NASA Contractor Report 172285

DEVELOPMENT OF AN IMPACT- AND SOLVENT-RESISTANT THERMOPLASTIC COMPOSITE MATRIX

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Contract NAS1-16808

April 1984

NASA
National Aeronautics and
Space Administration

Langley Research Center
Hampton, Virginia 23665

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SUMMARY

Several aliphatic-aromatic thermoplastic polymers in neat resin form have been identified which hold promise as solvent-resistant matrices for application in composites for aerospace vehicles. During this initial 24-month technical effort, 16 compositions representing polyimides and two types of polybenzimidazoles were synthesized, molded, and characterized. Polyimides from pyromellitic dianhydride with 1,6-hexane- and 1,8-octanediamines and polybenzimidazoles from 3,3',4,4'-tetraamino biphenyl with suberic and sebacic acids and 1,12-dodecanedicarboxylic acid demonstrated excellent unstressed resistance to chloroform, acetone, and tricresyl phosphate. N-arylenepolybenzimidazoles and polyimides from 3,3',4,4'-benzophenonetetracarboxylic dianhydride with aliphatic diamines were susceptible to chloroform absorption. Modification of the aliphatic polyimides from 3,3',4,4'-benzophenonetetracarboxylic dianhydride and 1,6-hexane- and 1,8-octanediamine, with m-phenylenediamine, reduced the chloroform susceptibility to acceptable values.

Three polymers were subjected to 500-hr exposure under stress to chloroform, acetone, and tricresylphosphate with no evidence of cracking or crazing. These polymers were the polybenzimidazole from 3,3',4,4'-tetraaminobiphenyl with sebacic acid; and the polyimides from pyromellitic dianhydride with 1,8-octanediamine, and 3,3',4,4'-benzophenonetetracarboxylic dianhydride with 1,8-octanediamine and m-phenylenediamine. Selection of the latter polymer for further investigation occurred. This selection was based on the cited stressed solvent testing as well as its tensile, hardness, and Tg properties.

It was then discovered that heat treatment of the selected polymer for 1 hr at 316°C (600°F) produced opacity in originally clear polymer moldings. Opacity was not produced in closely related compositions, i.e., the selected polymer with reduced m-phenylene content and the selected polymer where 1,8-octanediamine was replaced with 1,6-hexanediamine. Clear moldings are qualitatively much tougher than opaque moldings. Further, the as-prepared polymer must provide a clear cresol solution to produce clear moldings.

Reaction conditions as well as compositional variations of the selected composition were studied in detail. Rapid heatup to the final 180°C reaction temperature was found to play a key role in obtaining clear cresol solutions. Substitution of the 1,8-octanediamine with 1,6-hexanediamine in the composition appears to be advantageous and this latter composition has been scaled up to produce ~250 gm quantities. Preliminary composite work was initiated with this polymer.

SECTION 1

INTRODUCTION

This report describes efforts conducted during the first 2 years of a program to develop improved thermoplastic resins for application in composite structures for aerospace vehicles. Included in this section is a brief description of the advantages of such resin systems and the Acurex approach to the development of new impact- and solvent-resistant thermoplastic resins.

With solvent resistance tests conducted to date (under stress), the aliphatic-aromatic polyimides show outstanding promise in view of the state-of-the-art thermoplastic polymers, particularly in regard to their resistance to halogenated solvents. While this feature is not unusual for aromatic polyimides, the observed insolubility in combination with the good moldability of the aliphatic-aromatic polyimides is unique. Polyimides from both pyromellitic and 3,3',4,4'-benzophenonetetracarboxylic dianhydrides (PMDA and BTDA) show promise. The polyimide from BTDA with 1,6-hexanediamine and m-phenylenediamine was selected as the best candidate from the present effort. It should be noted that this selection is based on a number of factors which are consistent with current requirements of composite resins.

Less understood are the composite properties which might be obtained from the PMDA-based polyimides. Molded samples of these resins show the unusual ability to support a 450-psi compressive load at temperatures close to their molding temperatures. Differential scanning calorimetric (DSC) measurements suggested that crystalline polymers were obtained, which was confirmed by NASA-Langley personnel with X-ray analysis of the polyimides from PMDA with 1,8-octanediamine and 1,12-dodecanediamine. Both were determined to be highly crystalline. The use of crystalline polymers as composite matrix resins is not state of the art and a basis for their use has not been established. These thermally crystallizable polyimides showed remarkably low weight gains after 24-hr water boil (1,8-octanediamine = 0.2 percent and 1,12-dodecanediamine = 0.0 percent). Polyetheretherketone (PEEK) is crystalline and under investigation by several companies as a composite matrix[1,2].

Further characterization of the polyimides from BTDA with 1,6-hexanediamine and m-phenylenediamine and PMDA with 1,8-octanediamine and their copolymers are planned for third-year efforts.

1.1 BACKGROUND

The successful development of impact- and solvent-resistant thermoplastic systems for glass and graphite composites is particularly attractive from the standpoint of their demonstrated streamlined manufacturability. Hypothetically, thermoplastics only require simple heating and cooling cycles for component manufacture, whereas thermosets require more precise, and possibly extended, heating schedules which must be consistent with the cure chemistry.

Very high modulus (matrix properties) and crosslink density (solvent resistance) are the excellent features of thermosets, which currently make them the preferred matrices for graphite composites. Further, since the B-staged resins are liquids, excellent fiber collimation is achievable in the prepregs. The impact response of graphite composites to low-speed impact has been of concern for a number of years. Kevlar, glass, and other fibers are used with graphite fibers to provide more impact-resistant composites. Such "hybrids" involve loss of initial mechanical properties (modulus, compressive strength) to provide improved impact properties. Thermoplastics, on the other hand, offer impact resistance not attainable with thermosets.

Aircraft design requires lifetime prediction of their components. Any material which exhibits environmental degradation will compromise the design safety margins for the selected material. Structural designs are currently overweight because of the lower properties resulting from moisture absorption. The sensitivity of existing thermoplastics to aircraft fluids and other solvents preempts their serious consideration in aircraft components. This is the basic reason that Acurex proposed insolubility in aircraft solvents as the starting point for the program effort. Exposure to fuel, deicing fluids, and hydraulic fluids are serious concerns.

1.2 APPROACH

The Acurex approach is based on the development of thermoplastic polymers with rigid, crystallizable segments interconnected with flexible, energy-absorbing segments. The rigid segments can act as pseudocrosslinks between polymer chains and provide high modulus and solvent resistance. The interconnecting flexible segments provide impact resistance and melt processibility. The aliphatic-aromatic heterocyclics have received only limited attention in the literature; however, they appear as a class to offer both good solvent resistance and impact properties.

The aliphatic-aromatic heterocyclics selected were the polyimides, N-arylenepolybenzimidazoles, and polybenzimidazoles. Candidate rigid and flexible segments for these systems are given in Figure 1. The selected segments encompassed several features:

- Polyimides: Both stiff and kinked dianhydrides were selected for investigation. Although the long-term moisture stability of these systems may require careful characterization, they are readily prepared from relatively low-cost raw materials. An aliphatic dianhydride was included.

- Polybenzimidazoles: The polybenzimidazole from 3,3',4,4'-tetraaminobiphenyl (TAB) and sebacic acid was the subject of prior Acurex efforts and demonstrated many desirable features with notched Izod impact strengths comparable to polysulfone and unmodified polyphenylene oxide. The solvent resistance of this polymer class appeared to be excellent. The imidazole hydrogen provides hydrogen bonding, and several properties of the system reflect the effects of the hydrogen bonding.

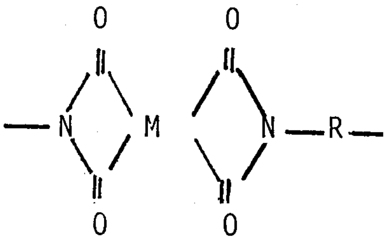
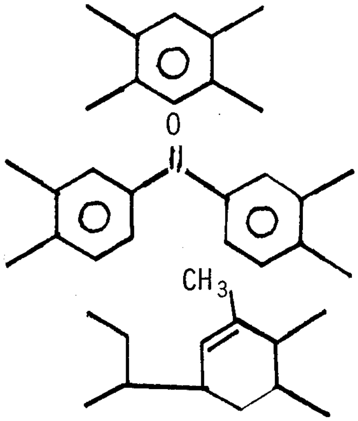
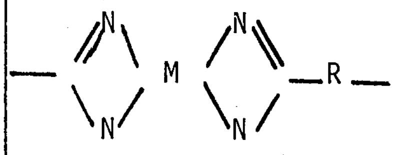
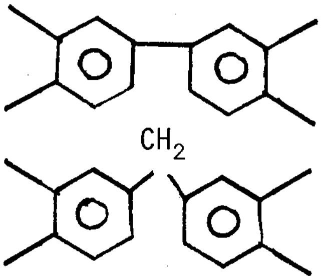
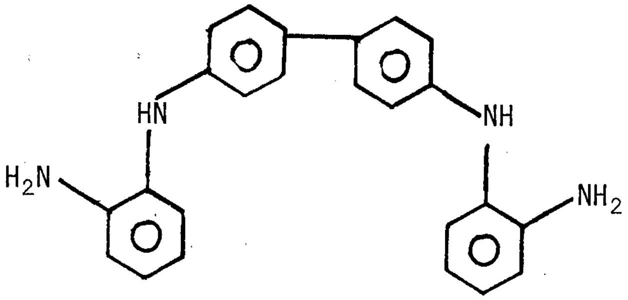
Resin Class/Structure	Rigid Segments M	Flexible Segments R
Polyimides 		$-(\mathrm{CH_2})_n-$ n = 6, 8, 12
Polybenzimidazoles 		$-(\mathrm{CH_2})_n-$ n = 6, 8, 12
N-Arylenepolybenzimidazoles		$-(\mathrm{CH_2})_n-$ n = 6, 8, 12 Aromatic/aliphatic anhydrides

Figure 1. Candidate aromatic/aliphatic heterocyclics

- N-Arylenepolybenzimidazoles: The all-aromatic polymers in this class were also investigated previously by Acurex. The aliphatic polymers were expected to be low melting, and may have required copolymerization or blending with aromatic systems to have useful heat-distortion temperatures. The aromatic polymers are insoluble in common solvents.

SECTION 2

OBJECTIVE

The overall objective of this program is the development of new thermoplastic laminating resin(s) that can be used with glass or graphite filament reinforcement to provide impact- and solvent-resistant composites for potential use on aerospace vehicles. These composites must have mechanical properties equivalent to state-of-the-art 177°C (350°F) curing epoxy systems. Although several routes can be pursued to improve the impact strength of composites (such as increasing the strain-to-failure capability of the reinforcement) this effort specifically pertains to resin development. Even though the tensile strength and tensile modulus of the reinforcement are considered to be the dominant contributors to impact strength of composites, the matrix also plays an important role by transferring strength and dissipating stress.

Target properties for the polymers are listed below.

- Amenable to impregnation of a reinforcement using conventional equipment
- Long prepreg shelf life at ambient conditions (>6 months)
- Acceptable processibility (maximum curing temperature of 316°C (600°F), maximum curing pressure of 0.69 MPa (100 psi), maximum time at final temperature of 1 hr, insensitive to heatup rate, and no volatile evolution)
- Thermoformability (thermoform flat-sheet stock to desired configurations at maximum temperature and pressure of 316°C and 0.69 MPa, respectively; ability to undergo thermoforming process twice)
- Acceptable mechanical properties over temperature range of -54° to 93°C (-65° to 200°F) after environmental exposure (humid aging and long-term aging at 93°C)
- Resistant to airplane fluids and solvents (under stress)
- Impact resistance and damage tolerance

SECTION 3

RESULTS AND DISCUSSION

This section has been divided into subsections which deal with different key aspects of the development effort. For example, methods to attain high molecular weight polymers from the numerous candidates is described under synthesis, Section 3.1. Comparison of the moldability of the several polymer compositions is provided in Section 3.2, Polymer Flow Properties; and comparison of their solvent resistance provided in Section 3.3, Screening of Molded Polymers.

Selection of a promising composition occurred after 12 months as described in Section 3.4. However, difficulties were encountered in obtaining the selected composition reproducibly and the originally planned composite efforts were postponed. Efforts directed at the reproducibility problem are described in Section 3.5, Polyimides From BTDA with Aliphatic and Aromatic Amines. A brief description of initial scaleup activities are described in Section 3.6 and composite efforts attempted thus far are described in Section 3.7.

3.1 SYNTHESIS

Efforts on the first 6 months of the program focused on the synthesis of high molecular weight polymers from the numerous polymer candidates since high molecular weight is a prerequisite for toughness. Preparation of high molecular weight, soluble, aliphatic polyimides was found to be more difficult than anticipated. Melt or modified-melt condensations carried out at final temperatures above 200°C led to crosslinked products, particularly with BTDA. Condensation in cresol solution at a 10 percent solids level provided high-molecular-weight soluble aliphatic polyimides.

Preparation of tough, aliphatic polybenzimidazoles proceeded as expected via melt condensation techniques.

Preparation of aliphatic N-arylenepolybenzimidazoles was more difficult than expected. Cyclic anhydrides produce high-molecular-weight polymers with 4,4'-bis(o-aminoanilino)biphenyl from purified monomers, which were not qualitatively tough. Aliphatic diacids do not react in a predictable manner. High-molecular-weight, tough polymers were obtained from suberic and sebacic acids, and a modest-molecular-weight polymer from 1,12-dodecanedicarboxylic acid.

At the end of the first 6 months of the program, efforts shifted to evaluation of the on-hand polymers in place of continuing with preparation of more candidates. The inherent viscosities of the 16 polymers characterized for moldability and solvent resistance in subsequent sections of the report are provided in Table 1. Discussion on the preparation of the polymers is provided in the following paragraphs.

TABLE 1. POLYMERS CHARACTERIZED FOR MOLDABILITY

Polymer[a]	Viscosity, dl/gm (solvent)[b]
Polyimides	
PMDA with 1,6-hexanediamine	1.05 (H_2SO_4)
with 1,8-octanediamine	3.32 (H_2SO_4)
with 1,12-dodecanediamine	1.16 (H_2SO_4)
BTDA with 1,6-hexanediamine	1.70 (H_2SO_4)
with 1,8-octanediamine	1.66, 1.54 (H_2SO_4 -- <1% insolubles)
with 1,12-dodecanediamine	1.00 (H_2SO_4 -- 24% insolubles)
with isophorone diamine	0.35 (H_2SO_4)
MCTC with 1,8-octanediamine	0.84 (H_2SO_4)
Polybenzimidazoles	
TAB with suberic acid	1.59 (H_2SO_4 -- 33% insolubles)
with sebacic acid	2.69 (H_2SO_4 -- 22% insolubles)
with 1,12-dodecanedicarboxylic acid	2.31 (H_2SO_4 -- 7.2% insolubles)
N-Arylenepolybenzimidazoles	
4,4'-Bis(o-aminoanilino)biphenyl	
with suberic acid	1.10 (H_2SO_4)
with sebacic acid	0.88 (cresol)
with 1,12-dodecanedicarboxylic acid	0.68 (H_2SO_4 -- 3.5% insolubles)
with methylhexahydrophthalic anhydride	Clear 1.10; opaque 1.62 (cresol)
with phthalic anhydride	0.92 (H_2SO_4)

[a] PMDA = pyromellitic dianhydride
BTDA = 3,3',4,4'-benzophenonetetracarboxylic dianhydride
MCTC = 5-(2,5-diketotetrahydrofuryl)-3-methyl-3-cyclohexane-1,2-dicarboxylic anhydride
TAB = 3,3',4,4'-tetraaminobiphenyl
[b] At 0.5% concentration

3.1.1 Aliphatic Polyimides

Investigation of several methods to prepare aliphatic polyimides eventually led to the development of a solution-condensation procedure, which provides sulfuric acid soluble polymers with high inherent viscosities. As described below, melt or modified-melt (fluxed) procedures invariably lead to crosslinked polymers, particularly with BTDA.

The three selected anhydrides were purified, and two were titrated for total acid. These results are given in Figure 2. Discrepancy between the titrated acid values and theory was attributed to residual purification solvent.

Three of the four selected diamines were purified by vacuum distillation to remove water and carbonate. They are shown in Figure 3.

The preparation of aliphatic polyimides with 1,8-diaminooctane by the procedure described by Sorenson and Campbell for polynonamethylenepyromellitimide was carried out[3]. This procedure requires formation of the dimethyl ester of the dianhydride in refluxing methanol; addition of the diamine to form the salt; methanol removal; and treating the salt for 2 hr at 139°C and 2 hr at 325°C (see the Appendix).

The polyimides from PMDA and BTDA were reasonably tough, whereas the polyimide from MCTC was brittle. The cited polynonamethylenepyromellitimide was reported to have an inherent viscosity of 0.8 to 1.2 dl/gm in m-cresol. The polyoctamethylenepyromellitimide was unaffected by this solvent, whereas the BTDA polymer produced swollen gel particles, suggesting that crosslinking had occurred. The polyoctamethylenepyromellitimide provided a highly swollen gel in sulfuric acid, suggesting that it was also crosslinked. It was also opaque, suggesting the presence of crystallinity.

Since the Sorenson and Campbell procedure is tedious and requires very high temperatures, alternative "melt" approaches to produce the aliphatic polyimides were investigated. Details are provided in the Appendix of this report. Briefly, the phenol-fluxed melt of PMDA and 1,8-octanediamine provided a product which was spectrally inconsistent with the product obtained from the Sorenson and Campbell procedure after overnight reaction at 105°C. Heating the product to 218°C led to spectral consistency and approximately the same "toughness" as the product obtained from the Sorenson and Campbell procedure. The sulfuric acid inherent viscosity of the soluble portion of the polymer (treated at 218°C for 1 hr) was 1.40 dl/gm. After correction for the 26 percent sulfuric acid insolubles determined on the sample, the inherent viscosity would be 1.89 dl/gm. Heat treatment of this polymer at 325°C for 2 hr rendered it essentially insoluble in sulfuric acid (slight swelling).

Efforts were then directed toward solution methods to obtain soluble aliphatic polyimides. These efforts met with success. PMDA and 1,8-octanediamine provided a polymer with an inherent viscosity of 3.32 dl/gm in sulfuric acid (overnight at 60°C was required to facilitate its dissolution). The originally developed procedure is outlined below and, as discussed in later sections, minor modifications have occurred to facilitate scaleup of BTDA polyimides containing 1,6-hexanediamine and <u>m</u>-phenylenediamine:

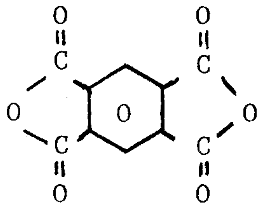
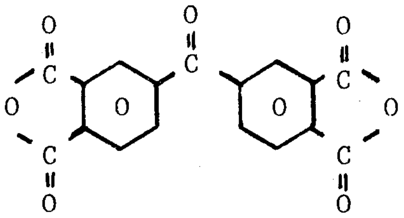
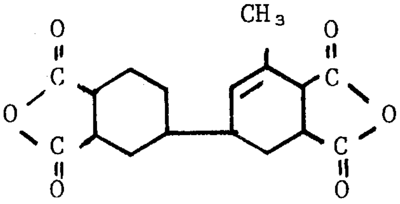
Anhydride	Acid Equivalent Weight	
	Determined	Theory
 Pyromellitic dianhydride (PMDA)	Sublimed - not determined	63.54
 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA)	81.3	80.56
 5-(2,5-Diketotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride (MCTC)	66.8	66.05

Figure 2. Anhydrides selected for polyimide investigations

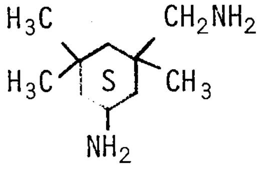
	Boiling Point	Amine Equivalent Weight	
Amine	Temperature/Pressure	Determined	Theory
$H_2N(CH_2)_6NH_2$ 1,6-Hexanediamine	--	Used from unopened bottle	58.1
$H_2N(CH_2)_8NH_2$ 1,8-Octanediamine	67°C/0.5 mm Hg	72.3	72.1
$H_2N(CH_2)_{12}NH_2$ 1,12-Dodecanediamine	124°C/0.6 mm Hg	Not soluble in titrating medium	100.2
 Isophoronediamine	59°C/0.1 mm Hg	85.6	84.6

Figure 3. Amines selected for polyimide investigations

1. Dissolve the dianhydride in hot, distilled m-cresol using tertiary amine. Only partial conversion to the phenyl ester occurs, as only a few drops of base are added; however, the dianhydride does not crystallize upon cooling the m-cresol solution to below 60°C. A 10 percent solids solution is prepared.

2. Add the selected diamine and complete its transfer to the dissolved dianhydride solution with a few milliliters of m-cresol.

3. Immerse the flask equipped with nitrogen purge and magnetic stirring bar into an oil bath at 180°C.

4. Hold the reaction for 1 hr at close to 180°C (190°C oil bath temperature). The reaction will boil until imidization is complete and water is driven from the reaction. The reaction thickens markedly during the first few minutes of reaction above 170°C.

5. Pour slowly into methyl alcohol in a Waring blender on slow speed.

6. Upon completion of the addition of the m-cresol solution of the aliphatic polyimide to the methyl alcohol, turn the blender to full speed for 20 to 30 sec.

7. Filter the polymer suspension, wash with fresh methyl alcohol, and resuspend the solid in fresh methyl alcohol.

8. Stir the suspension and boil the methyl alcohol for 10 min. Filter, wash, and dry the polymer under vacuum at 80°C for a minimum of 2 hr.

Viscous, clear polymer solutions were obtained at the final reaction temperature for the following monomer combinations:

- PMDA with 1,8-octanediamine and 1,12-dodecanediamine
- BTDA with 1,6-hexanediamine, 1,8-octanediamine and 1,12-dodecanediamine
- MCTC with 1,8-octanediamine

PMDA with 1,6-hexanediamine gave an orange, opaque slurry at the final reaction temperature.

The MCTC with 1,8-octanediamine polymer provided an elastomeric product which hardened only slowly (days). It is expected that a better procedure for isolation of the polymer from m-cresol would lead to a nonelastomeric product at the outset.

A viscous polymer solution was also obtained with isophoronediamine (IPDA) and BTDA; however, the stoichiometric mixture was not viscous, and high viscosity was obtained by incremental addition of excess isophoronediamine.

Table 1 provides the inherent viscosities of the polymers previously described.

Based on the observed behavior of the polymers in cresol at the reaction temperature, it is expected that the PMDA-based polymers will exhibit a range of crystallinity. That is, PMDA with 1,6-hexanediamine was only partially soluble, whereas with 1,8-octanediamine an insoluble polymer formed at the surface of the polymerization which could be redissolved slowly at 180°C. The BTDA-based polymers were all homogeneous at the reaction temperature. The crystallinity of the PMDA polymers was verified by X-ray analysis (Section 1).

This behavior is very close to that sought for the flexible, rigid-segment polymer approach to meet the program's objectives. For instance, replacement of some percentage of BTDA by PMDA to produce a copolymer with 1,6-hexanediamine as coreactant would be expected to lead to increased crystallinity to produce enhanced solvent resistance.

3.1.2 Aliphatic Polybenzimidazoles

Prior Acurex Efforts

Preparative methods for aliphatic benzimidazole polymers were reviewed in detail. The majority of these Acurex efforts occurred prior to Acurex's acquisition of Whittaker R&D in 1975.

The inherent viscosities obtained from carefully purified monomers for several aliphatic benzimidazole polymers is provided in Table 2. Condensation in either the melt or PPA is successful in producing high molecular weights. Molecular weight control was not attempted in these experiments.

Sebacic acid was selected for scaleup efforts. This required investigation of polymerization conditions and successful stoichiometries for as-received raw materials. The as-received sebacic acid typically analyzed 99.5 percent pure, and

TABLE 2. INHERENT VISCOSITIES OBTAINED FOR ALIPHATIC BENZIMIDAZOLE POLYMERS FROM TAB

Diacid	Condensation Method	Inherent Viscosity of Polymer(s)[a]	Reference
Glutaric	Melt	1.15	AA 2039
	PPA	0.83, 1.28	AA 2039
Adipic	Melt	1.04	AA 3024
Suberic	Melt	0.81, 0.90, 3.08 (1% insol.)	AA 3041
	Melt	1.15	AA 3053
Azelaic	Melt	0.61	AA 3041
Sebacic	Melt	0.93, 1.04	AA 3041
	Melt	0.65, 0.88, 2.19	AA 2039
	PPA	1.43	AA 2039

[a] dl/gm at 0.5 percent concentration in H_2SO_4

the TAB was required to have a 97.0 percent minimum purity. Holding the melt condensed polymers at 316°C for injection-molding investigations led to further advancement of polymers from equimolar raw materials.

Empirical studies with the as-received raw materials led to the results given in Tables 3 and 4. Polymers containing excess sebacic acid eventually became insoluble with extended 316°C treatment, whereas polymers with excess TAB or 5 percent phenylbenzoate were stable, showing only slight increases in inherent viscosity. Several batches of end-capped polymers were successfully injection molded a number of times (inherent viscosities from 0.7 to 1.2).

Program Efforts

For program purposes, it appeared that two materials could be useful:

- The end-capped polymer, which exhibits minimal change with high-temperature exposure
- The unend-capped, stoichiometric polymer, which crosslinks at elevated temperature and provides insolubility in sulfuric acid. (The crosslinking reaction likely occurs to some extent even with highly purified monomers; however, exposure to refluxing 40 percent KOH solutions usually increases the H_2SO_4 inherent viscosities in place of lowering them, as would be expected with any significant quantity of amide linkages present. Crosslinking may involve other mechanisms.)

Crystallization of the three selected diacids was carried out from water-ethanol mixtures and acid equivalent weights determined. This data is provided in Table 5. Sebacic acid, in particular, gains weight during weighing, which may account in part for its indicated nearly 1 percent impurity level.

TABLE 3. EFFECT OF EXCESS SEBACIC ACID ON ALIPHATIC POLYBENZIMIDAZOLE

Moles Sebacic Acid: Moles TAB	Inherent Viscosity (dl/gm)	
	After 1 Hr at 316°C	After 3 Hr at 316°C
1.0100:1.0000	0.69	Insoluble and infusible
1.0256:1.0000	1.16	
1.0526:1.0000	Insoluble and infusible	
1.0000:1.0000	0.50	

TABLE 4. EFFECT OF PHENYL BENZOATE OR EXCESS TAB ON ALIPHATIC POLYBENZIMIDAZOLES

Moles TAB: Moles Sebacic Acid	Inherent Viscosity (dl/gm)	
	After 1 Hr at 316°C	After 3 Hr at 316°C
1.0526:1.0000	0.48	0.55
1.0256:1.0000	0.70	0.94
1.0100:1.0000	0.85	1.21
1.0000:1.0000 + 0.0526 phenyl benzoate	0.63	0.78

TABLE 5. DIACIDS SELECTED FOR POLYBENZIMIDAZOLE INVESTIGATIONS

Diacid	Acid Equivalent Weight	
	Determined	Theory
Suberic	87.3	87.1
Sebacic	102.1	101.2
1,12-Dodecanedicarboxylic acid	131.2	129.2

Benzimidazole polymers from TAB with suberic, sebacic, and 1,12-dodecanedicarboxylic acids were prepared. They were qualitatively tough. The inherent viscosities are provided in Table 1.

3.1.3 Aliphatic N-Arylenepolybenzimidazoles

Prior Acurex Efforts

As with the aliphatic polybenzimidazoles discussed above, Acurex records show that sebacic acid was successfully melt-condensed with 4,4'-bis(o-aminoanilino)-biphenyl to provide a tough polymer with an inherent viscosity of 0.82. Condensation of suberic acid with the tetraamine provided a polymer with a viscosity of only 0.33 (H_2SO_4). Both were phenol-fluxed and did not give measureable amounts of decarboxylation. Heat schedules for the melt condensations, however, varied. The low inherent viscosity of the second polymer appeared to be consistent with the subsequent results for the polymer from phthalic anhydride with the tetraamine: long heating times at reduced temperatures have a significant effect on final molecular weight, as shown in Table 6[4]. The sebacic acid condensation was held overnight between 100° and 162°C, whereas the suberic acid condensation was allowed to cool to room temperature overnight prior to its final high-temperature treatment.

Program Efforts

A number of polymerizations were conducted with 4,4'-bis(o-aminoanilino)-biphenyl which was crystallized from benzene/tetrahydrofuran. The polymers prepared are given in Table 7 with their inherent viscosities. Based on the low inherent viscosities obtained for these polymers, the amine was recrystallized from 1,2-dichloroethane for new polymerizations. As discussed below, the polymer from methylhexahydrophthalic anhydride (MHHPA) showed improvement in inherent viscosity (0.70) with amine purified from 1,2-dichloroethane from that given in Table 7. Detailed discussion of amine purity determination by DSC is provided in Reference 5. Melting-point determination by visual method is inadequate. Reference 5 also contains detailed preparative procedures on the polymerization of cyclic anhydrides with the amine.

TABLE 6. INFLUENCE OF HEATING SCHEDULE ON THE MOLECULAR WEIGHT OF N-ARYLENEPOLYBENZIMIDAZOLES[a]

Heat Schedule	Inherent Viscosity (dl/gm)	Heat Schedule	Inherent Viscosity (dl/gm) (H_2SO_4)
1 hr at 215°C	N/A		N/A
+1 hr at 250°C	0.33	+1 hr at 400°C	1.14
+16 hr at 250°C	1.14	+1 hr at 400°C	3.25

[a] Phthalic anhydride with 4,4'-bis(o-aminoanilino)biphenyl

TABLE 7. N-ARYLENEBENZIMIDAZOLE POLYMERS PREPARED FROM SEVERAL DIACIDS

Diacid	Inherent Viscosity (dl/gm) (0.5% in m-cresol)
Suberic acid	0.12, 0.17
Sebacic acid	0.12, 0.14
1,12-Dodecanedicarboxylic acid	0.10
Phthalic anhydride	0.10, 0.13
Methylhexahydrophthalic anhydride (MHHPA)	0.07, 0.12

1,2-dichloroethane crystallized 4,4'-bis(o-aminoanilino)biphenyl polymerized with methylhexahydrophthalic anhydride (MHHPA) and sebacic acid provided high-molecular-weight N-arylenepolybenzimidazoles. With unpurified MHHPA, a polymer with an inherent viscosity of 0.70 (m-cresol) was obtained. With freshly distilled MHHPA, two products were obtained in the polymerization tube, one opaque and the other clear. Details are provided in the Appendix of this report. The clear polymer is slowly converted to the opaque polymer by reaction at 250°C (final heat treatment was 300°C). The inherent viscosities of clear and opaque polymers in m-cresol were 1.10 and 1.62 dl/gm, respectively. Neither polymer, however, was considered "tough." Both polymers were sufficiently hand-pulverizable for obtaining a Nujol mull.

Melt polymerization of sebacic acid with 4,4'-bis(o-aminoanilino)biphenyl (twice crystallized from 1,2-dichloroethane) was carried out. The heating schedule employed is indicated in Table 8, along with comments on the polymer samples removed from the progressing polymerization.

Based on the high-molecular-weight product obtained from the polymerization of sebacic acid described previously, an attempt was made to prepare the polymer in a shorter timespan. After overnight condensation of the monomers (15 percent by weight m-cresol flux) in a 218°C oil bath, the majority of the polymer was set aside. A small portion of the polymer was heated overnight in a 258°C oil bath, followed by increasing the temperature to 300°C over an 8-hr period. The inherent viscosity of this polymer was only 0.17 dl/gm, and its infrared spectrum showed the presence of unreacted acid carbonyl.

A partial understanding of the failure of the abbreviated heating schedule polymerization to produce high-molecular-weight polymer is derived from infrared spectra. It was concluded that greater than 50 percent of the free acid is converted to the m-cresol ester by 24-hr heating at the reflux temperature of m-cresol. The ester carbonyl is not detected by spectral analysis of the prepolymers due to its more rapid reaction rate with the amine than the free acid.

TABLE 8. POLYMERIZATION OF SEBACIC ACID WITH 4,4'-BIS(o-AMINOANILINO)BIPHENYL

Oil Bath Temperature (°C)	Days at Temperature (total time)	Comments on Polymer Samples; Inherent Viscosities at 0.5 Percent m-Cresol
218	3	Spectra showed acid carbonyl
218	3 (6)	Spectra showed no reduction in acid content. Spectra required wiggle bug to obtain Nujol mull; η_{inh} = 0.24 dl/gm.
258	3 (9)	Spectra showed no carbonyl; η_{inh} = 0.58 dl/gm
302	1 (10)	Samples too tough to be pulverized by wiggle bug; η_{inh} = 0.88 dl/gm
302	1 (11)	η_{inh} = 0.88 dl/gm

Suberic and 1,12-dodecanedicarboxylic acids with 4,4'-bis(o-aminoanilino)-biphenyl and 65 and 61 percent m-cresol (based on total weight) were polymerized by heating in an oil bath for 24 hr each at 225°, 247°, 266°, and 300°C. The previously cited prepolymer from sebacic acid, which had received only overnight treatment at 218°C, was also given the same treatment with fresh m-cresol. The polymer from suberic acid was pink and opaque. The clear thick polymer turned opaque with the 300°C overnight treatment. The polymers were removed from their polymerization tubes by dissolution in refluxing m-cresol. The polymer from suberic acid behaved as if it were crosslinked (swollen gel), and the polymer from 1,12-dodecanedicarboxylic acid contained both gel and soluble polymer. Gel was removed from the soluble polymer by retaining the gel on a 50-mesh screen. The polymer from sebacic was soluble. All of the polymers were treated overnight at 200°C under high vacuum for m-cresol removal. The polymer from suberic acid turned slightly opaque, but not to the degree previously witnessed after 300°C treatment. The gel portion of the 1,12-dodecanedicarboxylic acid polymer was very tough. Inherent viscosity measurements on the polymers led to the results given in Table 9.

Only the polymer from suberic acid provided high molecular weight. The lack of advancement of the sebacic acid polymer strongly suggests that the original 24-hr treatment of the monomers with only 15 percent m-cresol was critical to the achievement of high molecular weight.

The polymers selected for subsequent characterization efforts are summarized in Table 1.

3.2 POLYMER FLOW PROPERTIES

Numerous methods exist to index the flow properties of polymers. Laboratory methods are tailored to end use, e.g., flow at atmospheric pressure for rotomolding versus flow at 6.9 MPa (1000 psi) for injection molding. Further, some information

TABLE 9. ALIPHATIC N-ARYLENEPOLYBENZIMIDAZOLES FROM PURIFIED TETRAAMINE

Polymer From	Inherent Viscosity, dl/gm (solvent)
Suberic acid	1.10 (H_2SO_4)[a]
Sebacic acid	0.18 (m-cresol)
1,2-Dodecanedicarboxylic acid	
Soluble portion	0.41 (m-cresol)
Gel portion	0.68 (H_2SO_4 with 3.5% insolubles)

[a] Completely soluble

on the creep properties of the thermoplastic at elevated temperature would be useful if obtainable in the screening tests.

With this in mind, screening the flow properties of the polymers was attempted in such a manner that sound decisions on the merits of the various systems could be made and further guidance on copolymer compositions obtained. As discussed below, comparison of the flow curves obtained at low and moderate pressures accompanied by DSC analysis lead to a good preliminary understanding of the potential of the candidates to meet the program objectives.

Flow properties were conducted on the as-prepared powdered or fibrous polymer specimens at low pressure and on molded polymer specimens by Distortion Temperature Under Load (DTUL) measurements at 3.1 MPa (450 psi). Conditions to obtain the molded polymer specimens is described in Section 3.3. It is useful, however, to include the curves obtained from DTUL tests on the molded specimens in this section for comparative purposes.

3.2.1 Test Method Development

Polymer melt/flow behavior with increasing temperature can be determined by placing the polymer in a press equipped with an accumulator and measuring the platen travel with a dial gage indicator as the temperature is increased. The melt/flow characteristics indexed by the press method were found to be essentially replicated with the DuPont TMA at lower pressures (calculated to be about 0.069 MPa (10 psi) on a polymer film, but actual pressure depends on polymer form, e.g., powder). Both methods are described in the following paragraphs.

Press Method

Polymer flow characteristics can be conveniently screened in the laboratory by placing 3.0 gm of powdered resin between two pieces of aluminum foil into a press at room temperature. A constant force is applied to the powder using an accumulator, and a dial gage indicator is placed between the bottom press platen and the press frame. The press platens are then heated as desired, slow or fast. The dial gage readings are plotted against temperature. The first event observed is expansion of the press platens, which gives the dial gage versus temperature plot a positive slope.

Polymer flow is obtained as the platens close, and finally a second press platen expansion curve is obtained. The curves obtained are very reproducible using identical press conditions of heatup rate and applied pressure. The flow midpoint is reproducible to within 1° or 2°C with the same raw material. Residual solvent, moisture, and other contaminants can have a significant effect on the flow properties.

Figure 4 provides an example of the flow properties of polymethylmethacrylate and two polyphenylquinoxalines (PPQ's). PMMA exhibited expected behavior with the initial heatup, flow, and final heating. The two PPQ samples upon heatup suggested the presence of solvent or other impurities; however, flow and final heatup are as expected.

The flow properties of the polybenzimidazole from sebacic acid and TAB were explored in detail by the press method. An unexpected finding was that the polymer exhibited two flow temperatures: one at ~215°C and one at ~400°C. (Injection molding of this PBI is accomplished at 300° to 330°C.)

Figure 5 shows the flow behavior of a single batch of aliphatic polybenzimidazole from sebacic acid under two pressures. At low pressure (57 Kg (125 lb)), flow onset occurs distinctly at 210°C and ceases at about 260°C to give the baseline platen expansion curve. At higher pressures, however, flow cessation is not clearcut, and upon heating to 400°C a second flow is observed. The polymer was dried under high vacuum for 1 hr to determine if the first flow could be eliminated. It was not, as shown in Figure 5 (dried polymer). The TGA curve for the dried polymer is provided in Figure 6. The high-temperature flow curves at 400°C seen in Figure 5 are 50°C below the polymer's decomposition temperature. The high-temperature flow phenomena is not due to polymer decomposition since the resulting disc was light in color.

The inherent viscosity (0.5 pct, H_2SO_4) of the polymer discussed above was 0.76 dl/gm. Flow characteristics of two other aliphatic PBI polymers with different histories are provided in Figure 7. The inherent viscosities of these polymers were not significantly different; however, their thermal histories were. The solid line was obtained on a sample of ground, injection-molded polymer, whereas the dashed line was as-prepared polymer. The ground, injection-molded material essentially shows no flow at ~215°C compared to the as-prepared polymer. Since the injection-molded polymer was soluble and flows at 400°C, absence of low-temperature flow is probably not due to crosslinking.

Inherent viscosities of aliphatic polybenzimidazole samples after various pressout treatments were determined. Samples were removed from the press at several temperatures and inherent viscosities determined on the heat-treated samples. All of

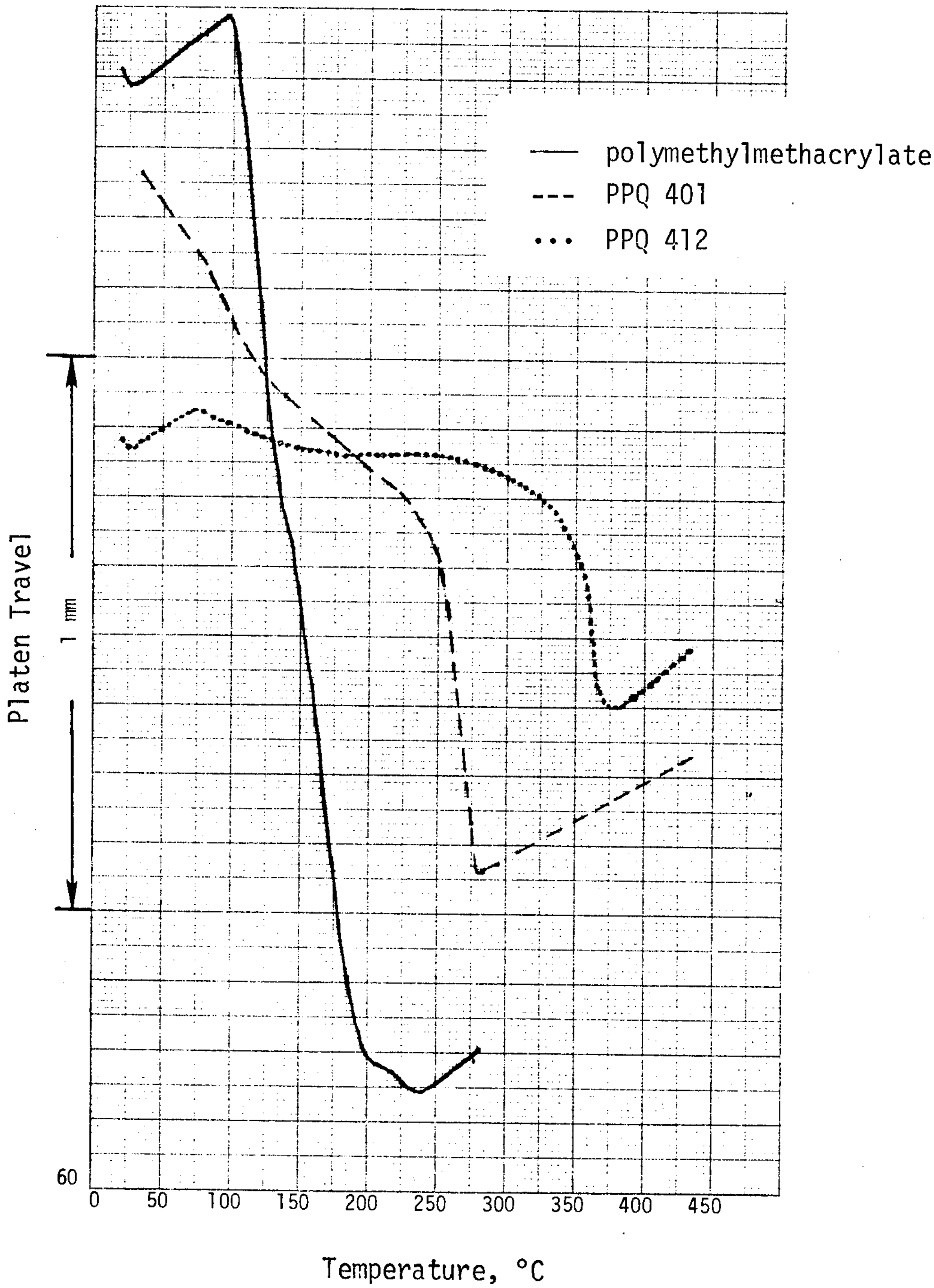


Figure 4. Example curves of polymer flow versus temperature

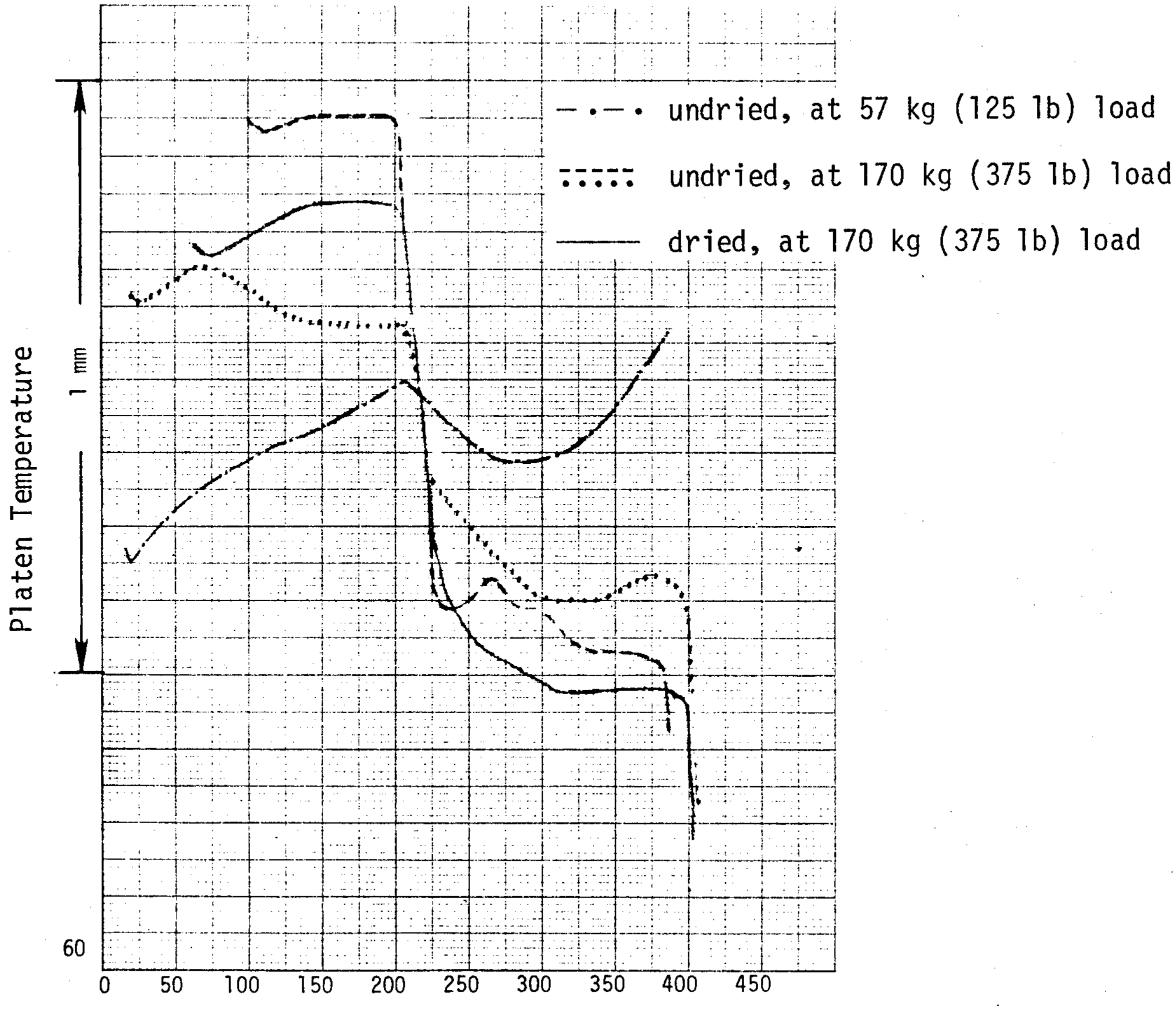


Figure 5. Flow curves for aliphatic polybenzimidazole

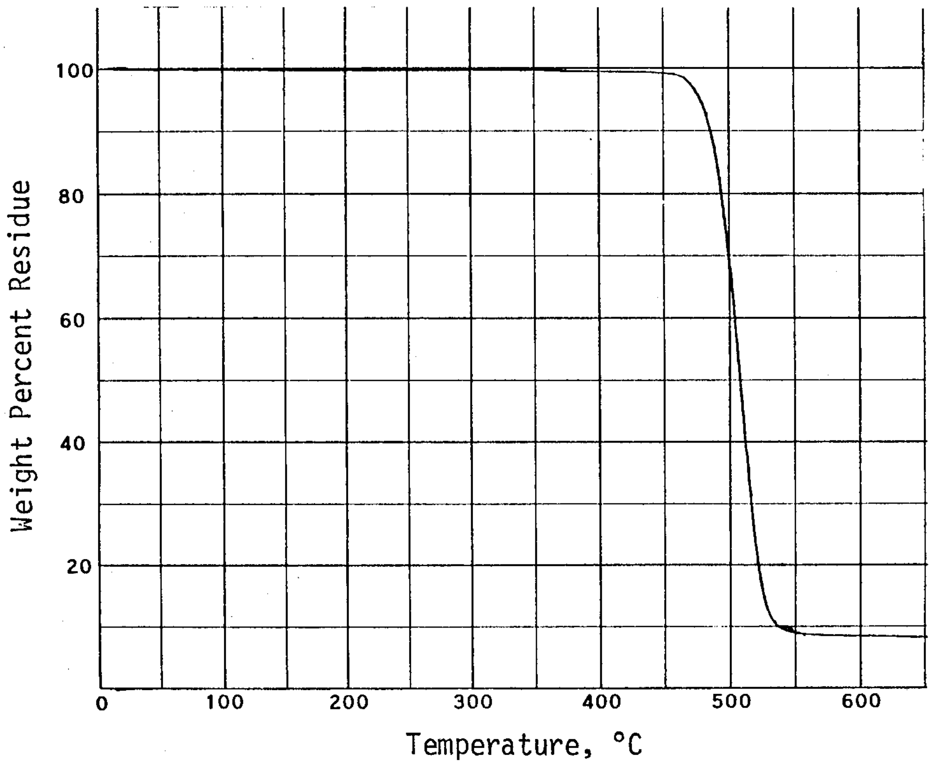


Figure 6. Anaerobic TGA curve of aliphatic polybenzimidazole

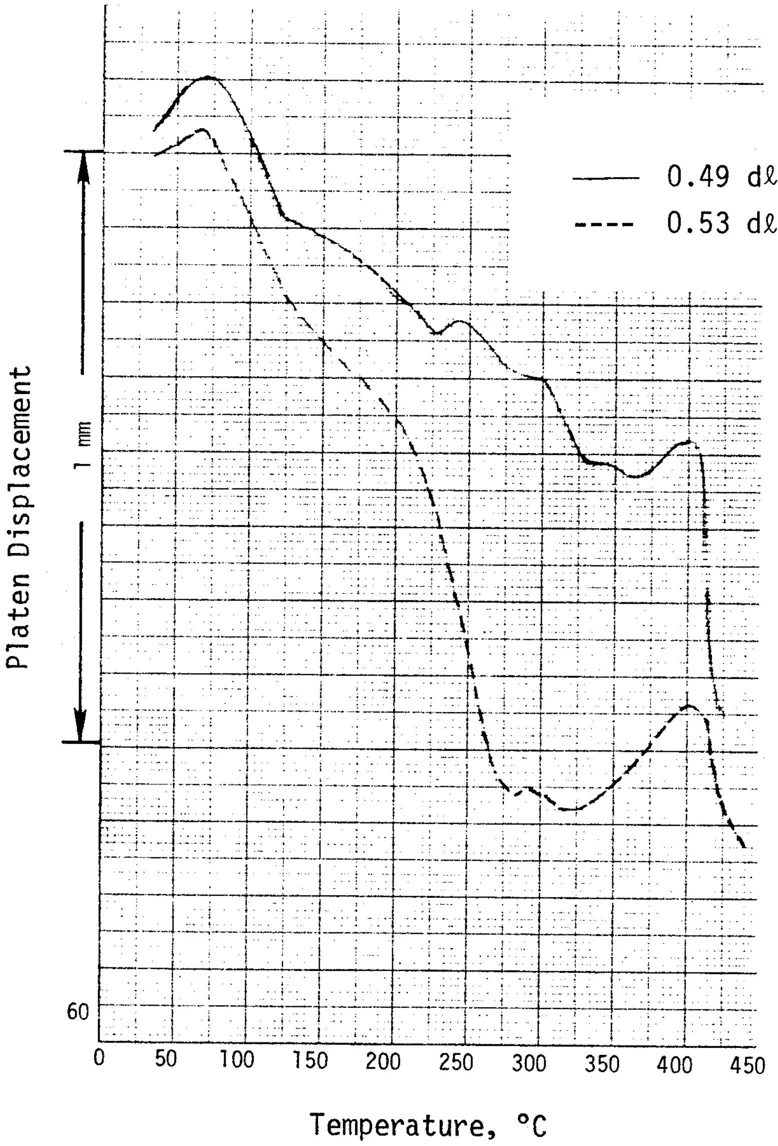


Figure 7. Flow curves for aliphatic polybenzimidazole

the polymer samples contained some insolubles in the solvent. Insoluble contents were not quantitatively determined. These results are given in Table 10.

The results of the pressout-inherent viscosity study indicate that the polymer does not degrade at temperatures up to 350°C, and in fact appears to advance. Very high temperatures (420°C) appear to degrade the polymer; however, as previously mentioned, it is not thought to be responsible for the high-temperature flow phenomena.

It was concluded that the melt-flow behavior of the aliphatic PBI from sebacic acid and TAB is sensitive to its processing history, as well as to its molecular weight and molecular weight distribution.

Thermal Mechanical Analysis (TMA) Method

The developed test method for the polymer is shown in Figure 8.

The TMA flow curve for the aliphatic polybenzimidazole characterized by the press method in Figure 7 (bottom curve) is provided in Figure 9. Comparison of the curves in these two figures representing the two methods shows that the two methods are essentially equivalent.

With the exception of a slight upward temperature shift for the flow events with the TMA method (probably due to lower molding pressures), the flow curve obtained by TMA has all of the features of the flow curve obtained with the press. In the press method, complete fusion is not obtained at 250°C (about the midpoint of the flow curve), whereas complete fusion is obtained at 325°C and the baseline curve is observed shortly thereafter (positive slope line due to platen expansion). The TMA method with its quartz probe gives a baseline which is parallel to the x-axis. Baselines for the two methods can be seen between room temperature and about 75°C,

TABLE 10. INHERENT VISCOSITIES OF ALIPHATIC POLYBENZIMIDAZOLE AFTER VARIOUS PRESS HEATUP CONDITIONS

Temperature (°C)	Sample Fusion	Inherent Viscosity (dl/gm)
125	No	0.88
255	Partial	0.92
350	Yes	1.32
420	Yes	0.65
420[a]	Yes	0.35

[a] Sample not removed, but left in press to cool (slow cooldown)

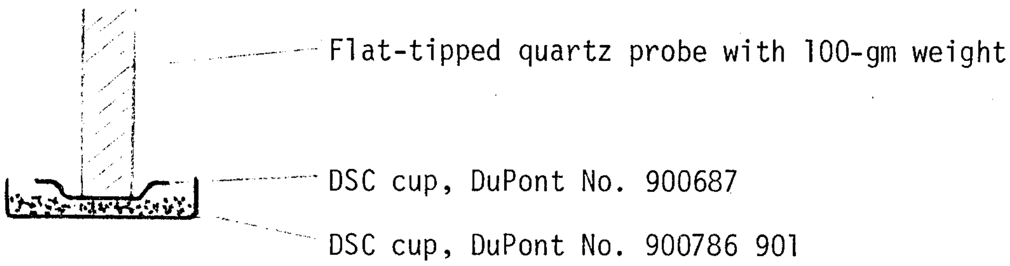


Figure 8. Microflow test by DuPont TMA

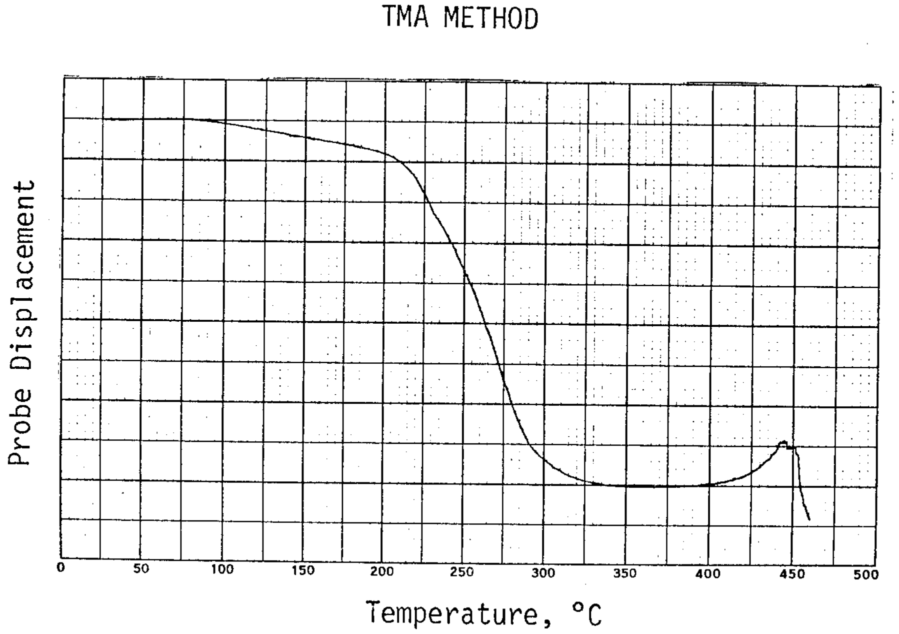


Figure 9. TMA of polymer flow with temperature

and again between 350° and 400°C. The apparent expansion observed for the polybenzimidazole sample by the TMA method between 400° and 440°C may be due to foam formation caused by further condensation and/or tenaciously held water.

With polymers which demonstrate a precipitous flow curve, such as the PMDA-based polyimides discussed in the next section, the TMA method appears to be related to polymer melt temperature (PMT), as described by Sorenson and Campbell[3]. DSC testing of the PMDA-based polyimides indicated that they were crystalline and a relationship between PMT and flow is expected. Flow of noncrystalline polymers by the TMA method appears to be associated with the polymer's Tg.

3.2.2 Aliphatic Polyimides

Figures 10 and 11 provides flow curves for aliphatic-PMDA polyimides with the solid triangles representing Tgs and the open triangles indicating Tms. All of the aliphatic PMDA polymides in Figure 10 were liquids at the end of the low-pressure test. As discussed above, complete fusion has likely occurred when the flow curve intercepts the bottom baseline curve. Downward baseline drift is thought to be due to continued melt flow during heatup. DTUL measurement on fused discs shows that flow occurs at temperatures close to those observed in the low-pressure tests. DSC measurements on the PMDA polymers from 1,8-octanediamine and 1,12-dodecanediamine showed endotherms on heatup and exotherms on cooldown, demonstrating the presence of crystallinity in these polymers.

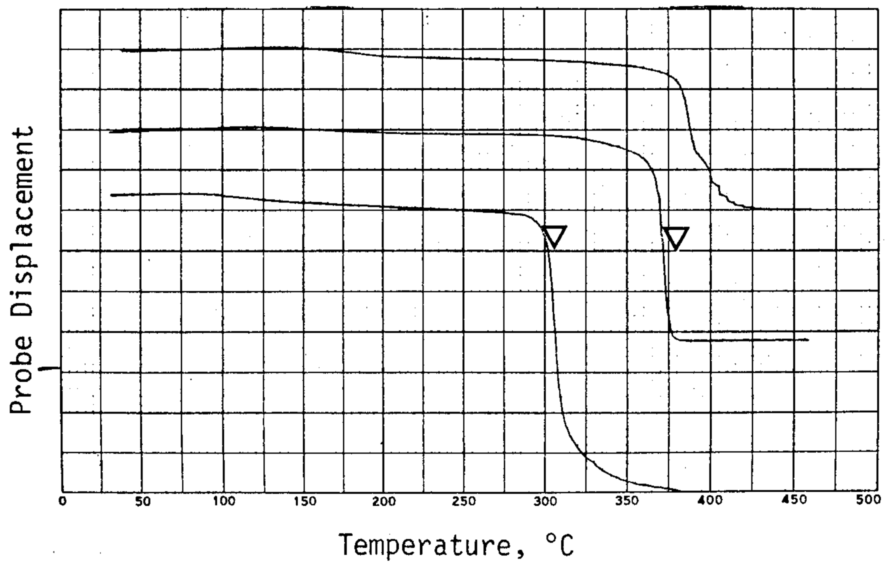
The Tg of the PMDA-nonamethylene diamine polyimide is 110°C[6] and would be close to that for the PMDA-octanediamine polymer. A slight break in the flow curves of the PMDA-octanediamine polymer occurs close to this temperature and is probably associated with the polymer's Tg and may explain the slight shrinkage of the three polymers indicated by slight downward pen movement prior to melt. The high flow temperature of the PMDA-1,12-dodecanediamine polymer was surprising, in view of its behavior after isolation. The day it was prepared it was isolated as fibers by precipitation in methanol. However, the next morning the fibrous mat had coalesced to give a much smaller and thinner single piece of polymer in which the fibers were nearly indistinguishable. This unusual behavior was initially thought to be due to obtaining a low-temperature melting polymer. However, it may be due to crystallization of the polymer accompanied by solvent loss. As seen in Figure 10, the Tm is above 300°C. This latter interpretation is also supported by the form in which the PMDA polymers were isolated. The C_6 and C_8 diamine polymers were isolated as powders, suggesting that crystallization had occurred in solution prior to isolation.

The three PMDA polymers showed very high flow temperatures compared to the flow temperatures of the "kinked" BTDA polymers. The flow curves of the aliphatic-BTDA and MCTC polyimides are given in Figure 11. The Tg of these polymers is clearly controlling the flow properties of these systems.

The three polyimides from 1,8-octanediamine with PMDA, BTDA, and MCTC show decreasing flow temperatures for each of the three dianhydrides, respectively. The flow curve of the MCTC/1,8-octanediamine polymer suggests little use for this polymer in the intended application. Copolymers with this dianhydride, e.g., MCTC with BTDA or aromatic amines, could provide higher flow temperatures.

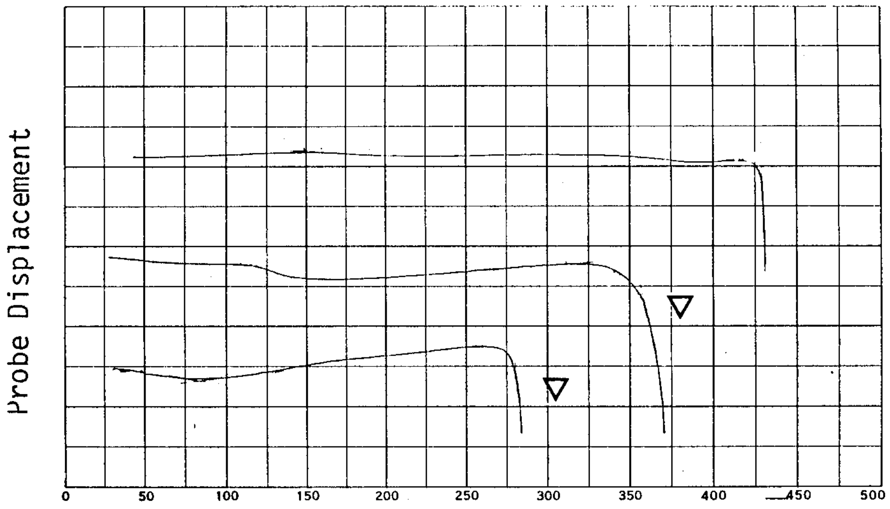
The cyclohexane ring containing isophoronediamine (ten carbon atoms) has higher melt/flow temperatures than the linear diamines, as expected.

Low Pressure Curves



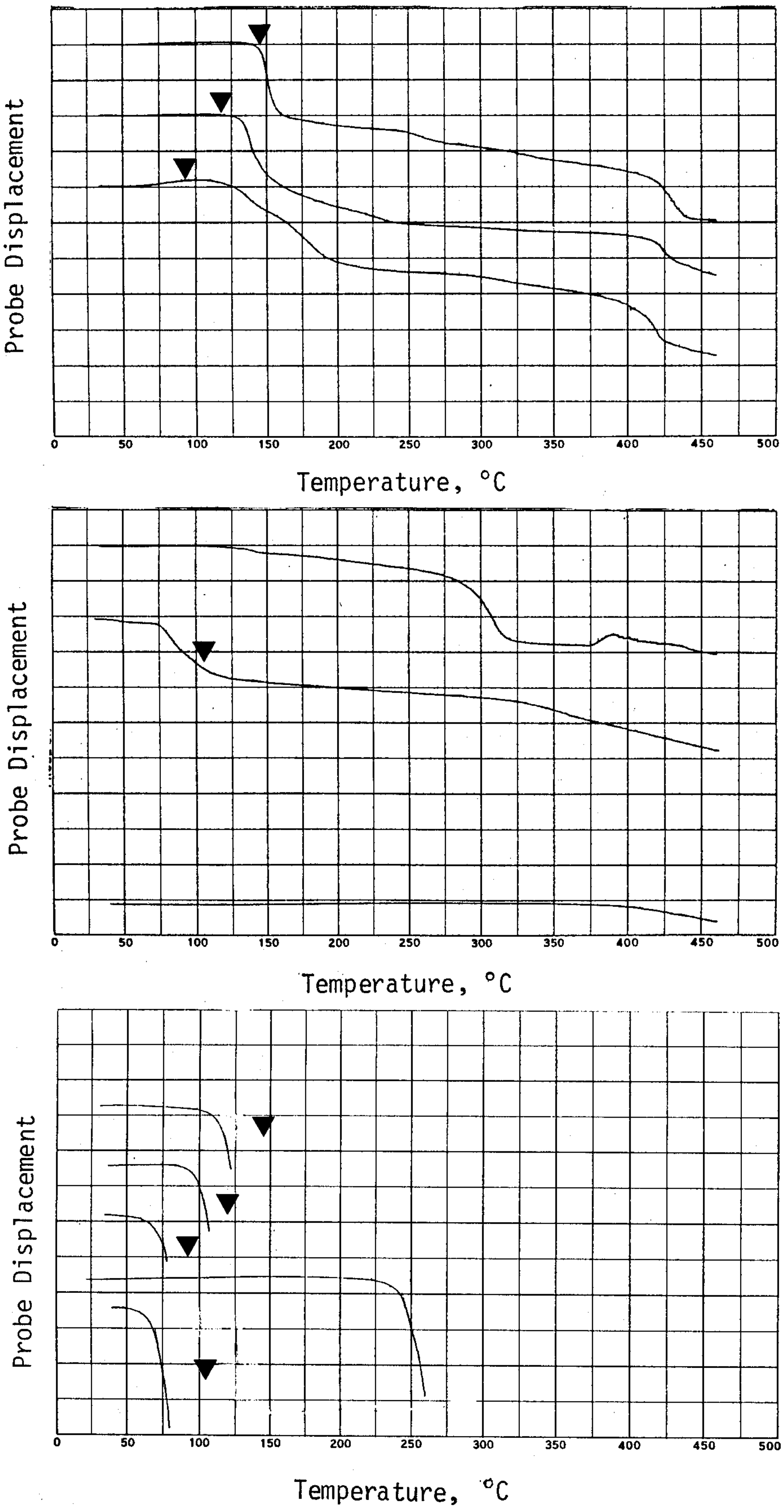
PMDA with C_6, C_8, and C_{12} diamines (top to bottom curves, respectively)

DTUL Curves



Curves ordered as indicated above

Figure 10. Flow curves for aliphatic-PMDA polyimides



Low pressure curves:

BTDA with C_6, C_8, and C_{12} diamines (top to bottom curves, respectively)

Low pressure curves:

BTDA with isophoronediamine (top) and MCTC with 1,8-octanediamine (middle)

Baseline curve with no sample

DTUL curves:

Curves top to bottom include three curves from first diagram and two curves from second diagram, respectively

Figure 11. Flow curves for aliphatic BTDA and MCTC polyimides

It should be noted that loss of polymerization solvent or water from the samples, if not completely removed from the polymers prior to test, will lead to apparent sample flow due to shrinkage. Flow behavior of the polyimide from BTDA with 1,6-hexanediamine is provided in Figures 11 and 12. After the major flow phenomenon between 125° and 175°C, two additional "flows" appear: between 250° and 275°C and between 415° and 440°C. These flows can also be due to sample shrinkage, e.g., imidization, crystallization, and/or decomposition. The flow curve provided in Figure 12 is a second determination on the same polymer, but the fibrous polymer was not compacted in the DSC cup prior to measurement.

3.2.3 Aliphatic Polybenzimidazoles

Figure 13 provides the flow properties of the aliphatic polybenzimidazoles prepared from suberic, sebacic, and 1,12-dodecanedicarboxylic acids with TAB. None of these polymers provided low-pressure flow characteristics consistent with the previously obtained result given in Figure 9. In fact, flow curves consistent with the injected molded polybenzimidazole from sebacic acid and TAB were obtained for all three polymers. The absence of low-temperature flow (top curve in Figure 7) in the injection-molded polymer was previously discussed.

The notebook record indicates only two exceptions from the standard recipe; the use of highly purified raw materials (which the standard method does not require) and a several-week storage time between prepolymer preparation and 2 hr at 600°F advancement. Examination of Table 1 reveals that although some insoluble polymer was isolated from the polymerizations, relatively high inherent viscosities were obtained which can be attributed to use of highly purified monomers.

DTUL curves, clearly show that flow occurs under 3.1 MPa pressure just prior to the Tg event with all three polymers at much lower temperatures than observed for the low-pressure flow test.

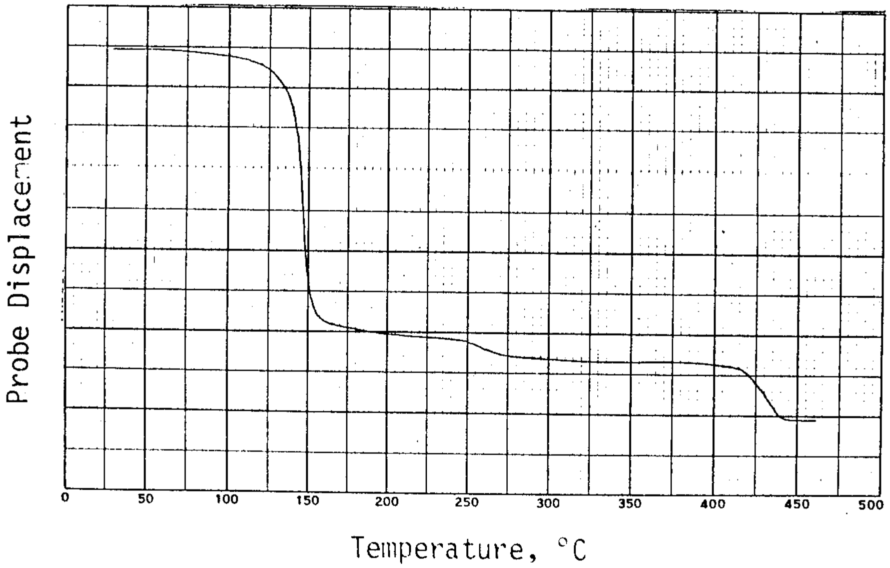
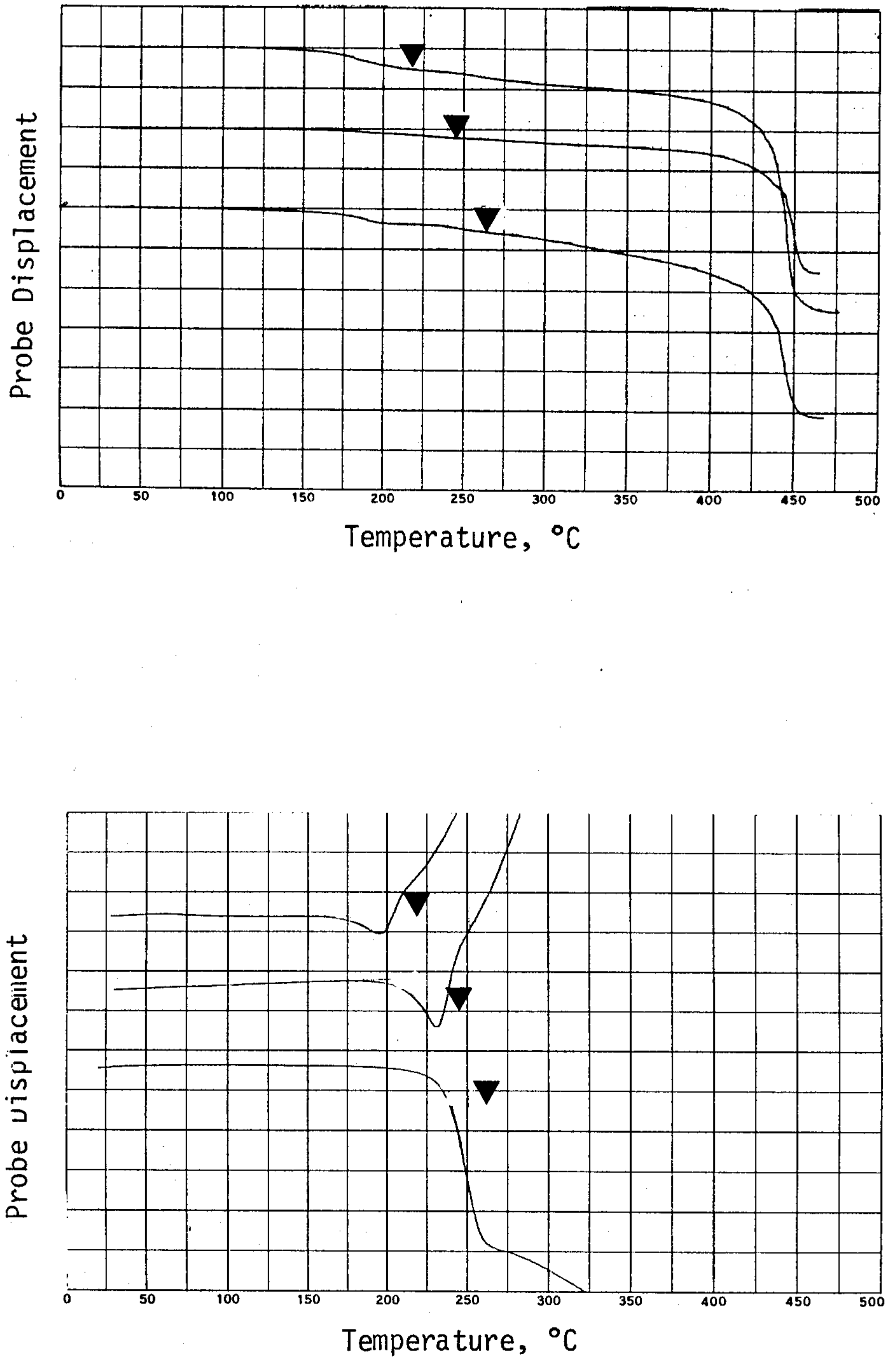


Figure 12. Flow curve of uncompacted BTDA with 1,6-hexanediamine polyimide fibers



Low Pressure Curves:

TAB with C_{12}, C_8, and C_6 dicarboxylic acids (top to bottom curves, respectively)

DTUL Curves:

Curves as indicated above

Figure 13. Flow curves for aliphatic polybenzimidazoles

The 200°$^+$C difference in flow temperatures between TMA and DTUL methods is not understood. DSC measurement revealed the Tg but not Tm up to 450°C, where decomposition occurred. Slight crystallinity in the polymers, intermolecular hydrogen bonding, or similar effects appear to be playing a role to produce the observed differences and the difference in flow properties between the polymers tested by the press method in Figure 7.

The three low-pressure flow curves, however, are interesting from the standpoint of polymer behavior. All three polymers showed that excellent flow had occurred, and inspection of Figure 13 shows that all three polymers melted at approximately the same temperature (425° to 450°C). This is unlike both the previously discussed polyimides from homologous diamines and N-arylenepolybenzimidazoles from homologous diacids, discussed in the next section.

3.2.4 N-Arylenepolybenzimidazoles

Figure 14 depicts the flow behavior for polymers from 4,4'-bis(o-aminoanilino)biphenyl with suberic, sebacic, and 1,12-dodecanedicarboxylic acids, as well as for polymers from phthalic and methylhexahydrophthalic anhydrides.

The amine with the homologous diacids provided different melt temperatures, as expected.

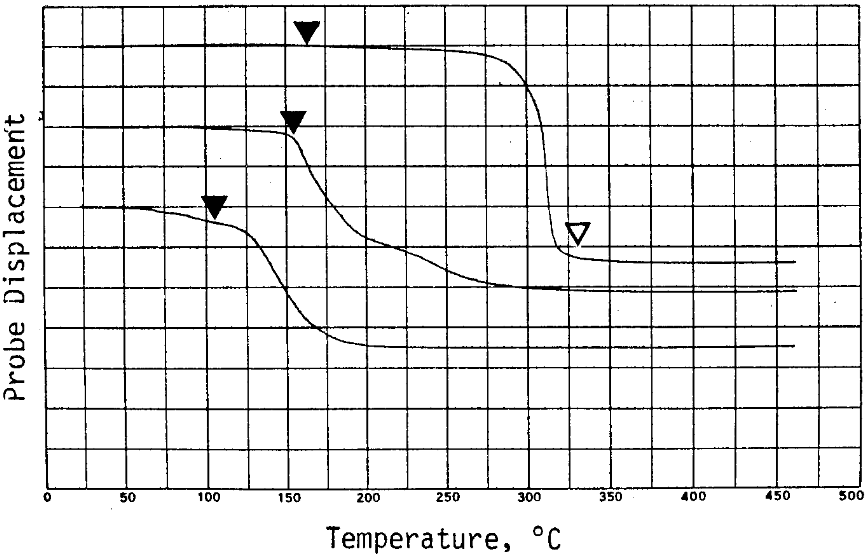
The suberic acid polymer is slightly opaque and thought to be crystalline. It has a slight endotherm in the as-prepared condition, as well as after molding at 330°C. No exotherm on cooldown is detected. If the suberic acid polymer is heated to a clear condition prior to DSC analysis and quenched, the 330°C endotherm is no longer detected. All three polymers showed evidence of good melting upon removing from their DSC cups.

The phthalic anhydride polymer did not exhibit a sharp low-pressure flow temperature. Upon removing, only partial fusion had occurred (sufficient, however, that the individual particles had fused together). Both the opaque and clear polymers from methylhexahydrophthalic anhydride were tested. The opaque polymer showed good evidence of melt, whereas the clear polymer showed only partial fusion, even though the flow curve suggested good flow. It was much like the phthalic anhydride polymer in regard to its degree of fusion. DTUL curves on these polymers suggest good mechanical performance to temperatures in excess of contract goals. They could be useful to form copolymers with the straight chain aliphatic dicarboxylic acids.

3.3 SCREENING OF MOLDED POLYMERS

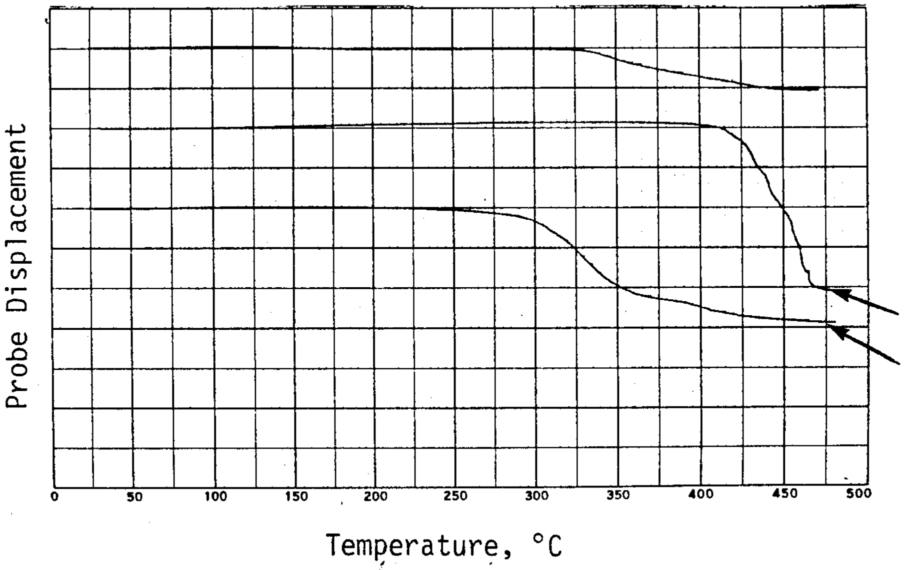
The 16 polymer compositions indicated in Table 1 were screened for moldability. Several homopolymers were not moldable at the maximum target temperature of 316°C (600°F). Moldings were prepared by addition of 1g of the polymer to a mold preheated to a temperature selected from the low-pressure TMA flow curves.

DTUL measurements were conducted on the molded specimens. Several polymers showed softening under the 3.1 MPa (450 psi) compressive load in DTUL measurement below the target composite performance temperature of 93°C (200°F). To increase the Tg of the polyimide from BTDA with 1,8-octanediamine, m-phenylenediamine was added as a coreactant amine. Moldings of this polymer were included in subsequent tests.



Low Pressure Curves:

4,4'-bis(o-aminoanilino) biphenyl with C_6, C_8, and C_{12} dicarboxylic acids (top to bottom curves, respectively)

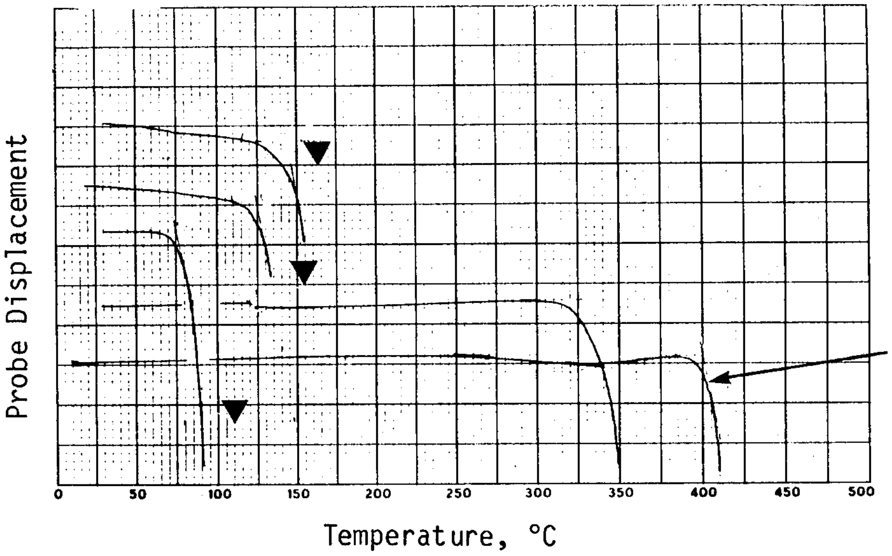


Low Pressure Curves:

4,4'-bis(o-aminoanilino) biphenyl with phthalic anhydride (top) and methylhexahydrophthalic anhydride (middle and bottom curves)

Opaque polymer

Clear polymer



DTUL Curves:

Curves ordered as indicated above (opaque polymer not shown)

Clear polymer

Figure 14. Flow curves for N-arylenepolybenzimidazoles

The molded polymer compositions were screened for Tg and solvent resistance in acetone, chloroform, and tricresyl phosphate (TCP). Several polymers were found to have low weight gains after 50-day exposure to all three solvents. Three polymers were selected and successfully scaled up (50g), molded, and tested for stressed solvent resistance. All did well in this test. Further discussion on solvent resistance is provided in Sections 3.3.2 and 3.3.3.

The polyimide from BTDA with 1,8-octanediamine and m-phenylenediamine showed excellent initial resistance to solvents, excellent tensile strength and Barcol hardness. At this juncture, the program efforts focused on scale-up and composite work with the composition.

Details of the characterization of the molded polymers are discussed below and discussion of the m-phenylenediamine-modified BTDA/aliphatic polyimide is provided in Section 3.5.

3.3.1 Moldability and Upper Performance Temperature (DTUL)

Table 11 gives the molding conditions used to obtain fused samples from the 16 polymers. Other data are included in the table.

In several instances, flash removal from the molded buttons suggested a degree of toughness of the molded polymers which differed from previous toughness estimates on the unmolded polymers. The PMDA/1,8-octanediamine polymer, the three BTDA/linear diamine polymers, and the N-arylenepolybenzimidazole from suberic acid were judged in their as-prepared state to have marginal toughness properties, but after molding are tough. The PMDA/1,8-octanediamine polymer shows stress whitening, probably due to crystallization with elongation. The N-arylenepolybenzimidazole from sebacic acid was judged to be very tough in its as-prepared state. Its lack of toughness after molding may be due to the low temperature used to prepare the molding, even though it was clear.

Table 12 gives the results of both dry and 24-hr water-boiled DTUL measurements on the moldings. Hardness and specific gravity measurements are also provided. In all instances, except for the N-arylenepolybenzimidazoles, the expected variation occurred with the linear aliphatic (C_6, C_8, and C_{12}) content of the polymers. Specific gravity, hardness, moisture absorption, and DTUL are decreased with increasing chain length. A regular decrease in the values is also observed for the N-arylenepolybenzimidazoles, except for moisture weight gain due to 24-hr water boil, where little effect is observed for the three diacids used.

Comparison of polymer Tg's obtained by DCS scans and DTUL (deviation from linearity) shows the DTUL's to be about 50°C below the Tg's. This agrees with Tobolsky's suggestion that upper use temperature for rigid plastics should be approximately 50°C below the Tg[7]. To obtain state-of-the-art properties at elevated temperatures, Acurex has further suggested that the dry DTUL (deviation from linearity value) should be 50°C above the performance temperature. In the present case, this would be 150°C (Tg ≅200°C).

Consequently, to obtain this DTUL in combination with good moldability and modulus (hardness) with linear aliphatic aromatic heterocyclics, only the PMDA-based polyimides and the polybenzimidazoles show adequate DTUL's. Shorter aliphatic

TABLE 11. MOLDING CONDITIONS AND PHYSICAL CHARACTERISTICS OF POLYMERS

Polymer	PMT (°C)	DSC Analysis[a]		Mold Temperature[b] (°C)	Molding Pressure, psi, MPa (psi)	Molding Thickness (mm)	Transmitted Light	Inherent Viscosity of Polymer (dl/gm)
		Midpoint of Baseline Shift (Tg)	Endotherm (Tm)					
Polyimides								
PMDA with C_6 diamine	420	None to 420°C	None to 420°C	415	0.69 (100)	0.94	Opaque	1.05
with C_8 diamine	360	None detected	383	321		1.07	Haze	3.32
with C_{12} diamine	340	None detected	312	330		0.46	Haze	1.16
BTDA with C_6 diamine	310	146	None detected	315		0.71	Clear	1.06
with C_8 diamine	360	117		327		1.02		1.54
with C_{12} diamine	360	89		327		1.14		1.00
with isophoronediamine	None to 450°C	NA		325		0.76		0.35
MCTC with C_8 diamine	325	106		280		0.76		0.84
Polybenzimidazoles								
TAB								
with C_6 dicarboxylic acid	none	265		343		1.9	Slight haze	1.59
with C_8 dicarboxylic acid	480	244		327	1.4 (200)	1.9	Clear	2.69
with C_{12} dicarboxylic acid	470	217		327	1.4 (200)	1.9	Clear	2.31
N-Arylenepolybenzimidazoles								
4,4'-Bis(o-aminoanilino)biphenyl								
with C_6 dicarboxylic acid	320	165	330°C[c]	293	0.69 (100)	1.02	Haze	1.10
with C_8 dicarboxylic acid	225	156	None detected	138		0.89	Clear	0.88
with C_{12} dicarboxylic acid	170	110		143		1.02	Clear	0.41
with phthalic anhydride	410	NA		399		1.02	Opaque	0.92
with methylhexahydrophthalic anhydride	None to 420°C	NA		371		0.64	Haze	1.10

[a] Polymers fused into cups briefly at high temperature prior to DSC analysis

[b] Molding occurred by preheating mold on hotplate to temperature shown, adding polymer and hot plunger to mold and inserting into press for pressure application

[c] No cooldown exotherm detected compared to PMDA polyimides which both showed cooldown exotherms

TABLE 12. DRY AND WET POLYMER PROPERTIES

Polymer	Specific Gravity (g/cc)	Hardness of Molding		DTUL Measurements (°C)				Sample Weight Gain Due to 24-Hr Water Boil (Percent)
				Initial Dry		24-Hr Water Boiled	Intercept Shift Due to Moisture (°C)	
		Barcol	Shore D	Deviation from Linearity	Intercept	Intercept		
Polyimides								
PMDA with C_6 diamine	1.38	a	a	148	428	278	-150[b]	0.9
with C_8 diamine	1.28	6	--	108	353	350	-3[c]	0.2
with C_{12} diamine	1.20	0	65	Not clear	278	282	+4	0.0
BTDA with C_6 diamine	1.32	20	--	98	113	102	-11	3.9
with C_8 diamine	1.28	0	65	79	98	85	-13	1.6
with C_{12} diamine	1.21	0	45	59	72	63	-19	0.9
with isophoronediamine	1.14	a	a	222	242	130	-112	3.6
MCTC with C_8 diamine	1.12	0	60	48	67	62	-5	9.2
Polybenzimidazoles								
TAB with C_6 dicarboxylic acid	1.14	45	--	197	235	126	-109	7.9
with C_8 dicarboxylic acid	1.12	30	--	185	207	127	-80	5.6
with C_{12} dicarboxylic acid	1.08	18	--	160	175	134	-41	4.3
N-Arylenepolybenzimidazoles								
4,4'-Bis(o-aminoanilino)biphenyl								
with C_6 dicarboxylic acid	1.17	15	--	115	143	118	-25	3.1
with C_8 dicarboxylic acid	1.13	10	--	108	125	102	-23	3.6
with C_{12} dicarboxylic acid	1.12	a	75	58	75	63	-12	2.9
with phthalic anhydride	--	a	a	300	321	319	-2	1.2
with methylhexahydrophthalic anhydride	1.10	a	a	260	400	407	+7[d]	1.1

[a] Sample breaks during hardness testing

[b] Deviation from linearity after water boil occurs at 125°C suggesting -23°C shift

[c] Deviation from linearity after water boil occurs at 95°C suggesting -13°C shift

[d] Deviation from linearity after water boil occurs at 83°C

segments such as 1,4-diaminobutane for BTDA-based polyimides or succinic acid for N-arylenepolybenzimidazoles would provide higher DTUL polymers; however, addition of less flexible diamines or diacids, e.g., cycloaliphatics, to form copolymers would also provide sufficient DTUL's in these polymers. For example, the following copolymers would be expected to provide the recommended minimum, dry DTUL properties:

- Polyimide from BTDA with 1,8-octanediamine and m-phenylenediamine -- it is assumed that m-phenylenediamine will have DTUL properties similar to isophorone diamine and the DTUL of the 50/50 wt pct blend of amines will be the midpoint of these two temperatures ((79 + 222) ÷ 2 = 150°C)
- N-arylenepolybenzimidazole from 4,4-bis(o-aminoanilino)biphenyl from suberic acid and phthalic anhydride -- reasoning as described above for the BTDA polymers, this polymer would require modification with only 20 percent by weight phthalic anhydride to have a DTUL of ≅150°C (80 percent by weight suberic acid)

3.3.2 Solvent Screening

Initial susceptibility to solvent attack was determined on molded specimens of the 16 polymers. Due to the small size of the specimens, the measured percent weight gain values are only accurate to ±1 percent. Acetone, chloroform, and TCP were used for test solvents; and sample weight gain (percent) after 1-, 7-, and 50-day exposure to these solvents are given in Table 13.

PMDA-based polyimides (crystalline) and polybenzimidazoles are the only two polymer systems which showed any resistance to chloroform. The BTDA- and MCTC-based polyimides, as well as all of the N-arylenepolybenzimidazoles, showed poor chloroform resistance. The acetone resistance of most of the polymers was better than their resistance to chloroform. The polymers' resistance to TCP (on a weight percent gained basis) is not as good in some instances as their resistance to acetone and chloroform. In particular, the suberic and sebacic acid polybenzimidazoles show weight gains with TCP in excess of weight gains with acetone or chloroform. A second batch of polybenzimidazole from sebacic acid, however, showed no weight gain upon exposure to TCP for 50 days. Some difficulty was encountered in wiping all of the TCP from the samples surfaces, and the percent weight gain may be high. The loss in weight obtained with two of the N-arylenepolybenzimidazoles in Table 13 after TCP exposure is probably attributable to dissolution of the polymer at the surface.

With the exception of a few data points, the data in Table 13 also suggest that resistance of the aliphatic-aromatic polymers to organic solvents is proportional to the chain length of aliphatic diamine or dicarboxylic acid used in the polymer. Polymers containing longer aliphatic segments are less resistant to attack by organic solvents. Of interest is the inverse relationship between weight gain due to 24-hr water boil seen in Table 12 and weight gain due to organic solvents.

The polyimide from BTDA with octanediamine and m-phenylenediamine has been included in the table and shows marked improvement in solvent resistance over the BTDA/octanediamine polymer.

After 10 days exposure to the three solvents, several specimens were tested for DTUL shift. These specimens are noted in the table by footnote e. These tests

TABLE 13. SOLVENT SCREENING OF MOLDED POLYMERS[a] (PERCENT WEIGHT GAIN)

Polymer	Acetone			Chloroform			TCP[b]		
	1 Day	7 Days	50 Days	1 Day	7 Days	50 Days	1 Day	7 Days	50 Days
Polyimides									
PMDA with C_6 diamine	0	0	0	0	0	f	1	2	0
with C_8 diamine	0	0	e	3	5	e	1	0	e
with C_{12} diamine	1	1	3	12	30	29	0	0	0
BTDA with C_6 diamine	0	0	2	Swells			1	0	0
with C_8 diamine	2	6	11	Swells			0	0	0
with C_{12} diamine	7	9	9	Swells			1	1	0
with isophoronediamine	0	0	6	Swells			2	1	0
with C_8 diamine and m-phenylenediamine	1	--	1	2	--	6	0	--	0
MCTC with C_8 diamine	Swells			Dissolved			Swells	Dissolved	
Polybenzimidazoles									
TAB with C_6 dicarboxylic acid	0	0	0	0	0	f	4	4	5
with C_8 dicarboxylic acid	0	0	e	0(0)[c]	0(0)[c]	e(f)	1(0)[c]	2(0)[c]	e(0)[c]
with C_{12} dicarboxylic acid	0	0	e	2	4	e	1	1	e
N-Arylenepolybenzimidazoles									
	4	14	14	Swells			0	0	0
4,4'-Bis(o-aminoanilino)biphenyl									
with C_6 dicarboxylic acid	11	18	16	Dissolved			-2	-1	0
with C_8 dicarboxylic acid	23	14	-2	Dissolved			-2	-5	Half dissolved
with C_{12} dicarboxylic acid	6	--	--	Swells			--	--	--
with phthalic anhydride	15	15	2	Dissolved			3	4	4
with methylhexahydrophthalic anhydride									

[a] Sample weights of polymers varied between 0.1 and 0.2 grams. Samples were towel wiped.

[b] Seven-day TCP samples were acetone washed and towel wiped prior to weighing

[c] Second sample of polymer

[d] Surface degraded, polymer TCP cloudy

[e] Sample used for DTUL measurement

[f] Solvent evaporated

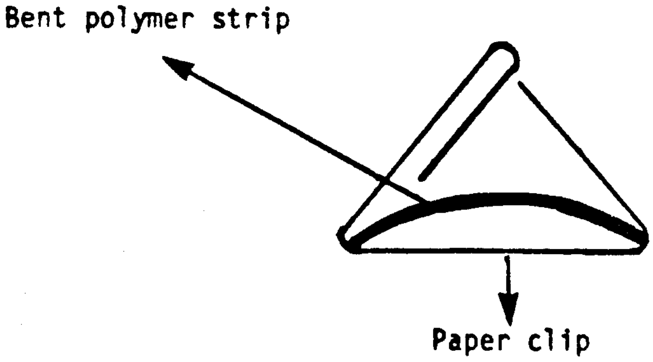
were discontinued when essentially no effect was noted for the nine samples tested except the polybenzimidazole from TAB with 1,12-dodecanedicarboxylic acid and chloroform. DTUL curves for this polymer after exposure to the three solvents are given in Figure 15. The arrow in the figure indicates sample shrinkage, probably due to chloroform being lost from the specimen and premature sample softening. Acetone and TCP show no change in DTUL behavior from original dry DTUL curves.

3.3.3 Solvent Resistance Under Stress

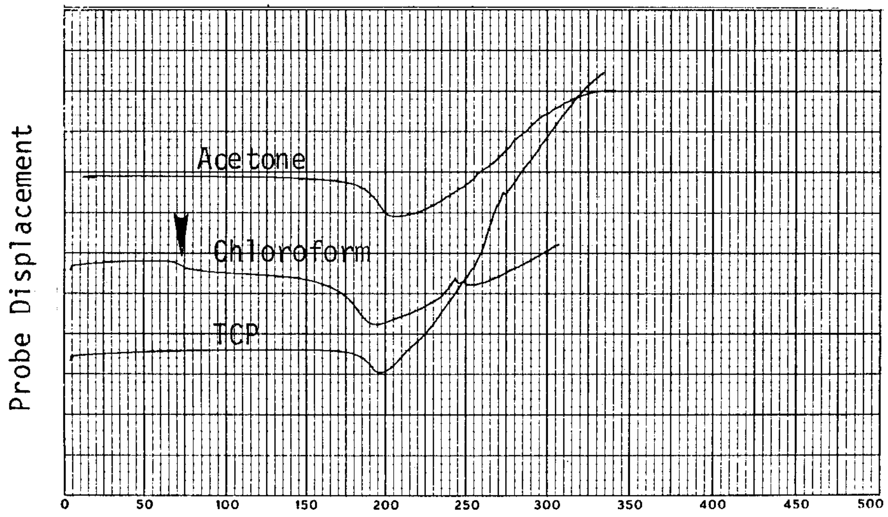
Based on the DTUL and solvent screening results previously discussed, the three polymers indicated below were prepared in 50g quantities for molding and subsequent solvent resistance testing under stress.

- Polyimides
    - PMDA with 1,8-octanediamine (η_{inh} = 4.1)
    - BTDA with 50/50 weights of m-phenylenediamine and 1,8-octanediamine (η_{inh} = 0.98)
- Polybenzimidazoles
    - TAB with sebacic acid

The PMDA/octanediamine polymer, during preparation, progressed to a very high molecular weight. The 10 percent solids solution of this polymer at 180°C required dilution with additional solvent to reduce its viscosity for pouring into the nonsolvent for isolation. The above polymers were molded at 6.9 MPa (1000 psi) at 393°C (740°F), 266°C (510°F), and 385°C (725°F), respectively. Polymer strips cut from the moldings were placed (bent) into large paper clips as sketched below and immersed into acetone, chloroform, and TCP.



After 500 hr exposures to the three solvents, no evidence of cracking or crazing was observed in any of the test strips from the three polymers. However, removal of the test strip from the paper clip did not lead to a completely flat specimen. Control strips which were aged in air also did not return to completely flat specimens. Qualitatively, the polybenzimidazole specimens appear to retain their stiffness in all three solvents better than the two polyimides. The m-phenylenediamine modification to the BTDA/octanediamine polymer has a DTUL of 155°C (deviation from linearity). The DTUL intercept temperature is 187°C. Fifty-day weight gains in acetone, chloroform, and TCP were 1, 6, and 0 percent, respectively.



Temperature, °C

Figure 15. DTUL curves for polybenzimidazole from 1,12-dodecanedicarboxylic acid after 10-day exposure to solvents

Efforts to demonstrate stressed durability resistance at finite stress levels (tensile tests) under the influence of solvents led to discovering that the polymers became anisotropic when pressed into thin films. If a narrow strip of 7.6 mm-thick polymer is pressed to a 1.3 mm thickness, most of the flow occurs to increase the width of the sample and little flow occurs to increase the sample's length. Creasing the thin films leads to failure when the crease is parallel to the flow direction and no failure when perpendicular to the flow direction. It appears as if these tests may be more properly conducted on composites prepared from the candidate resins.

The three polymers were then exposed (unstressed) to more severe solvents: formic acid, N-methyl-2-pyrrolidone (NMP), and dimethyl sulfoxide (DMSO). The 50-day results of these tests are given in Table 14.

3.4 INITIAL POLYMER SELECTION

The three polymers which passed the stressed solvent resistance testing alone or with modification are good candidates for further characterization. Their key properties are reiterated and compared in Table 15, with their tensile properties determined on strips from molded films. Molding temperature of the films is also indicated in the table.

The PMDA/octanediamine polymer was opaque after molding and was crack-sensitive, compared to earlier moldings from a different synthesis (same monomers). Although molding was accomplished by placing the polymer (powder, and fibers) evenly over the bottom of the mold prior to molding, the samples may be slightly anisotropic due to polymer flow from the mold. The tensile strength of the polybenzimidazole specimen is higher than obtained from prior Acurex efforts and the high strength of of the polyimide from BTDA with octanediamine and m-phenylenediamine is consistent with those obtainable from aromatic polyimides.

TABLE 14. SOLVENT SCREENING OF SELECTED POLYMERS, 50-DAY TESTS (PERCENT WEIGHT GAIN)

Polymer	Formic Acid	N-methyl-2-pyrrolidone (NMP)	Dimethyl Sulfoxide (DMSO)
<u>Polyimides</u>			
PMDA with C_8 diamine	14	0	0
BTDA with C_8 diamine and <u>m</u>-phenylenediamine	2	-0.4	0
<u>Polybenzimidazoles</u>			
TAB with sebacic acid	Dissolved	Dissolved	Attacked

The initial modulus of the samples must be redetermined. The tangent modulus is given in the table.

The good Barcol hardness of the BTDA/1,8-octanediamine and m-phenylenediamine polyimide, its low molding temperature, and good tensile properties made it the first choice for further characterization efforts.

3.5 POLYIMIDES FROM BTDA WITH ALIPHATIC AND AROMATIC AMINES

Continuing investigation of the polyimide from BTDA/1,8-octanediamine and m-phenylenediamine (50/50 wt pct amines) led to the discovery that two types of products were obtained when apparently prepared by the same procedure: clear and opaque moldings. Further, when clear moldings were heat treated at 316°C (600°F) they usually turned opaque. Lowering the m-phenylenediamine content from 50 wt pct based on total amine content to 43 percent (equimolar for 1,8-octanediamine and m-phenylenediamine) produced clear moldings.

Twenty-one molded buttons of numerous polymers were treated under nitrogen for 1 hr at 316°C (600°F). Moldings which were opaque prior to heat treatment became more opaque. Seven clear polyimide moldings of the 50/50 wt pct amine composition turned opaque. Polymers which did not become opaque with the 1-hr heat treatment are listed below:

- BTDA/1,6-hexanediamine, one each
- BTDA/1,8-octanediamine, one each
- BTDA/1,6-hexanediamine/m-phenylenediamine (equimolar amines), two each

TABLE 15. POLYMER SELECTIONS

	Mold Temperature (°C)	Barcol Hardness	Dry[a] DTUL (°C)	Wet[a] DTUL (°C)	Tensile Properties
Polyimides					Strength, MPa/elongation, %/modulus, MPa[b]
PMDA with C_8 diamine	385	10	108 (353)	95 (350)	30.3/3/1144
BTDA with C_8 diamine and *m*-phenylenediamine	266	40	155 (187)	148 (180)	117/14/1220
Polybenzimidazole					
TAB with sebacic acid	385	25	185 (207)	120 (126)	101/10/1144

[a] Deviation from linearity values; intercept values are in parenthesis
[b] Tangent modulus, not initial modulus

- BTDA/1,8-octanediamine/m-phenylenediamine (equimolar amines), one each, and 50/50 wt pct amines, one each

- BTDA/1,6-hexanediamine/4,4'-methylenedianiline (equimolar amines), one each

- BTDA/1,8-octanediamine/4,4'-methylenedianiline (equimolar amines), one each

- BTDA/1,8 octanediamine/2,6-diaminotoluene (equimolar amines), one each

Only polymers containing m-phenylenediamine turn opaque with heat treatment. All three polyimides from equimolar amines containing m-phenylenediamine did not turn opaque compared to only one of the many polyimides containing 50/50 wt pct amines.

These results, which are discussed in more detail below, prompted more in-depth investigations of the aromatic amine modified aliphatic polyimides. The results of these investigations are discussed in the next few pages and finally led to selection of the polyimide from BTDA with equimolar 1,6-hexanediamine and m-phenylenediamine. Scaleup of this polymer is described in Section 3.6 and prepregging and composite efforts in Section 3.7.

3.5.1 Considerations of Forming Polyimides From Amines With Different Basicities

Addition of aromatic amines as the coreactant with more basic aliphatic diamines to form polyimides with aromatic dianhydrides results in the potential to form a number of new polyimides. Block, random, and alternating copolymers are hypothetically possible. Formation of specific mer sequences would be expected to be related to methods of preparing the polyimide. For example, principally block copolymers would be expected from condensation of equimolar quantities of one amine with a dianhydride followed by continuing reaction with equimolar quantities of the second amine with the same dianhydride or alternate dianhydride.

The mer sequences which are actually obtained during condensation are further complicated by the chemistry involved. Consider the simultaneous addition of both amines to a solution of the dianhydride at temperatures below imidization temperature(s). As pendant acid groups are formed from reaction of aliphatic amine with anhydride, they would be expected to preferentially react with the strongest base in the mixture, the unreacted aliphatic amine. Thus, at ~50 percent of aliphatic amine reacted due to salt formation of unreacted aliphatic amine with pendant acid groups, the aromatic amine may become the amine available for reaction with anhydride.

It is apparent that formation of random and alternating copolymers of polyimides from aliphatic-aromatic amines with BTDA will be very sensitive to reaction conditions. The molding properties, solvent resistance, and crystallinity of such polymers would be expected to vary with mer sequencing and further mer crystallizability. Thus, block copolymers with long sequences of mers containing the aliphatic amine and long sequences containing the aromatic amine would be expected to produce moldings with both amorphous (aliphatic) and ordered or crystalline (aromatic) regions. On the other hand, alternating copolymers due to their regular sequencing may have a stronger tendency to crystallize than random copolymers.

The previous brief discussion is further complicated by at least two additional considerations: macrocycle formation and crystallizability of polymers containing the m-phenylene moiety. As the progressing condensation depletes the concentration of monomers and dimers, potential for macrocycle formation is increased. Neglecting molecular geometries (e.g., intermediates) which may be required to actually obtain such macrocycles, it is noted that Fischer-Hirschfelder-Taylor models can readily be constructed (strain free) for numerous potential macrocycles including the highly unlikely BTDA-derived structure wherein the 3,3'-dicarboxylic amides are bridged with m-phenylene and the 4,4'-dicarboxylic amides are bridged with hexamethylene. Two crystalline forms of the aromatic nylon from isophthaloyl chloride and m-phenylenediamine are discussed in detail in Reference 8. Both the soluble, coiled alpha form (intramolecular hydrogen bonded) and insoluble beta form (intermolecular hydrogen bonded) of the polymer are described. These polymers may be similar to the clear, hazy, and/or opaque BTDA polyimides obtained with m-phenylenediamine as coreactant with 1,6-hexane or 1,8-octanediamine compared to clear BTDA polyimides from the aliphatic amines and/or with methylenedianiline and 2,6-diaminotoluene as coreactants.

3.5.2 BTDA With Equimolar Aliphatic and Aromatic Amines

Characterizature of BTDA polymers from equimolar aliphatic and aromatic diamines appeared to be in order based on the clarity of the moldings obtained at 316°C from these compositions. These results are given in Table 16. All of the polymers were molded to clear buttons at target conditions with the exception of Polymer 7, (see Sections 3.5.3 and 3.5.4) which was the initially selected polyimide composition.

The three items noted below are evident from the results presented in Table 16. Polymer 7 is apparently an exception to the general trends seen in Table 16:

- Polymers derived from hexanediamine provide moldings with higher Barcol hardness than polymers derived from octanediamine. Polymers from octanediamine have greater resistance to moisture than polymers from hexanediamine.
- Aromatic amines incorporated into the hexanediamine based polymers increase hardness, DTUL, and resistance to both water and chloroform. Similar effects are observed for octanediamine polymers except for moisture resistance, where little effect is observed.
- No obvious relationships exist between weight percent of individual constituents, i.e., hydrocarbon portion of aliphatic amine versus hardness, DTUL, chloroform, or moisture resistance

Polymer 7 in Table 16 appears to be different than Polymers 6 and 8. It has significantly higher hardness and resistance to chloroform than would be predicted by extrapolation from the compositions of Polymers 6 and 8. There appears to be a discontinuity in properties as the m-phenylene content of the polymer is increased to values above its content in the equimolar polymer. For example, if the quantity of m-phenylenediamine were increased from 43 percent (Polymer 6) to 60 percent (10 percent more than Polymer 7), a polymer with a Barcol hardness of 50+ might be expected. The polymer from 100 percent m-phenylenediamine with BTDA would not be expected to have a hardness much greater than 50.

TABLE 16. PROPERTIES OF POLYIMIDES FROM BTDA WITH ALIPHATIC AND ALIPHATIC-AROMATIC DIAMINES

Polymer Number	Amines		Weight Percent Contribution of Structures			Inherent Viscosity (dl/gm), H_2SO_4	Barcol Hardness	Properties of Molded Polymer			50-Day Chloroform Weight Gain (percent)
				Amines (Hydrocarbon Portion)				DTUL; °C (Intercept)		Water Weight Gain (percent)	
	Aliphatic	Aromatic	BTDA (imide)	Aliphatic	Aromatic			Dry	After 24-Hr Water Boil		
1	1,6-Hexanediamine	None	79	21	0	1.32	20	113	102	3.9	266[a]
2	1,6-Hexanediamine	*m*-Phenylenediamine	80	11	9 (equimolar)	0.82	43	195	155	2.4	11
3	1,6-Hexanediamine	Methylenedianiline	72	9	19 (equimolar)	1.55	40	193	158	2.0	96
4	1,6-Hexanediamine	2,6-Diaminotoluene	79	10	11 (equimolar)	1.25	45	205	175	2.3	294[b]
5	1,8-Octanediamine	None	74	26	0	1.28	0	98	85	1.6	250[a]
6	1,8-Octanediamine	*m*-Phenylenediamine	77	14	9 (equimolar)	0.74	30	155	136	1.9	91
7	1,8-Octanediamine	*m*-Phenylenediamine	78	11	11	1.4	40 to 48	185	159	1.5	6
8	1,8-Octanediamine	Methylenedianiline	70	12	18 (equimolar)	1.18	30	155	133	0.9	87

[a] 1-day result

[b] Heat treated for 1 hr at 316°C (600°F)

The results previously described suggest that the composition (morphology) of Polymer 7 is unusual. This appears to be confirmed by the difficulties encountered in synthesizing it reproducibly, as discussed in the next section.

The toughness of the molding from Polymer 3 was noteworthy: samples for tests were cut from the molded bottom with a trim knife without fracture propagation.

3.5.3 BTDA With Equal Weight Percent 1,8-Octanediamine and m-Phenylenediamine

After demonstration of the good solvent resistance (stressed) and tensile strength of the polyimide from BTDA with 1,8-octanediamine and m-phenylenediamine, composite property efforts were scheduled. Numerous subsequent attempts to prepare this polymer were not successful. Specifically, molded resin specimens from the numerous attempts varied in degree of opacity from clear to very opaque. Table 17 provides a log of the reactions conducted.

Polyimides 1 and 2 were the first two reactions from the 50/50 wt pct amine/BTDA reactants. Polymer 2 was tested for its tensile properties (Section 3.4). Not evident in the table is the direct correlation between clarity of the polymer solution at the end of the 180°C reaction temperature and molding clarity. If the solution is clear, the molding is clear.

It appears that the difference in producing a clear versus opaque molding is due to differences in polymer segment sequences. For example, if m-phenylene/BTDA sequences include two to three mers, that portion of the molecule is insoluble in m-cresol and precipitates in conjunction with similar segments as a colloid or highly visible particle. The polymers from equimolar amines were both clear, suggesting that the sequence BTDA/m-phenylenediamine/BTDA does not lead to opaque moldings per se.

3.5.4 Properties of Heat-Treated BTDA Polyimides

Molded buttons of numerous polymers were treated under nitrogen for 1 hr at 316°C (600°F). This differs from the standard heat treatment for button molding wherein the polymer was placed into a preheated mold, the mold placed into a cold press, and 100 psi applied. The 1 hr at 600°F treatment did not significantly affect the color of the moldings; however, improvements in both hardness and resistance to chloroform were observed. Since the original purpose of the experiment was to determine if more complete fusion could be obtained with a hold time at 316°C (600°F), it was surprising to find that the heat treatment led to more opaque moldings with the 50/50 wt pct amine polymers.

Table 18 provides property differences observed on molded polymer discs from the two heat treatments. Attention is directed to the H_2SO_4 solubility tests on the polymer samples. In many instances, there are several entries for the same sample. The first entry was after 13 days at room temperature on the shaker (S = soluble, T = trace insolubles, and I = insoluble). The majority of the as-molded samples were dissolved by this treatment, compared to the nondissolution of nearly all of the heat-treated samples. The second entry is after 4-hr oven treatment at 43°C with overnight room temperature shaker treatment plus a second identical treatment. Samples which still demonstrated H_2SO_4 insolubility were finally heated for an additional 4 hr at 43°C and 3 days on the shaker at room temperature. Trace insolubles in the final solution are considered to be essentially equivalent to

TABLE 17. RECORD OF POLYMERS OBTAINED FROM THE REACTION OF BTDA WITH 50/50 WT PCT 1,8-OCTANEDIAMINE AND m-PHENYLENEDIAMINE

Number	Notebook Reference	Weight of Reactants (g)	Method[a]	Catalyst Amine	Inherent Viscosity, dl/g (H_2SO_4)	Clarity of Molding to Transmitted Light[b]
1	65-103	5.5	Standard method	EMI	1.10	Slight haze
2	65-107	55	Standard method	EMI	0.98	Clear[c]
3	65-121	111	Standard method	Et_3N	0.46	Opaque
4	65-122	11	Standard method (new BTDA)[d]	EMI	2.29	Clear[e]
5	65-123	55	Standard method	EMI	1.04	Opaque
6	65-125	11	Standard method (recrystallized mPDA[f])	EMI	1.00	Opaque
7	65-130	180	Standard method (new BTDA)	EMI	0.74	Hazy
8	65-132	5.5	Standard method	None	0.74	Opaque
9	65-133	5.5	Octanediamine added at RT, 2.5 hr later mPDA added	None	0.78	Opaque
10	65-134	5.5	mPDA added at RT, 24 hr later octanediamine added (distilled mPDA)	None	0.59	Opaque
11	65-135	5.5	Standard method	Pyridine	0.66	Opaque
12	65-136	5.5	Octanediamine, heat, cool, add mPDA	None	0.48	Hazy
13	65-137	5.5	Standard method	EMI (new batch)	0.55	Opaque

[a] Standard method is preparation of a clear cresol solution of BTDA with catalyst amine, cooling to below 60°C, addition of reactive amines and heating through 1 hr at 180°C.

[b] Molded by preheating mold to 320°C, adding 1g of polymer to mold and immediately placing 100 psi on polymer.

[c] Tensile and solvent resistance conducted on this polymer.

[d] Slurried with THF in addition to acetone slurry for purification.

[e] Molding does not propagate fracture when cut with trim knife (very tough and insensitive to fracture via crack initiation).

[f] mPDA = m-phenylenediamine

TABLE 18. PROPERTY DIFFERENCES BETWEEN AS-MOLDED AND MOLDED HEAT-TREATED BTDA POLYIMIDES

Polymer	Reference Number	Polymer Composition[b]	Barcol Hardness		Solubility in H_2SO_4[a]		50-Day Chloroform Weight Gain of Heat-Treated Moldings[d] (percent)	Clarity of Molding to Transmitted Light	
			As Molded[c]	Molded,[d] Heat Treated	As Molded[c]	Molded,[d] Heat Treated		As Molded[c]	Molded,[d] Heat Treated
1	65-107	BTDA with ODA and m-PDA (50/50 wt pct amines)	40	46	S	I,T	2.5	Clear	Partly clear
2	65-121		0→5	2	T,T	I,I,I	27.0 (foam?)	Partly clear	Opaque
3	65-122		44	51	T,S	I,S	0.9	Clear	
4	65-123		46	52	S	I,T	1.3	Clear	
5	65-125		41	50	S	I,T	2.5	Opaque	
6	65-130		42	49	S	I,T	1.0	Clear	
7	65-131	Same as above except amines at 50/50 mole pct	30	0[e]	S	T,S	16.1 (foam)	Clear	
8	65-132	Same as above except amines at 50/50 wt pct	35	40	S	I,S	22.9	Opaque	
9	65-133		44	48	S	I,T,T	25.4	Opaque	
10	65-134		44	52	I,S	I,I,I	1.6	Hazy	
11	65-135		45	48	S	I,S	1.9	Opaque	
12	65-136		42	52	S	T,S	1.3	Clear	
13	65-137		42	52	S	I,T,S	2.7	Clear	
14	65-138	BTDA with ODA and MDA (50/50 mole pct amines)	30	30	I,I,I	I,I,I	96.5	Clear	Clear
15	65-142	BTDA with ODA and mPDA (50/50 wt pct amines)	45	44	S	I,S	3.5	Hazy	Opaque
16	65-143	BTDA with HDA and mPDA (50/50 mole pct amines)	40	42	S	I,S	1.7	Clear	Clear
17	65-145	BTDA with ODA and mPDA (50/50 wt pct amines)	44	46	S	I,S	2.1	Clear	Clear
18	65-146	BTDA with HDA and MDA (50/50 mole pct amines)	40	43	I,I,I	I,I,I	46.2	Clear	Clear
19	65-151	BTDA with HDA and 2,6-diaminotoluene (50/50 mole pct amines)	45	(foam)	S	T,S	294.0 (foam)	Clear	Clear

[a] S = soluble, T = trace insolubles, I = insoluble

[b] BTDA = benzophenonetetracarboxylic dianhydride; ODA = 1,8-octanediamine; mPDA = m-phenylenediamine; MDA = methylenedianiline; HDA = 1,6-hexanediamine

[c] Molded by preheating mold to 320°C (608°F), adding 1g of polymer to mold and immediately placing 100 psi on polymer and fan cooling to room temperature

[d] The as-molded polymers were vacuum bagged and heated to 316°C (600°F) for 1 hr under nitrogen after venting the vacuum

[e] The molding foamed internally

completely soluble samples and is judged to not necessarily represent significant structural variance between the polymers.

With only the few exceptions discussed below, there appears to be no major difference between the H_2SO_4 solubility response of the samples given the two heat treatments. Dissolution time of the samples heated for 1 hr at 316°C (600°F) is longer, but the final result is essentially the same -- complete solubility in sulfuric acid. Consequently, it was concluded that the improved chloroform resistance observed for the heat-treated samples over the as-molded polymers is not principally due to crosslinking.

Variation in solubility response between as-molded and heat-treated samples is observed for polymers 2 and 10 shown in Table 18. Polymer 2 was obtained from use of triethylamine as catalyst. Polymer 10 was prepared with no amine catalyst. Polymers 8, 9, and 12 were also prepared without catalyst. Polymer 10 differed from the others in regard to the order of the amine addition. The m-phenylenediamine was added 24 hr prior to the 1,8-octanediamine. Polymer 2 and 10 may be crosslinked after 1 hr at 316°C (600°F) in view of the complete solubility of the other polymers from the same constituents. The methylenedianiline polymers (14 and 18) are insoluble in sulfuric acid with both heat treatments; however, a decision on the cause of this insolubility (structure versus crosslinking) is premature without further tests. These polymers as isolated from the reaction are soluble in sulfuric acid (see Table 16).

Comparison of the chloroform resistance of as-molded to heat-treated samples is provided in Table 19.

At this juncture it was suspected that the enhanced chloroform resistance after to the 1-hr heat treatment at 316°C (600°F) might be attributable to changes in structure. Three polymers were selected for more extensive investigation. All three polymers were made using m-phenylenediamine. Both methylenedianiline and 2,6-diaminotoluene based polymers gave high chloroform weight gains. As shown in Table 20, two polymers were made from 50/50 wt pct amines (1,8-octanediamine/m-phenylenediamine) with BTDA; one was opaque (65-137) after 1 hr at 316°C (600°F) treatment, whereas the other remained clear (65-145). The third polymer was from BTDA with equimolar amines (1,6-hexanediamine/m-phenylenediamine) (65-143).

The TGA data on the as-prepared polymers show residual cresol or imidization water is lost. Imidization weight losses expressed as percent of original polymer weight for Polymers 65-137 and -145 is 8.0 percent and for Polymer 65-143, 8.3 percent. If the weight loss for 65-143 was entirely due to further imidization, the 0.2 percent weight loss measured would represent only about 2 to 3 percent of the total water loss required for complete imidization.

Since heat treatment was not conducted under pressure, the slight increase in density measured for the heat-treated samples appears valid and suggests the occurrence of some chemical or physical change. Based on the increased Barcol hardness values measured for the heat-treated samples (compare to Table 20), increased polymer densities would be predicted. The polymer which was opaque after heat treatment was also the densest.

The tetrachloroethane (TCE) soluble portion (90^+ percent) of several as-prepared polymers were cast onto salt plates and infrared spectra taken of the films after TCE removal at room temperature, after 1-min treatment at 316°C (600°F)

TABLE 19. COMPARISON OF CHLOROFORM RESISTANCE BETWEEN "AS MOLDED" AND "MOLDED HEAT TREATED" BTDA POLYIMIDES

Reference Number	Polymer Composition[a]	1-Day Chloroform Weight Gain (Percent)		11-Day Chloroform Weight Gain (Percent)		50-Day Chloroform Weight Gain (Percent)	
		As Molded[b]	Molded Heat Treated[c]	As Molded[b]	Molded Heat Treated[c]	As Molded[b]	Molded Heat Treated[c]
65-107	BTDA with ODA and m-PDA (50/50 wt pct amines)	1.8	1.0		1.7	9.0	2.5
65-131	Same as above except amines at 50/50 mole pct	6.0	2.5 (foam)	64.0	7.7 (foam)	91	16.1 (foam)
65-138	BTDA with ODA and MDA (50/50 mole pct amines)	9.0	4.3	85.0	35.6	87	96.5
65-146	BTDA with HDA and MDA (50/50 mole pct amines)	2.7	1.6		7.9	96	46.2
65-143	BTDA with HDA and m-PDA (50/50 mole pct amines)	3.9	0.5		0.9	11	1.7

[a] BTDA = benzophenonetetracarboxylic dianhydride; ODA = 1,8-octanediamine; m-PDA = m-phenylenediamine; MDA = methylenedianiline; HDA = 1,6-hexanediamine

[b] Molded by preheating mold to 320°C (608°F), adding 1g of polymer to mold and immediately placing 100 psi on polymer and fan cooling to room temperature

[c] The "as molded" polymers were vacuum bagged and heated to 316°C (600°F) for 1 hr

TABLE 20. POLYMERS SELECTED FOR FURTHER INVESTIGATION

Reference Number	50-Day Chloroform Weight Gain of Heat-Treated Moldings (percent)	Weight Loss of As-Prepared Polymer Through 300°C (percent)	Density (g/cc)		
			As Molded	Molded, Heat Treated	Percent Change
65-137	2.7	1.2	1.362	1.369	+0.5
65-145	2.1	0.4	1.355	1.362	+0.5
65-143	1.7	0.2	1.354	1.364	+0.7

under vacuum, and after 60-min treatment at 316°C (600°F) under vacuum. Figures 16, 17, and 18 provide the spectra of Polymers 65-137, -145, and -143, respectively. The figures contain three spectra representing, from top to bottom, the three conditions cited.

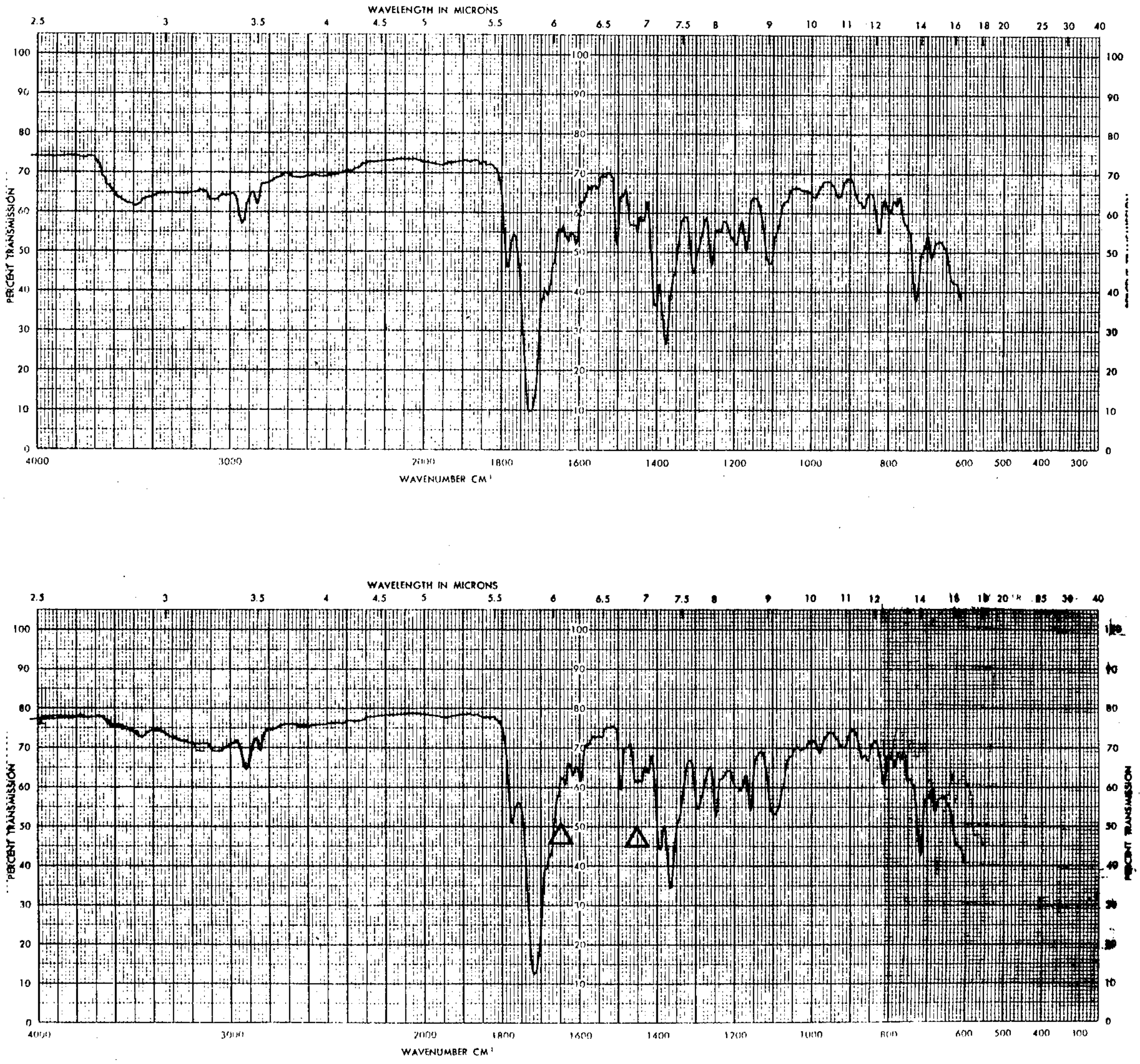
With continued heat treatment there is loss in all spectra of the weak absorptions at 2930 cm^{-1} and 2970 cm^{-1}, as well as general loss of the weak absorptions in the entire 2800 cm^{-1} through 3700 cm^{-1} region. Further loss of the 1700 cm^{-1} shoulder on the imide doublet to provide better resolution of the BTDA carbonyl at 1680 cm^{-1} occurs in all three polymers. Appearance of a broad weak absorption at 3300 cm^{-1} occurs in all three polymers. The percent transmission between the imide absorptions at 1730 cm^{-1} and 1780 cm^{-1} is improved. Two differences exist between films cast from TCE and Nujol mulls of the polymers. A weak absorption at 820 cm^{-1} and a broad absorption at 3600 cm^{-1} (HOH?) are present in the TCE films but not the mulls of the polymers. The carbonyl region appears to be unaffected by sample preparation method.

It was concluded that similar changes occur in all three polymers with heat treatment (density and hardness increases and subtle changes in the carbonyl region of their infrared spectra), and it appears likely that these changes are responsible for the improved chloroform resistance. As to whether these changes are chemical or physical can only be elucidated by further experimentation.

3.5.5 BTDA With Equimolar 1,6-Hexanediamine and *m*-Phenylenediamine

Numerous attempts to prepare the clear polymer were eventually successful. Table 23 provides a log of the first reactions conducted. Monomer batches were the same throughout the study.

The principal observation relevant to formation of clear polymers from detailed analysis of the Table 21 results is that if the polymerization is held below about 120°C (but above some lower temperature) for ~2 hr prior to rapid heatup to 180°C, a clear polymer is produced. This differs from the standard method of preparation in that, with the standard method, cooling the BTDA cresol varnish to some temperature below 60°C prior to simultaneous addition of both amines is



△= Transient specie?

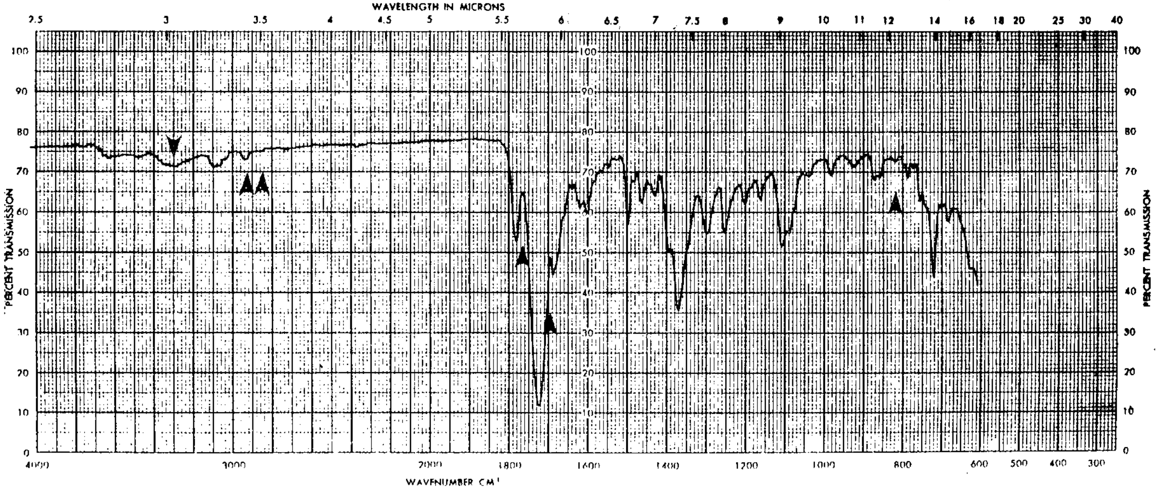


Figure 16. Spectra of BTDA/ODA/mPDA (65-137) polyimide film from TCE

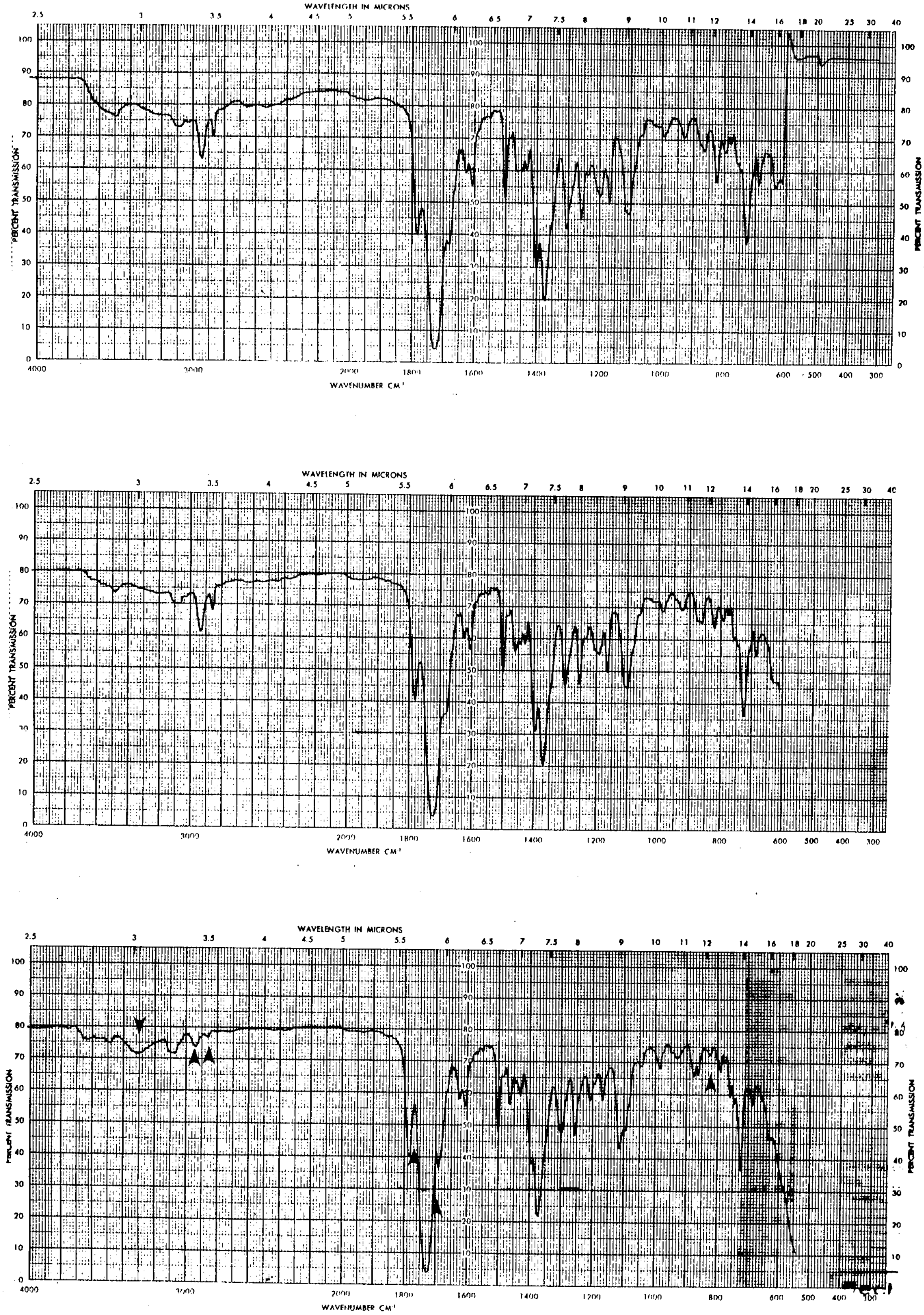
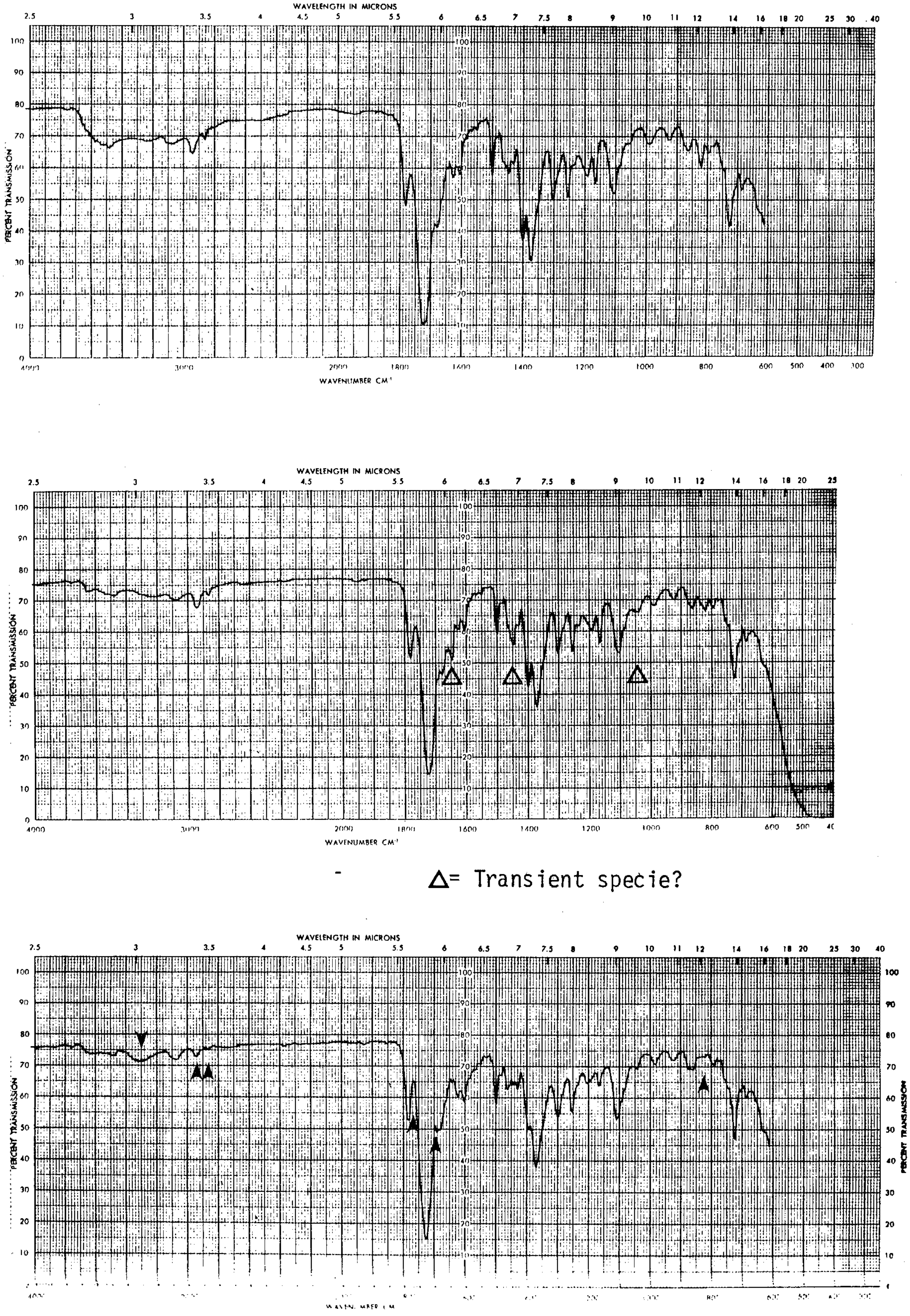


Figure 17. Spectra of BTDA/ODA/mPDA (65-145) polyimide film from TCE



Δ= Transient specie?

Figure 18. Spectra of BTDA/HDA/mPDA (65-143) polyimide film from TCE

TABLE 21. RECORD OF POLYMERS OBTAINED FROM THE REACTION OF BTDA WITH 1,6-HEXANEDIAMINE AND *m*-PHENYLENEDIAMINE

Table Number	Notebook Reference	Weight of Reactants (g)	Solids Content (percent)	Method[a]	Catalyst Amine	Inherent Viscosity, dl/g (H_2SO_4)	Reaction Clarity
1	65-143	5.5	10	Standard method	Pyridine	0.82	Hazy
2	78-1	5.5	10	Standard method	Pyridine	1.04	Clear
3	78-2	5.5	10	Standard method	Pyridine	1.07	Clear
4	338-64	11	30	Standard method	Pyridine	0.51	Opaque (110°C)
5	338-69	11	10	BTDA solution prepared at RT (16 hr), standard method	Pyridine	0.72	Opaque (130°C)
6	338-72	5.5	10	Solution of amines added all at once at 130°C	Pyridine	0.70	Hazy (35 min)
7	338-73	5.5	10	Solution of amines added at RT	Pyridine	0.81	Trace haze
8	338-75	5.5	10	BTDA/HDA at 180° 2.5 hr, add mPDA, react 2.5 hr	Pyridine	0.24	Clear
9	338-78	5.5	10	BTDA/mPDA at 180°C 10 min, cool, add HDA	None	0.81	Hazy (160°C)
10	338-79	5.5	10	BTDA/mPDA at 180°C 1.5 hr, add HDA	None	0.26	Opaque
11	338-80	5.5	10	Dropwise addition of amines in solution at 180°C	Pyridine	0.33	Opaque
12	338-82	5.5	5	BTDA/HDA add mPDA after 2 hr at 120°C	Pyridine	0.52	Clear
13	338-85	5.5	5	BTDA/HDA reacted at 0°C, then at 120°C to constant spectra, add mPDA	None	1.18	Clear
14	338-88A	5.5	5	As above	5x pyridine	0.63	Clear
15	338-88B	1/2 of 88A	5	5 percent excess mPDA added, 16 hr at 180°C	5x pyridine	0.31	Clear
16	338-90	5.5	10	Standard method	5x pyridine	0.70	Opaque (140°C)
17	338-96[b]	5.5	10	BTDA/HDA reacted at 128°C to constant spectra, add mPDA	None	0.51	Opaque
18	338-98[b]	5.5	5	Same as previous	None	0.48	Hazy
19	338-101	5.5	5	Dropwise addition of amines in solution (3 hr at 110°C). After 1 hr at 180°C, 16 hr at 147°C.	None	0.63	Clear

[a] See Footnote a, Table 17, all reactions heated through 1 hr at 180°C

[b] Amines at 97.5 percent of stoichiometry

required. The amines could be added at room temperature or 60°C and after dissolution, the reaction vessel placed into a 180°C oil bath.

The variation in inherent viscosities suggests that attainment of a high molecular weight polymer is also sensitive to preparation method. In general, polymerizations which turned opaque do not achieve molecular weights as high as clear polymerizations.

It is noted that the carbonyl region of the infrared spectra for all of these polymers, whether clear or opaque, is identical. It is further noted that once a clear polymer has been prepared, it is not readily convertible to an opaque polymer by seeding the cresol solution with opaque polymer, evaporation to dryness, addition of water or salts to the cresol solution. Attempts have not been made to convert opaque polymers to clear polymers.

Since polymer 13 of Table 21 had the highest inherent viscosity of the 19 polymers shown in the table another polymerization was carried out using techniques similar to those employed in the preparation of polymer 13, i.e., solids concentration and exotherm moderation of the BTDA/HDA reaction. Since both polymerizations employed the same monomers, inherent viscosity differences between the polymers produced are related to polymerization conditions.

Polymer 13 was prepared by hot dissolution of the BTDA at 5 percent solids in cresol followed by cooling with an ice bath prior to addition of solid aliphatic amine. The BTDA/HDA prepolymer was then heated to constant spectra at 120°C (1 hr) and solid m-phenylenediamine was added. The temperature was increased to 180°C for its 1-hr reaction. With the second reaction the BTDA flake was added to a cresol solution of the aliphatic amine at room temperature, which gave a clear 16 percent solids solution after 1.5 hr. The BTDA/HDA prepolymer was then condensed for 0.5 hr at 140°C and cooled to room temperature. After room temperature addition of a cresol solution of m-phenylenediamine to the precondensed HDA/BTDA prepolymer solution, the reaction was divided into four parts. Table 22 provides the heating conditions and inherent viscosities of the four resulting products.

Table 22 clearly demonstrates that "rapid" heatup to 180°C after m-phenylenediamine addition to the BTDA/HDA prepolymer solution is required to obtain a clear polymer. Polymerization conditions appear to have a marked effect on inherent viscosity, however, it should be noted that the solids content of the first polymer was nearly twice that of the other polymers during the 180°C reaction condition. After stirring ceased in the first polymer at 180°C, 5 ml cresol was added to thin the reaction mixture. Five ml of cresol was added to each of the other portions of the reaction prior to heatup to eliminate potential for stirrer cessation.

3.6 SCALEUP

Based on the finding that rapid heatup to the reaction temperature was required to obtain clear cresol varnishes of the BTDA/HDA/mPDA polyimide, several scouting experiments directed toward demonstrating scaleup feasibility were conducted. Several small-scale reactions (~11g of solids) were carried out with the items listed below in focus:

- Production of clear cresol varnishes
- Attainment of high molecular weight polymers

TABLE 22. BTDA/HDA/mPDA POLYIMIDE REACTION CONDITIONS VERSUS POLYMER PROPERTIES

Condition	Solution Clarity	Inherent Viscosity (dl/gm)
Solution placed into 180°C oil bath, reacted for 1 hr at 180°C	Clear	1.66
Overnight reaction at room temperature, overnight reaction at 120°C, 1 hr at 180°C	Opaque[a]	1.20
2 days reaction at room temperature, into cold oil bath, reacted for 1 hr at 180°C	Clear	0.96
Aliquot of above reacted overnight at 120°C	Clear	1.13

[a] Minimum opacity

- Can the procedure be used to prepare pound quantities of polymer

Several options exist for achieving rapid heatup of the reaction. Rapid addition of refluxing cresol to a high solids content cresol varnish of the monomers holds potential. Efforts focused on the stepwise amine addition route wherein the m-phenylenediamine is added to the varnish prepared from BTDA and HDA. Addition of m-phenylenediamine to a 180°C cresol solution of the BTDA/HDA prepolymer was successfully used to prepare 247g of polymer (13 percent solids). Only a trace of insolubles was observed in the cresol varnish. The inherent viscosity of the polymer was 1.09 dl/gm in sulfuric acid.

Isolation of the polymer by slow addition of the varnish to a Waring blender containing methyl alcohol provided of large chopped fibers. The product, after standard workup (refluxing methyl alcohol and 60°C vacuum oven dry), contained 2.7 percent by weight cresol by TGA analysis.

Methods to remove residual cresol from the 247g batch of BTDA/mPDA/HDA polyimide were investigated. The as prepared polymer still contained 2.7 percent residual volatiles (TGA) after 5-day treatment under high vacuum at 60°C. Increasing the drying temperature to 200°C (high vacuum) and/or reducing the particle size of the alcohol-precipitated polymer both succeeded in reducing the residual volatiles to <0.3 percent (at 316°C by TGA). A 10.2 x 15.2 x 0.76 cm thick molding was prepared from 152g of this polymer (13.8 MPa, 316°C) after treatment for 16 hr at 200°C under high vacuum. The polymer's moldability seemed to be unaffected by this heat treatment.

3.7 COMPOSITES

An 8-harness Celion 3000 fabric (24 x 23) was treated with chloroform for epoxy size removal, dried, and impregnated with a 13 percent solids (BTDA/mPDA/HDA) cresol varnish. Half of the varnish was added to one side and, after partial drying, half to the other side. Final dry conditions were 16 hr at 150°C under vacuum to give a prepreg with a volatile content of 2.7 percent (30 min at 260°C). Composites were fabricated from the prepreg by molding for 1 hr at 316°C under three different pressures; 0.69, 6.9, and 34.5 MPa (100, 1000, and 5000 psi). Properties for the three preliminary composites are given in Table 23. Calculated zero void content composite properties for this fabric are as follows:

Fiber Volume (percent)	Resin Weight (percent)	Ply Thickness (mm)
55	38.8	4.01
60	34.1	3.66

Figures 19 and 20 provide indication of the resin, void, and fiber distribution in the 0.69 and 6.9 MPa processed composites. The 34.5 MPa processed composite had essentially the same features as the 6.9 MPa processed composite and is not shown.

The void contents calculated for the high-pressure processed composites (Table 23) clearly reside in the individual fiber bundles since Figure 20 demonstrates essentially no voids are present in the interply resin. Processing at 0.69 MPa (100 psi) failed to consolidate the composite, and numerous large voids are observed in the composite. The shear strengths obtained for the high-pressure composites of 34 MPa is surprisingly high considering the void content of the composites. Epoxy resins provide up to 70 MPa with this fabric.

TABLE 23. PROPERTIES OF POLYIMIDE CELION 3000 COMPOSITES

Processing Pressure, MPa (psi)	Resin Weight (percent)	Ply Thickness (mm)	Void[a] Content	SBS, MPa[b] (psi)
0.69 (100)	34	4.77	23	24.9 (3610)
6.9 (1000)	36.2	4.42	17	33.7 (4880)
34.5 (5000)	36.2	4.19	13	34.8 (5040)

[a] Calculated from mm/ply observed for composite versus mm/ply for zero void composite

[b] Average of four specimens

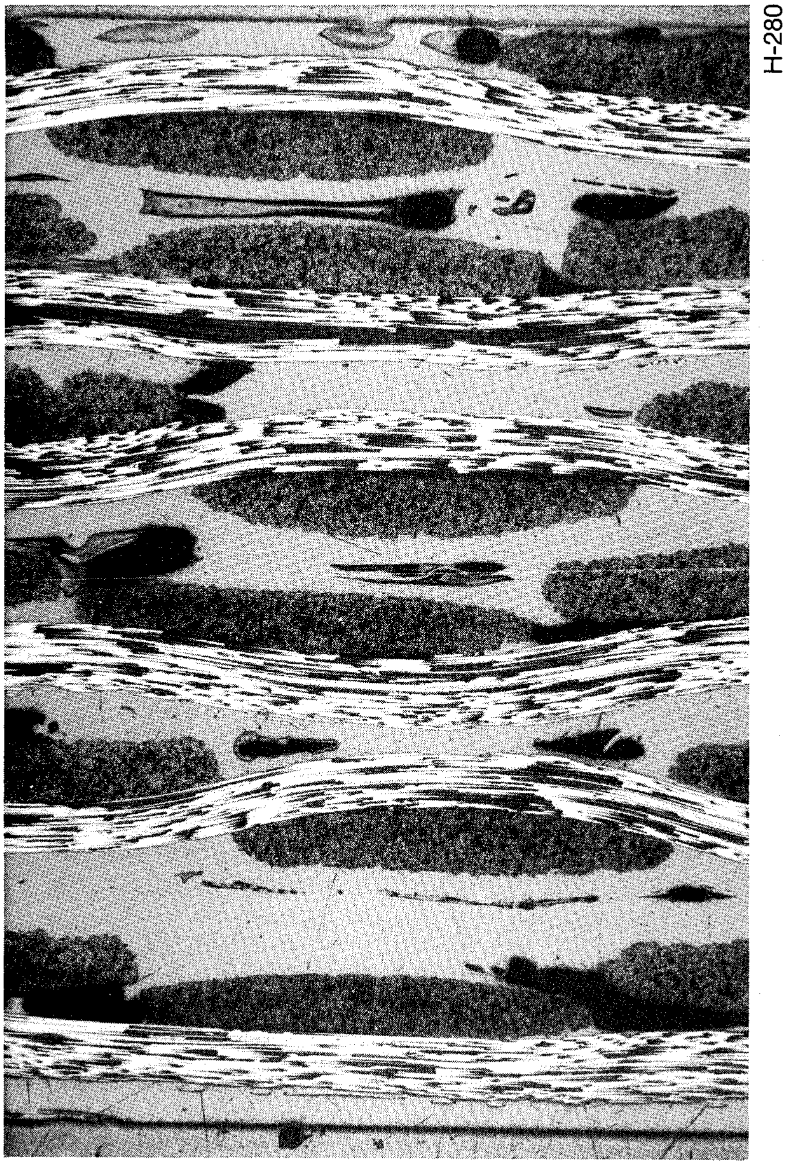


Figure 19. Polyimide Celion 3000 composite processed at 0.69 MPa

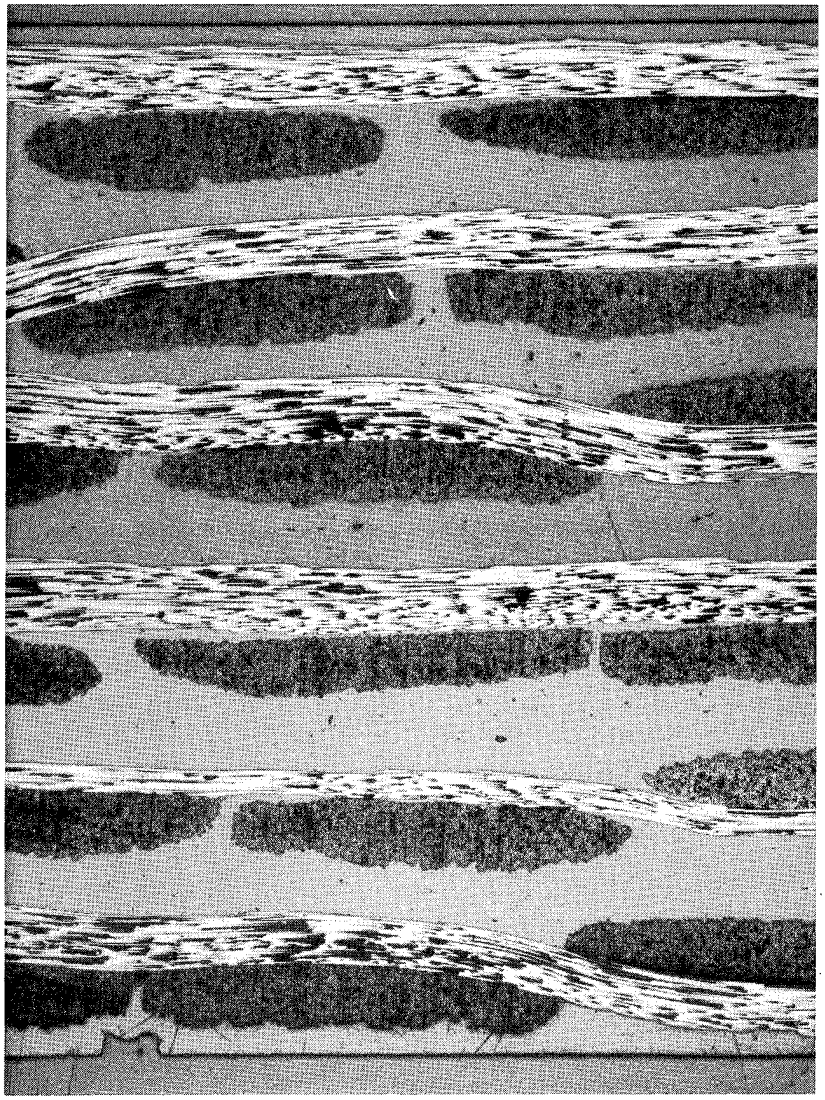


Figure 20. Polyimide Celion 3000 composite processed at 6.9 MPa

Based on the photomicrographs of the composites, it is obvious that more resin must be introduced into the fiber bundles and that placing half of the varnish on one side of the prepreg all at once is unacceptable.

The Acurex procedure for obtaining prepregs from PPQ-cresol varnishes was attempted with the 13 percent solids polyimide-cresol varnish. This tedious procedure requires multicoats of the varnish with partial cresol removal (at 132°C) and squeegeeing between each new application of varnish. A composite with a 3.71 mm per ply thickness was obtained from such a prepreg with 13.8 MPa processing pressure at 316°C. The void content calculated for this composite based on its per-ply thickness is 2.7 percent. This is a distinct improvement over the calculated void contents seen in Table 23.

The 50x photomicrographs of the low void content composite, however, revealed distinct resin knit lines between the carbon fiber plies. The origin of the knit lines is not clear. This composite was prepared from prepreg from which the epoxy size was not removed prior to impregnation by the polyimide varnish. Several subsequent composites were prepared wherein the epoxy size was removed and the knit lines do not appear to be present in such composites.

Mechanical properties were determined on one composite which had a low void content and no knit lines. Its room temperature properties are comparable to strengths obtained from epoxy resins and are indicated in Table 24.

TABLE 24. PROPERTIES OF LOW VOID CONTENT POLYIMIDE COMPOSITE[a,b]

Flexural Strength MPa (ksi)/Modulus GPa (msi)		
Test Temperature °C (°F)		
Ambient	82 (180)	121 (250)
751 (109)/ --	551 (80)/49 (7.1)	427 (62)/46 (6.7)
696 (101)/ --	503 (73)/47 (6.8)	372 (54)/47 (6.8)
Short Beam Shear Strength MPa (ksi)		
76 (11.0)	59 (8.6)	56 (8.1)
81 (11.8)	47 (6.8)	37 (5.3)

[a] Individual specimen strengths

[b] Celion 3000, 8-harness satin weave, epoxy size solvent removed, prepreg treated 16 hr at 200°C under vacuum molded 1 hr at 316°C, 2000 psi

SECTION 4

CONCLUSIONS AND RECOMMENDATIONS

1. Preparation of fully imidized polyimides is achieved by condensation in cresol at less than 15 solids content. Rapid heatup to the final reaction temperature of 180°C is not required for polyimides prepared from aliphatic amines but when such polyimides are modified with m-phenylenediamine, rapid heatup is important for the attainment of clear polyimide cresol varnishes.

2. Preparation of polybenzimidazoles from 3,3',4,4'-tetraaminobiphenyl with aliphatic diacids proceeds to high molecular weight products with melt condensation techniques.

3. Preparation of N-arylenepolybenzimidazoles from 4,4'-bis(o-aminoanilino)biphenyl from cyclic anhydrides readily provides high molecular weight polymers with modified (cresol fluxed) melt condensation techniques. High molecular weight polymers have also been attained from aliphatic diacids, but polymerization conditions are not well defined.

4. Without modification, only the polyimides from PMDA with aliphatic diamines and the polybenzimidazoles from 3,3',4,4'-tetraaminobiphenyl with aliphatic diacids have adequate heat distortion temperatures to suggest utility as composite matrix resins for 93°C application. Addition of less flexible diamines to the polyimides from BTDA or diacids to the N-arylenepolybenzimidazoles to form copolymers provides good heat distortion temperatures.

5. Solvent resistance testing of the polymers showed three classes of polymers to have excellent resistance to chloroform and other solvents. The polyimides from PMDA with aliphatic amines are crystalline and show excellent resistance to common organic solvents and humidity. Polyimides from BTDA with aliphatic amines and m-phenylenediamine as well as polybenzimidazoles from 3,3',4,4'-tetraaminobiphenyl with aliphatic diacids also demonstrated good resistance to common organic solvents and humidity. Elucidation of the operative mechanisms by which the latter two polymer classes achieve their solvent resistance did not occur. Postmolding, heat treatment of the m-phenylenediamine-modified aliphatic BTDA polyimides at 316°C improves the solvent resistance of these compositions.

6. Stressed solvent resistance testing of one polymer from each of the three polymer classes described above showed no evidence of attack or failure after 500-hr exposure to chloroform, acetone, or tricresyl phosphate.

7. It is recommended that efforts to optimize the solvent-resistant polymer compositions described above be continued. Optimization efforts must include identification of methods to successfully impregnate bundles of reinforcing

filaments, i.e., carbon or glass, as well as demonstration of the sought composite properties (i.e., strength, impact, and solvent resistance).

8. The polymer which appears to have the best balance of properties at this time is the polyimide from BTDA with 1,6-hexanediamine and m-phenylenediamine. Efforts should continue with this polymer composition.

9. Based on the outstanding solvent resistance of the polyimide from PMDA with 1,8-octanediamine, efforts should also continue with this crystalline composition.

APPENDIX

EXPERIMENTAL DETAILS AND PROCEDURES

A.1 PREPARATION OF ALIPHATIC POLYIMIDES

From Decomposition of the Salt

The polymer described immediately below is patterned after the preparation of polynonamethylenepyromellitimide, described in Reference 3. Into a 100-ml three-necked, round-bottom flask, protected by a drying tube, was placed 6.08 gm (0.279 mole) pyromellitic dianhydride and 30 ml absolute methyl alcohol. A clear solution was obtained in 20 min by gently swirling the mixture in a steam bath. Upon quantitative addition of 4.02 gm (0.0279 mole) 1,8-diaminooctane to the flask, a mild exotherm occurred. Distillation of the methyl alcohol from the salt left a thick, clear syrup which became a white, opaque foam upon application of vacuum to remove the last of the solvent.

The salt was transferred to a side-arm test tube fitted with a capillary inlet reaching to the bottom. Alternate vacuum and nitrogen purge was performed. With a slow nitrogen bleed through the capillary, the test tube was introduced into an oil bath at 137°C. The salt melted and foamed, which required collapsing by spatula to keep the melt below the oil level. Foaming again occurred. After 2.5 hr reaction at 137°C, the test tube with contents was placed into a 325°C oil bath for 2.5 hr.

A semitough, off-white foam was obtained, which was insoluble in hot m-cresol and cold sulfuric acid. Warming the surfuric acid to 60°C and holding at that temperature overnight provided a clear, swollen polymer gel. With additional heating of the neat resin foam for 2 hr under nitrogen at 350°C, the product turned brown and lost its toughness.

1,8-Octanediamine condensed with BTDA and MCTC, using the above conditions, produced a rubbery, tan product and an orange-brittle glass, respectively. Isophoronediamine with MCTC produced a black, low-viscosity liquid. It became obvious that even though proper conditions might be found for PMDA-based aliphatic polyimides, BTDA-based systems were very highly crosslinked. A more general synthesis procedure was needed.

From Decomposition of the Salt Using Phenol as a Fluxing Agent

Condensation using aromatic esters to produce polyimides[9] was investigated. On a 0.01-mole scale, PMDA was refluxed in 10 gm of phenol with 0.1 gm ethylmethylimidazole (EMI 24) base. The octanediamine was added to the cooled PMDA solution and reacted overnight in an oil bath at 105°C. An orange precipitate formed in the first hour of reaction, and no visible change occurred with overnight reaction.

The test tube was immersed into an oil bath at 218°C, and the reaction became homogeneous. After 1 hr, pump vacuum was applied and the polymer heated in the bath for an additional hour. The product was not soluble in refluxing m-cresol, even though it was previously soluble in phenol. It had an inherent viscosity of 1.40 dl/gm in sulfuric acid, with insolubles of 26 percent (overnight warming at 60°C required). Several additional attempts to achieve 100 percent sulfuric-acid-soluble polymer by phenol-fluxed melts invariably led to insoluble polymers.

By Solution Methods

Attempts were then directed toward solution condensation methods. Prior art discloses that several solvents are useful for achieving high-molecular-weight polyimides. However, a patent[10] discloses that cresol with additives is useful for obtaining polyamic acids at low temperatures (below 40°C), as expected for basic solvents such as N,N-dimethylacetamide. Further, the tetracarboxylic acid is disclosed as producing high-molecular-weight polymers in m-cresol[11]. The addition of tertiary amines to phenolic solutions of dianhydrides and diamines is disclosed[12].

PMDA With 1,8-octanediamine

In a 50-ml flask equipped with magnetic stir bar and nitrogen purge, 1.807 gm (0.125 mole) 1,8-diaminooctane and 30 ml cresols (distilled Koppers tar acids) were introduced. Powdered PMDA (2.73 gm; 0.125 mole) was added to the stirring solution rapidly. After 40-min reaction at 40°C, the PMDA had dissolved, and the reaction was very thick. Infrared spectra were conducted periodically on the progressing reaction. These analyses indicated unreacted anhydride in all samples taken through 140°C when the imide doublet began to appear.

The reaction was heated for 1 hr each at 40°, 60°, 100°, and 140°C and 30 min each at 160° and 180°C. The homogeneous reaction mixture was poured slowly into stirring methyl alcohol, filtered, and dried for 30 min at 110°C under vacuum. The product was insoluble in warm cresol, but completely soluble in warm sulfuric acid (60°C). Its inherent viscosity was 0.60 dl/gm.

BTDA With 1,8-octanediamine

BTDA and 1,8-octanediamine (0.0101 mole each) were reacted in 30 ml cresol and 0.2 gm (4 drops) EMI 24. The anhydride was predissolved in cresol with the base and heat. Upon cooling to below 60°C, the amine was added and the reaction heated as indicated in Table A.

A second reaction was carried out with heatup occurring over a 2-min period from 60° to 165°C. The reaction was reacted for an additional 2 hr at 170°C. The reaction was poured slowly into 300 ml methyl alcohol in a Waring blender on slow speed. Upon completion of the addition, the blender was turned up to full speed for 20 to 30 s. The isolated polymer was boiled for 10 min in fresh methyl alcohol, isolated, and dried. The inherent viscosity of the polymer was 1.54 dl/gm with a trace of insolubles, which was not observed in the slow heatup reaction described above.

TABLE A. POLYMERIZATION OF BTDA WITH 1,8-OCTANEDIAMINE IN CRESOL

Reaction Time (hr)	Temperature (°C)	Comments
1.25	84	
2	90	
3	100	
4.5	98	
5.75	112	Spectrum shows imide doublet, ester, and amine carbonyls. Sample into MeOH is stringy.
7	136	Imide doublet crisp, ester carbonyl absent, amine carbonyl disappearing. Sample into MeOH is stringy.
7.5	140	Sample gave η_{inh} of 0.38 dl/gm
18	140	Sample gave η_{inh} of 1.38 dl/gm
22	140	
25	170	
25.5	175	Reaction thicker than at 140°C. Sample gave η_{inh} of 1.30 dl/gm.
42	170	Reaction thicker. Sample gave η_{inh} of 1.66 dl/gm.

PMDA with 1,8-octanediamine (Rapid Heat Up)

To 40 ml cresol solution at 40°C containing 3.92 gm (0.0180 mole) PMDA and 4 drops EMI was added 2.60 gm (0.0180 mole) 1,8-octanediamine. The stirring mixture was immersed into an 180°C oil bath. The oil-bath temperature was increased to 190°C. After the reaction temperature reached 180°C, it was held at that temperature for 1 hr and worked up with methyl alcohol, as described above. The polymer was completely soluble in sulfuric acid with overnight warming at 60°C. Its inherent viscosity was 3.32 dl/gm.

A.2 PREPARATION OF ALIPHATIC POLYBENZIMIDAZOLES

To a 22 l flask were added 4.04 kg (20 mole) sebacic acid and 4.29 kg (20 mole) 3,3',4,4'-tetraaminobiphenyl which were thoroughly mixed together. The reactants were heated under nitrogen to a pot temperature of 185°C, and then poured into a large stainless steel box also capable of nitrogen purge. The closed purging box was placed into an air-circulating oven at 371°C. The polymer was heated to 315°C and held there for 2 hr. Upon removal of the polymer, it was diced with a band saw and finally coarse ground. Typical inherent viscosities of the polymer are between 0.7 and 1.2 dl/gm (H_2SO_4).

A.3 PREPARATION OF N-ARYLENEPOLYBENZIMIDAZOLES FROM ANHYDRIDES

To a side arm test tube was added 3.66 gm (0.01 mole) 4,4'-bis(o-aminoanilino)biphenyl, 1.68 gm (0.01 mole) methylhexahydrophthalic anhydride, and 3.0 ml cresols (distilled Koppers tar acids). Stirring and nitrogen purge were initiated. After 15 min at room temperature, an oil bath preheated to 240°C was placed immediately under the test tube such that the oil level was immediately below the test tube. After 30 min, the oil bath was raised to cover the bottom 2 inches of the test tube. Stirring was continued for an additional 30 min and the stirrer removed from the thickening polymerization.

After 16 hr at 240°C, the oil-bath temperature was increased slowly to 300°C (4 hr). After overnight treatment at 240°C, about 50 percent of the polymer had turned opaque (lump in bottom of test tube), and the remainder was clear. When the oil-bath temperature reached 300°C, vacuum was applied for 1 hr. Both opaque and clear polymer were present in the test tube upon cooldown; however, the quantity of clear polymer was only about 20 percent of the yield. Both polymers were soluble in cresol at room temperature. The clear polymer's inherent viscosity was 1.10 dl/gm, and the opaque polymer's was 1.62 dl/gm.

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1. Report No.
NASA CR-172285

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
Development of an Impact- and Solvent-Resistant Thermoplastic Composite Matrix

5. Report Date
1 April 1984

6. Performing Organization Code

7. Author(s)
C. B. Delano and C. J. Kiskiras

8. Performing Organization Report No.

9. Performing Organization Name and Address
Acurex Corporation/Aerotherm Division
555 Clyde Avenue, P.O. Box 7555
Mountain View, California 94039

10. Work Unit No.

11. Contract or Grant No.
NAS1-16808

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
Washington, D.C. 20546

13. Type of Report and Period Covered
Contractor Report

14. Sponsoring Agency Code

15. Supplementary Notes
Langley Technical Monitor: P. M. Hergenrother, NASA-Langley Research Center, Hampton, Virginia 23665

16. Abstract

Synthesis, moldability and chloroform, acetone and tricresyl phosphate resistance of 16 polymer compositions are described. These aliphatic heterocyclic polymers include polyimides, polybenzimidazoles, and N-arylenepolybenzimidazoles. A solution condensation (cresol) method to prepare imidized aliphatic polyimides is described. Two polyimides and one polybenzimidazole demonstrate no crazing or cracking during 500-hr exposure to the cited solvents under stress. Modification of one aliphatic polyimide with several aromatic amines suggests that m-phenylenediamine is singular in its behavior to improve the chloroform resistance of that class of polyimides.

17. Key Words (Suggested by Author(s))
Aliphatic polyimides
Aliphatic polybenzimidazoles
Synthesis
Molding
Solvent resistance
Physical properties

18. Distribution Statement
Unclassified -- unlimited

19. Security Classif. (of this report)
Unclassified

20. Security Classif. (of this page)
Unclassified

21. No. of Pages
69

22. Price

N-305

For sale by the National Technical Information Service, Springfield, Virginia 22161