CONDENSATION POLYIMIDES

P. M. Hergenrother

NASA Langley Research Center
Hampton, VA 23665-5225

February 1989

Chapter for Encyclopedia of Composites;
Stuart M. Lee, editor; VCH Publishers, Inc.
New York, NY; To be published in 1990

(NASA-TM-103467) CONDENSATION POLYIMIDES (NASA) 47 p CSCL 11C

N90-26129

Unclas
G3/27 0292242

CONDENSATION POLYIMIDES

Paul M. Hergenrother

NASA Langley Research Center

Hampton, VA 23665-5225

INTRODUCTION

Polyimides belong to a class of polymers known as polyheterocyclics. Since their initial disclosure in the later 1950s, hundreds of polyimides with different chemical structure and molecular order (morphology) and accordingly, different physical, mechanical and chemical properties have been reported. Numerous reviews on polyimides are available.[1-6] The impetus to develop polyimides was the demand for a polymer to operate in a high temperature environment. Initial applications were in the electrical field where higher temperature insulation was needed. High temperature organic polymers were also required for use in structural components in advanced high speed aircraft, weapon systems and space vehicles.

Although many different families of high temperature polymers have been disclosed, polyimides have attracted the attention of the scientific community. Their popularity arises as a result of a unique combination of thermal stability, chemical and solvent resistance, mechanical properties, reasonable cost and the ability to be processed into useful forms.

Unlike most other high temperature polymers, polyimides can be prepared from a variety of inexpensive monomers by several synthetic routes. By judicious choice of starting materials, a polyimide can be tailor-made for a specific application. For example, the glass transition and crystalline melt temperature, thermooxidative stability, toughness, dielectric constant, coefficient of thermal

expansion, chemical stability, mechanical performance, etc. of polyimides can be controlled within certain boundaries. This versatility has permitted the development of various forms of polyimides. These include adhesives, composite matrices, coatings, films, moldings, fibers, foams and membranes. Polyimides are currently commercially available in the form of adhesive tapes, composite prepreg, molding powders, moldings, films and foams.

Polyimides are synthesized through both condensation (step-polymerization) and addition (chain growth polymerization) routes. The precursor materials used in addition polyimides or imide oligomers are prepared by condensation method. This chapter will deal only with high molecular weight polyimide made via polycondensation or step-growth polymerization. The purpose of this chapter is to acquaint the reader with the various synthetic routes to condensation polyimides, structure/property relationships of condensation polyimides and composite properties of condensation polyimides. No attempt was made to comprehensively review condensation polyimides since this would be beyond the scope and space limitation of this chapter. Instead, the focus is on the synthesis and chemical structure/property relationships of polyimides with particular emphasis on materials for composite application.

FEATURES OF POLYCONDENSATION PROCESS

Before beginning a discussion on condensation polyimides, a brief review on the features of polycondensation or step-growth polymerization is worthwhile. In polycondensation processes, monomeric molecules react to give off a small molecule as a by-product. As a result, the molecular weight of the polymer is less than the total molecular weight of the monomers used to form the polymer. Condensation polymerization is a step-growth process where molecular weight

increase is slow. One monomer will react with a different monomer to form a dimer which subsequently reacts with other monomers or dimers to form trimers or tetramers and so on. All polymer chains grow at about the same rate, one step at a time, until high molecular weight polymer is formed or the reaction ceases. The number average degree of polymerization, DP, is defined as the average number of repeat units per molecule and is obtained from the Carothers equation, DP = 1/1-p, where p equals the extent of reaction. Hence, a polycondensation which has gone to 95% completion will have formed a polymer with 20 repeat units (1/1-0.95) in the average chain. Accordingly 98% completion will provide a polymer with 50 repeat units in the average polymer molecule. The theory is based upon the polymerization of an A-B monomer. For condensation polymers such as polyimides prepared from two monomers (AA + BB type), the average number of repeat units is one half of DP.

The polyimide from the reaction of pyromellitic dianhydride and 4,4'-oxydianiline has a repeat unit molecular weight of 366 g/mole. Therefore at 98% reaction, this polyimide would have a number average molecular weight of 50/2 x 366 or 9,150 g/mole. A polymer with an M_n of 9,150 g/mole would not normally be expected to have mechanical integrity. However, polyimides are unusual polymers and because of the strong intermolecular association through primarily polar and charge transfer interactions, polyimides at seemingly low M_n can exhibit good mechanical properties.

To obtain a high molecular weight polyimide via condensation polymerization, the purity of the monomers must be high (> 99%) and no side reactions that consume monomers or functional groups can occur. Equal molar amounts of AA + BB type monomers are required. (Only a few high molecular weight polyimides have been reported from A-B monomers). When highly pure monomers are used in stoichiometric amounts, polyimides with very high molecular

weights can be obtained. These high molecular weight polyimides exhibit high melt viscosities and accordingly poor flow in composite fabrication. To alleviate this problem, the stoichiometry can be upset to limit the molecular weight and the polymer chains can be end-capped with inert groups to improve melt flow and provide melt stability.

To determine the stoichiometry to obtain a polymer with a desired DP from AA + BB monomers, the Carothers equation is modified to that given below

$$DP = \frac{1 + r}{2r(1 - p) + 1 - r}$$

where r = the ratio of AA to BB monomers. If p, the extent of reaction is 1, the equation reduces to DP = 1 + r/1 - r. At 4% excess of the A-A monomer, r = 0.96 and theoretically a DP of 49 is attainable. Thus, for a polyimide from the reaction of 3,3',4,4'-benzophenonetetracarboxylic dianhydride and 3,3'-diaminobenzophenone with a repeat unit molecular weight of 498 g/mole, the number average molecular weight of the polymer would be 49/2 x 498 or 12,201 g/mole. This is adequate molecular weight in this polyimide to afford good mechanical properties.

Polyimides can be prepared by several methods using solution or melt polycondensation processes. Various factors affect the polymer in each of these polymerizations. For example, in solution polycondensation, stirring rate, mode of monomer addition, form of monomer when added, temperature, time, atmosphere and concentration are variants. If these factors are properly controlled, high molecular weight polymer can be readily obtained from high purity monomers.

Several different polymerization routes leading to polyimides will be discussed in the following section. Only those routes or variations thereof which have provided high molecular weight polyimides will be covered.

POLYIMIDE SYNTHESIS

1. The most popular and versatile route to aromatic polyimides involves the reaction of an aromatic tetracarboxylic dianhydride with an aromatic diamine to initially form a precursor, configurationally unordered, polyamide acid (polyamic acid). The precise isomer distribution is unimportant from a practical standpoint and is primarily a function of the reactivity of the dianhydride. The precursor polymer can be chemically or thermally converted to the polyimide. As an example, 3,3',4,4'-benzophenonetetracarboxylic dianhydride is depicted to react with 3,3'-diaminobenzophenone in Eq. 1 to yield the polyamide acid which is converted to the polyimide (structure 1). Although this general route appears to be relatively straightforward, it is actually very complex.[1]

The experimental procedure for the preparation of a polyamide acid will vary from one laboratory to another. In addition, the particular monomers and solvents may necessitate a modification in the procedure. A typical synthesis is generally conducted by adding the dianhydride in the form of a fine powder, slurry or solution to a stirred solution or slurry of the diamine in a highly polar solvent such as N,N-dimethylacetamide (DMAc) or N-methylpyrrolidinone (NMP) at ambient temperature under nitrogen at solids content of 15 to 25% (weight/volume). High molecular weight polyamide acid readily forms by the nucleophilic attack of an amino group on an anhydride carbonyl group, opening the anhydride ring to form the amide acid. Dianhydride (structure 2) containing electronic attracting groups such as CO or SO_2

2

where x = nil, -CO-, $-SO_2-$, $-C(CF_3)_2-$, $-\overset{O}{\overset{\|}{C}}-C_6H_4-\overset{O}{\overset{\|}{C}}-$, O, S, $-C(CH_3)_2-$, etc

are more reactive than those containing electron donating groups such as O or $C(CH_3)_2$. Similarly diamines (structure 3) containing electron donating groups are

n + n H_2N ... NH_2

Diglyme, 15% solids

(1)

$-2nH_2O$

1

$$H_2N-C_6H_4-X-C_6H_4-NH_2$$

3

where x = same as for structure 2

more reactive than those containing electron attracting groups. Certain diamines such as 4,4'-diaminodiphenyl sulfone or 4,4'-diaminobenzophenone are poor nucleophiles such that the formation of high molecular weight polyamide acid through reaction with a dianhydride, especially a less reactive dianhydride, is often difficult to attain. High molecular weight polyamide acids, however, have been prepared from the reaction of aromatic dianhydrides with 4,4'-diaminobenzophenone[7] and 4,4'-diaminodiphenyl sulfone.[9]

The reverse addition,[7] that is, the addition of a diamine to a dianhydride is not recommended for the preparation of a high molecular weight polyamide acid. An excess of anhydride groups is thought to attack the polyamide acid causing chain cleavage.[9] Thus only dianhydrides such as pyromellitic dianhydride that are virtually insoluble in the polymerization medium will form high molecular weight polyamide acid by the reverse addition route.

Other solvents, particularly ether solvents such as tetrahydrofuran[10] or bis(2-methoxyethyl)ether (diglyme),[10,11] have also been used to prepare high molecular weight polyamide acids. However, only certain polyamide acids can be prepared in high molecular weight in ether solvents whereas most polyamide acids can be prepared in high molecular weight in the more universal, highly polar, solvents such as DMAc and NMP. The reactivity of the monomers as well as the solubility of the polyamide acid is different in the ether solvents versus the highly polar solvents.

The nature of the polyamide acid, particularly the molecular weight distribution, is influenced by several factors such as the solubility of the monomers, reaction time, solvent, concentration and stirring rate. For example, with insoluble dianhydrides or improper mixing, there can be interfaces or zones where the polymerization is proceeding independent of the total system, thereby providing

molecules of significantly different molecular weight, with a preponderance on the high molecular weight end. Ether solvents tend to yield somewhat lower molecular weight polyamide acids having a broad molecular weight distribution and in many cases, a bimodal molecular weight distribution.

The stability of the polyamide acids is also a concern. These materials are known to undergo molecular weight equilibration[12-14] and chain cleavage[9,15] as a function of time under various conditions. This instability is of practical importance since the properties of the polyamide acid and corresponding polyimide are directly effected. Polyamide acids in solution should be stored cold (0°C) under nitrogen. Chain cleavage is faster at higher temperatures and lower concentrations.

The preceding discussion briefly outlined some of the problems associated with the polyamide acids. More details on these problems can be found in a single review.[1] In spite of these problems, high molecular weight polyamide acids are successfully prepared and converted to polyimides for use as adhesives, composite matrices, coatings, fibers, films, foams, moldings and membranes.

The conversion of the polyamide acid to polyimide can be accomplished by chemical or thermal inducement. The thermal cyclodehydration of polyamide acids to polyimides occurs generally with a partially reversible change in molecular weight.[15-17] As the polyamide acid is heated and converted to polyimide, it undergoes a decrease in the molecular weight and then an increase as the temperature is raised. High molecular weight polyamide acids free of solvent cannot be isolated from solutions in highly polar solvents. Polyamide acids with low solvent content can be isolated from solutions in ether solvents, particularly tetrahydrofuran. However, polyamide acids made in ether solvents are more difficult to thermally convert to polyimides, exhibiting more foaming than those from highly polar solvents. The polar solvents apparently enhance the cyclodehydration process and also serve as a plasticizer, providing flow, during compression or

injection molding. The detrimental effect of the polar solvents is that small amounts are held tenaciously by certain polymers, particularly those having high glass transition temperatures (e.g. > 250°C). Temperatures in excess of the glass transition are required to remove the last amount of solvent. In certain forms, particularly thicker components such as bonded parts, composites and moldings, porosity, delimination or large bubbles develop in the part due to volatization of the last traces of solvent. These voids lower the mechanical properties and thermooxidative stability.

Polyamide acids have been successfully used in combination with a reinforcement to fabricate small, essentially void-free, composites with high mechanical properties by careful control of cure conditions to accommodate volatile evolution (e.g. condensation by-products and residual solvent). However, this is an exception rather than a norm. The fabrication of quality composites from polyamide acids becomes more of a problem as the size of the composite increases. Larger quality composites can be fabricated through long cure cycles which translates into high manufacturing cost and unacceptability for many applications.

Polyamide acids can be chemically converted to polyimides or polyisoimides through the use of cyclodehydrating chemicals such as acetic anhydride and triethylamine and dicyclohexylcarbodiimide or trifluoroacetic anhydride respectively. The utility for composite application lies primarily in the formation of small particle powders (e.g. 1-2μ) that can be used to powder or slurry impregnate reinforcements. Another use of the chemically converted materials is that certain polymers can be dissolved and the resulting solution used to impregnate a reinforcement. Although solution impregnation is undesirable due to the generally poor quality of the prepreg and solvent removal problems, small composites of good quality have been made from solution coated prepreg. The polymer must be fusible under the conditions of fabrication. The glass transition temperature or crystalline melt temperature, melt

viscosity and volatile content are the most important factors in a polymer to obtain good consolidation in a composite.

The preceding discussion pertained to the preparation of polyimides via polyamide acids and concentrated on the reaction of aromatic dianhydrides with aromatic diamines. The properties of the polyimides can obviously be substantially altered through chemical structure variations by introducing connecting groups such as alkylene, alkylenedioxy, perfluoroalkylene and the like in both the dianhydride and the diamine. Heteroorganic monomers such as silicon containing, phosphorus containing and other unusual dianhydrides and diamines have also been used to make high molecular weight polyamide acids. In addition, alicyclic dianhydrides can be used to form high molecular weight polyamide acids. However, alicyclic and aliphatic diamines will not form high molecular weight polyamide acids when reacted with dianhydrides primarily because the basicity of the amine allows for salt formation with the carboxylic acid of the polyamide acid. Alternate synthetic methods are available to make polyimides from the reaction of alicyclic or aliphatic diamine with dianhydrides.

Chemical structure/property relationship studies on polyimides have been extensively conducted. Several tables will be used to explain these relationships. Since the studies were conducted in different laboratories, the method employed to determine certain properties may vary. As a result, discretion should be exercised in comparing the properties of a polyimide in one study with one from another study because the method of measurement, thermal history of the polymer, molecular weight of the polymer, etc. may vary. In Table 1, the T_gs of several polyimides derived from a common dianhydride that was reacted with different diamines are presented. As evident in theTable, polyimides containing the more rigid moieties (p-phenylene, 1,5-naphthalene and 4,4'-biphenylene) have the highest T_gs while

those containing flexible moieties [4,4'-diphenyl ether and 1,3-bis(4-phenoxy)benzene] have lower T_gs.

In Table 2, three isomers of a diamine were used to prepare polyimides. Again the most flexible diamine (3,3'-diaminobenzophenone) provided polyimides with the lowest T_gs. This study also clearly shows the effect of a rigid dianhydride (pyromellitic dianhydride) versus a more flexible dianhydride (3,3',4,4'-benzophenonetetracarboxylic dianhydride) on the polyimide T_g. Table 3 shows T_gs of five polyimides where a common diamine was reacted with five dianhydrides. The T_gs are all relatively low because polyimides from this particular diamine are relatively flexible.

A series of semi-crystalline polyimides containing carbonyl and ether connecting groups between the aromatic rings is presented in Table 4. The T_gs ranged from 215 to 246°C and the T_ms were from 350 to 427°C. The properties of a semi-crystalline polyimide in structure 4, designated LARC-CPI (Langley Research Center-Crystalline Polyimide), are given in Table 5.

4

The relationship of chemical structure to T_g and color in polyimide films is given in Table 6. Conventional polyimide films are yellow to orange in color. The intensity of the color can be essentially alleviated by the proper design of the molecule. The use of the bulky hexafluoroisopropylidene and sulfone groups coupled with the use of the meta isomers in the diamine was particularly effective. Disruption of the conjugation and the intermolecular association is important for obtaining essentially colorless films as well as soluble polyimides. Most of the polyimides in Table 6 are soluble in chloroform.

Within certain boundaries, the dielectric constant of polyimides can be controlled through the chemical structure of the molecules. Linking groups that disrupt conjugation, dissymmetry and bulky groups that interrupt molecular continuity, molecular packing and intermolecular polar association all contribute to lower dielectric constant in polymers. The effect of these factors on the dielectric constant of polyimides is evident in Table 7. The hexafluoroisopropylidene group and meta catenation lowers the dielectric constant of polyimides significantly.

Although many studies were conducted to correlate the chemical structure of polyimides with certain physical properties, there is no detailed published study where the effect of chemical structure, molecular weight and molecular weight distribution and various end-groups was correlated with compression moldability or melt viscosity and mechanical properties. Studies of this type have been done by industrial companies active in the polyimide field but these studies are not published. Those active in the synthesis of polyimides for adhesive and composite work realize that with many polyimides, especially those with high T_gs, the molecular weight must be controlled to obtain adequate flow during compression molding to yield panels with high mechanical properties. In addition, the molecules are frequently end-capped with a stable group to afford better melt stability. The very factors in a polyimide that contribute to a high T_g also result in high melt viscosity and accordingly, difficult compression moldability. As a result, the properties of the polymer are frequently compromised to obtain better processability.

As an example, high molecular weight polyimide (T_g ~ 260°C) in structure 1 has a melt viscosity of ~ 10^6 Pa·sec (~ 10^7 poise) at 350°C under a shear rate of 10^{-1} sec^{-1}. The molecular weight of this polymer has been controlled by upsetting the stoichiometry followed by end-capping to provide a grade of LARC-TPI (inherent viscosity of 0.37 dL/g and T_g of ~ 236°C) with a melt viscosity of 6 x 10^3 Pa·sec (6 x 10^4 poise) at 340°C under a shear rate of 10^{-1} sec^{-1}.[24] The stoichiometric

adjustment and end-capping group may vary slightly from one polyimide to another. As a general rule, the stoichiometry can be upset by 3 to 5 mole % in favor of the diamine and phthalic anhydride used as the end-capper.

Several other synthetic routes to condensation polyimides will be briefly reviewed. The reaction of a dianhydride with a diamine to yield a precursor polyamide acid is the most versatile and widely used route to polyimides.

2. Certain variations on route 1 to avoid the unstable polyamide acid have been reported. For example, the diester diacid or diamide diacid from the reaction of a dianhydride with an alcohol[25] or secondary amine[26] respectively has been converted to the corresponding diacid chloride and subsequently reacted with an aromatic diamine to yield a stable precursor polyamide ester or polyamide amide. The precursor polymer has been thermally converted to polyimide.

3. An aromatic or alicyclic dianhydride or tetracarboxylic acid is thermally reacted with an aromatic or aliphatic diamine in a phenolic solvent such as m-cresol using a catalytic amount of an organic base such as quinoline to form the polyimide.[27-28] The polyimide must be soluble in the phenolic solvent to obtain high molecular weight.

4. An aromatic tetracarboxylic acid or half ester (diester diacid) is initially reacted with an aromatic diamine in solvents such as diglyme, ethanol or NMP. Upon heating and removing the solvent, polymerization occurs to yield high molecular weight polyimide. To obtain high molecular weight, adequate molecular mobility must occur during the polymerization. This route has been successfully used to prepare the Avimid® K-III polyimide.[29]

5. An aromatic activated dinitro compound undergoes aromatic nucleophilic displacement by reaction with a diphenoxide anion [e.g. a bis(nitrophthalimide) and a bisphenol salt] to form a polyetherimide.[30] This route has been claimed as that used to make the Ultem® series of polyetherimides.

6. Melt polycondensation of an aromatic or alicyclic dianhydride or appropriate derivative with an aromatic diamine has been successfully used to make high molecular weight polyimides.[31] The polyimide must remain fusible during the polymerization to allow for adequate molecular mobility for chain growth. This route is suspected to be that used to prepare Ultem® 1000.

7. An exchange reaction between a bisimide and an aromatic diamine using an organometallic catalyst has been successfully used to prepare high molecular weight polyimide.[32-33]

8. Other exchange reactions have also been reported to yield polyimides. As an example, 3,3',4,4'-benzophenonetetracarboxylic dianhydride is reacted with less than a stoichiometric amount of caprolactam in the presence of ethanol. The resulting partially imidized product is subsequently thermally reacted with an aromatic diamine such as 4,4'-methylenedianiline to yield a polyimide.[34] Intermediates from this route have been formulated and successfully used to prepare low density, ductile, fire resistant, foams via microwave curing.

9. The polyamic acid as discussed in item 1 has been converted to polyisoimide by treatment with certain chemical cyclodehydrating agents such as dicyclohexylcarbodiimide.[35] The polyisoimide rearranges to polyimide upon heating. The attractive feature of this route is that the polyisoimide is significantly more soluble and exhibits better melt flow than the corresponding polyimide. This route is currently being used to prepare a series of acetylene terminated isoimide oligomers.[36]

10. Derivatives of diimides for example N,N-bis(ethoxycarbonyl)-pyromellitimide can be reacted with aromatic diamines to yield stable precursor polyamide amides. These precursor polymers are subsequently thermally converted to polyimides.[37] Unlike polyamic acids, the polyamide amides and solutions thereof are stable. A variation of this route involves reacting the N,N'-

di(ethoxycarbonyl) pyromellitimide with an aliphatic diamine via interfacial polymerization.[38]

11. An aromatic dianhydride is reacted with an aromatic diisocyanate to form a seven membered ring which eliminates carbon dioxide to yield the imide.[39] The polyimide, formerly known as Upjohn Polyimide 2080, was prepared by this route.

The stoichiometry can be altered and end-capping agents can be used in routes 2 to 11, similar to that discussed in route 1, to obtain polymer of lower molecular weight with better solubility and compression or injection moldability. Most of the preparations in routes 2 to 11 do not offer the versatility in chemical structure variation as route 1. Melt fusibility or solubility of the polyimide are required to obtain high molecular weight in several of the routes 2 to 11.

COMPOSITE PROPERTIES

Several condensation polyimides have been evaluated as composite matrices primarily in combination with continuous fiber reinforcements. Most of the work has concentrated on glass and carbon/graphite filament reinforcements although boron and quartz reinforcements have seen minor evaluation. In addition, superficial work has been done with a few inorganic fibers and fibers from the new high modulus rigid rod polymers such as the polybisbenzthiazole. Kevlar® is not a reinforcement of choice because of the high temperatures required in composite fabrication with most polyimides. The following discussion will be restricted primarily to condensation polyimide composites using continuous carbon/graphite reinforcements.

Several methods have been employed to prepare carbon/graphite prepreg. Solutions of polyamide acids, mixtures of monomers, polyimides, polyisoimides and various modifications (e.g. B-staged precursor polymer consisting of a mixture of

polyamide acid and polyimide) have been used to impregnate fibers. Prepreg has also been prepared from slurries of polyimide powders and mixtures of polyamide acids solutions with polyimide powders. In addition, preliminary work has involved the deposition (e.g. electro, electrostatic and gravity) of dry polyimide powders onto carbon/graphite tow. Another form of condensation polyimide prepreg which has been evaluated is a hybrid where polyimide fibers have been co-mingled with carbon/graphite fibers. Melt impregnation using polyimide film or powder have also received attention as a means of prepreg preparation. Of the five methods of prepreg preparation (solution, slurry and melt impregnation, powder deposition and co-mingling), solution coating has been the method most extensively used to evaluate polyimides as composite matrices.

Prepreg quality is very important because with inferior prepreg, the fabrication of large high quality polyimide composites is virtually impossible. Unlike forgiving systems, such as epoxies, where high quality composites can be obtained from poor quality prepreg, precursors to and polyimides themselves are unforgiving materials. Volatiles in the prepreg can cause significant fabrication problems such fiber wash during consolidation and voids. With the current state of technology, tack in polyimide prepreg is due to residual solvent. Prepreg with drape but not volatiles can be made by dry powder impregnation. Each prepreg form appears to have certain advantages and disadvantages. High melt viscosity which necessitates the use of high temperatures and pressures [e.g. $\geq$ 1.38 MPa (200 psi)] is frequently a problem for volatileless polyimide prepregs.

The following discussion pertains to the composite work recently reported on condensation polyimides. No attempt was made to comprehensively cover all the condensation polyimide composite work. Instead, the emphasis will center on representative condensation polyimides that have been evaluated as composite matrices.

A family of Avimid® K polymers,[29] amorphous linear condensation polyimides, formed from the reaction of a monomeric mixture of an aromatic diethyl diacid with an aromatic diamine in NMP have received considerable attention. The exact chemical composition of the polymers have not been disclosed although they are presumably covered in a patent.[40] The synthetic scheme of one polyimide (structure 5) of particular interest is that shown in Eq. 2.

$$n\ H_5C_2O-\overset{O}{\overset{\|}{C}}\ \ \overset{O}{\overset{\|}{C}}-OC_2H_5,\ HO_2C\ \ CO_2H\ +\ n\ H_2N\ \ O\ \ O\ \ NH_2 \xrightarrow{\Delta\ -\ 2n\ C_2H_5OH,\ -\ 2n\ H_2O} 5 \qquad (2)$$

The T_g of high molecular weight polymer (structure 5) is 284°C.[41] The Tg and melt viscosity of this polymer can be lowered considerably by upsetting the monomer stoichiometry to lower the molecular weight and subsequently end-capping. In Eq. 2, the molecular weights of the diethyl pyromellitic acid and the 1,4-bis(4-aminophenoxy)-2-phenylbenzene are 310 and 368 g/mole respectively. On a one mole scale, the combined weight loss of ethanol and water in going from monomers to polymer is 128 g/mole or 18.9%. This obviously represents a significant weight loss which must be handled if the monomeric reaction approach is employed to make prepreg and subsequently composites. In most instances, "B staging" is performed to reduce the volatile evolution and increase the melt viscosity.

A polyimide, designated Avimid® K-III, has the neat resin properties in Table 8. An NMP solution of a mixture of monomers was used to impregnate a carbon/graphite fiber reinforcement such as Magnamite AS-4 to yield a tacky, drapable prepreg which contains ~ 15-17 weight % volatiles (~ 50% are polymerization by-products and the remaining 50% residual solvent). Laminates

were fabricated by conventional vacuum bag/autoclave molding technique using a cure cycle of ~ 9 hours which involved heating to 343°C during ~ 6 hours under vacuum, applying 1.34 MPa (200 psi) at 343°C, and maintaining at 343°C for ~ 2 hours followed by a cool-down under pressure during 1 hour to 200°C.[29] The mechanical properties of representative laminates are presented in Table 9.

Although Avimid K-III prepreg contains high volatile content which can cause severe composite processing problems, cure cycles as long as 14 hours have been employed primarily to accommodate the volatile evolution during the fabrication of sizable low void content (e.g. 0.5%) laminates [e.g. 0.6 m x 2.2 m x 32 plies (2 ft x 7 ft)]. Avimid K-III is one of the leading condensation polyimide candidates for high performance composite applications. Limited quantities of Magnamite AS-4 prepreg currently costs ~ $220 to $440 per kilogram (~ $100 to $200 per pound) depending on the size of the order. Work is still underway with Avimid K-III primarily to reduce the time required for composite fabrication and also to develop a larger mechanical property data base. Another condensation polymer (formerly called NR150B2), Avimid N, with higher temperature performance than Avimid K-III is also under development.

The polyimide of structure 6 was prepared via the polyamic acid in NMP and subsequently converted to polyimide by heating in NMP.[42] The properties of the polyimide are presented in Table 10. As prepared by

6

imidization in hot NMP, the polyimide exhibited crystallinity as evidenced by wide angle x-ray diffraction and differential scanning calorimetry showing a T_m at 236°C. However, the crystallinity disappears after heating above 250°C and could not be recovered by simply annealing under ambient conditions. The fractured compact

tension specimens of amorphous polymer which gave an average critical strain energy release rate (G_{Ic}) of 3200 J/M^2 showed pronounced crazing and moderate roughness due to yielding, creating new surface area to dissipate the stress. The melt viscosity in Table 10 is similar to that of the polyetherimide Ultem® 1000 (T_g = 220°C, run at 276°C) and polysulfone UDEL® P-1700 (T_g = 190°C, run at 240°C). The tensile shear strengths are the highest average value reported for a polyimide and comparable to the highest values ever reported for an organic adhesive. The excellent adhesive strength has been attributed to the high flow and accordingly good wetting of the adherends.

Preliminary unsized AS-4 unidirectional composite properties are also listed in Table 10. Prepreg was prepared by coating tow with an NMP solution of the polyimide which was subsequently wound on a drum and air dried to a tack-free state. The prepreg was then placed unrestrained in a circulating air oven and further dried by heating to ~ 200°C for 1 hour to yield volatile content of $<$ 1.0%. Prepreg prepared and dried in this manner is generally of poor quality with high resin content on the non-drum side, curled and boardy. Although the preliminary adhesive and composite properties of this polyimide were encouraging, no further work was performed in our laboratories because the polyimide is sensitive to solvents encountered in aerospace composite applications (e.g. hydraulic fluid and paint stripper).

A polyimide of structure 7 was prepared by reacting 1,3-bis(aminomethyl)-

7

where R = - CH_2 –(cyclohexane)– CH_2 - (25%), -$(CH_2)_6$- (25%) and –(methylbenzene, CH_3)– (50%)

cyclohexane (0.25 mole) and 1,6-hexanediamine (0.25 mole) with 3,3',4,4'-benzophenonetetracarboxylic dianhydride (0.99 mole) and phthalic anhydride (0.002 mole) in m-cresol at ambient temperature under nitrogen for 0.5 hour. 2,4-Diaminotoluene (0.50 mole) was added and the reaction mixture (solids content of 20%) was stirred under nitrogen for 24 hours at 185 to 195°C.[44] The polyimide had a surprisingly narrow molecular weight distribution with a polydispersity factor (M_w/M_n) of only 2.04. The polydispersity factor for most polyimides is significantly higher. The tensile and compression properties of the polyimide as well as the fracture energy in Table 11 are excellent. The preliminary adhesive properties were also impressive with high 25°C strength and good retention of strength at 200°C. The major disadvantage of this polyimide was the use of m-cresol as the polymerization solvent. Other solvents were not investigated as the polymerization medium. Meta-cresol has an unpleasant odor, irritates the skin upon contact and is difficult to remove.

Unidirectional and fabric carbon/graphite prepreg were prepared by solution coating and subsequently dried to 250°C to reduce the volatile content to < 1%. Laminate fabrication involves heating to 300°C under 1.34 MPa (200 psi) and maintaining at 300°C under pressure for 0.5 hour. Preliminary laminate properties presented in Table 12 are comparable to that of the state-of-the-art 177°C epoxy systems.

The polyimide of structure 1 in Eq. 1 commonly referred to as LARC-TPI has undergone extensive evaluation. Although different properties (e.g. T_g, fracture energy and adhesive strength) have been reported for LARC-TPI due largely to the difference in quality of the polymer, thermal history and method of measurement, the properties in Table 13 are typical. The laminates were fabricated from prepreg prepared from a 2:1 by weight slurry of LARC-TPI powder and polyamic acid. The

powder is from chemically imidized polyamic acid and exhibits a transient crystallinity and excellent melt flow characteristics. LARC-TPI laminates fabricated without the powder exhibited significantly lower mechanical properties. More recent composite work with LARC-TPI has provided excellent mechanical properties [49]. Since this initial work with the semi-crystalline LARC-TPI powder, a new experimental form of powder designated LARC-TPI-1500 has been introduced.[50] One grade of this new end-capped, controlled molecular weight, powder form of LARC-TPI (inherent viscosity of 0.37 dL/g and Tg of ~ 236°C) as mentioned earlier had a relatively low melt viscosity [6 x 10^3 Pa·sec (6 x 10^4 poise) at 340°C under a shear rate of 10^{-1} sec^{-1}].[24] Composites from this material are being evaluated.

A polyimide similar to LARC-TPI is the polyimidesulfone in structure 8. The sulfone group in place of the carbonyl group results in more intermolecular

8

association (polar interaction) and accordingly a higher T_g (273°C versus 250°C) and higher modulus [4.96 GPa (720 ksi) versus 3.72 GPa (540 ksi)].[51] Polyimidesulfone/112E-glass with an A-1100 finish adhesive tape was used to fabricate Ti/Ti tensile shear specimens at 325°C under 1.38 MPa (200 psi) for 15 minutes. Tensile shear strength of 32.1 MPa (4650 psi) at 25°C, 18.1 MPa (2620 psi) at 232°C, and 24.5 MPa (3560) at 232°C after 5000 hours at 232°C in air were obtained.[51] A postcure effect (higher strength after aging) is evident at 232°C similar to that observed for LARC-TPI. This polyimide has also been evaluated as a composite matrix. Two parts of the LARC-TPI semi-crystalline powder were blended with one part (by weight) of the polyamic acid of the polyimidesulfone and the resulting slurry used to prepare prepreg. The composite properties were slightly better than those reported in Table 13 for LARC-TPI. Further work is underway to

optimize the formulation and the composite fabrication conditions[49] with the polyimidesulfone.

Two relatively new thermoplastic polyetherimides recently developed as composite matrices are similar in chemical structures to that of Ultem® 1000 polyetherimide[52] in 9. Although the chemical composition of these two new

9

polyetherimides, Cypac 7005 and 7156-1, have not been disclosed, Cypac 7005 presumably uses a different diamine than Ultem® 1000 whereas Cypac 7156 uses a different dianhydride and diamine than Ultem® 1000. The neat resin properties of Ultem® 1000, Cypac 7005 and Cypac 7156-1 are presented in Table 14. The T_g of Cypac 7156 (275°C) is higher than that of Cypac 7005 (230°C) which permits better retention of mechanical properties at elevated temperatures.

Laminate properties for Cypac 7005 are summarized in Table 15. In addition, compression strength at 23°C after 1500 in lb/in impact for fabric laminates was 46,000 psi while quasi-isotropic AS-4 laminates gave 42,000.[54,55] Unidirectional AS-4 laminate also gave 23°C short beam shear strengths of ~ 16,000 psi,[54] a relatively high value for a thermoplastic matrix. The Cypac 7005 laminates were reported[53] to show little effect after exposure to jet fuel (JP-4) and hydraulic fluid (Skydrol). The current price of Cypac 7005 AS-4/3K70P fabric prepreg is ~ $330/kg (~ $150/lb).

A controlled molecular weight, end-capped version of the semi-crystalline polyimide of structure 4 (neat resin properties in Table 5) was recently evaluated in composite work.[56] Unidirectional unsized AS-4 laminates fabricated at a final

temperature of 365°C under 3.4 MPa (500 psi) for 15 minutes followed by a postcure at 300°C under 3.4 MPa for 3 hours from solution-coated drum-wound tape containing 2.1% volatiles gave the preliminary properties in Table 16. Good retention of flexural properties was observed at temperatures as high as 232°C (above the T_g) due to increased crystallinity from aging at 316°C for 100 hours. The short beam shear strengths are low because of the poor quality of the prepreg (e.g. fiber misalignment, resin rich areas, fiber wetting, etc.). Regardless, short beam shear specimens tested at 232°C retained 60% of their room temperature strength. Further work is underway on LARC-CPI to optimize the polymer (improve processability, crystallization rate, etc.), obtain better quality prepreg and conduct more extensive laminate properties.

Another condensation polyimide, JD861, has been evaluated as a composite matrice and is commercially available.[57] The exact chemical composition has not been disclosed although the polyimide is thought to be from the reaction of the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid and two diamines, one of which may be 1,3-bis(3-aminophenoxy)benzene. JD861 has a T_g of 266°C; 23°C flexural strength and modulus of 170 MPa (24.7 Ksi) and 4.1 GPa (590 Ksi) respectively; 23°C tensile strength, modulus and strain of 120 MPa (17.4 Ksi), 3.4 GPa (500 Ksi) and 4.2% respectively; and a fracture toughness of 1400 J/M^2 (8 in lb/in^2).[58] Preliminary carbon/graphite fabric composite properties are presented in Table 17. Residual compressive strengths of quasi-isotropic Toho HTA-7 laminates after 6750 J/M (1500 in lb/in) impact were ~ 220 MPa (32 Ksi).[58]

CONCLUSIONS

Although condensation polyimides can be prepared for many applications where the T_g, T_m, thermooxidative stability, toughness, color, dielectric constant,

coefficient of thermal expansion, chemical stability, mechanical properties, etc. can be controlled within certain boundaries, a readily processable, low cost, high temperature condensation polyimide with high overall composite properties has not been realized. Depending upon the approach to condensation polyimide composite matrices (e.g. mixture of monomers, polyamide acid, polyimide, mixtures of polyamide acid and polyimide, etc.), certain shortcoming still exist. These include:

- limited flow which necessitates the use of high fabrication temperatures and pressures
- volatile evolution leading to processing problems and poor mechanical properties
- high cost which may discourage their use except in specialty high performance applications
- low compression strength

To overcome these limitations, research and development is being directed towards the following areas:

- Improving the processability of polyimides that do not evolve volatiles
- Development of an in-situ polymerization route to high T_g, solvent resistant, tough polyimides without volatile evolution
- Cost reduction through use of less expensive monomers and better processability
- Increased durability at high operating temperatures
- Higher compression strength
- Innovative low cost process to prepare prepreg and composites

A single polyimide matrix system cannot perform in all the different applications because the requirements vary significantly. As a result, composite matrices are generally developed for particular applications. Polyimide matrix

development during the last two decades has been sporadic primarily because of a questionable market. New markets are developing particularly in the military arena, jet engine applications and in high speed commercial transports (formerly called supersonic transports) which demand high temperature performance. These areas offer the potential for a sizable market for polyimide composite matrices. As polyimides evolve with good processability and mechanical performance, larger markets will develop which will lower the cost and stimulate their use in other structural applications.

The use of trade names or manufacturers does not constitute an official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.

REFERENCES

1. M. I. Bessonov, M. M. Koton, V. V. Kudryavtsev and L. A. Laius, Polyimides, Plenum Publishing Co., New York, 1987
2. J. P. Critchley, G. J. Knight and W. W. Wright, Heat Resistant Polymers, Plenum Press, New York, 1983
3. P. E. Cassidy, Thermally Stable Polymers, Marcel-Dekker Inc., New York, 1980
4. S. E. Sroog, Polyimides in Encyclopedia of Polymer Science and Technology, ed. H. F. Mark, N. G. Gaylord and N. M. Bikales, Interscience Publishers, New York, Vol. 11, 1969, p. 247
5. Polyimides, ed. K. L. Mittal, Plenum Press, New York, Vols. 1 and 2, 1984
6. Recent Advances in Polyimide Science and Technology, ed. W. D. Weber and M. R. Gupta, Society of Plastics Engineers, Inc., Poughkeepsie, New York, 1987
7. V. L. Bell, B. L. Stump and H. Gager, J. Polym. Sci. Polym. Chem. Ed. 14, 2275 (1976)
8. A. H. Egli and T. L. St. Clair in Recent Advances in Polyimide Science and Technology, ed. W. D. Weber and M. R. Gupta, Society of Plastics Engineers, Inc. Poughkeepsie, New York, 1987, p. 57
9. G. M. Bower and L. W. Frost, J. Polym. Sci. Pt. A1, 3135 (1963)
10. R. A. Orwoll, T. L. St. Clair and K. D. Dobbs, J. Polym. Sci. Polym. Phys. Ed., 19, 1385 (1981)
11. T. L. St. Clair and D. J. Progar in Adhesion Sci. Tech., ed. L. H. Lee, Plenum Press, New York, 1975, p. 187
12. W. Volksen and P. M. Cotts in Polyimides, ed. K. L. Mittal, Plenum Press, New York, Vol. 1, 1984, p. 163
13. P. Cotts and W. Volksen, ACS Symp. Ser. 242, 227 (1984)

14. C. C. Walker, J. Polym. Sci.: Pt. A: Polym. Chem. 26, 1649 (1988)
15. R. A. Dine-Hart and W. W. Wright, J. Appl. Polym. Sci. 11, 609 (1967)
16. V. Y. Smirnova, L. A. Laius, M. I. Bessonov, S. V. Bushin, T. I. Garmonova, M. M. Koton, V. S. Skazka and L. M. Shcherbakova, Polym. Sci. USSR 17(10), 2549 (1975)
17. P. R. Young and A. C. Chang, Soc. Adv. Matl. Proc. Eng. Series 32, 1051 (1987)
18. H. H. Gibbs and C. V. Breder, Polym. Prepr. 15(1), 775 (1974)
19. A. K. St. Clair, T. L. St. Clair and K. T. Shevket, Polym. Matl. Sci. Eng. Prepr. 51, 62 (1984)
20. P. M. Hergenrother, N. T. Wakelyn and S. J. Havens, J. Polym. Sci.: Pt. A: Polym. Chem. 25, 1093 (1987)
21. P. M. Hergenrother and S. J. Havens, SAMPE J. 24(4), 13 (1988)
22. A. K. St. Clair, T. L. St. Clair and W. S. Slemp, in Recent Advances in Polyimide Science and Technology, ed W. D. Weber and M. R. Gupta, Soc. of Plastics Engineers, Inc., Poughkeepsie, NY, 1987, p. 16.
23. A. K. St. Clair, T. L. St. Clair and W. P. Winfree, Polym. Matl. Sci. Eng. Proceedings, 59, 28 (1988)
24. M. Sugita and M. Ohta, Mitsui Toatsu Chemicals, Inc., Tokyo, Japan, private communication
25. S. N. Kharkov, E. P. Krasnov, Z. N. Laurova, S. A. Baranova, V. P. Aksenova and A. S. Chegola, Vysokomol. Soedin A13(4) 833 (1971)
26. P. Delvigs, L. Hsu and T. T. Serafini, J. Polym. Sci. B, 8(1), 29 (1970)
27. M. Dorr and M. Levy, J. Polym. Sci. Polym. Chem. Ed. 13, 171 (1975)
28. F. W. Harris, W. A. Feld and L. H. Lanier, J. Polym. Sci. Polym. Let. Ed. 13(5), 238 (1975)

29. R. J. Boyce, T. P. Gannett, H. H. Gibbs and A. R. Wedgewood, Sci. Adv. Matl. Proc. Eng. Series 32, 169 (1987)

30. T. Takekoshi, J. G. Wirth, D. R. Heath, J. E. Kochanowski, J. S. Manello and M. J. Webber, J. Polym. Sci. Polym. Chem. Ed., 18, 3069 (1980)

31. J. P. Critchley, P. A. Grattan, M. A. White and J. S. Pippett, J. Polym. Sci. Pt. A-1, 10, 1789 (1972)

32. T. Takekoshi, U.S. Patent 3,847,870 (1974) and 3,850,885 (1974) (To General Electric Co.)

33. T. Takekoshi, Paper presented at IUPAC 32nd Intl. Symposium on Macromolecules, Kyoto, Japan, Aug. 1-6, 1988

34. J. Gagliani and J. V. Long, U.S. Patent 4,394,464 (1983)

35. R. J. Angelo, U.S. Patents, 3,282,898 (1963) and 3,345,342 (1967) (To DuPont)

36. See Thermid IP-600, IP-615, IP-630 and IP-6001 from National Starch and Chemicals Corporation, Bridgewater, NJ 08807

37. Y. Imai, J. Polym. Sci. B, 8(8), 555 (1970)

38. K. Taguchi, Ibid., B, 18(8), 525 (1980)

39. W. F. Farrisey, J. S. Rose and P. S. Carleton, Polym. Prepr. 9, 1581 (1968)

40. T. P. Gannett, H. H. Gibbs and R. J. Kassal, U.S. Patent 4,485,140 (1984) (To E. I. DuPont de Nemours and Company)

41. P. M. Hergenrother and S. J. Havens, NASA Langley Research Center, unpublished work

42. F. W. Harris, M. W. Beltz and P. M. Hergenrother, SAMPE J. 23(1), 6 (1987)

43. P. M. Hergenrother, NASA Langley Research Center, unpublished work

44. C. Delano and C. Kiskiras, paper presented at Workshop on Chemistry and Properties of High Performance Composites, sponsored by the Div. Polym.

Chem. and Div. Polym. Matl.: Sci. Eng., American Chem. Soc. March 28-31, 1988, Jackson, WY

45. D. J. Progar, NASA Langley Research Center, private communication

46. N. J. Johnston, NASA Langley Research Center, private communication

47. D. J. Progar and T. L. St. Clair, Natl. SAMPE Tech. Conf. Series 7, 53 (1975)

48. C. L. Hendricks and T. N. Hale in Welding, Bonding Fastening 1984 Sym. Proceedings, NASA Conf. Publ. 2387 (1985), p. 351

49. N. J. Johnston, T. L. St. Clair, R. M. Baucom and T. W. Towell, Sci. Adv. Matl. Proc. Eng. Series 34, 000 (1989)

50. Mitsui Toatsu Chemicals, Inc., 140 E. 45th St., New York, NY 10017

51. T. L. St. Clair and D. A. Yamaki in Polyimides, ed. K. L. Mittal, Plenum Press, New York, Vol. 1, 1984, p. 99

52. General Electric Company, Pittsfield, MA 01202

53. S. Peake, A. Maranci, D. Megna, J. Powers and W. Trzaskos, 10th Intl. SAMPE European Chapter Conf. and Exhibition Proceedings, 10 000 (1989)

54. S. Peake, American Cyanamid Company, Stamford, CT 06904-0060, personal communication

55. Preliminary Data Sheet on Cypac X7005, American Cyanamid Company, Polymers Products Division, Wayne, NJ 07470

56. P. M. Hergenrother, M. W. Beltz and S. J. Havens, Soc. Adv. Matl. Proc. Eng. Series 34, 000 (1989)

57. BP Advanced Materials, Ltd., Bristol, England

58. D. Wilson, A. G. Aldred, A. Fernyhough and F. C. Robertson, paper presented at "Recent Advances in Polyimides and Other High Performance Polymers," Reno, NV, July 13-16, 1987

Table 1

Glass Transition Temperatures of Polyimides*

Ar =	n_{inh}, dL/g	T_g, °C
	0.35	326
	0.41	297
	0.64	365
	0.40	337
CH_2	0.38	291
O	0.46	285
S	0.35	283
SO_2	0.31	336
O O	0.35	229

* Ref 16

Table 2
Glass Transition Temperatures of Polyimides*

Ar	Ar'	η_{inh} of poly(amide-acid),dL/g	T_g, °C
BTDA	4,4'-DABP	0.73	295
BTDA	3,4'-DABP	0.64	283
BTDA	3,3'-DABP	0.55	264
PMDA	4,4'-DABP	0.98	380
PMDA	3,4'-DABP	0.84	339
PMDA	3,3'-DABP	0.83	321

* Ref 7

Table 3

Glass Transition Temperatures of Polyimides*

Ar =	η_{inh} of polyamide acid, dL/g	T_g, °C
[structure: aryl–O–aryl–S–aryl–O–aryl]	0.41	167
[structure: aryl–O–aryl]	0.87	187
[structure: aryl–C(=O)–aryl]	0.80	201
[structure: aryl–C(CF_3)$_2$–aryl]	1.20	206
[structure: benzene (tetrasubstituted)]	0.44	221

* Ref 19

Table 4

Glass Transition and Crystalline Melt Temperatures of Polyimides*

Ar	Polyamide acid η_{inh}, dL/g	Polyimide T_g, °C	Polyimide T_m, °C
1,4-phenylene	0.81	222	350
1,3-phenylene	0.62	233	427
–C6H4–CO–C6H4–	0.57	233	422
–C6H4–O–C6H4–	0.52	215	418
naphthylene	0.42	246	424

* Ref 20

Table 5

Properties of Polyimide 2 (LARC-CPI)*

Glass transition temperature: 222°C

Crystalline melt temperature: 350°C

Melt viscosity at 395°C at angular frequency of 0.1 rad/sec: 10^5 Pa·sec (10^6 poise)

Equilibrium moisture pickup: < 1%

Dielectric constant at 1 MHz: 3.1

Solvent Resistance: Excellent

Fracture Energy (G_{Ic}): 6650 J/M^2 (38 in lb/in^2)

Unoriented Thin Film Tensile Properties (Through 1 hr @ 300°C)

Test Condition	Strength, MPa (Ksi)	Modulus, GPa (Ksi)	Elongation, %
25°C	151.7 (22.0)	4.34 (630)	8.3
25°C after 100 hr soak in 30% aq. NaOH	139.9 (20.3)	4.07 (590)	5.0
177°C	104.8 (15.2)	3.72 (540)	21.1
232°C	35.8 (5.2)	1.69 (245)	76.1
232°C after 100 hr @ 316°C in air	57.9 (8.4)	2.35 (341)	9.6

Ti/Ti Adhesive Properties [RT → 400°C under 6.9 MPa (1000 psi), hold 15 min @ 400°C]

Test Condition	Tensile Shear Strength, MPa (psi)
25°C	43.1 (6250)
25°C after 1000 hr @ 232°C	49.1 (7120)
177°C	31.1 (4510)
232°C	4.1 (590)
232°C after 1000 hr @ 232°C	18.9 (2740)
232°C after 100 hr @ 316°C in air	25.3 (3670)

*Ref. 21

Table 6

Glass Transition Temperatures and Color of Polyimide Films*

X =	Ar =	Polyamide acid η_{inh}, dL/g	T_g, °C	Film color**
$-C(CF_3)_2-$	$-C_6H_4-O-C_6H_4-O-C_6H_4-$	1.20	206	Pale to colorless
$-C(CF_3)_2-$	$-C_6H_4-O-C_6H_4-$	1.00	244	Pale to colorless
$-C(CF_3)_2-$	$-C_6H_4-SO_2-C_6H_4-$	0.47	279	Colorless
$-C(CF_3)_2-$	$-C_6H_4-C(CF_3)_2-C_6H_4-$	0.60	260	Colorless
$-O-$	$-C_6H_4-O-C_6H_4-O-C_6H_4-$	0.87	187	Pale yellow
$-O-$	$-C_6H_4-O-C_6H_4-$	1.09	192	Pale to colorless
$-O-$	$-C_6H_4-SO_2-C_6H_4-$	0.51	258	Pale yellow

* Ref 22

** Film thickness, [0.0051 cm, (0.002 in.)]

Table 7
Dielectric Constants of Polyimides*

$$\left[-N\begin{matrix} C(=O) \\ C(=O) \end{matrix}Ar\begin{matrix} C(=O) \\ C(=O) \end{matrix}N-Ar'- \right]_n$$

Ar	Ar'	Dielectric constant at 10 GHz
C_6H_2	$-C_6H_4-O-C_6H_4-$	3.22
C_6H_2	$-C_6H_4-O-C_6H_4-$	2.84
$C_6H_3-C(=O)-C_6H_3$	$-C_6H_4-O-C_6H_4-$	3.15
$C_6H_3-C(=O)-C_6H_3$	$-C_6H_4-O-C_6H_4-$	3.09
$C_6H_3-O-C_6H_3$	$-C_6H_4-O-C_6H_4-$	3.07
$C_6H_3-O-C_6H_3$	$-C_6H_4-O-C_6H_4-$	2.99
$C_6H_3-C(CF_3)_2-C_6H_3$	$-C_6H_4-O-C_6H_4-$	2.79
$C_6H_3-C(CF_3)_2-C_6H_3$	$-C_6H_4-O-C_6H_4-$	2.73
$C_6H_3-C(CF_3)_2-C_6H_3$	$-C_6H_4-C(CF_3)_2-C_6H_4-$	2.39

* Ref 23

Table 8

Ambient Temperature Properties of Avimid® K-III*

Property	Value
Tensile Strength	102 MPa (14800 psi)
Tensile Modulus	3.76 GPa (546,000 psi)
Elongation	14%
Fracture Energy (G_{Ic})	1900 J/M^2 (10.9 in lb/in^2)
Shear Modulus	1.37 GPa (198,000 psi)
Poisson's Ratio	0.365
Density	1.31 g/cc
T_g	251°C

*Ref. 29

Table 9

Mechanical Properties of Magnamite AS-4/Avimid® K-III Laminates*

Test	Fiber Orientation	Test Temperature, °C		
		25	177	232
Flexural Strength, MPa (Ksi)	Quasi-isotropic	793 (115)	648 (94.0)	614 (89.0)
Flexural Modulus, GPa (Ksi)	Quasi-isotropic	36 (5220)	34 (4930)	29 (4205)
Short Beam Shear Strength, MPa (Ksi)	Quasi-isotropic	63 (9.1)	48 (7.0)	36 (5.2)
Interlaminar Fracture Toughness, J/M^2 (in lb/in^2)	0	1800 (10.3)	----	----
Transverse Tensile Strength, MPa (Ksi)	0	37-48 (5.4-7.0)	----	----
Transverse Tensile Modulus, GPa (Msi)	0	8.3-10.3 (12.0-14.9)	----	----
Compressive Strength, MPa (Ksi)	0	1000 (145)	----	----
Compressive Modulus, GPa (Msi)	0	110 (15.9)	----	----
Compressive Strength After 6750 J/M (1500 in lb/in) Impact, MPa (Ksi)	Quasi-isotropic	281 (40.0)	----	----

*Ref. 29

Table 10

Properties of Polyimide 6[1]

Glass transition temperature: 155°C

Crystalline Melt temperature: 236°C

Melt viscosity for amorphous polymer at 210°C under angular frequency of 0.1 rad/sec: 6×10^5 Pa·sec (6×10^6 poise)

Fracture energy (G_{Ic}): 3200 J/M^2 (18.2 in lb/in^2)

Thin Film Properties (dried through 2 hr @ 210°C)		
Test Temp., °C	25	93
Tensile Strength, MPa (Ksi)	86.2 (12.5)	64.8 (9.4)
Tensile Modulus, GPa (Ksi)	2.70 (391)	2.06 (298)
Elongation, %	4.0	5.0
Ti/Ti Adhesive Properties (RT → 260°C, 100 psi, held 15 min)		
Test Temp., °C	25	93
Tensile Shear Strength, MPa (psi)	54.1 (7850)	37.2 (5400)
Unsized AS-4 Unidirectional Laminate Properties[2] (RT → 260°C, 100 psi, held 30 min)		
Test Temp., °C	25	93
Flexural Strength, MPa (Ksi)	1716.6 (249)	1111.9 (162)
Flexural Modulus, GPa (Msi)	117 (16.9)	109 (15.8)
Short Beam Shear Strength, MPa (Ksi)	82.7 (12.0)	47.5 (6.9)

[1]Ref. 42

[2]Ref. 43

Table 11

Properties of Polyimide 7

Glass transition temperature: 233°C

Inherent viscosity at 25°C: 0.28 dL/g ($CHCl_3$), 0.55 dL/g (m-cresol)

Number average molecular weight: 24,500 g/mole

Weight average molecular weight: 50,000 g/mole

Density: 1.33 g/cc

Melt viscosity at 300°C at angular frequency of 0.1 rad/sec: 10^6 Pa·sec (10^7 poise)

Equilibrium water pickup: 2.5%

Solvent resistance: Resistant to hydraulic fluid, jet fuel, deicing fluid

Fracture energy (G_{Ic}): 2100 J/M^2 (12 in lb/in^2)

Properties of neat resin moldings[1]

Test Temperature, °C	25	93
Tensile Strength, MPa (Ksi)	128.2 (18.6)	93.8 (13.6)
Tensile Modulus, GPa (Ksi)	3.14 (456)	2.72 (395)
Elongation, (break), %	6.7	5.0
Compressive Strength, MPa (Ksi)	213.7 (31.0)	156.5 (22.7)
Compressive Modulus, GPa (Ksi)	3.82 (554)	3.16 (458)
Elongation (yield), %	9.5	8.6

Ti/Ti Adhesive Properties[2] [RT → 316°C under 0.34 MPa (50 psi), hold 0.5 hr @ 316°C]

Test Condition	Tensile Shear Strength, MPa (psi)
25°C	37.0 (5370)
25°C after 3 da water boil	26.1 (3790)
200°C	19.5 (2830)
200°C after 500 hr @ 200°C	18.7 (2710)

[1]Ref. 44

[2]Ref. 45

Table 12

Laminate Properties of Polyimide 7

Fiber	Property	Test Temperature, °C			
		25	93	150	177
Unidirectional	Flexural St., MPa (Ksi)	1882 (273)	----	1317 (191)	510 (74)
AS-4 Unsized[1]	Flexural Mod., GPa (Msi)	123 (17.9)	----	117 (16.9)	78.6 (11.4)
	Short Beam Shear, MPa (Ksi)	63.4 (9.2)	----	48.3 (7.0)	42.1 (6.1)
Celion 3000 Fabric	Flexural St., MPa (Ksi)	765 (111)	800 (116)	----	----
8 Harness Satin Weave[2]	Flexural Mod., GPa (Msi)	55.8 (8.1)	58.6 (8.5)	----	----
	Short Beam Shear, MPa (Ksi)	63.4 (9.2)	56.5 (8.2)	----	----

[1]Ref. 46

[2]Ref. 44

Table 13

Properties of Polyimide 1 (LARC-TPI)

Glass transition temperature: ~ 250°C
Density: 1.33 g/cc
Fracture energy (G_{Ic}): ~ 2600 J/M^2 (15 in lb/in^2)

Unoriented Thin Film Properties at 25°C (dried through 1 hr @ 300°C)[1]

Tensile Strength, MPa (Ksi)	13.6 (19.7)
Tensile Modulus, GPa (Ksi)	3.72 (540)
Elongation, %	4.8

Ti/Ti Adhesive Properties [RT → 343°C under 1.4 MPa (200 psi)]

Test Condition	Tensile Shear Strength, MPa (psi)
25°C	42.6 (6000)[2]
232°C	13.8 (2000)[3]
232°C after 1000 hr @ 232°C	15.2 (2200)[3]
232°C after 10000 hr @ 232°C	24.1 (3500)[3]
232°C after 37000 hr @ 232°C	24.1 (3500)[3]

Unidirectional AS-4 Laminate Properties [4,5] [cured through 1 hour @ 350°C under 2.1 MPa (300 psi)]

Test Temperature, °C	Flexural St., MPa (Ksi)	Flexural Mod., GPa (Msi)	Short Beam Shear St., MPa (Ksi)
25	1972 (285)	97.2 (14.1)	95.1 (13.8)
93	1751 (254)	97.2 (14.1)	86.9 (12.6)
149	1599 (232)	90.3 (13.1)	73.1 (10.6)
177	1372 (199)	91.7 (13.3)	----

[1]Ref. 7

[2]Ref. 47

[3]Ref. 48

[4]Ref. 49

[5]Fiber Vol ~ 48%, good C-scan

Table 14

Neat Resin Properties*

Property	Ultem® 1000	Cypac 7005	Cypac 7156-1
T_g, °C	217	230	275
Tensile St., MPa (Ksi)	105 (15,2)	95 (13.8)	102 (14.8)
Tensile Elong., %	60	20	15
Flexural St., MPa (Ksi)	145 (21.0)	130 (18.9)	128 (18.6)
Flexural Mod., GPa (Ksi)	3.3 (479)	3.0 (435)	3.1 (450)

*Ref. 53

Table 15

Cypac 7005 Graphite AS-4/3K7OP Laminate Properties*

Property	Value
T_g, °C	225
Fiber Vol., %	54
Flexural St., MPa (Ksi)	
23°C dry	838 (120)
150°C dry	559 (80)
150°C wet	405 (58)
Flexural Mod., GPa (Msi)	
23°C dry	56 (8.0)
150°C dry	54 (7.9)
150°C wet	53 (7.7)
Short Beam Shear St., MPa (Ksi)	
23°C dry	66 (9.5)
150°C dry	41 (5.8)
150°C wet	35 (5.0)
Compression St., MPa (Ksi)	
23°C dry	503 (73)
150°C dry	414 (60)
150°C wet	289 (42)

*Ref. 53

Table 16
LARC-CPI Unidirectional Unsized AS-4 Laminate Properties*

Test Temp., °C	Exposure	Flexural St., Ksi	Flexural Mod., Msi	Short Beam Shear St., Ksi
25	None	267	15.0	8.7
177	None	212	14.4	3.0**
204	None	196	14.4	---
232	None	110**	11.9	---
25	100 hr @ 316°C, air	265	14.3	8.9
177	100 hr @ 316°C, air	----	----	6.9
204	100 hr @ 316°C, air	214	14.0	5.9
232	100 hr @ 316°C, air	209	13.3	5.3

*Ref. 56; fiber volume ~ 53%; fabricated by heating to 365°C under 500 psi, holding 0.5 hr @ 365°C under 500 psi, and postcuring at 300°C for 3 hr under 500 psi

**Thermoplastic failure

Table 17

JD-861 Toho HTA-7, 5-Harness Satin Fabric
Laminate Properties (Weft direction)*

Property	Value
Flexural St., MPa (Ksi)	
23°C	790 (114)
200°C	500 (72.4)
Flexural Mod., MPa (Msi)	
23°C	57 (8.3)
200°C	56 (8.1)
Short Beam Shear St., MPa (Ksi)	
23°C	56 (8.1)
200°C	36 (5.2)
Compressive St., MPa (Ksi)	
23°C	369 (53.6)
200°C	199 (28.8)

*Ref. 58