatile by-products. **Table 12** shows a comparison of the processing requirements for linear polyimides, SIPN blends of linear polyimides and acetylene-terminated imide oligomers, and SIPN blends of linear polyisoimides and acetylene-terminated isoimide oligomers. The isoimide SIPN blends allow for processing at lower temperatures and pressures with no evolution of volatiles during the cure/consolidation process.

As indicated previously, the thermal isomerism of isoimide to imide is readily discernible from the infrared spectra. **Figure 18** shows an example of the variation in infrared spectra with temperature in the infrared region of 1500 cm^{-1} to 1900 cm^{-1}. As isomerization occurs from 190°C (374°F) to 290°C(554°F), the imide carbonyl absorption (symmetric) at about 1738 cm^{-1} is seen to increase strongly in magnitude. By contrast, the peak at about 1813 cm^{-1}, characteristic of isoimide, diminishes until it is no longer detectable [2, 29].

Preliminary structural adhesive bonding studies were conducted with a number of substrates including aluminum, aluminum-iron-cerium alloy CZ42, 1020 cold rolled steel, and a silicon carbide whisker reinforced metal matrix composite. The results are summarized in **Table 13**.


I

II

III

IV

I: LARC-TPI
II: Poly(imide-sulfone)
III: Polyisoimide LA-100
IV: Isoimide Oligomer IP-600

Figure 17. Chemical Structures of Polyimide Adhesive Components

Table 12. Comparison of Processing Conditions for Adhesives

ADHESIVE TYPE	SOLVENT	BONDING CONDITIONS		PROCESSIBLE MATERIAL FORM	VOLATILES DURING PROCESS
		Pressure (psi)	Temp, °C (°F)		
Linear Aromatic Polyimides	NMP, diglyme	200 - 1,000	343 - 399 (650 - 750)	Amic Acid	Yes
Linear Polyimide/ AT-Imide SIPN Blends	NMP, diglyme	50	260 - 288 (500 - 550)	Amic Acid	Yes
Linear Polyisoimide/ AT-Isoimide SIPN Blends	THF, DMAC, NMP	15 - 50	260 - 288 (500 - 500)	Isoimide	No

THF	tetrahydrofuran
DMAC	N,N-Dimethylacetamide
NMP	N-Methylpyrrolidinone
diglyme	Bis(2-methyoxyethyl)ether, or diethylene glycol dimethyl ether

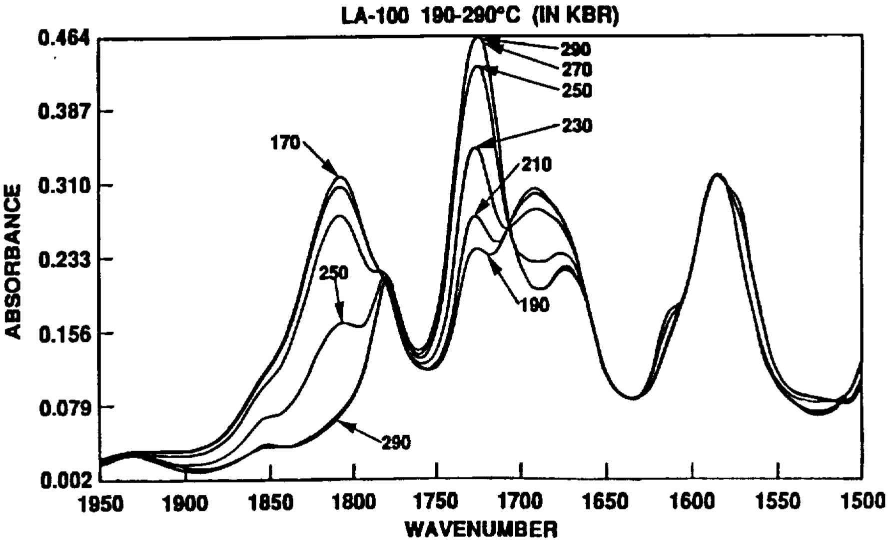


Figure 18. Expanded FTIR Spectrum Showing Isoimide-to-Imide Conversion in the 1500 to 1900 cm^{-1} Region

Table 13. Adhesive Strength Characterization

SUBSTRATE	POLYMER ADHESIVE	TEST CONDITION	LAP SHEAR STRENGTH (KSI)	FAILURE MODE
Aluminum Lap Shear	50% AT isoimide 50% LA-100	RTD	1.97 - 2.00	COHESIVE
Aluminum Lap Shear	75% AT isoimide 25% LA-100	RTD	1.40 - 1.50	COHESIVE
• Aluminum Flatwise Tensile	50% AT isoimide 50% LA-100	RTD	5.04	COHESIVE
• Aluminum Flatwise Tensile	75% AT isoimide 25% LA-100	RTD	3.69	COHESIVE
(w/scrim) Al-Fe-Ce CZ242 Lap Shear	50% AT isoimide 50% LA-100	RTD	4.00	90-100% COHESIVE
(no scrim) Al-Fe-Ce CZ242 Lap Shear	50% AT isoimide 50% LA-100	RTD	2.76	50% COHESIVE
Al-Fe-Ce CZ242 Lap Shear	50% AT isoimide 50% LA-100	260°C 30 min	1.47	COHESIVE
(SIPN primer) Al-Fe-Ce CZ242 Lap Shear	50% AT isoimide 50% LA-100	260°C 30 min	1.27	†ADHESIVE
(IP-600 primer) Al-Fe-Ce CZ242 Lap Shear	50% AT isoimide 50% LA-100	260°C 30 min	1.88	COHESIVE
1020 Cold Rolled Steel Lap Shear	50% AT isoimide 50% LA-100	RTD	2.01 - 2.46	COHESIVE
1020 Cold Rolled Steel Lap Shear	75% AT isoimide 25% LA-100	RTD	1.42	COHESIVE
MMC-Silicon Carbide whisker Aluminum Lap Shear	100% AT isoimide (IP-600)	196°C 100 hr	2.50	95/5 COHESIVE/ ADHESIVE
MMC-Silicon Carbide whisker Aluminum Lap Shear	100% AT isoimide (IP-600)	288°C 200 hr	1.80	95/5 COHESIVE/ ADHESIVE
MMC-Silicon Carbide whisker Aluminum Lap Shear	100% AT isoimide (IP-611)	196°C 100 hr	2.00	80/20 COHESIVE/ ADHESIVE

Bonding condition: 550°F, 50 psi, 1 hr RTD = Room Temperature Dry

† Primer/Substrate and Primer/Substrate Failure

SIPN adhesives were developed from poly(BTDA-APB)isoimide (LA-100) and the isoimide oligomer, Thermid IP-600. The neat resin blend has a melt viscosity in the 10^2- to 10^3-poise range, which is amenable to vacuum bagging or low-pressure molding techniques.

Unless otherwise specified, an adhesive carrier (scrim) consisting of 112 E glass fabric was solution impregnated with the SIPN polyisoimide blend adhesive until the resin content of the impregnated fabric was 70-80% by weight. Lap shear specimens were 1" by 4" with a 1/2" lap. Flatwise tensile specimens had a 2" X 2" bonding area.

For metal adherends, adhesive lap shear specimens were prepared by insertion of impregnated scrim cloth between metal adherends to allow a 1/2" lap. The specimens were cured in a preheated press or in an autoclave at 288°C(550°F) and 50 psi pressure for 1 hour, then cooled to ambient temperature under pressure.

The preliminary bonding data reported in **Table 13** clearly show that respectable adhesive strengths can be obtained, even at temperatures in the 260°C(500°F) range with a number of adhesive substrates having aerospace applications. It is clear that optimization of substrate treatment, primers and bonding conditions should further improve adhesive strength.

The aluminum flatwise tensile tests, designated by asterisks in **Table 13**, give an indication of the excellent bonding capability of the 1:1 and 1:3 LA-100/IP-600 SIPNs when pure tensile loads are applied. The observed cohesive failures thus provide good evidence of resin flow adequate to provide ample fabric impregnation and substrate wetting.

For polymer composite adherends, such as Skybond polyimides, lap-shear strength measurements were performed with coupons cut from a Skybond composites panel. The lap-shear specimens were molded at 316°C (600°F), 50 psi for 2 hours, with no post-cure. Lap-shear strengths of >3,200 psi were obtained.

For interlaminar tensile strength, a test configuration was made as shown in **Figure 19**. The observed failure mode was in the Skybond panel. The value for interlaminar tensile strength was 11,000 psi, but it did not reflect the strength of the adhesive bond due to the SIPN adhesive. An interlaminar tensile strength due to the SIPN adhesive was estimated at 20,000 psi.

The feasibility of achieving good structural bonding of aluminum alloys, steel alloys, and metal matrix composites using polyisoimide adhesives has been demonstrated. The use of thermoset/thermoplastic polyisoimide blends permits processing at relatively low temperatures and pressures.

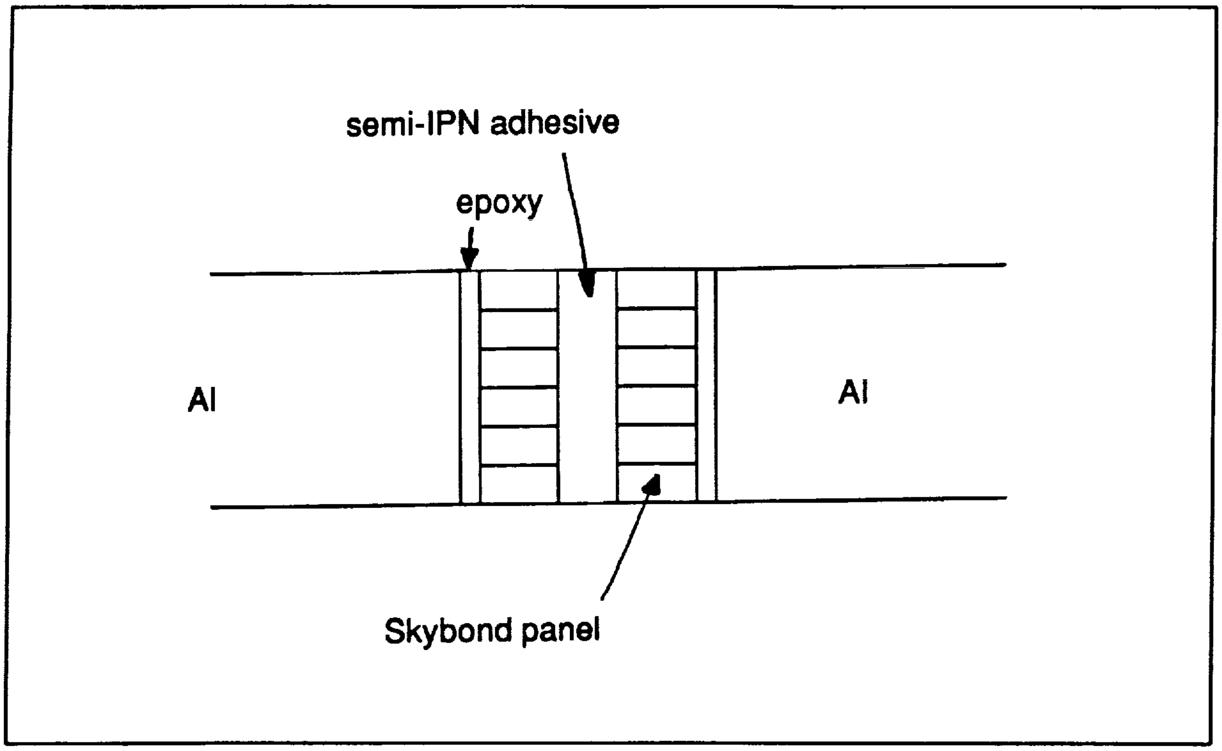
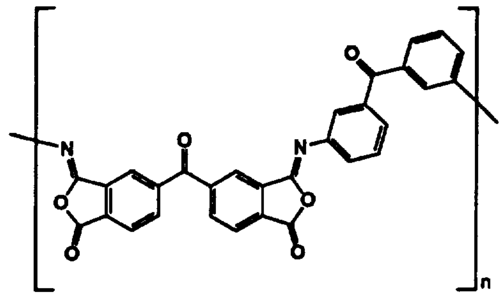


Figure 19. **Test Configuration for Interlaminar Tensile Strength Determination Using Composites Adherends**

In current work, other isoimides are being examined for application as SIPN isoimide adhesive systems. Some of the isoimide components of these systems include isoimide modifications of LARC-TPI, i.e., poly(BTDA-DAB)isoimide, V, and poly(isoimide-sulfone), VI. Two recently developed polyisoimide derivatives are poly(PMDA-APB)isoimide, VII, and poly(BTDA-BDAF)isoimide, VIII, which is the isoimide form of Ethyl's EYMYD L20N polymer (**Figure 20**).



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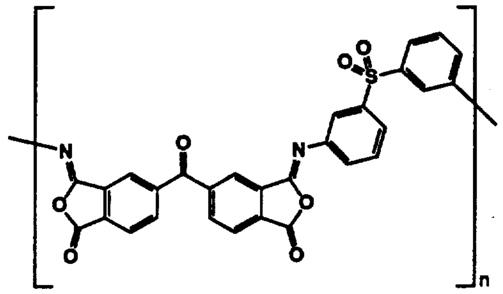

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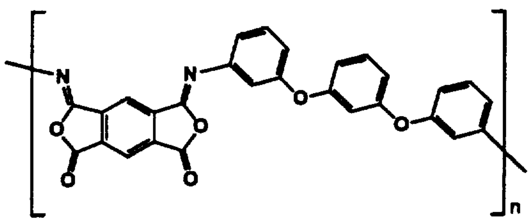
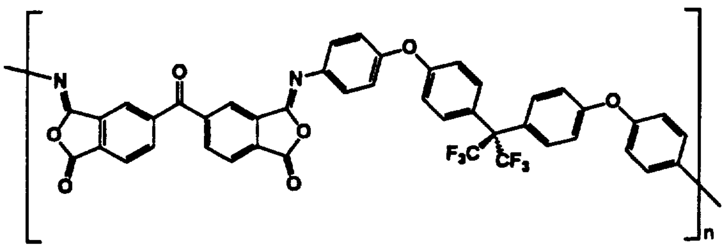


VII



VIII

V: Poly(BTDA-DAB)isoimide
VI: Poly(isoimide-sulfone)
VII: Poly(PMDA-APB)isoimide
VIII: Poly(BTDA-BDAF)isoimide

Figure 20. **Newer Materials for High-Temperature Adhesive Applications**

3.6 MATERIALS EVALUATION

During the course of materials development (details presented previously), each of the polyisoimide has been evaluated according to a predetermined characterization procedure. This procedure for materials evaluation entails three levels of characterization and evaluation prior to composite fabrication:

(1) Monomer, Polymer (and Polymer Blend) Characterization, at the 100-g and 500-g levels.

Level I:	Tg, rheology, physical and thermal properties
Level II:	Tensile strength and modulus, % strain

(2) Prepreg Evaluation and Consolidation.

(3) Small Laminate Fabrication and Level III Evaluation (fracture toughness, short beam shear strength, flexural/ tensile/ compressive strengths and moduli).

(4) Composite Fabrication and Level IV Evaluation (open-hole tensile/ compression, compression-after-impact).

Purity of materials was ascertained via physical characterization: (1) melting point, HPLC, GLC, uv, ir, nmr; (2) specific for polymers: GPC, MW dispersity. Processing characteristics of polymers including solubility in solvents, component miscibility, inherent viscosity, and melt rheology were determined.

One hundred grams of each potential candidate polymer were synthesized and characterized. Baseline neat resin properties were obtained. These data were later compared with those from 500-gram or larger scale-up batches (up to 20 kilograms).

3.6.1 Levels I/II Criteria and Characterization

Table 14 shows target properties for Levels I/II characterization. **Table 15** summarizes the test values for selective candidates whose properties met the target values.

3.6.2 Preliminary Evaluation of Prepregs/Laminates

For preliminary evaluation, fabric prepregs were fabricated by impregnation of fabrics and air-dried to remove excess solvent. Small laminates were consolidated and cured. The cured laminates were evaluated as to their C-Scan or microscopic appearance, resin content, void percentage, and ply thickness (micrometer).

Table 14. Target Properties For Levels I/II Evaluation

MATERIALS PROPERTIES	TARGET VALUES
Level I:	
min Tg (supersonic)	210°-230°C
min Tg (subsonic)	175°C
viscosity(η^*) (min)	10^3 to 10^5 poise
TGA degradation onset	> 500°C
Level II:	
Tensile Strength	14 KSI
Tensile Modulus	540 KSI

Table 15. Results of Levels I/II Evaluation

TARGET PROPERTIES	A	B	C	D	E	F	G	H	J
Level I:									
Tg (°C)	191	260	259	254	233	217	208	273	236
Melt viscosity ($\eta^* \times 10^{-3}$)	7.02	1.08	1.78	2.88	7.72	59.0	1.91	47.2	41.6
Temp of minimum η^*, °C	236	243	250	243	220	218	212	241	213
TGA degrad. onset (Air)	570	540	548	547	548	560	590	545	563
Level II:									
Tensile Strength (KSI)	19.6	19.7	19.0	21.0	---	---	---	15	22
Tensile Modulus (KSI)	613	465	540	600	---	---	---	714	600

A = LA-100 polyisoimide
B = LARC-TPI isoimide
C = LARC-ITPI isoimide
D = BTDA-3,4'-ODA isoimide
E = BTDA-3,4'-ODA/APB (3:1) isoimide
F = BTDA-3,4'-ODA/APB (1:1) isoimide
G = BTDA-3,4'-ODA/APB (1:3) isoimide
H = LARC-PIS isoimide
J = BTDA-BAPP isoimide

Criteria for selected mechanical properties (short beam shear strength, fracture toughness, tensile, compressive, and flexural strengths and moduli (**Table 16**) have been chosen to evaluate the cured laminates under room temperature, dry (RTD) and elevated temperature, wet (ETW) conditions. The range of acceptance for each property given is for unidirectional laminates. Fabric laminates generally have half of the unidirectional values.

In practice, only limited small laminate testing was performed due to small sample size achieved. Fabric laminates were fabricated for convenience. Testing at 350°F, wet was selected to demonstrate strength retention under the worst condition (**Table 17**). Since the consolidation of these small panels was not performed under optimal condition, the results are suitable only for qualitative assessment.

These first-round small laminates showed void contents of 5-10%. However, the optimal consolidation conditions were not applied. Comparison of the unoptimized data indicated that a longer consolidation time provided higher strength values. The important observation is that nearly all the polyisoimides tested showed the potential of strength retention under hot/wet conditions.

3.6.3 Prepreg and Small Laminate Fabrication and Evaluation

Improvement of the processing technique was made by adjusting the consolidation temperature, pressure, cure schedule, and prepreg characteristics. It is desirable to bring the consolidation pressure to below 250 psi, to be commercially practical. Throughout the laminate fabrication undertaking, pressures ranging from 200 to 500 psi have been used to effect good consolidation. Good consolidation is judged by C-scan results and mechanical property values approaching the desired ranges.

The initial laminates were fabricated with fabric reinforcements because of fabric availability and the relative ease of prepregging with fabrics. Comparison of mechanical property data can be made with similar fabric laminate data derived from BMI and PMR-15 developments.

Improvement of mechanical properties has been achieved by systematic adjustment of the processing parameters. Emphasis has been placed on poly(IPDA-MPDA)isoimide. The discussion is deferred to **Section 3.7.**

Table 16. Small Laminate Criteria

8-PLY LAMINATE EVALUATION CRITERION	RANGE OF ACCEPTANCE
short beam shear strength (unidirectional)	>8 ksi
interlaminar fracture toughness, G_{1C}, G_{2C}	4-6 lb/in^2
tensile/compressive moduli	> 20 Msi
tensile/compressive strength	200 - 240 Ksi

Table 17. Summary of Unoptimized Testing of Small Laminate at 350°F

POLYMER CONSTITUENT		PROCESSING CONDITION			FLEXURAL STRENGTH		FLEXURAL MODULUS	
Dianhydride	Diamine	T,°F	psi	hr	dry	wet	dry	wet
IPDA	MPDA	550	100	.25	39.1	39.0	4.7	5.0
		575	200	1.0	----	----	---	---
BTDA	DAB	550	100	.25	26.0	26.0	5.5	4.7
		575	200	1.0	----	----	---	---
BTDA	APB	550	100	.25	25.2	----	2.6	---
		550	500	1.0	55.6	25.8	13.9	5.6
BTDA	APB (3) 3,4'-ODA (1)	550	100	.25	26.0	26.0	6.0	5.9
		550	500	1.0	48.3	48.0	5.4	5.6
BTDA	APB (1) 3,4'-ODA (1)	550	100	.25	38.0	45.0	7.0	6.7
		550	500	1.0	----	----	---	---
BTDA	3,3'-DDS	550	100	.25	----	----	---	---
		600	200	1.0	39.0	36.1	4.7	4.2

Flexural Strength in units of KSI
Flexural Modulus in units of MSI

3.7 DEVELOPMENT OF POLY(IPDA-MPDA)ISOIMIDE

During the initial phase of Task 3, we have selected several potentially useful polyimide systems and synthesized their corresponding polyisoimides with the expectation that the isoimide modification would enhance the processibility of the materials. As a result of the preliminary study, we have recommended LARC-ITPI as the most attractive polyimide for further engineering evaluation for near-term applications.

The unexpected decision from Allco in August 90 to give up their production of the IPDA dianhydride and LARC-ITPI polymer has caused a major delay in the development of LARC-ITPI. They would have the potential to produce 50 to 100-pound level quantities on short notice. NASA and Lockheed's materials needs suffered an impasse in late 1990.

The establishment of a second source depended on the inherently attractive economics of LARC-ITPI. Both NASA and Lockheed have investigated in potential alternate sources. Imitec, Inc. (Schenectady, NY) began to develop a commercial line based on the amic acid of LARC-ITPI in early 1991.

While the bulk supply of LARC-ITPI amic acid eventually allowed us to proceed with the scale-up synthesis of LARC-ITPI isoimide, our needs for this material during this development period depended solely on small-scale synthesis in our laboratories. The synthetic technique for LARC-ITPI isoimide has been refined and transitioned to a scale-up process. The scale-up process, developed with collaboration from National Starch and Chemical Corporation, has been defined for batch size of 25 kilograms.

Because of their needs for more chemical studies, other Rank 1 polymers **(Table 18)** were not further evaluated. The 3,4'-ODA-based polyisoimides should remain as possibilities for advanced matrix resin applications. The strong attribute is that the small laminates made from these materials showed no significant deterioration of room-temperature mechanical properties at 350°F (hot, wet) testing. The laminates made from these polyisoimides gave expectedly low room-temperature properties because of high porosity. The difficulties in getting good laminates are with the flow characteristics as thermoplastics. Based on the results from the IPDA-MPDA system (see below in **Section 3.7.3)**, improvement on the 3,4'-ODA-based systems should also be possible with lower DP materials, and with SIPN blending with acetylene-terminated isomide oligomers. Other polyisoimides could be evaluated likewise in those directions as components of SIPNs.

Table 18. Ranking of Polyisoimides Prior to Scale-Up Development

RANKING	TRIVIAL NAME	POLYMER CONSTITUENT		CRITERIA					
		Dianhydride	Diamine	cost comp	Tg > 210°C	Td>500C (onset)	η^* (Tmin)	ease of synth	good prelim results
1	LARC-ITPI Polyisoimide	IPDA	MPDA	1	259	548	1780 (213)	1	yes
1	Polyisoimide O-10	BTDA	3,4'-ODA	1	254	547	2880 (243)	2	yes
1	Copolyisoimide O-31	BTDA	3,4'-ODA (3) APB (1)	2	233	548	7720 (220)	1	yes
1	Copolyisoimide O-11	BTDA	3,4'-ODA (1) APB (1)	2	217	560	59000 (218)	1	yes
2	Copolyisoimide O-13	BTDA	3,4'-ODA (1) APB (3)	3	208	590	19100 (212)	1	yes
2	LARC-TPI Polyisoimide	BTDA	DAB	3	260	540	1076 (243)	1	yes
2	Copolyisoimide B-10	BTDA	BAPP	2	236	563	41600 (213)	2	need more evaluation
2	OPDA-based Polyisoimides	OPDA	various diamines	2	270	570	-- --	2	need evaluation
3	LARC-CPI Polyisoimide	BTDA	1,3'-BABB	3	222	---	36200 (223)	3	need more evaluation
3	LARC-PIS Polyisoimide	BTDA	3,3'-DDS	3	273	545	47200 (241)	4	general low flow problm
3	UPILEX Polymers	DPDA	diamines	3	270	---	-- --	2	need evaluation

3.7.1 SCALE-UP SYNTHESIS DEVELOPMENT

We have selected poly(IPDA-MPDA)isoimide as our the target system based on preliminary data on cost and mechanical properties. The development comprises four stages. The very first important stage is to convert the bulk quantity of the polyamic acid lacquer to the isoimide. In the second and third stages, the isoimide is processed through prepregging and consolidation. The final stage is mechanical testing and analysis.

Imitec, Inc. supplied a 20-kg quantity of poly(IPDA-MPDA)amic acid as an NMP lacquer. The material was delivered to National Starch and Chemical Corporation, who assisted in evaluating the feasibility of process transition from bench-scale to a semi-pilot scale by duplicating some small-scale experiments originally done at Lockheed.

Quality Assessment

The IPDA dianhydride monomer and the NMP lacquer of the polyamic acid were within the accepted NASA guidelines (monomer: FTIR, HPLC purity 98.9%; polymer: 30% solids content, η_{inh} 0.50 - 0.80 dl/g; visually clear amber coloration).

Pilot Plant Safety Factors

In response to the OSHA requirements imposed on National Starch on laboratory/ pilot plant safety, replacement for the acetone work-up solvent was sought. The methyl ethyl ketone (MEK) work-up alternative was established as a safer method than the acetone work-up procedure. In the final analysis, the decision was to use a previously established and qualified solvent, isopropyl alcohol.

Resolving the Premature Gellation Problem

We have also resolved an unexpected problem due to premature gellation during the trial runs of isoimidization performed at National Starch. The problem was traced to a combination of the higher-than-desirable concentration of the reaction solution and the rapid addition of the N,N'-dicyclohexylcarbodiimide (DCC) reagent during the isoimidization step. We have demonstrated that the gellation problem can be circumvented by running the reaction at a concentration of <10% and a slow rate of addition of the DCC reagent.

Pilot Plant Experiment

The lab-scale experiment was duplicated at the pilot plant without any problem. The details pertaining to the step-by-step instruction for the pilot plant operators were then established. The production run (~30 lbs) took place in accordance with the estimated schedule. No complication was observed during the sequence of events. The work-up process continued for about 24 hours, during which the polyisoimide was precipitated and washed twice with high-purity isopropyl alcohol. The isolated powder was dried and conformance to specifications was verified.

National Starch was concerned earlier with the high volatiles content (9-10%) obtained from larger batch experiments with the high inherent viscosity (η = 0.8 dl/g) Imitec material. The high volatiles content, however, would not affect solution prepregging. In future work, where powder prepregging will be used, a lower than 3% volatiles content can be realized from a lower molecular weight end-capped polymer. Previous results did correlate lower volatiles contents with lower molecular weights.

3.7.2 SIPN DEVELOPMENT

The reproducibility of synthesis of the acetylene-terminated isoimide oligomer was also established. LARC-ITPI isoimide and its acetylene-terminated oligomer form the basis of the SIPN designs.

The synthetic procedure for various DPs of acetylene-terminated oligomer of Poly(IPDA-MPDA)isoimide (AT-ITPI) **(Figure 21)** has been established. Processing evaluation of the semi-interpenetrating polymer networks (SIPNs) with the Poly(IPDA-MPDA)isoimide/ AT-ITPI (DP=1) combination indicated markedly improved flow.

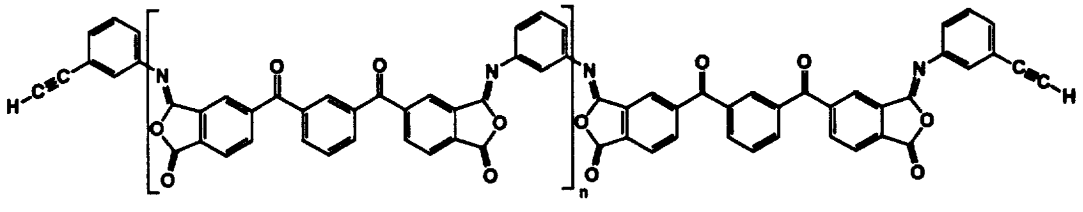


Figure 21. Acetylene-Terminated (IPDA-MPDA)isoimide Oligomer

3.7.3 PREPREGGING AND LAMINATE FABRICATION

Improvement of the mechanical strength of the 8-ply laminates (fabric) was obtained as better consolidation was achieved through adjustment of the processing parameters. Recent results with SIPNs indicated markedly improved flow, which resulted in better consolidation and higher values for tensile/flex strength and modulus of the fabric laminates. Consistent results have been obtained on the processing of void-free small laminates. Prepregging results obtained in N-methylpyrrolidinone (NMP) compared favorably with prepregging of similar polyisoimides in a mixture of 80% dioxolane/20% γ-butyrolactone (work done under a Lockheed IR&D joint project with Rohr Industries).

The preliminary SIPN formulations were prepared from poly(IPDA-MPDA)isoimide and AT-ITPI. The small-scale evaluation of SIPNs was conducted with materials synthesized at Lockheed. The synthetic procedures for all the phthalic anhydride-end-capped polyisoimides and acetylene-terminated isoimides, in particular, those of the IPDA-MPDA chemical system (which is the same as the LARC-ITPI system), have been proven to be scaleable. Because the AT-ITPI material is in short supply, a supplier not having been established, the subsequent SIPNs were made using the commercial IP-600 isoimide oligomer in place of AT-ITPI.

Fabric Prepregging and Laminate Consolidation

Table 19 summarizes the better laminate data for poly(IPDA-MPDA)isoimide via recent improvement on the adjustment of processing parameters.

The fabric data were 80.5 ksi flex strength and 8.4 msi flex modulus (almost twice of what were obtained earlier). Better consolidation was a result of using a preheated compression mold to reduce the time for the impregnated resin to reach processing temperature (minimum melt viscosity) for easier flow and fiber wetting. The modulus was in the acceptable range, although the strength was about 20 % low. However, these laminates had a high resin content of 38 %. Extrapolating to a 30-32% resin content range would bring the strength to an expected value of >100 ksi. As a rule of thumb, the unidirectional values should be twice the fabric values assuming similar levels of consolidation. The consolidation pressures were still slightly high (250-300 psi).

Another set of laminate data on the IPDA-MPDA system was obtained:

Ultimate Tensile Strength:	81.9 ksi	(range 75.7-88.4, 5 specimens)
Tensile Modulus:	9.40 msi	(range 9.66-9.86, 3 specimens)
Flex Strength:	84.3 ksi	(range 69.4-99.4, 10 specimens)
Flex Modulus:	8.60 msi	(range 8.3- 9.0, 10 specimens)
Interlaminar Short Beam Shear:	5.97 ksi	(range 5.46-6.32, 10 specimens)

Again, the high resin content of 44% probably reduced the actual values. Extrapolating to 32% resin content, the values probably improve by 27% (hence, FS = 115 ksi, FM = 11.8 msi). The expected corresponding unidirectional values would be 230 ksi and 23.6 msi, which would be well in the acceptable range. At this point, the consolidation pressure was still high. The DP=50 poly(IPDA-MPDA)isoimide requires >300 psi to achieve good consolidation (void content less than 5%). Using the SIPN approach (TP:TS = 75:25 or 50:50) has since reduced the processing pressures to 200 psi.

Table 19. **Physical Characteristics and Mechanical Properties for Small Laminates Made From Poly(IPDA-MPDA)isoimide on Fabric**

CHARACTERISTICS AND PROPERTIES	PANEL #1	PANEL #2
Specific Gravity	1.54	1.57
% Fiber Volume	62.0	56.0
% Void Content	2.2	2.6
Number of Plies	8	6
Flexural Strength, ksi (ASTM D-790)	80.5	84.3
Flexural Modulus, msi (ASTM D-790)	8.4	8.6
Short Beam Shear Strength, ksi (ASTM D-2344)	----	5.97
Tensile Strength, ksi (ASTM D-638)	----	81.9
Tensile Modulus, msi (ASTM D-638)	----	9.4

Table 20 shows the benefits of SIPN in processing. The void content for laminates made from a 50:50 SIPN blend of poly(IPDA-MPDA)isoimide and its corresponding DP=1 acetylene-terminated analog on 8 harness satin weave T300 fabric has been reduced to under 1%. The flex strength of 141.6 ksi is equivalent to 284 ksi for a unidirectional composite, assuming same level of consolidation.

Table 20. Physical Characteristics and Mechanical Properties for SIPN Small Laminates

CHARACTERISTICS AND PROPERTIES	PANEL #1	PANEL #2
Specific Gravity	1.58	1.56
% Fiber Volume	56.4	54.0
% Void Content	0.28	0.98
Number of Plies	8	6
Flexural Strength, ksi (ASTM D-790)	141.6	----
Flexural Modulus, msi (ASTM D-790)	8.6	----
Short Beam Shear Strength, ksi (ASTM D-2344)	13.4	----
Tensile Strength, ksi (ASTM D-638)	----	79.0
Tensile Modulus, msi (ASTM D-638)	----	8.8

Unidirectional Prepregging and Laminate Consolidation

A portion of the unidirectional prepreg work was performed by Applied Poleramic Incorporated (Benicia, CA), who used a modular prepregging machine that is currently being tested at NASA-Langley (**Figure 22**).

The fiber selected was unsized 12K IM7, and the resin was a 1:1 by wt blend of poly(IPDA-MPDA)isoimide and IP-600. The prepreg solvent was NMP. Prepreg characteristics of this batch are summarized in **Table 21.**

Table 21. Prepreg Characteristics of IM7 Unidirectional Tape

SAMPLE NUMBER	1	2	3
PREPREG WIDTH (cm)	17.2	17.2	16.5
WET PREPREG WEIGHT (grams)	2.72	2.72	2.60
DRY PREPREG WEIGHT (grams)	2.30	2.25	2.16
PERCENT VOLATILES	15%	17%	17%
EXTRACTION SOLVENT	N/A	N/A	N/A
DRY FIBER WEIGHT (grams)	N/A	N/A	N/A
APPROX FIBER AREAL WEIGHT (grams)	139	139	142
DRY RESIN CONTENT	39%	38%	34%

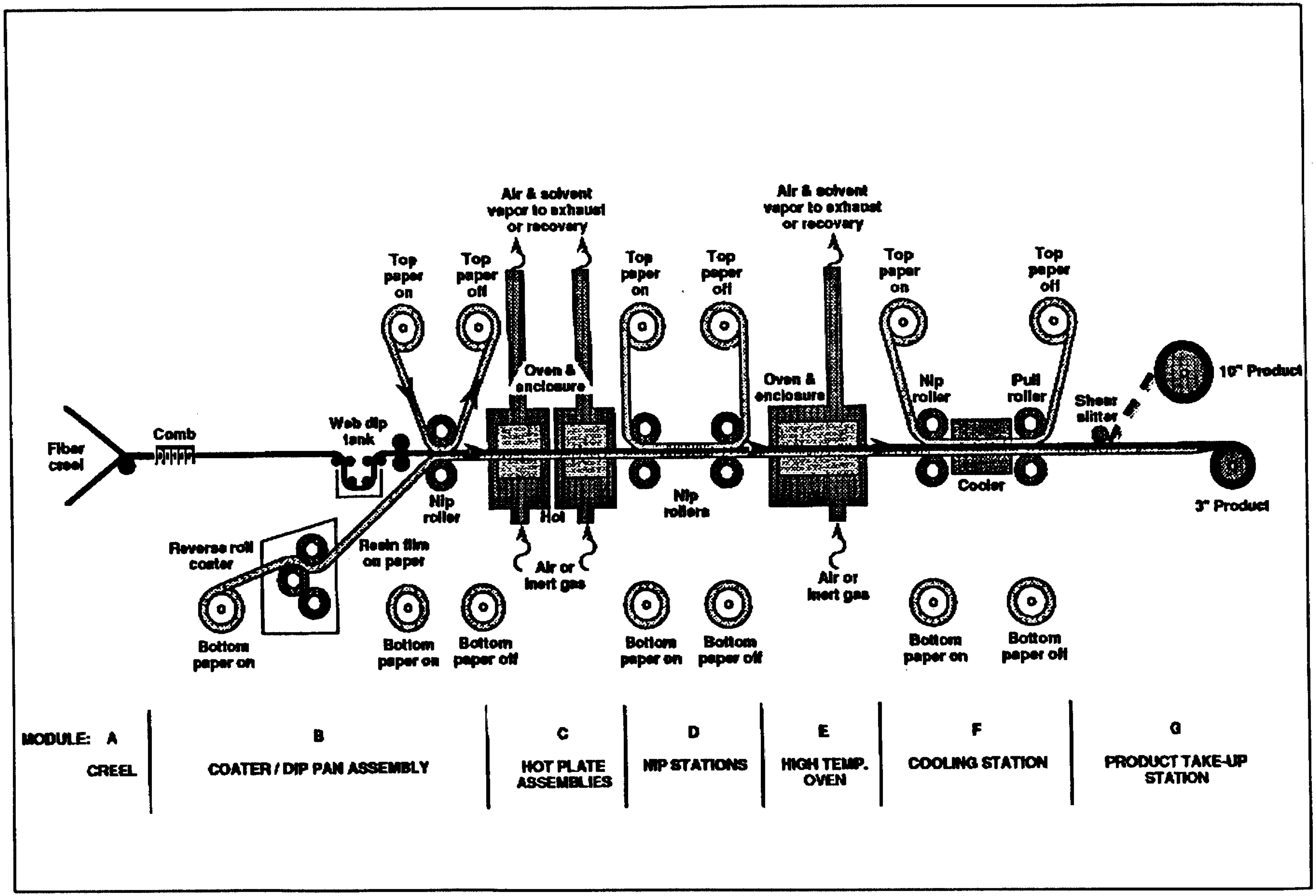


Figure 22. Schematic of Modular Prepregging Machine

Table 22 summarizes the test data on unidirectional IM7 laminates made with the SIPN blend of poly(IPDA-MPDA)isoimide and acetylene-terminated poly(BTDA-APB) oligomer (IP-600).

The 0° data were obtained for 8-ply and 16-ply 0° laminates. For one of the 16-ply 0° laminates, in particular, the 259.9 ksi tensile strength and 25.9 msi tensile modulus surpassed the general range of acceptance. The other similar laminates showed values within the range of acceptance, indicated previously in **Table 16**. The results suggested that SIPN systems made from poly(IPDA-MPDA)isoimide are acceptable candidates for advanced composite applications. The level of consolidation was shown by C-scan and specific gravity data as excellent (<5% void content). Good consolidation was achieved again by using a preheated compression mold to reduce the time for the impregnated resin to reach processing temperature (minimum melt viscosity) for easier flow and fiber wetting. The consolidation pressures were reduced to below 250 psi.

3.7.4 Future Plans for Testing

Confirmation of the above small laminate properties and additional properties (±45° and quasi-isotropic properties) are recommended to enhance the data base. The previous results showed significant correlation between consolidation and mechanical properties.

The next step for furthering the laminate evaluation would be to extend the consolidation technique to fabricate thicker composites, e.g., 48-ply, for engineering property measurements such as Tensile per ASTM D-3518, Open Hole Tensile/Compression per NASA 1142, and Compression After Impact per NASA 1092. The larger composites fabrication is material dependent. Larger batches (>25 kg) of poly(IPDA-MPDA)isoimide can be conveniently synthesized. Acetylene-terminated IPDA-MPDA oligomer can be developed either at Imitec, Inc. or National Starch.

With the large batches of polymers being made available, prepregs will be fabricated as unidirectional tapes. Panels (24" or 12" squared) will be fabricated as 24-plies, and 48-plies, cured and tested (C-scan, specific gravity, resin content, voids, moisture absorption at equilibrium, dry and wet Tg's). **Table 23** shows the range of acceptance for Compression After Impact (NASA 1092) and Open Hole Tensile/Compression (NASA 1142) properties.

Table 22. Physical Characteristics and Mechanical Properties for SIPN Unidirectional 0° Laminates

CHARACTERISTICS AND PROPERTIES	PANEL #1	PANEL #2	PANEL #3	PANEL #4
Specific Gravity	1.58	1.62	1.54	1.50
% Fiber Volume	65.5	66.7	60.0	57.1
% Void Content	0.0	0.0	2.8	5.0
Number of Plies	16	16	8	8
Flexural Strength, ksi (ASTM D-790)	----	187.0	245.0	202.0
Flexural Modulus, msi (ASTM D-790)	----	18.5	16.7	20.0
Short Beam Shear Strength, ksi (ASTM D-2344)	----	----	----	10.4
Tensile Strength, ksi (ASTM D-638)	259.9	250.3	216.6	234.0
Tensile Modulus, msi (ASTM D-638)	25.9	24.3	22.4	26.2

Table 23. 48-Ply Composite Evaluation Criteria

48-PLY LAMINATE EVALUATION CRITERION	RANGE OF ACCEPTANCE
compression after impact (275°F, wet)	> 4,000 $\mu\varepsilon$
open hole tension/compression	> 6,000 $\mu\varepsilon$ (T) > 4,000 $\mu\varepsilon$ (C)

3.8 EXPERIMENTAL

3.8.1 Instrumentation

Melting points were determined with an Electrothermal IA 8100 digital melting point apparatus. All melting points were uncorrected.

High-performance liquid chromatography (HPLC) was performed using an Altex Model 100 instrument. Inherent viscosity measurements were made using a thermostatted Oswald viscometer. Molecular weight determination by gel permeation chromatography was conducted using a Waters Model 150-C instrument.

Fourier-Transform infrared spectroscopy (FTIR) was performed on a Nicolet model 60SX spectrometer. FTIR studies generally provide qualitative information on the batch-to-batch variance in synthesis and the conversion of isoimide to imide. Quantitative measurements of the isoimide/imide ratio were performed as needed.

Differential scanning calorimetric (DSC) data were obtained from 10- to 15-mg samples in a nitrogen atmosphere at a 10°C min^{-1} heating rate, using a Perkin-Elmer DSC-7 analyzer. Thermogravimetric (TGA) data were obtained from 5- to 10-mg samples both in nitrogen or in air at a 10°C min^{-1} heating rate using a Perkin-Elmer TGS-2 or a TGS-7 thermogravimetric analyzer.

3.8.2 Rheological Characterization

Preparation of Molded Samples

Specimens suitable for rheological measurements were prepared from the powdery polyisoimides by pressing circular pellets from a vacuum compression mold, using a hydraulic press at ambient temperature. A predetermined quantity (1 gram) of polyisoimide powder was first placed inside the mold cavity, and was pumped at 10^{-3} mm pressure for 10 minutes to remove trapped air and residual traces of solvent. Then a pressure of 12,000 psi was applied to the plunger which compresses the powder into a pellet of 25 mm in diameter and 2 mm in thickness. Prior to forming a pellet, the powdery polymer was first pretreated at 175°C *in vacuo* for 30 minutes to remove residual solvent or moisture.

Measurement Procedure

The flow properties of polyisoimides as a function of temperature were obtained using a Rheometrics mechanical spectrometer, RMS-800, which is equipped with an environmental chamber for temperature control. Nitrogen purge was used during all runs to avoid oxidation of the samples. Oscillatory shear (dynamic shear) mode and parallel plates (8-mm and 25-mm diameters) were used to measure the dynamic viscosity at a frequency of 10 rad/s. A temperature sweep program was used to monitor the change in temperature.

After the specimen was placed between the parallel plates at ambient temperature, the temperature of the environmental chamber was allowed to equilibrate at 140°C (below the polymer melting temperature). The temperature was programmed to rise to 190°C at 10°C per increment, to 300°C at 5°C per increment, and then to 400°C at 10°C per increment. (In some cases, the program was terminated earlier due to sample outgassing). The dynamic viscosity, η^*, was measured after the chamber temperature stabilizes at each temperature step. The actual temperature of the specimen was monitored by a thermocouple in contact with the platen on which the specimen was placed. The specimen was subjected to a slight compression during the experiment to minimize slippage between the material and the platens. The percent strain applied to the specimen was chosen (using the auto strain option of the program) to ensure that the deformation was within the linear viscoelasticity range.

3.8.3 Dielectric Spectroscopy

Dielectric spectroscopic data were obtained using an Hewlett-Packard impendance analyzer and thin film samples impregnated onto interdigitizing electrodes. Measurements at frequency range of 100 Hz to 100 KHz were obtained as the temperature was increased at a rate of 5°C/min.

3.8.4 General Synthetic Technique for Polyisoimides

All solvents used were commercial and of reagent grade. Benzophenonetetracarboxylic dianhydride (BTDA) was from Allco High Purity Lots (recrystallized from acetic anhydride) and was used as received. Isophthaloyl bisphthalic dianhydride (IPDA) also was purchased from Allco. The diamine compounds were all commercial and of polymer grade, each being recrystallized once prior to use. 1,3-Bis(3-aminophenoxy)benzene (APB) was from National Starch (Bridgewater, NJ) and recrystallized from toluene. 3,4'-Oxydianiline (3,4'-ODA) and 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP) are Wakayama Seiko products, and supplies were purchased from Kennedy and Klim (Little Silver, NJ).

The general synthetic technique for the preparation of various polyisoimides of different molecular weights entails (1) the formation of the polyamic acid precursor by the reaction of stoichiometric amounts of acid anhydride, the diamine, and the end-capping agent phthalic anhydride (PA), in an appropriate solvent, such as tetrahydrofuran (THF), N,N-dimethylacetamide (DMAC), and N-methylpyrrolidinone (NMP); (2) cyclodehydration of the polyamic acid with a stoichiometric quantity of N,N'-dicyclohexylcarbodiimide (DCC) to yield the polyisoimide and the insoluble by-product, N, N'-dicyclohexylurea, (DCU), which can be removed by filtration; and (3) precipitation of the polyisoimide from the reaction solution with isopropyl alcohol, or acetone.

3.8.5 Illustrative Synthesis of End-Capped Poly(BTDA-APB)isoimide, DP=50

A five-liter, thermostatted, three-neck, round-bottom flask was fitted with a Tru-bore stirrer, dropping funnel, reflux condenser, constant pressure argon inlet fitting and a heating mantle.

The special thermostatted vessel comprises a concentric, spherical glass jacket, with inlet and outlet spouts for fluid circulation, built around a three-neck round-bottom flask of a predetermined size (500-ml to 5-liter size). During the reaction, a fluid thermostatted at a prescribed temperature is circulated through this jacket to maintain a constant temperature for the reaction mixture inside the vessel.

The flask was charged with 1,3-bis(3-aminophenoxy)benzene (APB) (135.0 g, 0.4623 Mol) and anhydrous tetrahydrofuran (2 L). To the flask, solid benzophenonetetracarboxylic dianhydride (BTDA) (145.95 g, 0.4533 Mol) was added. After stirring for 30 minutes, phthalic anhydride (2.680 g, 0.01813 Mol) was added. After stirring for 1 hour, 1 liter of THF was added and the solution cooled to 0-2°C by passing coolant through the jacket.

A solution of N,N'-dicyclohexylcarbodiimide (DCC) (190.5 g, 0.9247 Mol) in 600 ml of THF was added dropwise by means of a pressure equalized dropping funnel over a six-hour period. Too rapid addition of the DCC causes gelation. After the addition the reaction mixture was stirred at 0°C for 16 hours, filtered to remove the N,N'-dicyclohexylurea and the filtrate concentrated to 1.8 L on the rotary evaporator. The product was isolated by pouring 200 mL portions into 500 mL of isopropyl alcohol in a blender and filtering. After air-drying and vacuum drying at 80°C, a yield of 245 g of the product was obtained.

3.8.6 Illustrative Synthesis of End-capped Poly(IPDA-MPDA)isoimide, DP=50 (Acetone Work-up)

A 2-liter, 3-neck, jacketed flask fitted with a Tru-bore stirrer, pressure-equalized dropping funnel and a thermometer, is charged with m-phenylenediamine (MPDA)(25.86 g, 0.2394 Mol) and N-methylpyrrolidinone (NMP)(800 mL). To the solution, 1,3-bis(3,4-dicarboxybenzoyl)benzene dianhydride (isophthaloyl bisphthalic dianhydride, IPDA)(100.0 g, 0.2347 Mol) was added portion by portion as a powder. The reaction mixture was then stirred for 1 hour and phthalic anhydride (PA)(1.39 g, 0.00939 Mol) was added. The solution is stirred at ambient temperature for 16 hours to allow molecular weight equilibration.

Coolant was passed through the exterior jacket of the reaction flask and the reaction mixture was chilled to 0-1°C. A solution of N,N'-dicyclohexylcarbodiimide (DCC)(98.70 g, 0.4789 Mol) in 300 mL of NMP was then added dropwise over a 3-hour period. (Precipitation of N,N'-dicyclohexylurea (DCU) was evident after 20 minutes of stirring.) The reaction mixture was stirred at 0°C for 1 hour, the coolant turned off, the reaction mixture brought to ca. 20°C during 1 hour, and kept at that temperature for 16 hours. The precipitated DCU was filtered through a Whatman 541 filter paper in a Buchner funnel, and pressed with a rubber dam.

The polyisoimide was isolated by pouring the filtrate, in 150-mL portions, slowly into a blender containing 450 to 500 mL of acetone, and subsequent filtering through a Whatman Number 541 filter paper in a Buchner funnel. The solid cake was washed with acetone and pressed with a rubber dam to squeeze out as much of the mother liquor as possible. The combined mother liquor was saved for later determination of material loss during this work-up procedure. The solid cake was transferred to a large Erlenmeyer and broken up under 3.5 L of acetone. The solid was filtered, pressed with a rubber dam, and then broken up into a powder. The powder was placed in a shallow tray to air-dry at 25°C for 16 hours. The final drying was carried out in a stepwise process: first, 1 hour at 25°C/0.1 mm, then 1 hour at every 15°C increment, until the final temperature reached 85°C. The material was kept at 85°C under 0.1 mm pressure for 16 hours. A yield of 104 g of a light yellow fine powder was obtained.

The acetone washes were evaporated to dryness on the rotary evaporator at a bath temperature of 85°C, under slightly reduced pressure just enough to provide a steady distillation. The residue was dispersed in acetone, filtered and dried at 70°C under 0.1 mm pressure for 16 hours. The solids recovered weighed 10.4 gm.

3.8.7 Illustrative Synthesis of End-capped Poly(BTDA-3,4′-ODA)isoimide, DP=50

A 5-liter, 3-neck, jacketed flask fitted with a Tru-bore stirrer, pressure-equalized dropping funnel and a thermometer, is charged with 3,4′-diaminodiphenyl ether (3,4′-oxydianiline, 3,4′-ODA)(100.0 g, 0.5000 Mol) and N,N-dimethylacetamide (DMAC)(1,300 mL). To the solution, 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA)(157.84 g, 0.4902 Mol) was added as a powder. The reaction mixture was then stirred for 1 hour and phthalic anhydride (PA)(2.90 g, 0.0196 Mol) was added. The solution is stirred at ambient temperature for 16 hours to allow molecular weight equilibration.

Coolant was passed through the exterior jacket of the reaction flask and the reaction mixture was chilled to 0-1°C. Additional DMAC (800 mL) was added. A solution of N,N′-dicyclohexylcarbodiimide (DCC)(206.0 g, 1.000 Mol) in 600 mL of DMAC was then added dropwise over a 4-hour period. The reaction mixture was stirred at 0°C for 16 hours, the coolant turned off, the reaction mixture brought to ca. 20°C during 1 hour, and concentrated to 1,900 mL. The precipitated DCU was filtered through a Whatman 541 filter paper in a Buchner funnel, and pressed with a rubber dam.

The polyisoimide was isolated by pouring the filtrate, in 200-mL portions, slowly into a blender containing 450 to 500 mL of isopropyl alcohol, and subsequent filtering through a Whatman Number 541 filter paper in a Buchner funnel. The solid cake was washed with isopropyl alcohol and pressed with a rubber dam to squeeze out as much of the mother liquor as possible. The solid cake was transferred to a large Erlenmeyer and broken up under 3.5 L of isopropyl alcohol. The solid was filtered, pressed with a rubber dam, and then broken up into a powder. The powder was placed in a shallow tray to air-dry at 25°C for 16 hours. The final drying was carried out in a stepwise process: first, 1 hour at 25°C/0.1 mm, then 1 hour at every 15°C increment, until the final temperature reached 85°C. The material was kept at 85°C under 0.1 mm pressure for 16 hours. A yield of 234 g of a light yellow fine powder was obtained.

The FTIR of this material shows the characteristic isoimide bands at 1806, 1686, and 932 cm^{-1}, as well as the imide band at 1373 cm^{-1}. There is relatively little amic acid present (1540 cm^{-1}). The weight average MW is 20,823 and the number average is 8,404. A DSC scan (25-350°C) of the polyisoimide showed the onset of a exotherm at 263°C with a maximum at 292°C. Rescanning the sample to 350°C and cooled to room temperature gave a distinct Tg at 254°C. TGA at 10°C/min showed onset of degradation at 553°C (N_2), 547°C (air).

3.8.8 End-capped Copoly(BTDA-3,4′-ODA/APB (3:1))isoimide, DP=50

A 5-liter, 3-neck, jacketed flask fitted with a Tru-bore stirrer, pressure-equalized dropping funnel and a thermometer, is charged with 3,4′-diaminodiphenyl ether (3,4′-oxydianiline, 3,4′-ODA)(47.52 g, 0.2376 Mol), 1,3-bis(3-aminophenoxy)benzene (APB)(23.12 g, 0.07919 Mol) and N,N-dimethylacetamide (DMAC)(1,250 mL). To the solution, 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA)(100.0 g, 0.3106 Mol) was added as a powder. The reaction mixture was then stirred for 1 hour and phthalic anhydride (PA)(1.84 g, 0.0124 Mol) was added. The mixture was stirred at 25°C for 16 hours.

Additional DMAC (750 mL) was added. Coolant was passed through the exterior jacket of the reaction flask and the reaction mixture was chilled to 0-1°C. A solution of N,N′-dicyclohexylcarbodiimide (DCC)(130.5 g, 0.6335 Mol) in 600 mL of DMAC was then added dropwise over a 2-hour period. The reaction mixture was stirred at 0°C for 16 hours, the coolant turned off, the reaction mixture brought to ca. 20°C during 1 hour, and concentrated to 1,400 mL. The precipitated DCU was filtered through a Whatman 541 filter paper in a Buchner funnel, and pressed with a rubber dam.

The polyisoimide was isolated by pouring the filtrate, in 200-mL portions, slowly into a blender containing 500 mL of isopropyl alcohol, and subsequent filtering through a Whatman Number 541 filter paper in a Buchner funnel. The solid cake was washed with isopropyl alcohol and pressed with a rubber dam to squeeze out as much of the mother liquor as possible. The solid cake was transferred to a large Erlenmeyer and broken up under 3.5 L of isopropyl alcohol. The solid was filtered, pressed with a rubber dam, and then broken up into a powder. The powder was placed in a shallow tray to air-dry at 25°C for 16 hours. The final drying was carried out in a stepwise process: first, 1 hour at 25°C/0.1 mm, then 1 hour at every 15°C increment, until the final temperature reached 85°C. The material was kept at 85°C under 0.1 mm pressure for 16 hours. A yield of 165 g of a light yellow fine powder was obtained.

This polymer does not dissolve well in THF, and takes a long time to dissolve in NMP, but eventually it is castable into a tough film. The FTIR of this material shows the characteristic isoimide bands at 1806, 1686, and 932 cm^{-1}, as well as the imide band at 1373 cm^{-1}. There is relatively little amic acid present (1540 cm^{-1}). The FTIR gives a significant imide signal indicating a mixed imide/isoimide composition. Rescanning the sample to 350°C and cooled to room temperature gave a distinct Tg at 231°C.

3.8.9 End-capped Copoly(BTDA-3,4'-ODA/APB (1:1))isoimide, DP=50

A 5-liter, 3-neck, jacketed flask fitted with a Tru-bore stirrer, pressure-equalized dropping funnel and a thermometer, is charged with 3,4'-diaminodiphenyl ether (3,4'-oxydianiline, 3,4'-ODA)(31.68 g, 0.1584 Mol), 1,3-bis(3-aminophenoxy)benzene (APB)(46.25 g, 0.1584 Mol) and N,N-dimethylacetamide (DMAC)(1,200 mL). To the solution, 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA)(100.0 g, 0.3106 Mol) was added as a powder. The reaction mixture was then stirred for 3 hours and phthalic anhydride (PA)(1.84 g, 0.0124 Mol) was added. The reaction mixture was stirred at 25°C for 16 hours.

Additional DMAC (750 mL) was added. Coolant was passed through the exterior jacket of the reaction flask and the reaction mixture was chilled to 0-1°C. A solution of N,N'-dicyclohexylcarbodiimide (DCC)(130.5 g, 0.6335 Mol) in 500 mL of DMAC was then added dropwise over a 3-hour period. The reaction mixture was stirred at 0°C for 72 hours, the coolant turned off, the reaction mixture brought to ca. 20°C during 1 hour, and concentrated to 1,200 mL. The precipitated DCU was filtered through a Whatman 541 filter paper in a Buchner funnel, and pressed with a rubber dam.

The polyisoimide was isolated by pouring the filtrate, in 200-mL portions, slowly into a blender containing 500 mL of isopropyl alcohol, and subsequent filtering through a Whatman Number 541 filter paper in a Buchner funnel. The solid cake was washed with isopropyl alcohol and pressed with a rubber dam to squeeze out as much of the mother liquor as possible. The solid cake was transferred to a large Erlenmeyer and broken up under 3.5 L of isopropyl alcohol. The solid was filtered, pressed with a rubber dam, and then broken up into a powder. The powder was placed in a shallow tray to air-dry at 25°C for 16 hours. The final drying was carried out in a stepwise process: first, 1 hour at 25°C/0.1 mm, then 1 hour at every 15°C increment, until the final temperature reached 85°C. The material was kept at 85°C under 0.1 mm pressure for 16 hours. A yield of 172 g of a light yellow fine powder was obtained.

3.8.10 End-capped Copoly(BTDA-3,4'-ODA/APB (1:3))isoimide, DP=50

A 5-liter, 3-neck, jacketed flask fitted with a Tru-bore stirrer, pressure-equalized dropping funnel and a thermometer, is charged with 3,4'-diaminodiphenyl ether (3,4'-oxydianiline, 3,4'-ODA)(19.80 g, 0.09899 Mol), 1,3-bis(3-aminophenoxy)benzene (APB)(86.72 g, 0.2970 Mol) and N,N-dimethylacetamide (DMAC)(1,400 mL). To the solution, 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA)(125.0 g, 0.3882 Mol) was added as a powder. The reaction mixture was then stirred for 3 hours and phthalic anhydride (PA)(2.30 g, 0.0155 Mol) was added. Coolant was passed through the exterior jacket of the reaction flask and the reaction mixture was chilled to 0-1°C. Additional DMAC (1,500 mL) was added. A solution of N,N'-dicyclohexylcarbodiimide (DCC)(148.1 g, 0.7919 Mol) in 400 mL of DMAC was then added dropwise over a 2-hour period. The reaction mixture was stirred at 0°C for 16 hours, the coolant turned off, the reaction mixture brought to ca. 20°C during 1 hour, and concentrated to 1,900 mL. The precipitated DCU was filtered through a Whatman 541 filter paper in a Buchner funnel, and pressed with a rubber dam.

The polyisoimide was isolated by pouring the filtrate, in 200-mL portions, slowly into a blender containing 500 mL of isopropyl alcohol, and subsequent filtering through a Whatman Number 541 filter paper in a Buchner funnel. The solid cake was washed with isopropyl alcohol and pressed with a rubber dam to squeeze out as much of the mother liquor as possible. The solid cake was transferred to a large Erlenmeyer and broken up under 3.5 L of isopropyl alcohol. The solid was filtered, pressed with a rubber dam, and then broken up into a powder. The powder was placed in a shallow tray to air-dry at 25°C for 16 hours. The final drying was carried out in a stepwise process: first, 1 hour at 25°C/0.1 mm, then 1 hour at every 15°C increment, until the final temperature reached 85°C. The material was kept at 85°C under 0.1 mm pressure for 16 hours. A yield of 269 g of a light yellow fine powder was obtained.

A second lot of this polymer was prepared in a solvent mixture comprising 10% NMP and 90% THF. Using 100% THF caused premature gellation.

The FTIR of this material shows the characteristic isoimide bands at 1806, 1686, and 932 cm^{-1}, as well as the imide at 1373 cm^{-1}. Again, relatively little amic acid is present (1540 cm^{-1}). The weight average MW is 28,019 and the number average is 8,176. Rerunning a DSC on a sample which had been preheated to 350°C and cooled to room temperature gave a distinct Tg at 207°C. The TGA in nitrogen with a heating rate of 10°C/min showed the onset of decomposition at 565°C. The TGA in air showed the onset of decomposition at 590°C.

3.8.11 End-Capped Poly(BTDA-BDAF)isoimide, DP=50

A 500-mL, thermostatted, three-neck, round-bottom flask was fitted with a Tru-bore stirrer, dropping funnel, reflux condenser, constant pressure argon inlet fitting and a heating mantle. The flask was charged with 2,2-Bis[4-(4-Aminophenoxy)phenyl]hexa-fluoropropane (BDAF) (10.00 g, 0.01931 Mol) and anhydrous tetrahydrofuran (2 L). To the flask, solid benzophenonetetracarboxylic dianhydride (BTDA) (6.094 g, 0.01833 Mol) was added as a solution in 20 mL of THF. After stirring for 30 minutes, phthalic anhydride (0.120 g, 0.0008 Mol) was added. After the mixture was stirred for 20 minutes, a solution of N,N'-dicyclohexylcarbodiimide (DCC) (7.95 g, 0.386 Mol) in 40 ml of THF was added dropwise by means of a pressure equalized dropping funnel over a 15-minute period. After the addition, the reaction mixture was stirred at 25°C for 16 hours, filtered to remove the N,N'-dicyclohexylurea and the filtrate concentrated to 100 mL on the rotary evaporator. The product was isolated by pouring into 500 mL of isopropyl alcohol in a blender and filtering. After air-drying and vacuum drying at 45°C for 16 hours, a yield of 13.5 g of a yellow powdery product was obtained.

3.8.12 End-Capped Poly(BTDA-BAPP)isoimide, DP=50

A two-liter, jacketed three-neck, round-bottom flask was fitted with a Tru-bore stirrer and thermometer. The flask was charged with 2,2-bis(4-(4-aminophenoxy)phenyl)-propane (BAPP) (25.98 grams, 0.06335 mole), Wakayama Seiko Lot 34-110) and 250 ml of tetrahydrofuran (THF). To the solution, benzophenone-tetracarboxylic dianhydride (BTDA) (20.00 grams, 62.11 mmole) was added. The solution became quite viscous. After stirring for 30 minutes, phthalic anhydride (0.37 grams, 24.9 mmole) was added and the solution stirred at ambient temperature overnight. Then 350 ml of THF was added and the reaction mixture chilled to 0°C by passing coolant through the jacket. A solution of N,N'-dicyclohexylcarbodiimide (26.1 grams, 0.1267 mole) in 100 ml of THF was added dropwise over a four hour period. The reaction mixture was stirred at 0°C overnight, filtered and reduced in volume to 450 ml on the rotary evaporator. The product was isolated by pouring 150-ml portions in 450 ml of isopropyl alcohol in a blender and filtered. The combined filtrates were dried under vacuum to yield 45.4 gms of an orange-yellow powder.

The FTIR of this material shows the characteristic isoimide bands at 1806, 1686 cm^{-1} and 932 cm^{-1} as well as the imide at 1373 cm^{-1}. There is little amic acid present (1540 cm^{-1}). The weight average MW is 73,173 and the number average is 7,102, determined in THF solvent.

DSC analysis of the polyisoimide shows the onset of a exotherm at 277°C with a maximum at 333°C. It is somewhat possible to assign a shallow inflection point (227°C) to be the Tg of this polyisoimide from the thermogram. The exotherm is due to the thermal reversion of the isoimide to the imide structure. Rerunning a DSC on a sample which had been preheated to 350°C and cooled to room temperature gave a distinct Tg at 236°C. The TGA in nitrogen with a heating rate of 10°C/min showed the onset of decomposition at 617°C. The TGA in air showed the onset of decomposition at 443°C and a precipitous degradation at 563°C.

3.8.13 Synthesis of Acetylene-Terminated IPDA-MPDA Isoimide Oligomers, DP= 0, 1, 5

The acetylene-terminated IPDA-MPDA isoimide oligomers, DP= 0, 1, 5, are the required thermoset components for SIPNs based on LARC-ITPI. The following describes the detailed procedure to synthesize each of the thermoset oligomers.

Experiment Number	Reference Number	MW Range	Product Yield	Stoichiometry			Characterization		
				APA	IPDA	MPDA	FTIR	DSC	rheol
911119	11060X-41	DP=0	62 g	2	1	0	✓	✓	✓
911202	11060X-44	DP=1	49 g	2	2	1	✓	✓	✓
911209	11060X-45	DP=5	50 g	2	5	6	✓	✓	✓
911216	11060X-49	DP=1	224 g	2	2	1	✓	✓	✓
911217	11060X-50	DP=1	224 g	2	2	1	✓	✓	✓

Experiment 911119

A 2-liter, jacketed 3-neck flask fitted with an argon gas inlet, a Teflon-paddled Tru-bore stirrer, pressure-equalized dropping funnel and a thermometer, is charged with 1,3-bis(3,4-dicarboxybenzoyl)benzene dianhydride (isophthaloyl bisphthalic dianhydride (IPDA)(42.6 g, 0.100 Mol) and tetrahydrofuran (THF)(600 mL). To this slurry well-stirred with the mechanical stirrer, 3-aminophenylacetylene (APA)(23.4 g, 0.200 Mol) was added all at once. All of IPDA went into solution. The solution was stirred for 16 hr, and chilled to 0°C by circulating a coolant through the exterior glass jacket of the reaction flask. Then, a solution of N,N'-dicyclohexylcarbodiimide (DCC)(41.2 g, 0.200 Mol) in 200 mL of THF was added dropwise over a 0.75-hour period. The reaction mixture was stirred at 0°C for 2 hr under argon.

The slurry was warmed to 20°C and the precipitated dicylohexylurea (DCU) was filtered through a Whatman 541 filter paper in a Buchner funnel. The DCU solids collected in the filter was washed with a small amount of THF. The filtrate was concentrated to 200 mL on the rotary evaporator and filtered to remove a small amount of crystalline DCU. The concentrate was stirred into 1.2 L of isooctane to yield a fine precipitate. The precipitate was separated by filtration. The solid cake was broken up and the fine powder was placed in a shallow tray to dry under 0.1 torr at 37°C (16 hr) and then at 68°C (2 hr). The product melted within 85-105°C and cured at 220°C.

Experiment 911202

A 2-liter, jacketed 3-neck flask fitted with an argon gas inlet, a Teflon-paddled Tru-bore stirrer, pressure-equalized dropping funnel and a thermometer, is charged with 1,3-bis(3,4-dicarboxybenzoyl)benzene dianhydride (isophthaloyl bisphthalic dianhydride (IPDA)(42.6 g, 0.100 Mol) and tetrahydrofuran (THF)(600 mL). To this slurry well-stirred with the mechanical stirrer, a solution of m-phenylenediamine (MPDA)(5.4 g, 0.050 Mol) in 125 mL of THF was added dropwise. The solution was stirred for 30 minutes and 3-aminophenylacetylene (APA)(11.7 g, 0.100 Mol) was added all at once. The solution was stirred for an hour, and chilled to 0°C by circulating a coolant through the exterior glass jacket of the reaction flask. Then, a solution of N,N'-dicyclohexylcarbodiimide (DCC)(41.2 g, 0.200 Mol) in 200 mL of THF was added dropwise over a 2-hour period. The reaction mixture was stirred at 0°C for 16 hours under argon.

The slurry was warmed to 20°C and the precipitated dicylohexylurea (DCU) was filtered through a Whatman 541 filter paper in a Buchner funnel. The DCU solids collected in the filter had a yellow color even after washing with THF. It indicated that some insoluble isoimide (probably high-molecular-weight materials) was occluded in DCU. On washing these solids with N-methylpyrrolidinone (NMP), the yellow color was removed and the NMP washing was concentrated to a syrupy consistency.

The THF filtrate was concentrated to 150 mL on the rotary evaporator and allowed to stand for several hours. The small amount of crystalline DCU was removed by filtration. The syrupy NMP concentrate was combined with the THF-soluble fraction, concentrated to 75 mL and then stirred into 600 mL of 2-propanol (IPA) in a blender to yield a fine precipitate. The precipitate was separated by filtration, dispersed again in fresh IPA inside the blender and filtered. The solid cake was broken up and the fine powder was placed in a shallow tray to dry under 0.1 torr at 60°C (16 hr) and then at 80°C (2 hr).

Experiment 911209

A 2-liter, jacketed 3-neck flask fitted with an argon gas inlet, a Teflon-paddled Tru-bore stirrer, pressure-equalized dropping funnel and a thermometer, is charged with 1,3-bis(3,4-dicarboxybenzoyl)benzene dianhydride (isophthaloyl bisphthalic dianhydride (IPDA)(40.0 g, 0.0939 Mol), tetrahydrofuran (THF)(300 mL), and N-methylpyrrolidinone(NMP)(100 mL). To this slurry well-stirred with the mechanical stirrer, a solution of m-phenylenediamine (MPDA)(8.450 g, 0.07825 Mol) in 50 mL of THF was added dropwise during 15 minutes. The solution was stirred for 30 minutes and 3-aminophenylacetylene (APA)(3.66 g, 0.0313 Mol) was added all at once. The solution was stirred for an hour, and chilled to 0°C by circulating a coolant through the exterior glass jacket of the reaction flask. Then, a solution of N,N'-dicyclohexylcarbodiimide (DCC)(38.7 g, 0.1878 Mol) in 150 mL of THF was added dropwise over a 0.5-hour period. The reaction mixture was stirred at 0°C for 16 hours under argon.

The precipitated dicylohexylurea (DCU) was filtered through a Whatman 541 filter paper in a Buchner funnel. The filtrate was concentrated to 100 mL on the rotary evaporator. The concentrate was then poured, in 50-mL portions, into 450 mL of 2-propanol (IPA) in a blender to yield a fine precipitate. The precipitate was separated by filtration, dispersed again in fresh IPA inside the blender and filtered. The solid cake was broken up and the fine powder was placed in a shallow tray to dry under 0.1 torr at 65°C (16 hr).

Experiment 911216

A 5-liter, jacketed 3-neck flask fitted with an argon gas inlet, a Hershberg-type Tru-bore stirrer, pressure-equalized dropping funnel and a thermometer, was charged with 1,3-bis(3,4-dicarboxybenzoyl)benzene dianhydride (isophthaloyl bisphthalic dianhydride (IPDA)(175.0 g, 0.4108 Mol) and a solvent mixture comprising tetrahydrofuran (THF)(800 mL) and N-methylpyrrolidinone (NMP)(250 mL). To this slurry well-stirred with the mechanical stirrer, a solution of m-phenylenediamine (MPDA)(22.18 g, 0.2054 Mol) in 100 mL of THF was added dropwise during 30 minutes. The solution was stirred for 30 minutes and 3-aminophenylacetylene (APA)(48.1 g, 0.4108 Mol) was added all at once. The solution was stirred for 0.75 hr, and chilled to 0-5°C by circulating a coolant through the exterior glass jacket of the reaction flask. Then, a solution of N,N'-dicyclohexylcarbodiimide (DCC)(169.3 g, 0.8216 Mol) in 450 mL of THF was added dropwise over a 1.5-hour period. Precipitation of dicyclohexylurea (DCU) took place 15 minutes into the period of addition of DCC. It is noteworthy that in the preparation of the corresponding high-molecular-weight (DP=50) polyisoimide, half of the stoichiometric amount of DCC must be added before DCU begins to prepcipitate (approximately 1 hour into the period of DCC addition). The reaction mixture was stirred at 0°C for 16 hours under argon.

At 0°C, the precipitated DCU was filtered through a Whatman 541 filter paper in a Buchner funnel. The DCU solids collected in the filter were washed with THF and the washing was combined with the first filtrate. The filtrate was concentrated to 450 mL on the rotary evaporator. The isoimide oligomer was isolated by pouring the filtrate, in 100-mL portions, slowly into a blender containing 450 to 500 mL of 2-propanol (IPA), and subsequent filtering. The solid cake was washed with IPA and pressed with a rubber dam. The solid cake was pulverized and the powder was redispersed in IPA, filtered and the resulting solid cake broken up again. The fine powder was placed in a shallow aluminum tray to air-dry inside the hood for 30 minutes and then to dry under 0.1 torr at 80-88°C for 4 hr. The yield was 224 g.

Experiment 911217

This is a duplicate experiment of 911216: A 5-liter, jacketed 3-neckflask fitted with an argon gas inlet, a Hershberg-type Tru-bore stirrer, pressure-equalized dropping funnel and a thermometer, was charged with 1,3-bis(3,4-dicarboxybenzoyl)benzene dianhydride (isophthaloyl bisphthalic dianhydride (IPDA)(175.0 g, 0.4108 Mol) and a solvent mixture comprising tetrahydrofuran (THF)(800 mL) and N-methylpyrrolidinone (NMP)(250 mL). To this slurry well-stirred with the mechanical stirrer, a solution of m-phenylenediamine (MPDA)(22.18 g, 0.2054 Mol) in 100 mL of THF was added dropwise during 30 minutes. The solution was stirred for 30 minutes and 3-aminophenylacetylene (APA)(48.1 g, 0.4108 Mol) was added all at once. The temperature of the reaction mixture rose to 40°C. The solution was stirred for 0.75 hr, and chilled to 0-5°C by circulating a coolant through the exterior glass jacket of the reaction flask. Then, a solution of N,N'-dicyclohexylcarbodiimide (DCC)(169.3 g, 0.8216 Mol) in 450 mL of THF was added dropwise over a 1.5-hour period. Precipitation of dicyclohexylurea (DCU) took place 15 minutes into the period of addition of DCC. The reaction mixture was stirred at 0°C for 16 hours under argon.

At 0°C, the precipitated DCU was filtered through a Whatman 541 filter paper in a Buchner funnel. The DCU solids collected in the filter were washed with THF and the washing was combined with the first filtrate. The filtrate was concentrated to 450 mL on the rotary evaporator. The isoimide oligomer was isolated by pouring the filtrate, in 100-mL portions, slowly into a blender containing 450 to 500 mL of 2-propanol (IPA), and subsequent filtering. The solid cake was washed with IPA and pressed with a rubber dam. The solid cake was pulverized and the powder was redispersed in IPA, filtered and the resulting solid cake broken up again. The fine powder was placed in a shallow aluminum tray to air-dry inside the hood for 30 minutes and then to dry under 0.1 torr at 80-88°C for 4 hr. The yield was 224 g, identical to the previous run.

3.8.14 Processing of Polyisoimides

Fabric laminates were fabricated initially. The objective was to evaluate the relative ease of processing as compared to thermoset and thermoplastic polyimides and polyamic acids.

Preparation of Fabric Prepregs

A 40% by weight lacquer was prepared from poly(IPDA-MPDA)isoimide in NMP. The powdery polyisoimide was stirred into the solvent by portions to ensure complete dissolution. The fabric was dip-coated at a solution temperature of 123°C (250oF). The fabric was coated three times to consume all the lacquer prepared. The impregnated fabric was then dried inside a vacuum oven at 300°F for 2 hours.

The volatiles content was determined to be 5.2%. In subsequent prepreg preparations, drying at 300°F for 3 hours consistently produced prepregs with <3% volatiles.

Two exemplary processing procedures for these polyisoimides is given below:

Hot Pressing

A prepreg of poly(BTDA-APB)isoimide (LA-100) on Thornel F3T584 carbon fabric (13 mil/ply, 8 harness satin weave) was prepared from 25% by weight solution of LA-100 in THF. Drying was similarly staged to reduce volatile content to under 1%. The resin content was at 36-37% by weight. Prepregs were stacked eight plies high and consolidated between preheated platens at 288°C, 100 psi, for 0.5 hr. The system was cooled under 100 psi to 205°C over 1.5 hr, and held at 205°C for an additional 0.5 hr.

In addition to LA-100, other isoimide polymers were subjected to the same prepregging procedure. These polymers included poly(BTDA-DAB)isoimide, and copolymers of LA-100 and poly(BTDA-3,4-ODA)isoimide. These laminates were judged inferior (C-scan and mechanical properties) to those fabricated under an improved cure schedule.

Improved Hot Pressing

The prepreg was cut into 6" x 6" pieces, stacked to the desired number of plies, wrapped in 5-mil thick aluminum foil that was precoated with a mold release, and then placed in a preheated press at 450°F for comopression molding, according to the following schedule:

The initial molding temperature was kept at 450°F after an intial contact time (no pressure) of 15 minutes. The platens were forced to close to produce a molding pressure of 300 psi. The molding condition was 450°F (1 hr), and 575°F (1 hr). The cooling was under pressure over 1 hour.

Autoclave Process

Fabric prepregs were made with fabrics woven from either Celion 3000 or Fiberite T650 fibers. The fabric was impregnated with a 25%-by-weight solution prepared from the designated polymer or polymer blend in a mixture of 80% dioxolane/20% γ-butyrolactone (work done under a Lockheed IR&D joint project with Rohr Industries). The prepreg was dried in stages up to 110°C (24 hr).

Six to ten plies of prepreg 6" x 12" were stacked and enveloped in a Kapton vacuum bag with the appropriate thermocouple temperature sensors. The prepared vacuum bag was placed inside the autoclave which was preheated to 316°C. Contact pressure was applied. When the vacuum bag temperature reached 288°C (1 minute or so), the appropriate pressure (200 or 300 psi) was applied. The part reached 316°C and was held at 316°C for 12 hr. It was then cooled under pressure. C-scan analysis ascertained that the plaque was well consolidated.

3.8.15 Processing of Polyisoimide SIPNs

Processing of polyisoimide SIPNs followed a similar method as for the polyisoimides. It was determined that the consolidation pressure for SIPNs was generally between 200-250 psi. Much better flow was observed with the SIPN formulations than polyisoimides themselves.

Preparation of Unidirectional Prepregs

A 30% by weight solids lacquer was prepared by first dissolving the pre-weighed IP-600 isoimide oligomer in NMP solvent under high-speed air agitation. After 1 hour, the poly(IPDA-MPDA)isoimide powder was added. After stirring for 4 hours, numerous "jelly balls" still persisted.

The solution was allowed to stand under dry air and subambient condition overnight to allow time for further solvation of the powder. All particulates dissolved upon high-shear stirring for another 2 hr. The temperature of the solution rose to 110°F and the solution appeared homogeneous. Particulates (~2%) were removed by filtration.

The prepreg was prepared without difficulty, using the modular equipment. The conditioning of the prepregs was carried out in ovens set at 350°F and 250°F and hot plates set at 350°F. A 15-17% NMP retention resulted in a slight tack, which is the critierion for ease of fabrication. The prepregs were visually uniform in terms of even thickness and colinearity of the fiber tows. Quality control tests of the unidirectional prepregs showed that they were within the targeted fiber and resin areal weights **(Table 21, Section 3.7.3)**.

Laminate Fabrication from Unidirectional Prepregs

The prepreg was dried inside a vacuum oven at 300°F for 3 hours, cut and stacked 8 plies or 16 plies in a preheated compression mold at 450°F. The stack was held under contact pressure for 10 minutes to equilibrate. Force was applied to the press to slowly increase the pressure to reach 300 psi. The laminate was held at 450°F/300 psi for 1 hour and then at 600°F/300 psi for 1 hour. Coolong was under pressure over 1 hour.

Comparable cure was achieved using pressures under 250 psi. Several autoclave cure experiments were conducted at 225 psi, using a computer-controlled dielectric monitoring RESCAP system established at Programmed Composites, Inc.

Autoclave Process (National Starch)

In one case, a unidirectional fiber laminate was made with poly(BTDA-APB)isoimide at National Starch. A 6" x 6" x 0.083" unidirectional panel of poly(BTDA-APB)isoimide on AS4 carbon fibers was made. The prepreg was prepared by drum winding, using a 25% by weight solution of the polyisoimide in tetrahydrofuran (THF), and dried in stages up to 110°C (24 hr) to reduce the volatile content to 0.7%. The fiber content was 68.2% by weight (65.5% by volume).

Ten plies of prepreg 5-3/4" x 5-3/4" were stacked unidirectionally into a 6" x 6" closed mold. Frekote 44 was the release agent. The cold mold was inserted between the press platens which were preheated to 366°C. Contact pressure was applied. When the mold temperature reached 200°C, the pressure was released to allow volatiles to escape; then nine tons of compressive force (to produce 500 psi of pressure) was applied. The mold reached 288°C and was held at 280°-288°C for 1 hr. It was then cooled under 500 psi of pressure. Follow-up C-scan analysis showed that the plaque was well consolidated.

C-2.

3.8.16 Adhesive Characterization

The components of the SIPN polyimide blend are IP-600, a thermosetting acetylene-terminated polyimide prepolymer commercially available from National Starch and Chemical Corporation, and a thermoplastic linear polyisoimide prepared from 3,3′,4′4′-benzophenonetetracarboxylic dianhydride (BTDA) and bis(3-aminophenoxy)benzene (APB). The thermoplastic linear polyisoimide was originally prepared at Lockheed, but custom synthesized in larger quantities by National Starch. The IP-600/thermoplastic mixture was readily soluble in common solvents such as tetrahydrofuran (THF) and diglyme.

The isoimides, IP-600 and LA-100, were purchased from National Starch and Chemical Corporation, and were used without further purification. The poly(BTDA-APB)isoimide (LA-100) lot had a molecular weight of 40,000 to 50,000 as determined by gel-permeation chromatography. The polymer was not end-capped.

<u>1:3 Blend of LA-100 and IP-600</u>

A solution containing 37.5 g of LA-100 and 112.5 g of IP-600 in 350 g of chromatography grade purified THF was prepared to yield a 30% solids content, 1:3 LA-100/IP-600 adhesive lacquer.

<u>1:1 Blend of LA-100 and IP-600</u>

A solution containing 75 g of LA-100 and 75 g of IP-600 in 350 g of chromatography grade purified THF was prepared to yield a 30% solids content, 1:1 LA-100/IP-600 adhesive lacquer.

<u>Adherend Preparation</u>

The metal adherends were surface treated by FPL etch and primed by brush coating at THF solution of the appropriate primer on the freshly treated adherend surfaces. Adherend dimensions were 4" x 1" x 0.080". The applied polyimide coating protected the FPL etched surface of the adherends. Unless otherwise indicated, the primer consisted of the same adhesive that was used for bonding. The steel adherends were cleaned by light abrasion with sandpaper followed by isopropyl alcohol/scotchbrite treatment to remove burrs, and then desiccated prior to the bonding operation. No primer was used on the steel adherends.

<u>Scrim Cloth Preparation</u>

The scrim cloth, a glass fabric impregnated to a high resin content, serves to fix the bondline thickness. Unless otherwise noted, the scrim cloth consisted of 112E glass fabric (4 mils), which was heat-cleaned at 800°F until all contaminants were removed. Other fabrics utilized in this study included a non-woven glass fabric from International Paper Company, and a plain-weave, heat-cleaned glass fabric, style 1801, from J. P. Stevens Company. To prepare the adhesive scrim, the fabrics were brush-coated with a tetrahydrofuran (THF) solution of the isoimide adhesive mixture, and air-dried, followed by drying at 135°C (275°F). Successive coats of adhesive were applied until the adhesive scrim contained 70-80% resin. When non-woven scrim was impregnated, the fabric was lightly spray coated with a THF solution of adhesive and dried to preserve the structure of the fabric.

Lap-Shear Specimens

Adhesive lap-shear specimens were prepared by insertion of impregnated scrim cloth between metal adherends to allow a 1/2 inch lap. For lap-shear specimens containing no scrim cloth, specimens were prepared for bonding by brush coating a continuous layer of isoimide adhesive on the adherends. Primed metal adherends were dried at 140°C (284°F) to remove tack, and the primer was cocured with the adhesive scrim.

Adhesive specimens were cured in a preheated press or in an autoclave at 550°F and 50 psi minimum pressure for one hour, then cooled to ambient temperature under full pressure.

CONCLUDING REMARKS

The results from this study show the relevance of the IPDA-MPDA polymer system to advanced composite material. The isoimide modification offers the processing facility to polyimides in general. Specific to the IPDA-MPDA system, the isoimide form is a finely-divided powder, which is amenable to solventless powder prepregging methods.

8-ply and 16-ply unidirectional laminates made from poly(IPDA-MPDA)isoimide SIPNs yielded acceptable mechanical property values, establishing the potential of the poly(IPDA-MPDA)imide system for advance composite applications. The immediate future direction would be to conduct a comparative study using powder prepregs.

In addition, as the SIPNs are being developed, the specific acetylene-terminated IPDA-MPDA isoimide oligomer should be scaled up. Acetylene-terminated (AT) imide and isoimide oligomers are essential thermosetting components for SIPNs. Generally, AT materials yield higher toughness than BMIs in the final cured laminates. The phenylethynylated IPDA-MPDA isoimide oligomer can potentially be used in place of the acetylene-terminated IPDA-MPDA isoimide oligomer when an even higher Tg cured polyimide SIPN system is desired. With the use of phenylethynyl end-caps, thermosetting polyimides and polyisoimides can thermally cure to SIPN materials with Tg above 300°C. A final Tg of over 300°C is desirable for materials used in supersonic aircraft. The phenylethynyl end-capping agent has been explored at National Starch and Chemical Corporation [40].

A stepwise curing process can be formulated for processing phenylethynylated isoimide oligomers. The thermosetting phenylethynylated isoimide oligomers can be applied to graphite fabrics, unidirectional tapes, or 3-D preforms as a low-viscosity lacquer (due to the high solubility of the isoimide in solvents) or as a powder (isoimides readily form fine powders). The coated reinforcement forms can then be flash heated (convectionally or by electrical methods) in a B-stage to melt the isoimide to achieve flow and fiber-wetting. During this B-staging, partial conversion of the isoimide to the imide also takes place.

The final curing occurs during consolidation of the laminates. The phenylethynyl end-groups undergo chain-extension and cross-linking reaction at temperatures in the mid 300°C range.

Blending of AT isoimide oligomers (DP lower than 15) with BMIs offers the benefits of lower processing viscosity and melt temperature. The resulting IPNs have significantly higher toughness than BMIs due probably to the chain-extending reaction of the AT oligomers. Well-consolidated imide-based composites from this methodology would meet the durability requirements for future HSCT applications. The use of phenylethynylated end-caps yields high Tg composites to enable supersonic applications.

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY ***(Leave Blank)***

2. REPORT DATE
February 1993

3. REPORT TYPE AND DATES COVERED
Contractor Report June 1989 - June 1992

4. TITLE AND SUBTITLE
Advanced Composite Structural Concepts and Materials Technologies for Primary Aircraft Structures: Advanced Material Concepts

5. FUNDING NUMBERS
C NAS1-18888
WU 510-02-13-01

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Lockheed Aeronautical Systems Company
86 South Cobb Drive
Marietta, GA 30063

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
NASA Langley Research Center
Hampton, VA 23681-0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
NASA CR-4485

11. SUPPLEMENTARY NOTES
Langley Technical Monitor: Randall C. Davis

12a. DISTRIBUTION/AVAILABILITY STATEMENT
[redacted]

Subject Category 05

12b. DISTRIBUTION CODE

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

To achieve acceptable performance and long-term durability at elevated temperatures (350° to 600° F) for high-speed transport systems, further improvements of the high-performance matrix materials will be necessary to achieve very long-term (60,000-120,000 service hours) retention of mechanical properties and damage tolerance. This report emphasizes isoimide modification as a complementary technique to semi-interpentrating polymer networks (SIPN's) to achieve greater processibility and better curing dynamics, and possibly enhanced thermo-mechanical properties in composites. A key result is the demonstration of enhanced processibility of isoimide-modified linear and thermo-setting polyimide systems.

14. SUBJECT TERMS

Thermoplastic	Isoimide Modification
Polymide	Semi-interpentrating Polymer Network
Composites	

15. NUMBER OF PAGES
108

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
Unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT
Unclassified

20. LIMITATION OF ABSTRACT

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. 239-18
298-102

NASA-Langley, 1993