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Adhesively bonded structures offer weight savings, ease of fabrication, and absence of stress concentrations arising from holes and fasteners. However, the drawbacks of curent high performance resins, i.e. high paste viscosity and chemical cure shrinakge, often present uncertainties in the quality and durability of the bondlines. This program presents methodologies and approaches that seek to mitigate these difficulties through innovative chemical modifications and blending of monomers.

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Executive Summary

This Final Report describes the result gathered in the STTR Phase II program to develop (1) high temperature low viscosity adhesives and (2) high temperature adhesives with low cure shrinkage. Adhesively bonded structures offer weight savings, ease of fabrication, and absence of stress concentrations arising from holes and fasteners. However, the drawbacks of current high performance resins, i.e. high paste viscosity and chemical cure shrinkage, often present uncertainties in the quality and durability of the bondlines. This program presents methodologies and approaches that seek to mitigate these difficulties through innovative chemical modification and blending of monomers. Results in this program show that cure shrinkage in polymer networks can be mitigated and tailored by blending the resin with monomers that expand during polymerization, thus reducing the internal stress that arises from the reduction in chemical bond distances during polymerization. In addition, by modifying the chemical structures of these expanding monomers, thermophysical and adhesive properties of the adhesive joints can be improved over unmodified formulations. Modifications in the microstructural and blending ratios between monomers with various isomeric architectures have also been shown to improve the properties of high performance adhesives. Structure-property relationships of these adhesive formulations show that steric hindrance, rotation freedom, and chain lengths all play important roles in the processability of the formulations. Judicious selection and blending of these molecules can obtain adhesives with wider processing windows and lower cure pressures.

Part I. Development of Low Cure Shrinkage Adhesives

1. Introduction

Polymers are increasing used to fabricate high performance materials such as reinforced composites and adhesive joints. Each application has a specific set of property requirements that must be met or exceeded by the polymer. These requirements include a combination of various physical, mechanical, and electrical properties such as tensile strength, flexural strength, impact resistance, solvent resistance, dielectric constant and strength, hardness, and glass transition temperature, to name a few. Polymer properties are affected by several polymerization conditions such as monomer purity, cure schedule, catalyst stoichiometry, and degree of crosslinking.

Another factor, often overlooked, that influences the properties is volume change during polymerization. Negative volume change (shrinkage) is present to some degree during polymerization in all of the present monomer polymerization processes and has been tolerated and "lived with" for many years. The principal reasons for tolerating polymerization shrinkage were that no method was available to completely eliminate it, and no new monomers had been developed which produces positive volume change (expansion) during polymerization. If it were possible to "dial-in" the specific polymerization volume change required for each application, greatly improved polymer properties could be obtained and would result in the manufacture of more reliable and durable industrial and commercial products.

For example, for composites structures, it would be highly desirable to have monomers that exhibit near zero shrinkage during polymerization so as to produce strain-free materials. Adhesively bonded structures would also benefit from zero (or near zero) cure shrinkage so as to prevent crack initiation in the bond lines due to the shrinkage of the adhesive from the substrates. For other applications, such as precision casting, dental fillings, and fiber optic feedthrough seals, it would be advantageous to have monomers that produce slight.positive expansion during polymerization so as to achieve complete filling and mold replication.

The objective of this program is to understand and demonstrate the significance of monomers that expand during polymerization, specifically in the fabrication of adhesive bonds.

2. Experimental

Monomers

Bailey[1] first reasoned that to find monomers that would give near zero shrinkage or even positive expansion on polymerization, the most viable approach would be the study of bicyclic compounds. In bicyclic monomers, it is possible that for every bond that undergoes a shift from a van der Waals distance to a near van der Waals distance, producing an expansion. Among these bicyclic monomers is spiro orthocarbonates (SOC), which are more thermally stable and produce high volume expansions than other bicyclic monomers. We selected two SOC monomers to be investigated in this program, the syntheses of which are described below.

1. Diallyl Spiro Orthocarbonate

Diallyl spiro orthocarbonates (DASOC) was prepared from commercially available diethyl allylmalonate as shown in Figure 1[2]. The monomer is a low melting, waxy material (mp. 45°C).

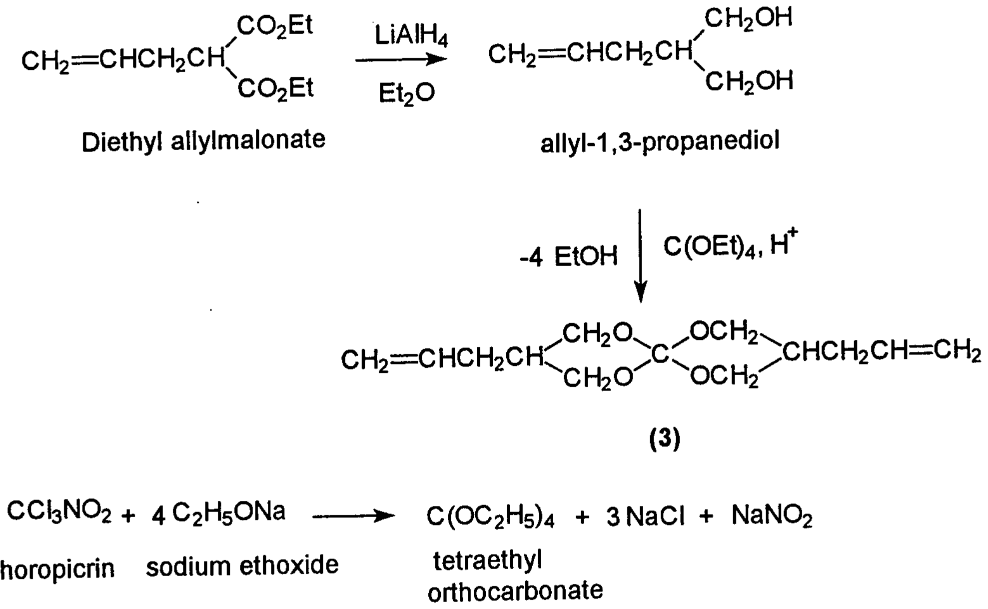

Figure 1. Synthesis of Dially Spiro Orthocarbonate (DASOC)

2. Dibenzo Spiro Orthocarbonate

Dibenzo Spiro Orthocarbonate (DBSOC) was prepared as shown in Figure 2[3]. The monomer is a crystalline material with a melting point of 240-245°C. Prior to use, DBSOC is pulverized by jar milling in acetone for seven days, resulting in a particle size of 2-5 microns.

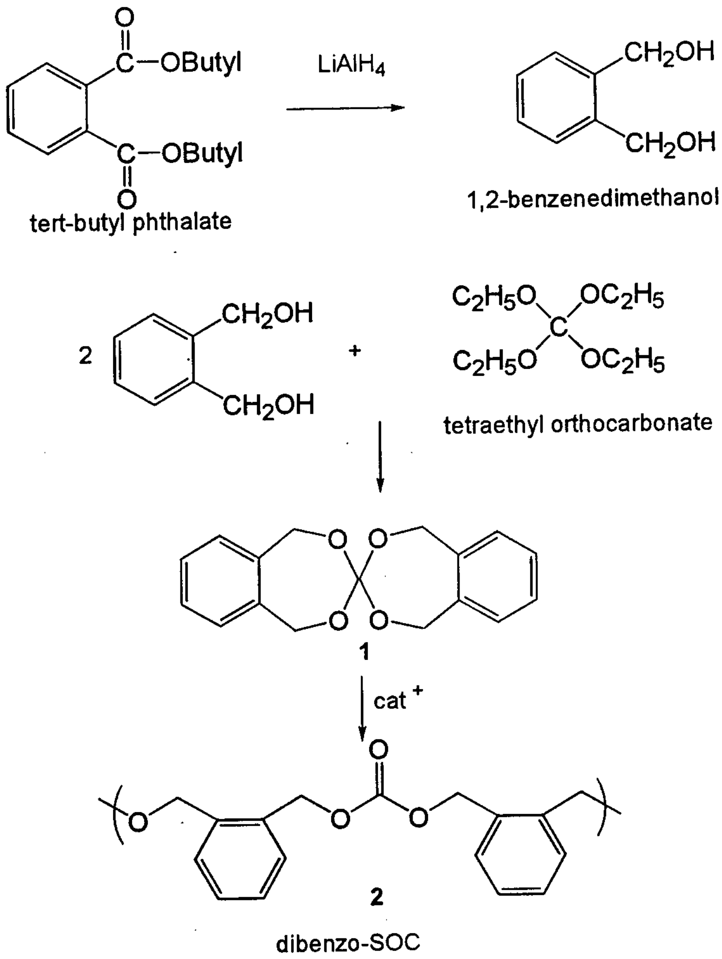

Figure 2. Synthesis of Dibenzo Spiro Orthocarbonate (DBSOC)

Polymer Blends with Expanding Monomers

The expanding monomers were blended with bismaleimides to demonstrate its effectiveness in reducing cure shrinkage. Matrimid® 5292 from Ciba Geigy is a high performance bismaleimide consisting of two components: a crystalline 1,1'-(methylenedi-4,1-phenylene)bismaleimide (Part A) and a viscous liquid diallyl bisphenol A (Part B). Since DASOC is a low melting solid, it was melt blended into the Matrimid formulation at elevated temperatures (about 150°C).

However, for DBSOC acetone slurry containing the required amount of the expanding monomer was pre-blended with Matrimid Part B, forming a paste. Acetone was then removed under reduced pressure, and the Part B/DBSOC mixture was then used to complete the formulation with Matrimid Part A at elevated temperature. Because of the presence of the high melting DBSOC as the dispersed phase, the blended formulation was opaque, as opposed to a clear formulation exhibited by the use of DASOC in the blend.

Preparation of Impregnated Scrim Cloth

Glass scrim cloth (112E, A1100 finish) was used. The cloth was impregnated with a solution of the bismaleimide/SOC blend at a concentration of about 25-30%. Because Matrimid Part A tends to precipitate out when the solvent was being evaporated, the usual method of repeated immersion could not be used, as the Part A powder tend to be dislodged in the solvent during repeated immersions. Instead, a pre-calculated amount of the resin blend necessary to yield a 60% solid content for the scrim cloth prepreg was dissolved in 1,3-dioxolane to form a 25-30% solution contained in a Teflon-lined tray, and the solution was allowed to evaporate overnight in a fume hood under a heat lamp. The 1,3-dioxolane, being a higher boiling solvent (bp. 74-75°C), enabled Matrimid Part A to adhere better to the cloth than with other low boiling solvents such as acetone or THF. They were cut to pieces measuring 0.5 inch wide for adhesive bonding.

Preparation of Lap Shear Joints

Because of the relatively lower temperature capability of bismaleimides than polyimides, the use of BMI adhesives is probably more suitable to the bonding of advanced composite laminates than metallic substrates. We therefore selected PMR-15 laminates as the substrates for adhesive bonding. Six-ply PMR-15 laminates were cut into 1" x 4" coupons, cleaned with acetone wipes, with a one-inch wide tab sanded with sandpaper to provide for mechanical roughening for bonding. Separately prepared primer solutions of the BMI/SOC blend as prepared previously for the prepregs was used to coat the roughened areas by brushing and the solvent removed under reduced pressure. The lap shear joints were then fabricated using a half-inch overlap of the scrim cloth using standard fabrication methods by compression molding. After cure, the excess scrims were cut and the joints were tested in a tensile tester for lap shear strengths.

3. Results and discussion

Formulation of Expandable Monomers

For a number of industrial applications, such as strain-free composites, it appears highly desirable to have monomers that will polymerize with near-zero shrinkage; while for other applications, such as high strength adhesives, it appears that slight positive expansion is beneficial. However, for either case, it is imperative that the polymer network be substantially formed before ring opening of the expandable monomer, so that the benefit of volume expansion can be utilized to compensate for the cure shrinkage. Therefore the blending of the expandable monomers in the matrix monomer is an important parameter in the development of low cure shrinkage composites and adhesives.

Bismaleimides are used as the matrix in this program. Matrimid® 5292, consisting of 1,1'-(methylenedi-4,1-phenylene)bismaleimide as Component A, and diallyl bisphenol A as Component B are used, with the diallyl spiroorthocarbonate (DASOC) replacing part of the Component B, so that the proper stoichiometry for the BMI is maintained. The processes of formulating processable BMI with reduced cure shrinkage include the following considerations.

1. Catalysed Initiation of Bismaleimide Polymerization

The polymerization of BMI resins occur via a Diels Alder reaction between the maleimide and the allyl functional groups, at a relatively high temperature of above180°C, as shown in Figure 3.

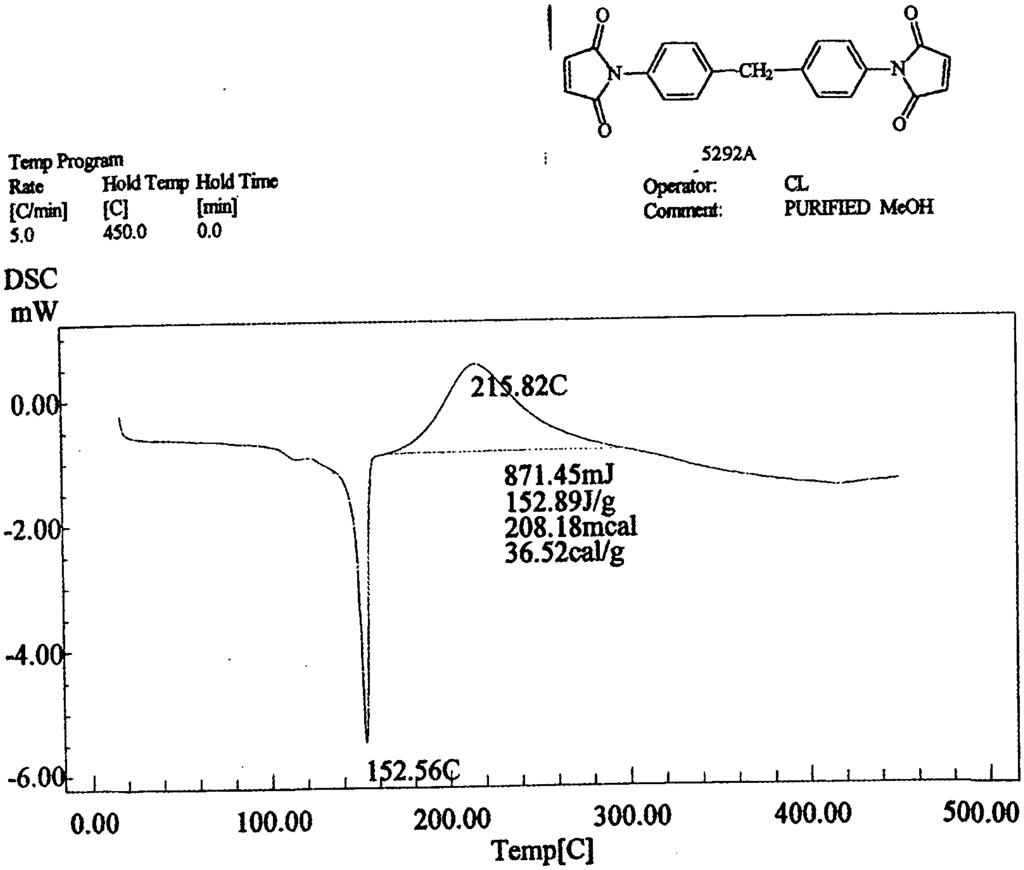

Figure 3. Cure thermogram of Matrimid 5292

However, this is also near the temperature for the cationic ring opening of the DASOC monomers, and therefore polymerization and ring opening reactions would be occurring simultaneously, adversely affecting the effectiveness of the expandable monomers. Since the Diels Alder reaction proceeds via a free radical method, a variety of peroxides were investigated to determine the effect of the type and concentration on bismaleimide polymerization. To be effective, the peroxide has to satisfy several conditions:

a. It must be miscible with the bismaleimide and SOC monomers.
b. The decomposition temperature must be higher than 150°C, which is the temperature at which Matrimid 5292 Component A melts and are blended with the Component B.

c. Upon decomposition, the reactivities of the free radicals must be high enough to initiate the Diels Alder reaction without evolution of by products such as moisture or gases.

Differential scanning calorimetry was used to screen various candidate peroxides. Tert-butylperoxybenzoate was selected because it satisfies all the above requirements. It is also a liquid, which enables a homogeneous blending into the monomer melts.

The concentration of the peroxide catalyst in the monomer blend is important because excessive free radicals concentrations in the blend will decrease the polymeric chain length and increase the crosslinking density, thus adversely affecting the mechanical and fracture properties of the cured polymer network. To determine the optimal concentration of peroxide catalyst, the cures of samples containing various concentrations of tert-butyl peroxybenzoate were studied, as shown in Figure 4. The plots show that at around 145-150°C, free radical polymerization of the bismaleimide monomers as initiated by the peroxybenzoate was proportional to the concentration of the free radical initiator. Interestingly, at the temperature region where the pure bismaleimide ordinarily starts to polymerize (210°C), the cure exotherm decreases as a function of peroxide concentration, indicating that the cure of the bismaleimide network has been shifted to lower temperature by the presence of the peroxybenzoate initiator. This would enable the creation of a two separate cure process: the polymerization of the bismaleimide resin at a lower temperature, followed by a ring opening polymerization of the expandable monomer at a higher temperature region.

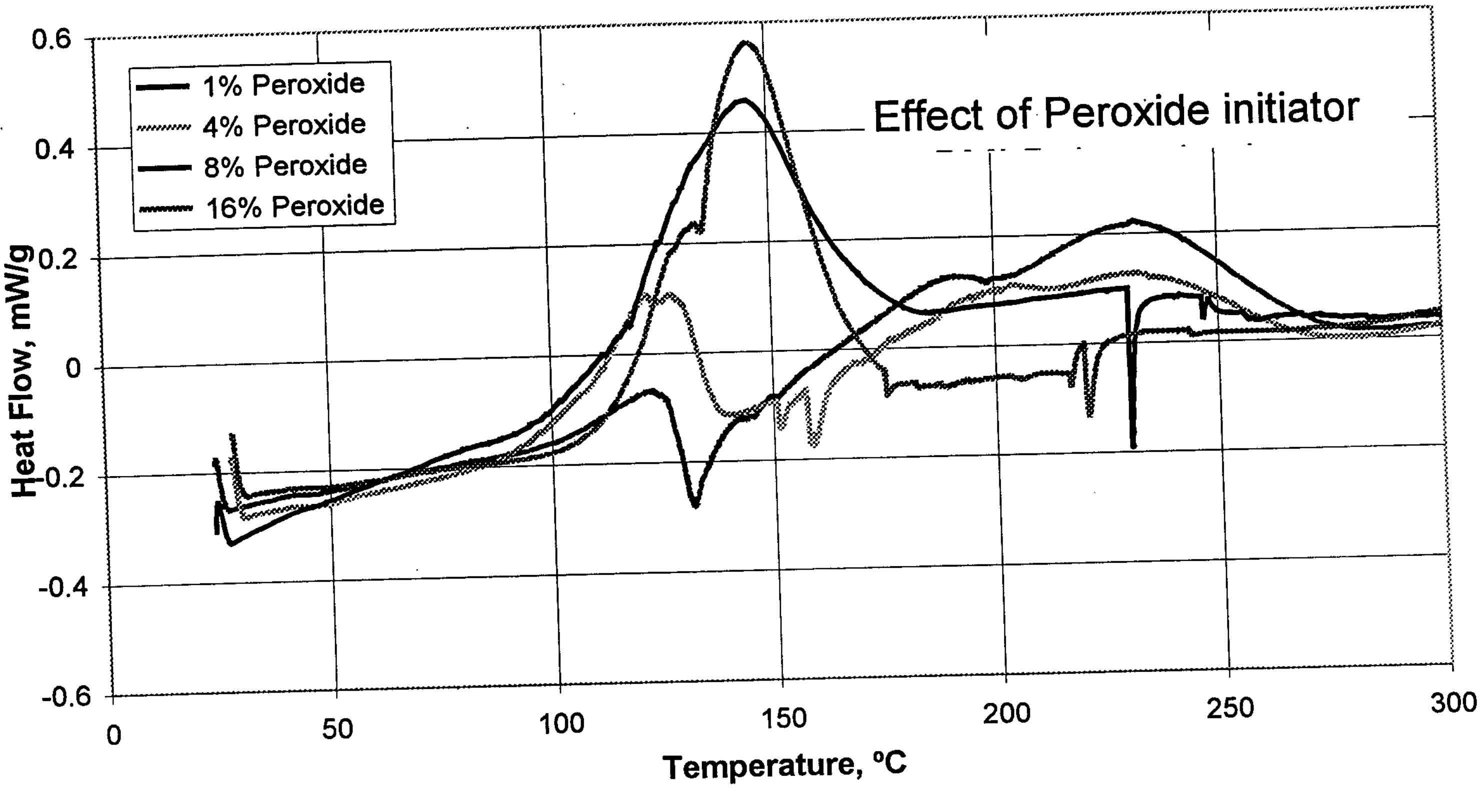

Figure 4. Effect of Peroxides on Polymerization of Matrimid 5292

Effect of Catalyst Type on Ring-Opening Efficiency

There are several cationic catalysts that can be used to polymerize spiro orthocarbonates monomers, such as Lewis acids or boron trifluoride-etherates. However, these catalysts are impractical to use in commercialized formulations because of its volatility, short shelf life and processing windows. New cationic catalysts for the high-energy cure of polymers (e.g. UV and e-beam) have been found to be more versatile than the BF_3 complexes. Such catalysts consist of a stable organic cation and an organometallic anion that does not readily decompose to a halogen acid. We examined the efficacy of three such catalysts: Triarylsulfonium hexafluoroantimonate (SbF_6), triarylsulfonium hexafluorophosphate (PF_6), and triarylsulfonium hexafluoroarsenate (AsF_6). The degrees of conversion by the respective catalysts as a function of reaction time were measured, as shown in Figure 5.

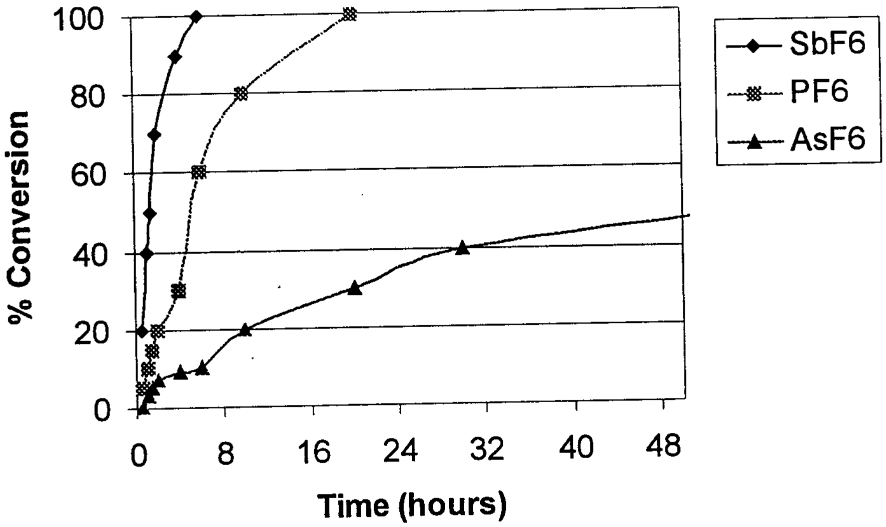

Figure 5. Ring-opening reactivity of cationic initiators at 150°C

The data show that triarylsulfonium hexafluoroantimonate and triarylsulfonium hexafluorophosphate are very similar in their respective reactivity towards ring opening, while triarylsulfonium hexafluoroarsenate is much less reactive, resulting in a cure time that is impractical for the processing of the formulated adhesive. One explanation for the difference in reactivity comes from the molecular modeling of the catalysts[4], in which the ionic distances between the anion and cation species for the catalysts increases in the order $AsF_6^- < PF_6^- \cong SbF_6^-$, as shown in Figure 6. The shorter ionic bond length for the triarylsulfonium hexafluoroarsenate implies that dissociation of the catalyst into cations which catalyses the ring opening reaction is less favorable than the other two catalysts, resulting in a lower polymerization rate. Thus either triarylsulfonium hexafluoroantimonate or triarylsulfonium hexafluorophosphate can be used as ring-opening initiators for the spiroorthocarbonate monomers.

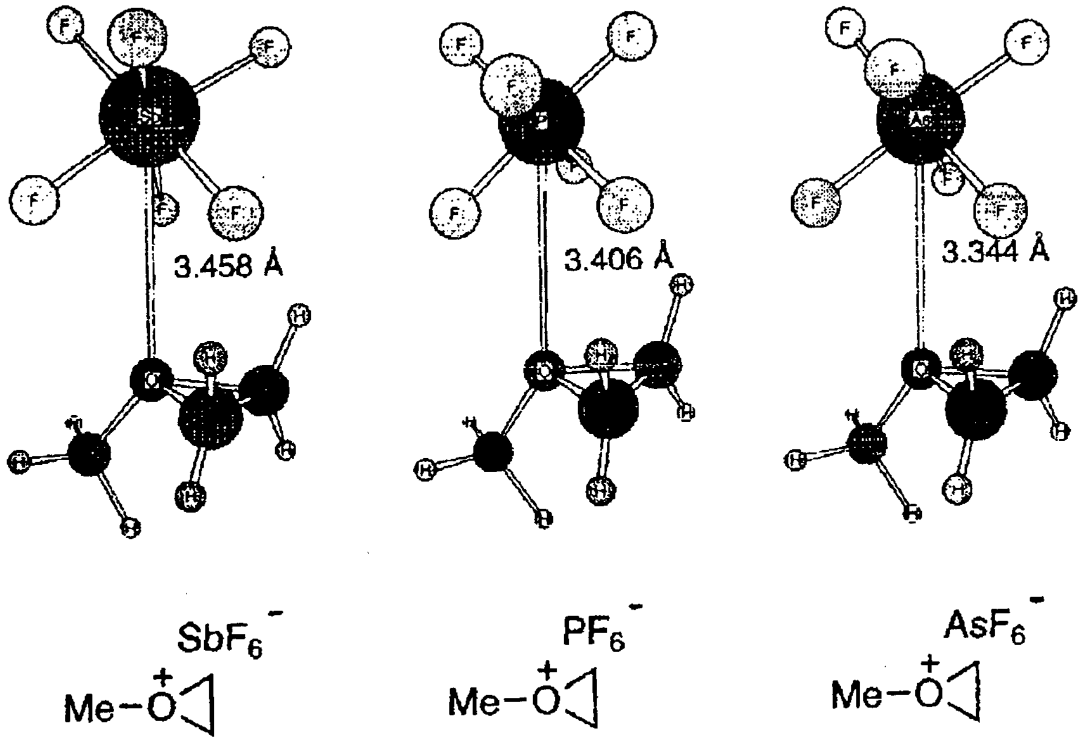

Figure 6. Ionic bond distances between various cationic catalysts

Effect of Cationic Catalyst Concentration on ring Opening of Spiro Orthocarbonate

We have shown that the efficiency of the catalyst is dependent on the acid strength of the cation-anion complex. Also, the efficiency of the catalyst as a terminator is related to the base strength of the complex anion. Thus, the more active a molecule is as a catalyst, the less active it is as a terminator. In general, the rate of initiation is

$$v_i = \mathrm{K}\,[\mathrm{A}][\mathrm{M}][\mathrm{RH}] \tag{1}$$

where A = catalyst, M = monomer, and RH = cocatalyst (if present). Since in strong contrast to radical polymerization, termination is first order for cationic polymerization,

$$v_t = k_t\,[\mathrm{M}^+] \tag{2}$$

where $[\mathrm{M}^+]$ is written as an abbreviation to the activated complex $[\mathrm{M}^+\ {}^-\mathrm{A}]$. By the steady-state assumption,

$$[\mathrm{M}^+] = \mathrm{K}\,(k_i / k_t)\,[\mathrm{A}]\,[\mathrm{M}]\,[\mathrm{RM}] \tag{3}$$

and the over-all polymerization rate is

$$v_p = k_p\,[\mathrm{M}][\mathrm{M}^+] = \mathrm{K}\,[\mathrm{A}][\mathrm{RM}][\mathrm{M}]^2 \tag{4}$$

Therefore Eqn. 4 shows that the rate of polymerization is proportional to the concentration of the initiator. The degree of polymerization depends on whether chain transfer or termination predominates. If termination predominates over transfer,

$$x_n = v_p / v_t = k_p\,[\mathrm{M}^+][\mathrm{M}] / k_t\,[\mathrm{M}^+] = [\mathrm{M}]\,k_p / k_t \tag{5}$$

whereas if transfer predominates,

$$x_n = v_p / v_{tr} = \{ k_p\,[\mathrm{M}^+][\mathrm{M}]\} / \{k_{tr}\,[\mathrm{M}^+][\mathrm{M}]\} = k_p / k_t \tag{6}$$

Since the reaction is carried in a solventless medium, and the bismaleimide polymerization is not a cationic reaction, we can assume that degree polymerization is determined by termination (Eqn. 5), i.e. independent of the initiator concentration. Figure 7 shows the curing thermogram of bismaleimide-DASOC blends at various levels of the cationic initiator triarylsulfonium hexafluoroantimonate. Samples in Figure 7 consist of blends containing the respective cationic initiators (in mol %) and 8 wt% of tert-butyl peroxybenzoate as described previously. The data show the initiation the bismaleimide resin, as catalyzed by the peroxybenzoate occurred at about 150°C. Subsequent to the BMI initiation, at about 190°C, the cationic initiation of the spiro orthocarbonates started. Integration of the heats of reactions show that samples containing various concentrations of the cationic initiators (in mol%) increases according to 5mol % (15 cal/g) < 10 mol% (17 cal/g) < 30 mol% (20 cal/g). This is in agreement with Eqn. 4, showing that the polymerization rate is proportional to the initiator concentration.

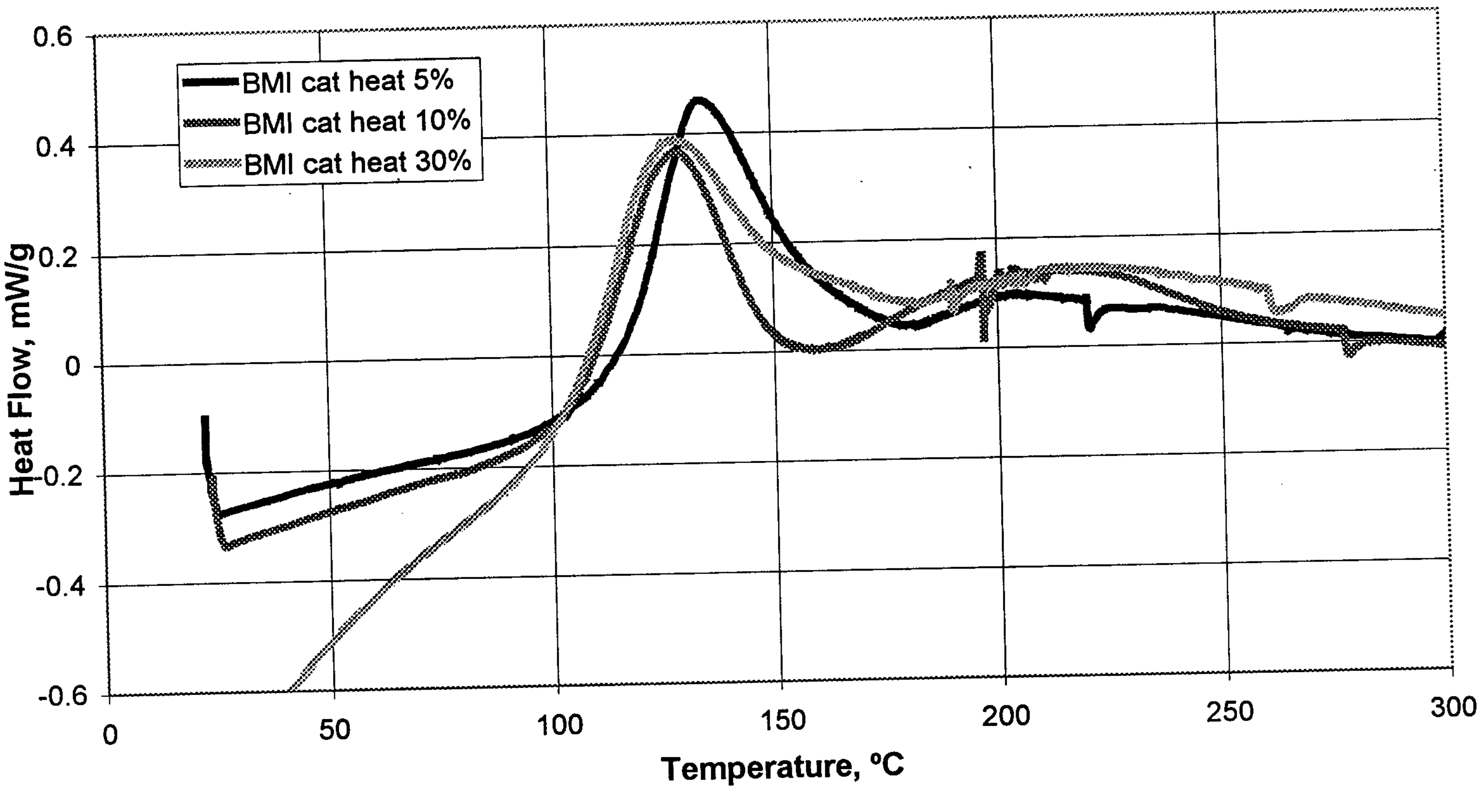

Figure 7. Cure Thermograms of BMI-DASOC as function of Catalyst Concentration

Volume Expansion Characterization

Volume expansion was characterized by dilatometry and specific gravity measurements of the fully cured BMI-DASOC samples.

1. Dilatometry

The visualization of volume change accompanying the cure reaction of samples with and without expanding monomers is important for the verification of the expanding monomer concept. Following the description provided by Snow and Armistead[5], a dilatometer was constructed from commercially available glassware. As shown in Figure 8, the dilatometer used in this work consists of three main parts: a detachable bulb, a graduated precision bore capillary, and a filling apparatus. Because most thermosets, including bismaleimides, adhere to glass, problems arose as a consequence of the adhesion of the resin to the glass bulb. Various glass surface treatments were tried to allow the removal of the cured resin plug from the bulb, but only the Glassclad 6C from Petrach Systems, Bristol, PA proved useful for this purpose. Following the procedures described by Snow and Armistead, samples were introduced into the bulb, and immersed into a silicone oil bath preheated to 150°C. Height of the mercury in the capillary was followed at regular intervals.

Data for unmodified bismaleimide and a BMI-DASOC sample containing 30 mol% of cationic initiator is shown in Figure 9. The data show that for the unmodified BMI, cure progressed with a decline in the mercury level, indicative of a cure shrinkage, leveling at about 30 minutes. However, for the BMI-DASOC sample, there was an increase in the height of the mercury column, indicative of an expansion of the resin, leveling at about 3 hours after the immersion into the silicone bath. This continual increase in volume agreed well with the chemistry of the cationic nature of polymerization, for which in the absence of chain transfer agents, maintains a "living polymer" stage until all monomers are consumed. This continual ring opening addition has been shown to be advantageous in mitigating the shrinkage as further post-curing continues.

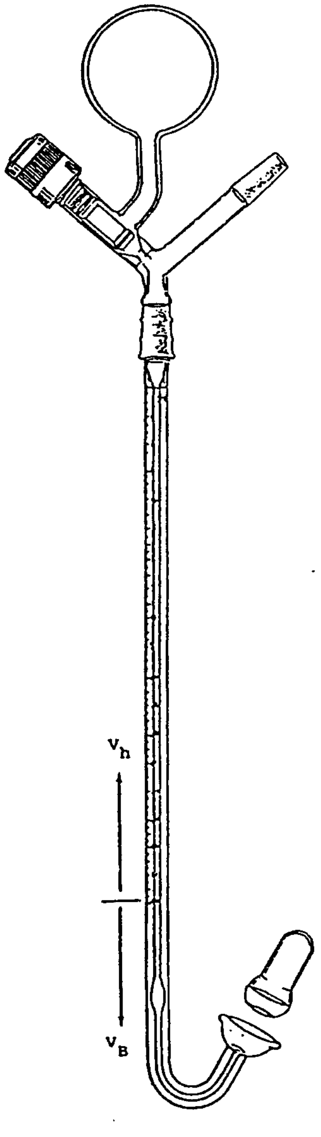

Figure 8. Dilatomer

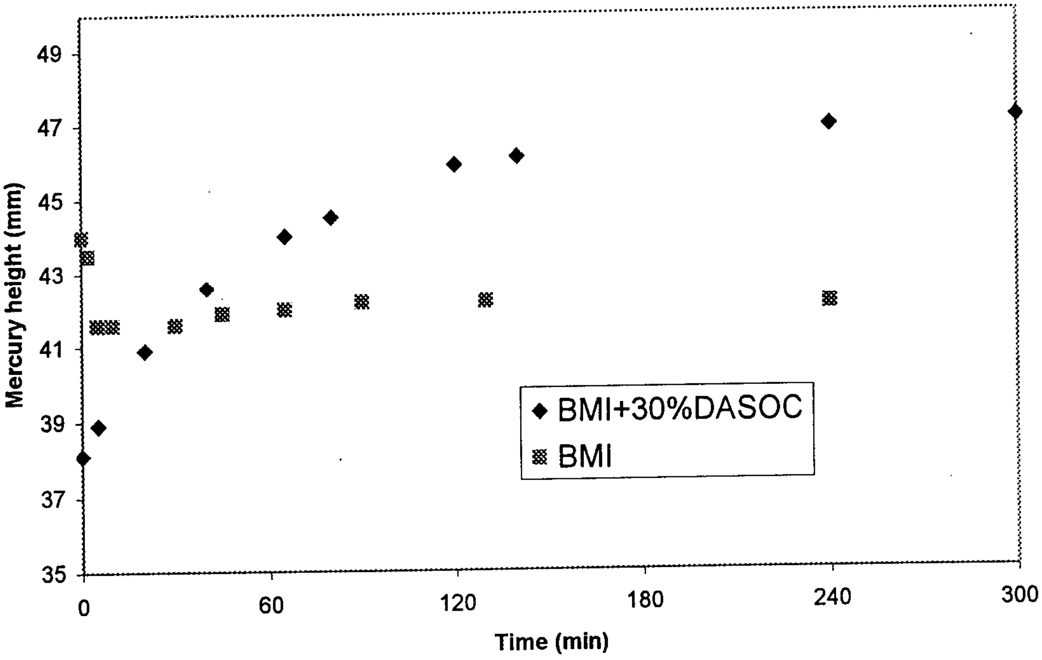

Figure 9. Dilatometry of BMI and BMI-DASOC at 150°C

Specific Gravity Measurements

While dilatometry provides visualization of the efficacy of the expanding monomer to mitigate cure shrinkage, the method is tedious and requires frequent recalibration of the capillary/bulb assembly after cleaning. In later experiments, specific gravity measurements were used. Samples were formulated with 8 wt% tert-butyl peroxybenzoate as free radical generator and 10 mol% triarylsulfonium hexafluoroantimonate as cationic initiator. To prepare the specimens, predetermined Matrimid 5292 Components A and B were premelted and thoroughly mixed to form a transparent liquid at 150°C, cooled to 125-130°C, and then the appropriate amount of the spiroorthocarbonate expanding monomer and the cationic initiator was stirred in the BMI melt at 130°C. After degassing at 130°C, the required amount of peroxybenzoate free radical generator was added. The hot mixture was then transferred to aluminum weighing dishes and cured with a cure schedule suggested by Ciba Geigy: 1 hour at 150°C, 2 hours at 200°C and 6 hours at 250°C. The specimens were dark brown, transparent, similar to unmodified Matrimid resins. Specific gravity measurements were carried out in deaerated distilled water, as shown in Table I.

Table I. Specific Gravity of BMI and BMI-DASOC Experimental Blends

Composition	% volume change
Matrimid 5292	-5.2
+7%DASOC	-2.5
+20%DASOC	-1.1
+30%DASOC	+0.4

The data show that the blending of DASOC was able to reduce the amount of cure shrinkage in BMI resins.

Thermophysical Properties

Glass transition temperatures, water absorption, and thermogravimetric measurement of the BMI-DASOC blends were measured, as shown in the following Tables.

Table II. Glass Transition Temperatures of BMI and BMI-DASOC Blends

Composition	Tg (C)
Matrimid 5292	318
+7%DASOC	312
+20%DASOC	302
+30%SASOC	300-305

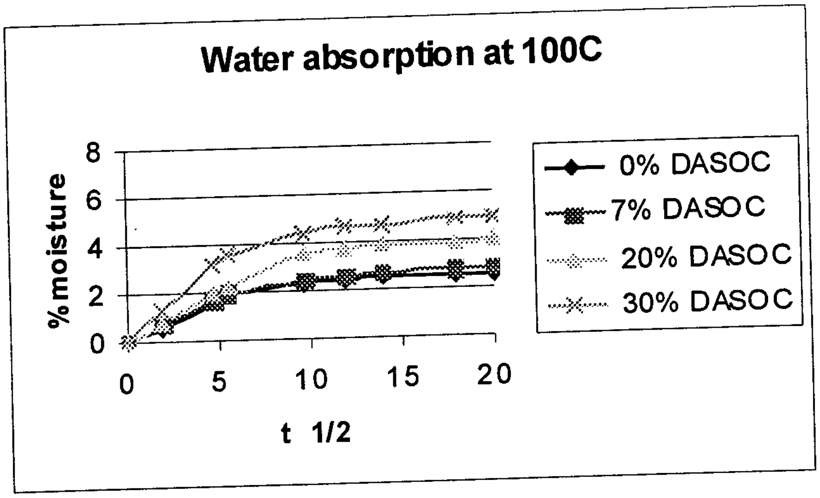

Figure 9. Water Absorption of BMI and BMI-DASOC Blends

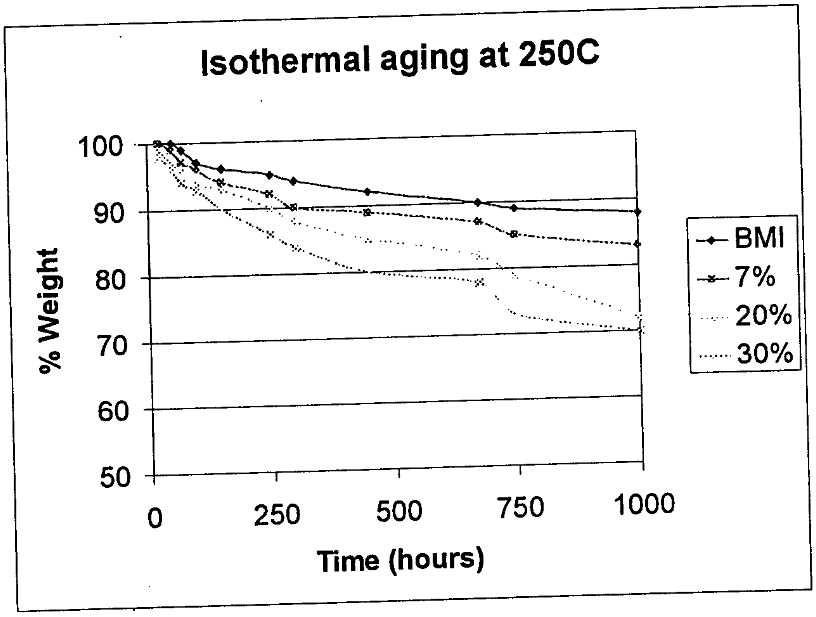

Figure 10. Isothermal Aging of BMI and BMI-DASOC Blends

The above data show that diallyl spiroorthocarbonate forms miscible blends with Matrimid 5292 bismaleimide resins, and when catalyzed with an appropriate cationic initiator, mitigating cure shrinkage due to the polymerization of the BMI monomers. More interestingly, at about 30% DASOC content, there appeared to be essentially no cure shrinkage. However, there are some drawbacks to the BMI-DASOC system when used as a high temperature matrix resin. The moisture sensitivity of the specimens containing DASOC was shown to be higher than that of the unmodified BMI, probably due to the increased polarity of the blend, which now contained carbonate groups. In addition, the isothermal aging characteristics of the blend also was lower than the unmodified bismaleimide, again potentially due to the more thermally labile ether linkages in the linear orthocarbonates functionality. Therefore in order to circumvent these deficiencies, and yet retain the benefits provided by the expanding monomer concept, a more thermally stable expanding monomer needs to be developed as an alternative to DASOC.

Dibenzo Spiroorthocarbonate

The decrease in thermooxidative stability of the BMI-DASOC blend during long-term testing was thought to be due to the aliphatic nature of the DASOC monomer. To test this hypothesis, a spiroorthocarbonate containing aromatic functionality was prepared, as shown in Figure 2. The dibenzo spiroorthocarbonate monomer (DBSOC) is a high melting crystalline (MP 240-245°C) material that must be reduced to micron-sized particles and used as a slurry with the matrix resin, thus adding several processing steps to the processing procedures. Table III compares the glass transition temperatures of the blends using DBSOC as the expanding monomer, showing that there is a slight increase in the Tg for the blend BMI-DBSOC.

Table III. Glass Transition Temperatures of BMI-SOC Blends

% SOC	+DASOC	+DBSOC
0 (baseline)	318	318
+10	312	314
+20	302	307
+30	300-305	303-305

The effect of using DBSOC in Matrimid 5292 on the volume change during polymerization is shown in Table IV. The data show that the % volume change is similar to that of DASOC, since the ring sizes between the two expanding monomers are quite similar.

Table IV. Volume Shrinkage of BMI-DBSOC

Composition	**% Volume Change**
Matrimid 5292	-5.2
+10% DBSOC	-3
+20% DBSOC	-1.9
+30% DBSOC	+0.9

Figures 11 and 12 show the comparison of thermooxidative stabilities between DA- and DB-SOC in Matrimid 5292. The data show that the presence of aromatic functionality in the DBSOC indeed improved the thermal stability of the BMI-DBSOC blend.

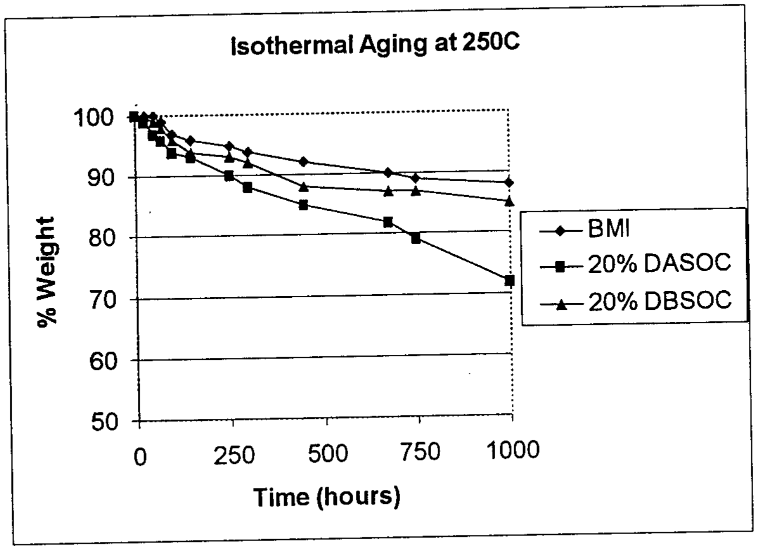

Figure 11. Isothermal Aging of BMI-SOC (20% blends) at 250°C

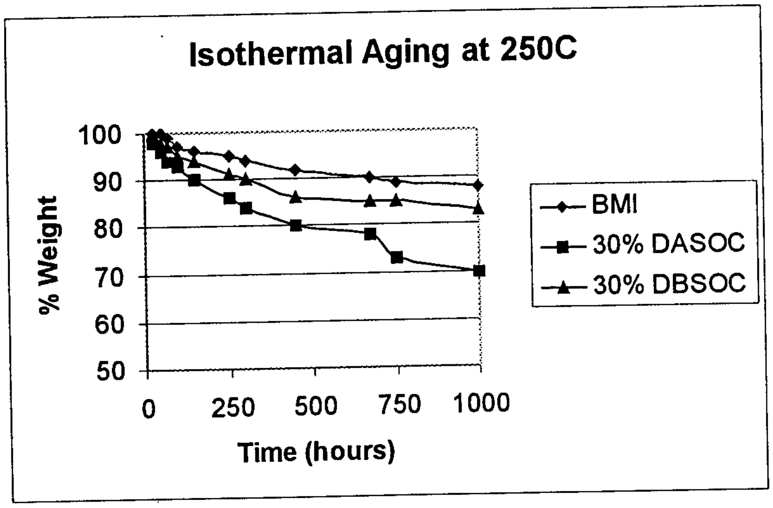

Figure 12. Isothermal Aging of BMI-SOC (30% blends) at 250°C

Adhesive Strengths

Lap shear joints with PMR-15 as substrates were fabricated as described in the experimental section. Five joints were made for each formulation. The average results of each of the formulations, cross-referenced with the percent cure shrinkage, are tabulated in Table V.

Table V. Lap Shear Strengths of BMI-SOC Blends

Composition	Lap Shear Strength (Mpa)	Cure Shrinkage (%)
Matrimid 5292	13.5	-5.2
+10%DBSOC	13.8	-3.0
+20%DBSOC	15.6	-1.9
+30%DBSOC	18.5	+0.9
+7%DASOC	14.0	-2.5
+20%DASOC	16.5	-1.1
+30%DASOC	17.9	+0.4

The results clearly demonstrated that by reducing cure shrinkage, the bond strengths of the joints are improved. Most significantly, when there is an overall expansion, the shear strengths indicated the most improvement in percentage over the other formulations. Another interesting observation is that the morphologies of the failure surfaces are similar among the samples. First of all, all as-fabricated joints show reasonable amounts of resin flow from the joint, indicating good coverage and wetting of the bond areas, as shown in Figure 13.

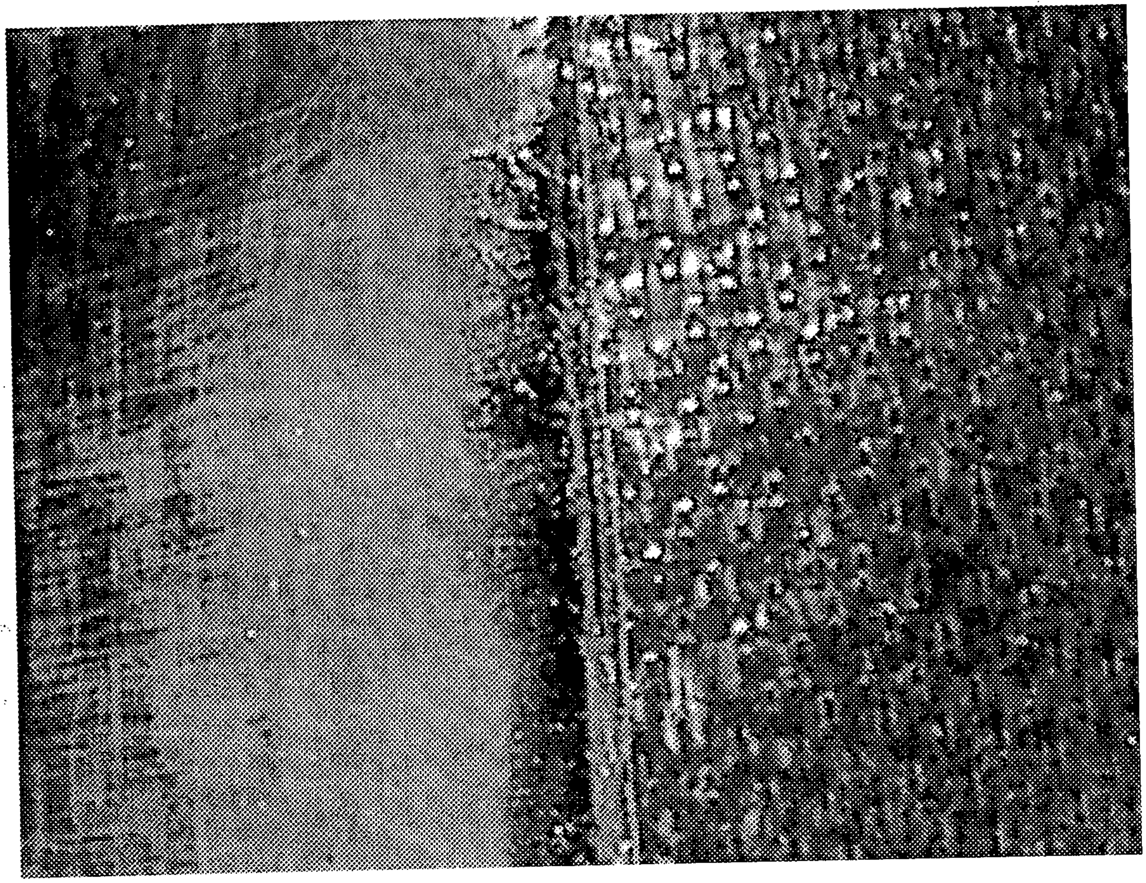

Figure 13. Optical Micrograph of Lap Shear Joint Showing Resin Flow (10x)

Optical micrographs of the joints, after lap shear tests, all showed that failure occurred cohesively at the glass scrim/adhesive interface, with the imprints of the scrim clearly visible on the failure surface (Figures 14 and 15).

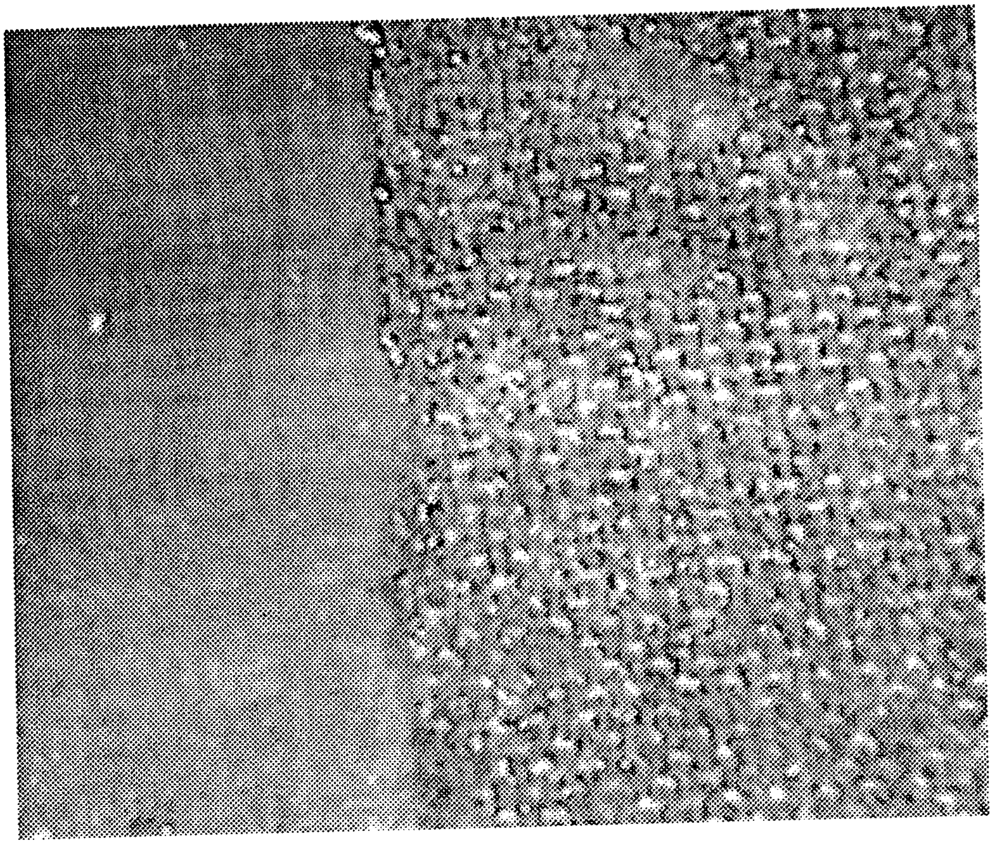

Figure 14. Optical Micrograph of Failed Adhesive Interface Surface Showing Scrim Cloth Imprint (10x)

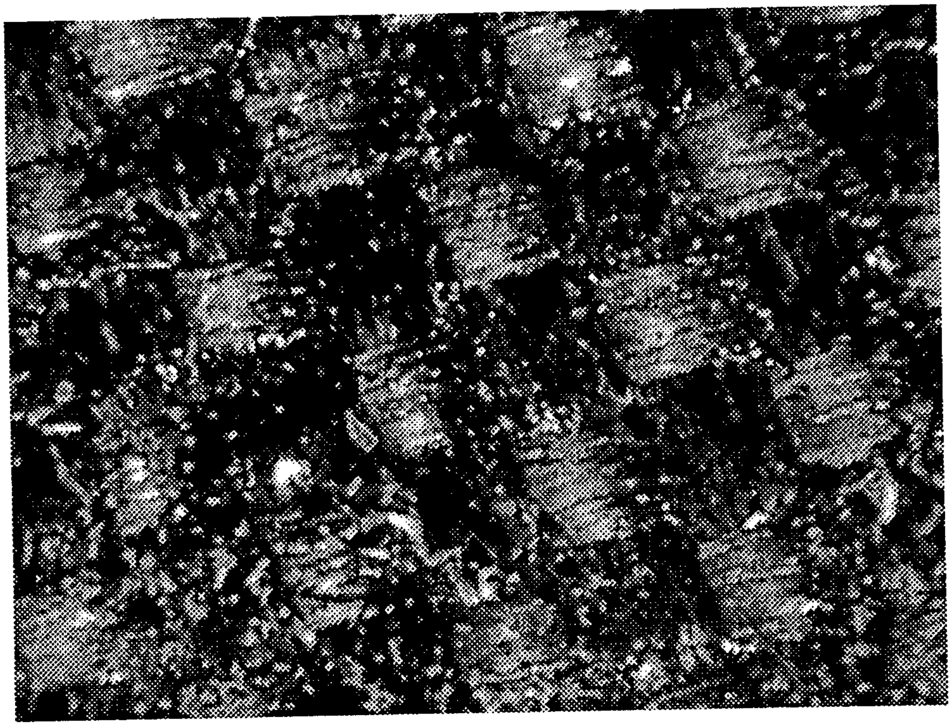

Figure 15. Optical Micrograph of Failed Adhesive Interface Showing Scrim Cloth Imprint (60x)

Since all lap joints showed adequately adhesive wet-out (by virtue of the modest bleed-out from the joint overlaps, and since all failure surfaces show the same morphology, i.e. failure by cohesive failure at the adhesive/scrim cloth interface, it can be reasonably argued that the difference in joint strengths is due to the internal stress distribution of the adhesives as a function of cure shrinkage (or lack thereof through mitigation by the expanding monomers). The mitigation of cure shrinkage therefore represents a method which adhesive joints can improve strengths, leading to more durable bonded structures.

4. Conclusions

The data in this program have demonstrated that the technology of expanding monomers is beneficial in the mitigation of cure shrinkage in polymer systems. The spiro orthocarbonates has been shown to hold great promise because of the relatively large volume expansion upon polymerization. With judicious design of the molecule, various chemical and thermophysical properties can be built into the formulations containing these monomers. The data show that the extent of shrinkage mitigation can generally be tailored by judicious blending of the expanding monomer into the matrix resin; however for wholly aliphatic monomers the thermal durability of the blend must also be considered. The data also show that while chemical modification of the expanding monomer can restore some of the thermooxidative stability, additional processing steps may be required. Adhesive bond tests showed that the incorporation of expanding monomers in a formulation most likely was due to the mitigation of the residual stress within the matrix, since the formulations, modified or unmodified, did not reveal differences in failure surface morphology.

Despite their usefulness, there are still hurdles for the wide spread use of expanding monomers. One major obstacle is that their synthesis is neither straightforward nor inexpensive, although for some critical applications their relatively high cost can be easily justified. In addition, to be effective, a two-stage cure cycle must be devised, resulting in a reformulation of matrix resins that are currently in use. Nevertheless for high performance resins for which a variety of curing agents exist and thus can be easily reformulated, for example epoxies and polyesters, the use of expanding monomers to mitigate cure shrinkage is highly advantageous.

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Part II. Development of Processable Polyimide Adhesives

SUMMARY

This is the Final Report (Part 2) on the STTR Phase II program to develop processable low cure shrinkable adhesives, under a U.S. Air Force Contract No. F49620-00-C-0025. This program was divided into two goals: (1) development of processable low cure shrinkable adhesives and (2) development of a low viscosity phenylethynyl end-capped fluorinated polyimide adhesive for high temperature applications. This was a joint program between Poly Comp. Technologies, Inc. of Del Mar, CA. and the University of Connecticut, Storrs, CT. The principal investigator (PI) for Poly Comp Technologies was Dr. Chuk L. Leung and the Principal Investigator for the University of Connecticut was Dr. Daniel A. Scola. The University of Connecticut phase of the program was carried under agreement No. 00-STTR-01 between Poly Comp Technologies, Inc. and the University of Connecticut. The period of performance was July 15, 2000 through July 14, 2002.

In the first year's effort, a series of phenylethynyl (PE) end-capped co-oligomides with molecular weight M_n 4,000 and 7,000 based on 4,4′-(hexafluoroisopropylidene) biphthalic anhydride (6FDA) and *para-* and *meta*-phenylenediamine containing 80/20 and 70/30 *para- / meta-* (*p/m*) mole ratio's in the repeat unit were synthesized and characterized for thermal and rheological properties. These PE end-capped co-oligomides (PE-6F-PDA-4K or –7K) were blended with a reactive diluent, namely 3,4′-bis(phenylethynyl) phthalimido diphenylether (PEPA-3,4′-ODA) at oligomer/diluent ratios of 90/10 and 80/20, and were also evaluated for thermal and rheological properties. The co-oligomides M_n 7,000 exhibited high melt viscosities relative to the co-oligomide, M_n 4,000, at both 80/20 and 70/30 *p/m* mole ratios. However, co-oligomides containing 70/30 *para- / meta-* bonding exhibited 25% lower viscosity than the co-oligomides with 80/20 *p/m* in the repeat unit. The biggest influence in viscosity was noted for PE-6F-PDA-4K (80/20) containing reactive diluent PEPA-3,4′-ODA at a 10 mole % level. Complex melt viscosity was decreased from 4,440 Pa. s at 343^{0}C to 1,460 Pa. s at 341^{0}C, a 68% decrease to a useful viscosity level. In contrast, at the levels investigated, molecular weight, *p/m* mole ratios, and reactive diluent, had a small influence on T_g.

In the second year's effort PE end-capped co-oligomides of molecular weight M_n 4,000 based on 6FDA and 4,4′-(2,2,2-trifluoro-1-phenylethylidene) diphthalic anhydride (3FDA) and *para-* and *meta*-phenylene diamine containing 80/20 and 70/30 *para/meta* (*p/m*) mole ratio's in the repeat unit were also synthesized and characterized for thermal and rheological properties.

The PE end-capped co-oligomides PE-6F-PDA-4K and PE-3F-PDA-4K were blended with reactive diluents PE-6F-*m*PDA and PE-3F-*m*PDA at 80/20 mole ratio and characterized for thermal and rheological properties.

On the basis of minimum melt viscosity and T_g, selected co-oligomides and co-oligomide blends were evaluated as adhesives in titanium-to-titanium tensile lap shear joints. The joints were fabricated and cured in stainless steel vacuum bags at one atmosphere at 370^0C/1 hr. The results indicate that the low viscosity PE end-capped co-oligomides, PE-6F-PDA-4K (70*p*/30*m*) and PE-6F-PDA (80*p*/20*m*)/PEPA-3,4′-ODA blend, both with T_g's of ~370 are excellent candidates for low pressure bonding, and high temperature adhesive applications. These two adhesive candidates exhibited tensile lap shear strengths of 3583 psi and 3378 psi, respectively, failing cohesively in the primer/ scrim cloth interface region.

1.0 Introduction

1.1 Objective

The objective of this program is to develop a low viscosity phenylethynyl end-capped fluorinated polyimide adhesive for high temperature applications.

1.2 Materials Investigated

The two year effort was based on the synthesis of phenylethynyl end-capped (4,4′-hexafluoro-isopropylidene) biphthalic anhydride (6FDA) co-oligomides (Fig. 1) and blends of these co-oligomides with two phenylethynyl end-capped reactive diluents, namely 3,4′-bis(phenylethynyl) phthalimido diphenylether (Fig. 2) and the phenylethynyl end-capped (PE) bisimide PE-6F-*m*PDA (Fig. 3), and the synthesis of phenylethynyl end-capped (4,4′-(2,2,2-trifluoro-phenylethylidene) diphthalic (3FDA) co-oligomides (Fig. 4) and blends of these co-oligomides with the fluorinated PE bisimide (PE-3F-*m*PDA), Fig. 5. PE-6F-PDA co-oligomides with number average molecular weights (M_n) of 4,000 and 7,000 were selected for evaluation initially. These were blended with the reactive diluents for further evaluation. The co-polyimides evaluated (prepared from 6FDA and phenylenediamine at para-/meta- ratios of 90/10 and 80/20 respectively), and the oligomer/reactive diluent blend ratios evaluated are listed in Table 1.

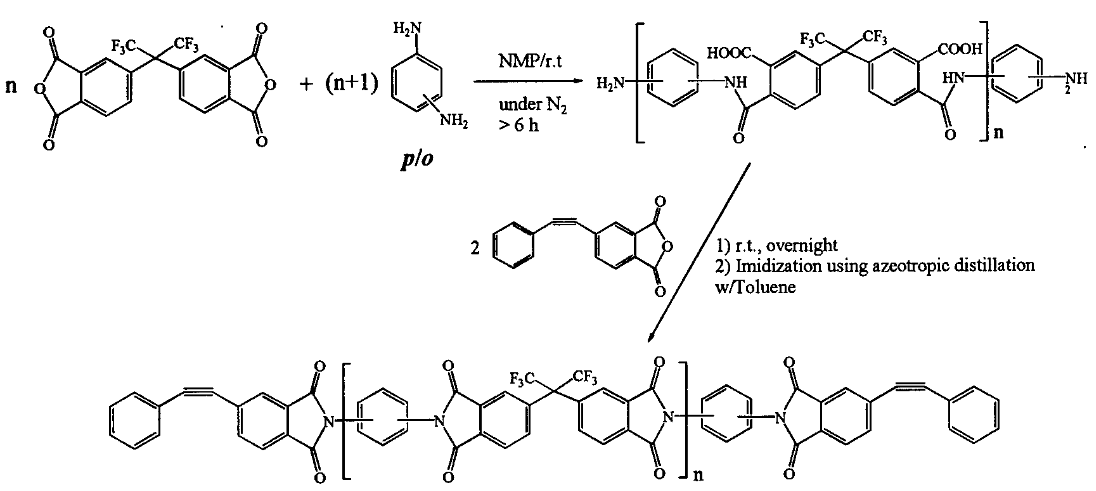


Figure 1. Synthesis of PE-6F-PDA(*p*/*m*) co-oligomides

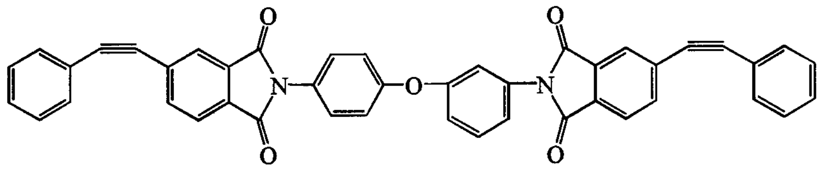


Figure 2. 3,4 ′- Bis[phenylethynyl-phthalimido-diphenylether as reactive diluent (PEPA-3,4′-ODA)

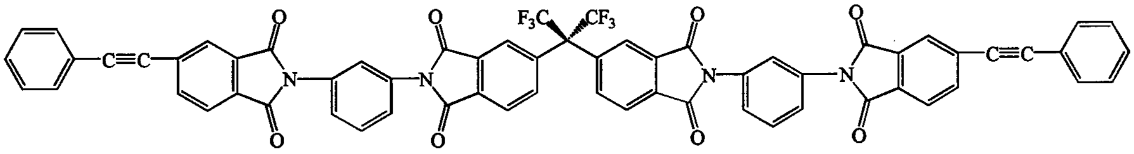


Figure 3. *N,N* ′- bis[(*N″,N‴*-1,3-phenylenephenylethynylphthalimido)]-4,4′-hexafluoroisopropylidenediphthalimide (PE-6F-*m*PDA)

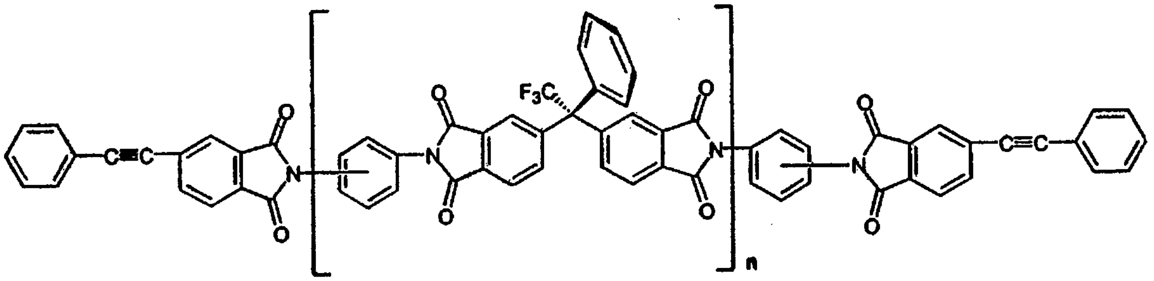


Figure 4. PE-3F-PDA 4K (80*p*/20*m*) Oligomides

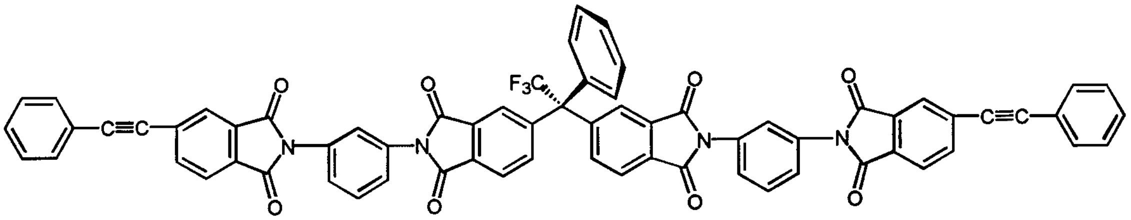


Figure 5. PE-3F-*m*-PDA reactive diluent

Table 1. Co-oligomides (PE-6F-PDA(*p/m*)) and PE-6F-PDA reactive diluent blends evaluated

Co-6F-PDA polyimide composition para/meta isomer ratio	Molecular weight (M_n)	Mole Ratio Oligomer/diluent	Reactive diluents evaluated	No. of blends
80*p*/20*m*	7000	90/10	Fig. 2	1
70*p*/30*m*	7000	90/10	Fig. 2	1
80*p*/20*m*	4000	90/10	Fig. 2, Fig. 3	2
80*p*/20*m*	4000	80/20	Fig. 2, Fig. 3	2
70*p*/30*m*	4000	90/10	Fig. 2, Fig. 3	2
70*p*/30*m*	4000	80/20	Fig. 2, Fig. 3	2

The PE-3F-PDA oligomide evaluated and the oligomide/reactive diluent blend evaluated is listed in Table 2.

Table 2. Co-oligomides (PE-3F-PDA (p/m) and PE-3F-*m*-PDA diluent blends evaluated

Co-3F-PDA polyimide composition para/meta isomer ratio	Molecular weight (M_n)	Oligomer/diluent mole ratio	Reactive blend evaluated
80*p*/20*m*	4000	80/20	PE-3F-*m*-PDA (Fig. 5)

2.0 Results and Discussion

The effect of three parameters, 1) molecular weight, 2) bonding (*para- / meta-*) ratio of phenylene diamine in the co-oligomide, and 3) co-oligomide blend composition on glass transition temperature and complex viscosity, which are important properties for processing and property retention at elevated temperatures, are discussed below.

2.1 Influence on glass transition temperature

Thermal data for the PE-6F-PDA(*p/m*) co-oligomides synthesized and co-oligomide/PEPA-3,4′-ODA reactive diluent blends are listed in table 3. Example DSC curves for PE-6F-PDA-4K, PE-6F-PDA-7K(80*p*/20*m*) and for PE-6F-PDA-7K (80*p*/20*m*)/PEPA-3,4-ODA(90/10) blend are shown in figures 6, 7 and 8.

Table 3. Thermal Data for PE-6F-PDA(p/m) Co-oligomides and Co-oligomide/PEPA-3,4′-ODA blends

Oligomer and Co-Oligomer Blend	T_g[3] (°C)		T_m[3] (°C)	T_{gel}[4] (°C) onset
	Oligomer	Cured Polyimide		
4K (80*p*/20*m*)[1]	265	366	none	368
4K (80*p*/20*m*)[1] / blend (90/10)[2]	257	369	none	374
4K (70*p*/30*m*)[1]	257	358	none	371
4K (70*p*/30*m*)[1]/blend (90/10)[2]	253	361	none	371
7K (80*p*/20*m*)[1]	286	357	none	379
7K (80*p*/20*m*)[1] / blend (90/10)[2]	285	363	none	396
7K (70*p*/30*m*)[1]	285	354	none	370
7K (70*p*/30*m*)[1] / blend (90/10)[2]	252	364	none	370

4K refers to M_n = 4,000 and 7K refers to M_n = 7,000

1. mole ratio of para-phenylene/m-phenylene diamines used in co-oligomide synthesis
2. mole ratio of co-oligomide/reactive diluent used in blend
3. from DSC measurements
4. from G′, G″ crossover in rheology measurements

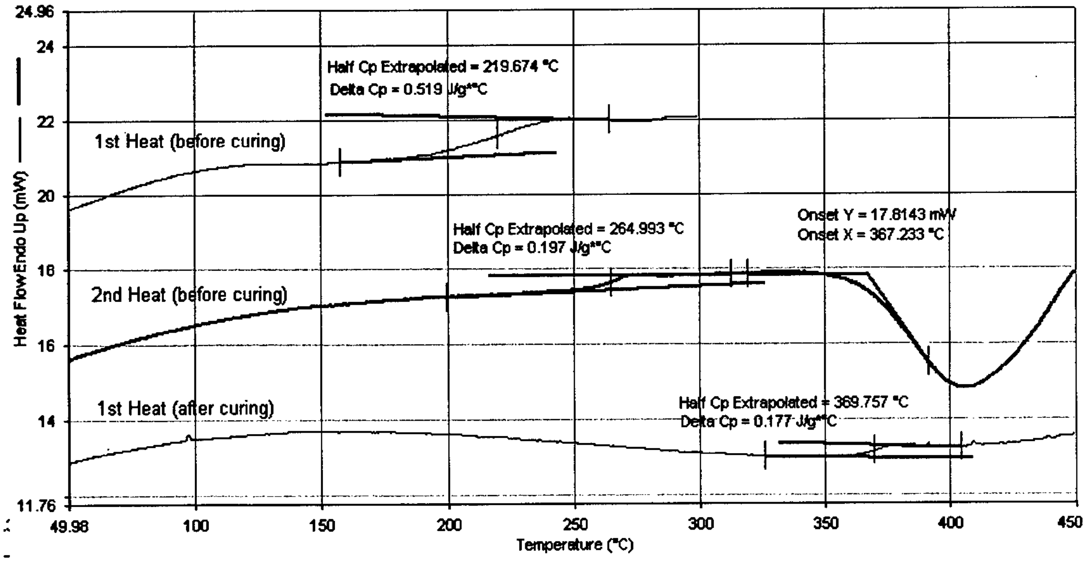


Figure 6. DSC thermogram of PE-6F-PDA-4K (80*p*/20*m*)

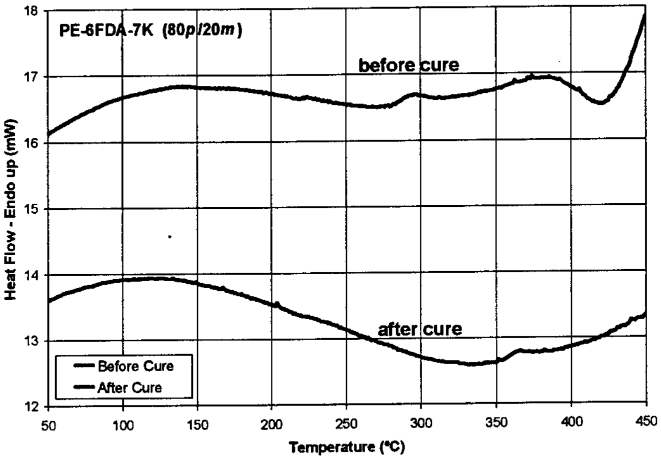


Figure 7. DSC Thermogram of PE-6F-PDA-7K (80*p*/20*m*) before and after cure

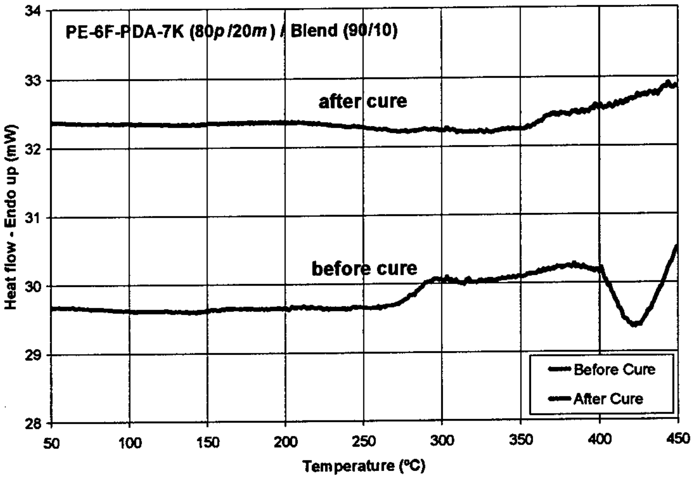


Figure 8. DSC Thermogram of PE-6-FDA-7K (80*p*/20*m*) /PEPA-3,4′-ODA Blend (90/10) before and after cure

Increasing the molecular weight (M_n) from 4,000 to 7,000 caused a small decrease in the glass transition temperature (T_g) (4°C to 9°C). A decrease in T_g is expected since the concentration of phenylethynyl end-capper is decreased as M_n increases. However, high T_g's are still maintained (~350°C). The high T_g's of the cured oligomers indicate that the materials are rigid, crosslinked structures, capable of sustaining loads close to the T_g's (~340°C). Decreasing the *para-/meta*-phenylenediamine ratio from 80/20 to 70/30 in the PE-6F-PDA co-oligomer repeat unit causes only a slight decrease (~8°C) in T_g, indicating little compromise in this property. Incorporation of 10 or 20 mole % PEPA-3,4′-ODA reactive diluent in PE-6F-PDA of molecular weight M_n 4000 also had very little effect on the glass transition temperature, T_g. However, 10 mole % of PEPA-3,4′-ODA in PE-6F-PDA of molecular weight M_n 7000 caused a 6 to 10^{0}C increase in the cured T_g.

2.2 Influence on Complex Viscosity

For low-pressure adhesive processing, it is desirable to have a material which has a low melt viscosity in the range 100 to 200 Pa. s. Complex viscosity data for the PE-6F-PDA co-oligomides and PE-6F-PDA co-oligomide/PEPA-3,4′-ODA blend compositions are listed in table 4. Selected complex viscosity versus temperature curves are shown in figure 9, and the rheological behavior for these systems are shown in figures 10-13.

Table 4. Thermal and Minimum Melt Viscosity Data for PE-6F-PDA (p/m) and Co-oligomide/PEPA-ODA Blends

PE-6F-PDA(p/m) and PEPA-3,4′-ODA blends	T_g (°C)[4] (DSC)		T_m DSC (°C)	η^*_{min}/T (Pa. s/°C)	T_{gel}[5] (onset, °C)
	Oligomer	Cured			
4K (80*p*/20*m*)[1]	265	366	No	4,440 / 343	365
4K(80*p*/20*m*)[1]/Blend(90/10)[2,3]	257	369	No	1,440 / 341	366
4K(80*p*/20*m*)/Blend (80/20)[2,3]	251	369	No	1446/344	365
7K (80*p*/20*m*)[1]	286	357	No	25,500 / 363	367
7K(80*p*/20*m*)/Blend (90/10)[2,3]	285	363	No	7,273 / 362	362
4K (70*p*/30*m*)[1]	257	358	No	3,510 / 352	371
4K(70*p*/30*m*)[1]/Blend (90-10)[2,3]	253	361	No	2,308 / 351	371
4K(70*p*/30*m*)/Blend (80/20)[2,3]	249	359	No	2398/337	360
7K (70*p*/30*m*)[1]	285	354	No	8,184 / 347	370
7K(70*p*/30*m*)/Blend (90-10)[2,3]	252	364	No	6,274 / 293	357

1. mole ratio of para-phenylene/m-phenylene diamines used in co-oligomide synthesis
2. mole ratio of co-oligomide/reactive diluent used in blend
3. prepared from same batch of co-oligomers
4. from DSC measurements
5. from G′, G″ crossover from rheology measurements

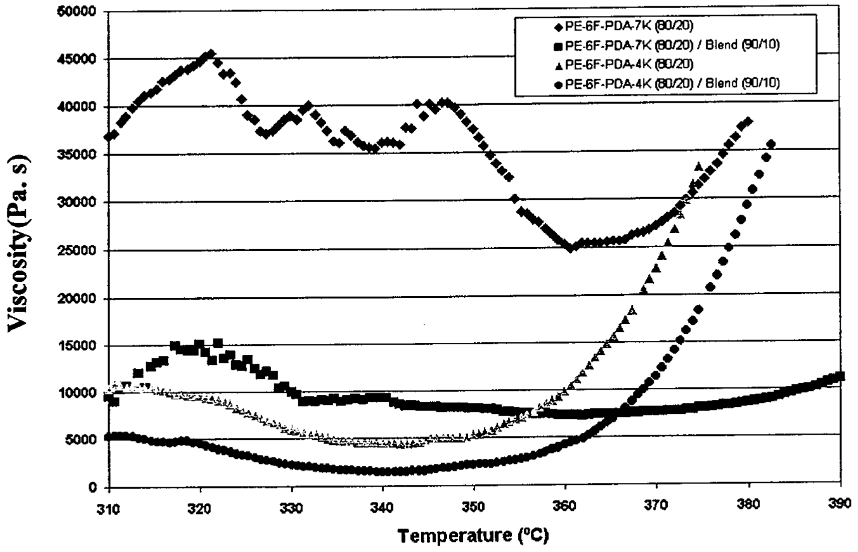


Figure 9. Complex Viscosity curves for 7K and 4K Co-oligomides and Blends with PEPA-3,4′-ODA

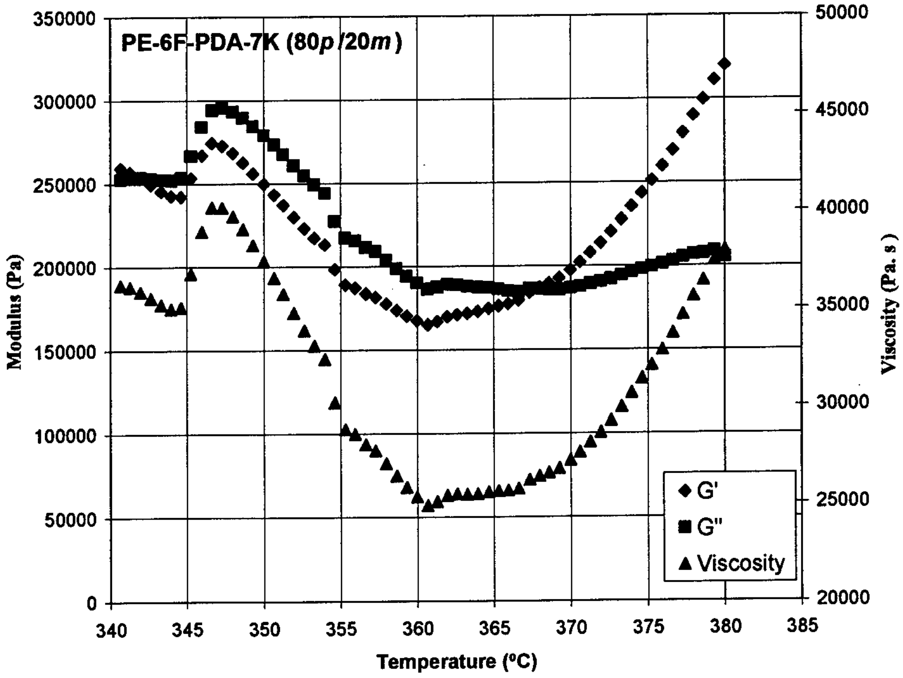


Figure 10. Rheological behavior for PE-6F-PDA-7K (80*p*/20*m*)

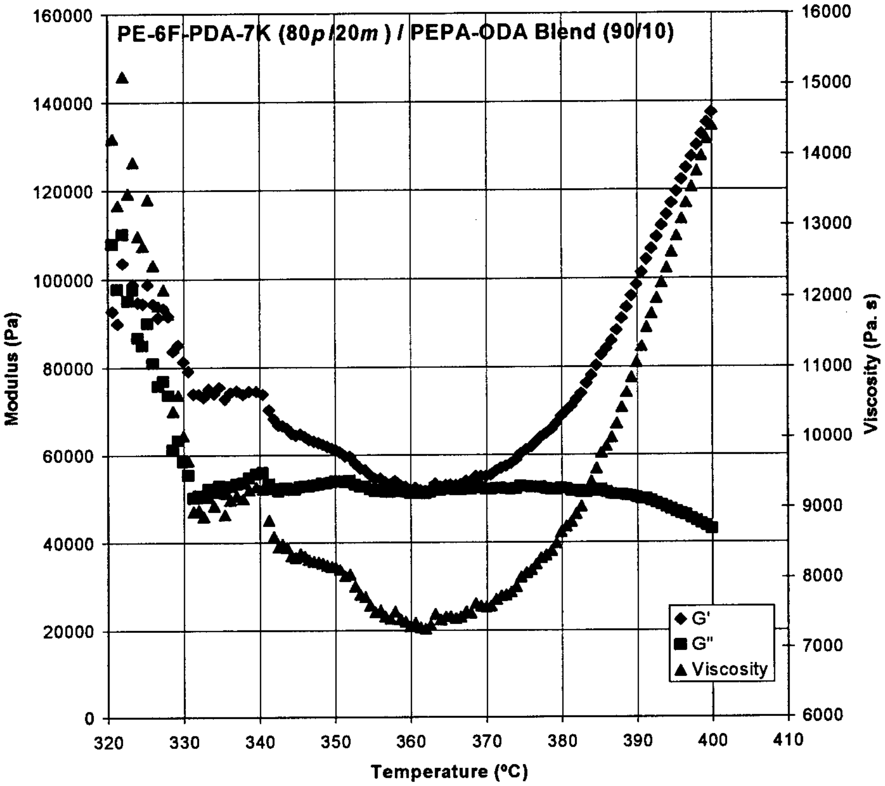


Figure 11. Rheological behavior for PE-6F-PDA-7K (80*p*/20*m*) / PEPA-3,4′-ODA Blend (90/10)

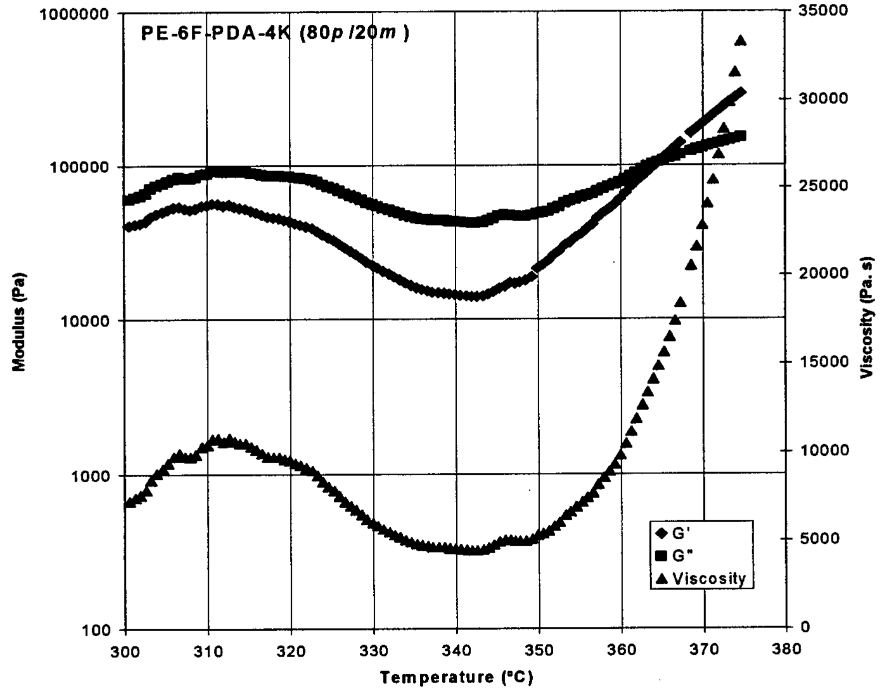


Figure 12. Rheological behavior for PE-6F-PDA-4K (80*p*/20*m*)

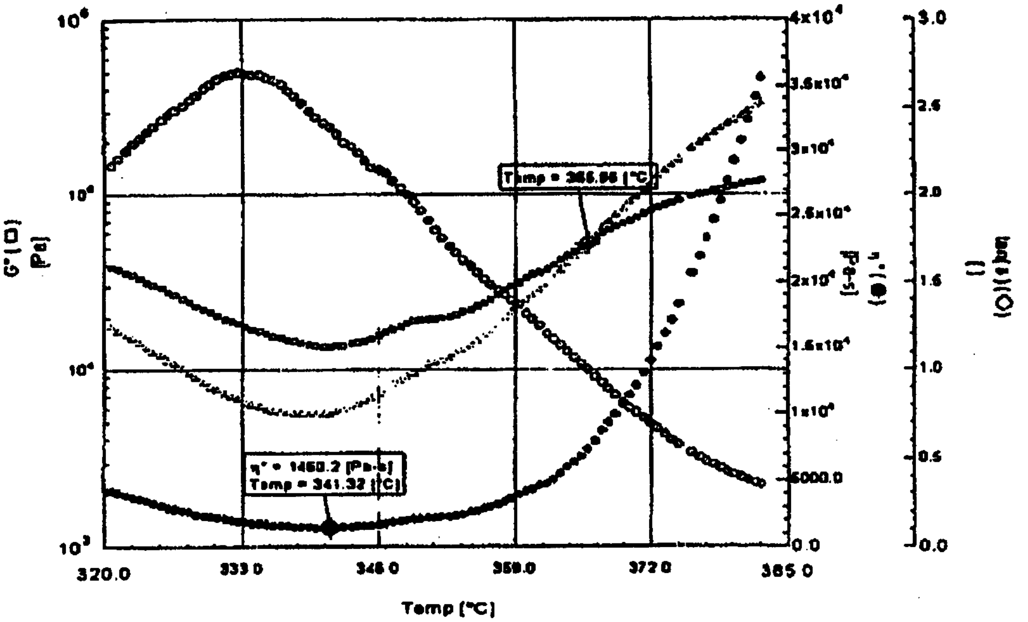


Figure 13. Rheometric Graph for PE-6F-PDA-4K (80*p*/20*m*) and PEPA-3,4′-ODA Blend at 90-10 Molar Ratio

2.2.1 PE-6F-PDA (*p*/*m*) Oligomide and Oligomide/PEPA-3,4′-ODA Blends

As expected, increased molecular weight causes a very sharp increase in complex viscosity; for example, PE-6F-PDA (80*p*/20*m*) with M_n = 4,000 exhibited a melt viscosity of 4440 Pa. s at 343°C, while PE-6F-PDA (80*p*/20*m*), M_n = 7,000 exhibited a melt viscosity of 25,500 Pa. s at 363°C. Clearly, the lower molecular weight co-oligomides are more desireable. Decreasing the mole ratio of *para- / meta-* bonding from 80/20 to 70/30 does cause a moderate decrease (20%) in viscosity for the low molecular weight M_n 4,000 co-oligomide, but a substantial decrease (68%) for the high molecular weight, M_n 7,000 co-oligomide. However, for the co-oligomide M_n 7,000 with 70/30 *para- /meta-* bonding, the viscosity (8,184 Pa. s) is considered too high for low pressure bonding.

Introduction of a reactive diluent PEPA-3,4′-ODA to form co-oligomide / reactive diluent blends causes substantial decreases in complex viscosity. For example, for the M_n 4,000 (80*p*/20*m*) co-oligomide, the complex viscosity decreases from 4,440 Pa. s at 340°C, to 1,460 Pa. s at 341°C for the 4K co-oligomide/10 mole % blend, a 68% decrease in viscosity. Increasing the blend concentration to 20 mole % caused no further decrease in viscosity.

Molecular weight, *para- / meta-* mole ratio, and reactive diluent caused substantial lowering of the viscosity, in contrast to the small influence of these parameters on T_g. Based on this data, additional studies were focused on lower molecular weight oligomers (M_n = 4,000) and their blends.

2.2.2 PE-6F-PDA (*p*/*m*) Oligomide and Oligomide/PE-6F-*m*-PDA Blends

Blends of PE-6F-PDA-4K (80*p*/20*m*) and PE-6F-PDA-4K (70*p*/30*m*), both of MW of 4000, with PE-6F-m-PDA at molar ratios of 90-10 and 80-20 were also investigated. Thermal data for these blends are summarized in Table 5. Melt viscosity data for the same materials are also included in Table 5.

Table 5. Thermal and Minimum Melt Viscosity Data of Co-oligomide PE-6F-PDA and of Co-oligomide/PE-6F-m-PDA Blends

PE-6F-PDA (*p*/*m*) and blends with PE-6F-*m*-PDA	**T_g (^{0}C)[4] (DSC)**		**T_m (DSC) (^{0}C)**	**η^*_{min}/T (Pa. s/^{0}C)**	**T_{gel}[5] (onset, ^{0}C)**	**T_d[6] (onset, ^{0}C)**
	Oligomer	Cured				
4K(80*p*/20*m*)[1]	263	369	No	4438/343	365	504
4K Blend (90-10)[2,3]	261	369	No	2163/347	365	503
4K Blend (80-20)[2,3]	256	360	No	1583/347	366	501
4K (70*p*/30*m*)[1]	257	358	No	3510/352	371	501
4K Blend (90-10)[2,3]	256	357	No	4019/341	361	501
4K Blend (80-20)[2,3]	252	261	No	2930/336	361	503

1. mole ratio of para-phenylene/m-phenylene diamines used in co-oligomide synthesis
2. mole ratio of co-pligomide/reactive diluent used in blend
3. prepared from same batch of co-oligomers
4. from DSC measurements
5. from G′, G″crossover (Rheometrics)
6. from TGA data curves

The thermal data show that the presence of the reactive diluent (PE-6F-m-PDA) has very little influence on the glass transition temperature, T$_g$, both before and after cure. The data also show little effect on the decomposition temperature, T$_d$, and gelation temperature, T$_{gel}$. The Tg findings are consistent with previous observations with PE-6F-PDA (p/m)/PEPA-ODA blends discussed above (Table 4). Moreover , the blends with PE-6F-m-PDA diluent show a substantial lowering of the melt viscosity for PE-6F-PDA 4K (80*p*/20*m*). With 10 mole % of reactive diluent, the viscosity of PE-6F-PDA-4K (80*p*/20*m*) was reduced from 4438 to 2163 Pa. s, a 51%

reduction. The reduction rate is somewhat less than it was for the PEPA-3,4′-ODA reactive diluent (Table 4). With 20 mole % of reactive diluent, the viscosity was further reduced to 1583 Pa. s, a 64% reduction. This further reduction of viscosity at 20 mole % was not observed for PEPA-3,4′-ODA blends (Table 4). In fact , for PE-6F-PDA-4K (70*p*/30*m*) oligomide/90/10 blend, no reduction in viscosity was observed, but the viscosity was actually increased from 3510 to 4019, a 15% increase. This obviously is an anomaly in the data. The complex viscosity was not repeated to verify this increase. However, a reduction in viscosity, from 3510 to 2930 Pa. s, a mere 17% reduction, was observed when the amount of the diluent increased to 20 mole %. These data suggest that PE-6F-m-PDA reactive diluent is less effective in reducing oligomer viscosity compared to PEPA-3,4′-ODA reactive diluent.

2.2.3 PE-3F-PDA (*p*/*m*) Oligomide and Oligomide/PE-3F-*m*-PDA Blend

The Complex Viscosity behavior of the PE-3F-PDA-4K (80*p*/20*m*) oligomer and the oligomer/PE-3F-m-PDA 80/20 blend is shown in Figure 14. The oligomer 80p/20m/ PE-3F-m-PDA 80/20 blend shows a minimum melt viscosity of 680 Pa. s at 325^{0}C which is considerably lower than the PE-6F-PDA-4K 80*p*/20*m*/PE-6F-m-PDA 80/20 blend system (1583 Pa. s/347^{0}C, Table 6). Data for the Pe-6F-PDA-4K (80p/20m) oligomide from table 4 is included for comparison with the PE-3F-PDA (80p/20m) oligomide. Since the complex viscosities of PE-6F-PDA (80p/20m) and PE-3F-PDA (80p/20m) are essentially identical, the reactive diluent PE-3F-m-PDA is more effective in lowering viscosity than is PE-6F-m-PDA.

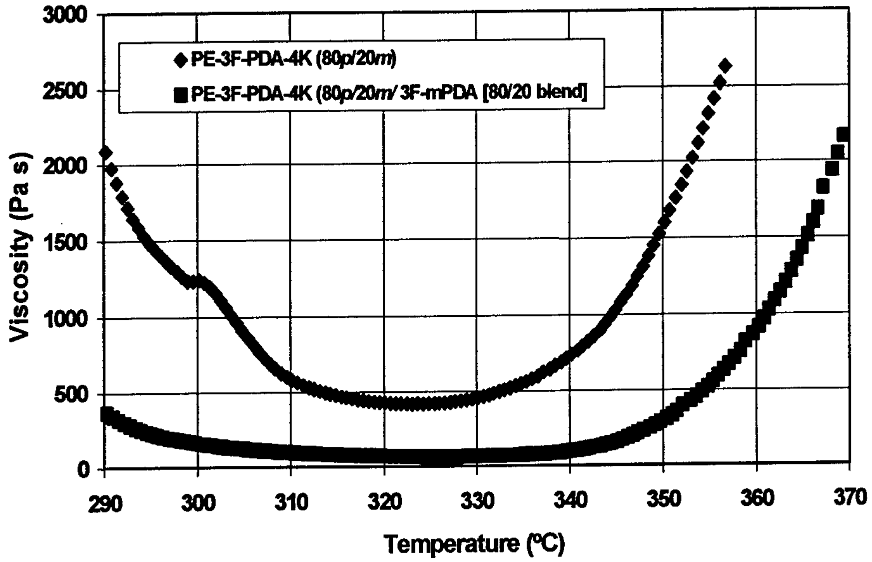


Figure 14. Complex Viscosity, temperature profile of PE-3F-PDA-4K (80*p*/20*m*) and PE-3F-PDA-4K (80*p*/20*m*)/PE-3F-*m*-PDA [80/20 blend]

The dynamic viscosity of the PE-3F-PDA-4K system at selected temperatures and minimum melt viscosity is listed in Table 6. Introduction of the reactive diluent PE-3F-*m*-PDA at a 20% level had a profound influence on the minimum viscosity of the PE-3F-PDA-4K 80p/20m oligomer, lowering it from 4210 Pa. s to 680 Pa. s. Comparison of the minimum melt viscosities of PE-3F-PDA-4K (80*p*/20*m*)/PE-3F-*m*-PDA blend with PE-6F-*m*-PDA blend (Table 6) indicates that the 3FDA unit has a greater influence in lowering the minimum melt viscosity than the 6FDA unit.

Table 6. Dynamic Viscosities of PE-3F-PDA-4K (80*p*/20*m*) System and Blend

	Complex Viscosity at selected temperatures (Pa. s) (Poise)		
	300°C	**325°C**	**350°C**
OLIGOMER			
PE-3F-PDA-4K (80*p*/20*m*)	1240 (12,400)	421 (4210)	1597 (15,970)
PE-3F-PDA-4K (80*p*/20*m*) PE-3F-mPDA [80/20 blend]	160 (1600)	68 (680)	292 (2920)

Oligomer	Minimum Melt Viscosity
PE-3F-PDA-4K (80*p*/20*m)*	448 Pa. s (4480 poise) at 342°C
PE-6F-PDA-4K (80*p*/20*m*)	4440 Pa. s (44400 poise) at 343°C
PE-3F-PDA-4K (80*p*/20*m*)/ PE-3F-mPDA [80/20 blend]	68 Pa. S (680 poise) at 325°C
PE-6F-PDA-4K (80*p*/20*m*) PE-6F-m-PDA [80/20 blend]	1583 Pa. s (15830 poise) at 347°C

2.3 Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) of the PE-6F-PI oligomides and several blends were carried out to determine dynamic thermal stability relative to other PE polyimides such as PETI-5. The samples were dried at 130^{0}C in vacuum overnight before TGA analysis. The temperatures at which 5 and 10 wt% losses occur, and char yields are also listed in Table 7. The data shows that a 2-3wt% loss occurs between 150 to 200^{0}C in all samples, indicating that residual solvent (NMP) or unreatced monomer remain in the sample after the 130^{0}C/vacuum drying overnight.

Table 7. Thermogravimetric Analysis Data of 6F-PDA(*p*/*m*) oligomides and oligomide/blends

6F-PDA-4K (80*p*/20*m*) oligomer and oligomer/PEPA-3,4'-ODA blend	**TGA Data**				
	$T_{d\,5\%}$	**$T_{d\,10\%}$**	***Char Yield***	***Comments***	**T_{cure} (onset, ^{0}C)^{3}**
4K (80*p*/20*m*)[1]	494	519	55.1	~3% wt loss from 150°C to 200°C	368
4K(80*p*/20*m*)[1]/Blend(90/10)[2]	490	520	55.6	~3% wt loss from 125°C to 200°C	374
7K (80*p*/20*m*)[1]	484	520	53.6	~3% wt loss from 125°C to 200°C	379
7K(80/20)/Blend (90/10)[2]	483	511	30.9	~2% wt loss from 150°C to 200°C	396
4K(70*p*/30*m*)[1]	498	522	54.9	~3% wt loss from 150°C to 200°C	361
7K (70*p*/30*m*)[1]	153	485	50.7	~7% wt loss from 100°C to 175°C	386
7K(70*p*/30*m*)/Blend (90-10)[2]	469	511	52.9	~3% wt loss from 125°C to 175°C	377

1. mole % para and meta-phenylene diamine in co-oligomide
2. mole % of oligomide/reactive diluent in blend
3. from G', G" crossover in rheology measurements

2.4 Molecular Weight Characterization

The oligomides synthesized with theoretical number average molecular weights M_n 4000g/mole and 7000g/mole were based on the stoichiometric quantities of reactants. However, this is an average theoretical number and includes molecules with a range of molecular weights. To determine experimentally how much the theoretical values deviate from actual values, the molecular weights of two co-oligomides 6F-PDA-4K (80*p*/20*m*) M_n 4,000 and 6F-PDA-7K (80*p*/20*m*), M_n 7000 were determined by proton nuclear resonance spectroscopy (^{1}H-NMR) for comparison with calculated molecular weights. Intrinsic viscosity measurements were also determined on these co-oligomides. The ^{1}H-NMR spectra of PEPA, 6FDA and PE-6F-PDA (*p*/*m*) co-oligomide are shown in Figures 15, 16 and 17, respectively.

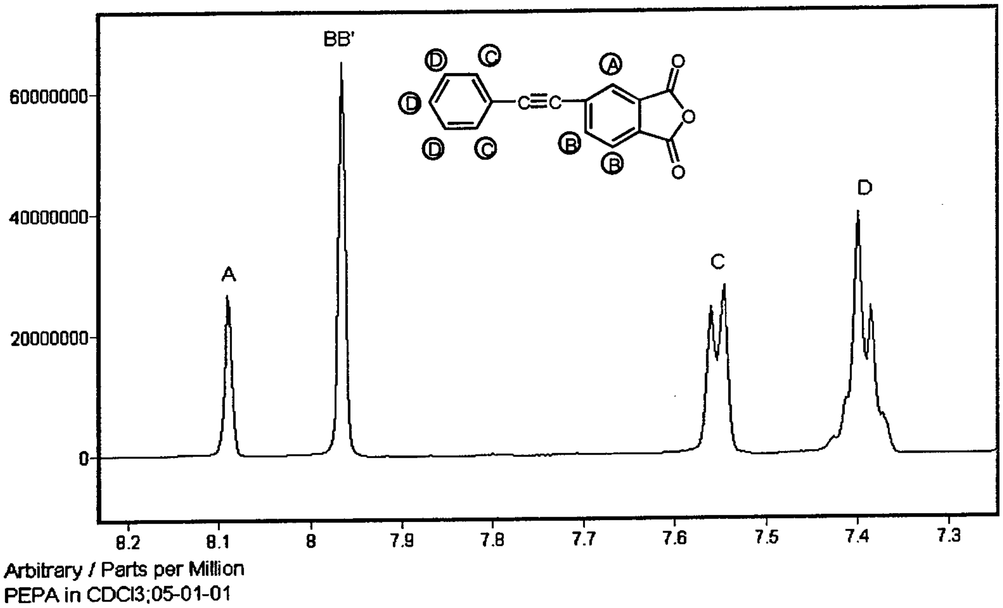


Figure 15: ^{1}H-NMR spectrum of PEPA with proton assignments noted

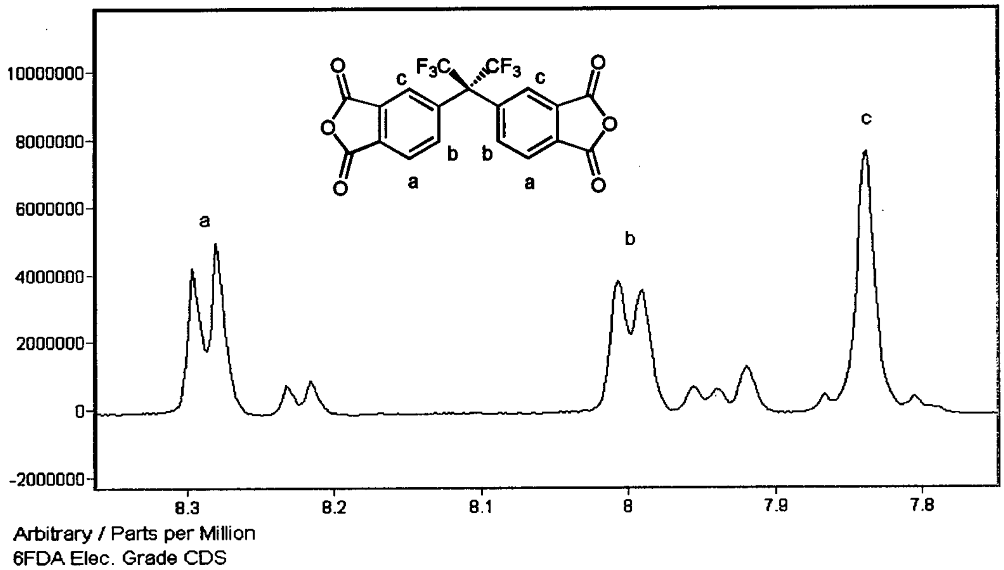


Figure 16: ^{1}H-NMR spectrum of 6FDA with proton assignments noted

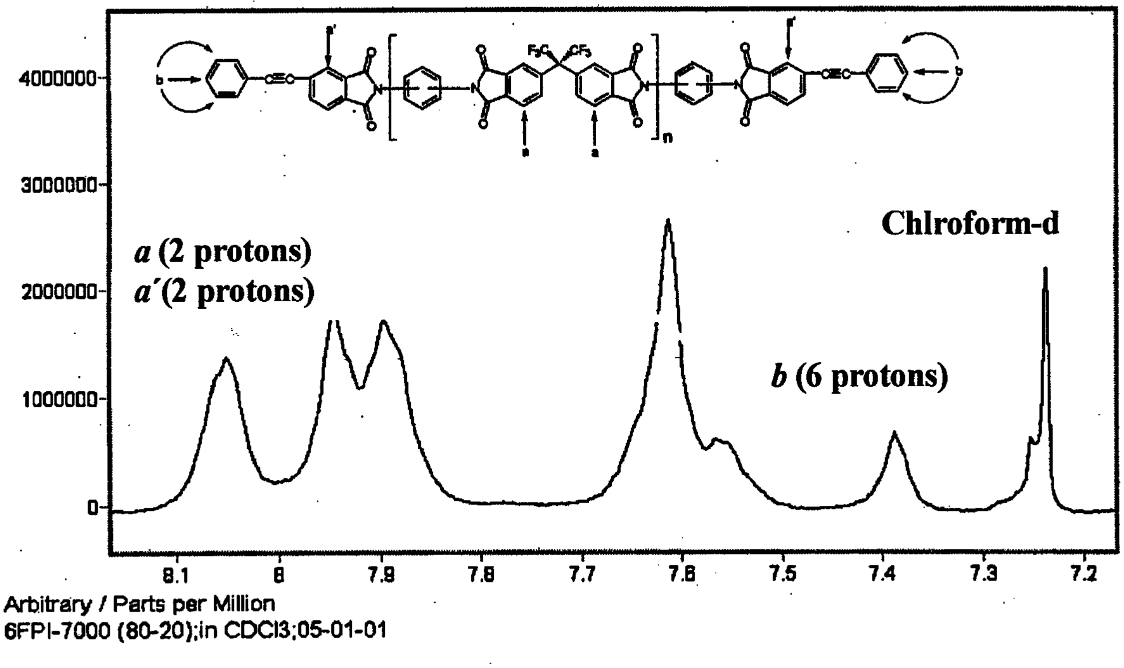


Figure 17: ^{1}H-NMR spectrum of PE-6F-PDA (*p/m*) co-oligomer with proton assignments noted

The spectra were run in $CDCl_3$. Based on the ^{1}H-NMR spectra of the 6FDA and PEPA units, the chemical shifts for quantifying the protons on the 6FDA repeat unit of PE-6F-PI (Fig. 18) and on the PEPA end-capping unit are designated in Figures 15, 16, and 17.

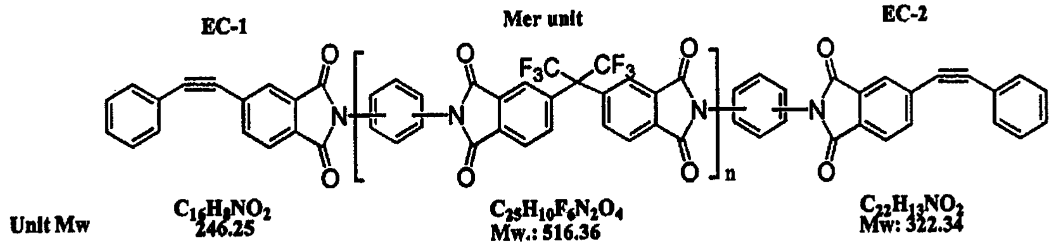


Figure 18. PE-6F-PDA (*p/m*)

The peak at 8.1 ppm in PEPA (Fig. 15) is due to the one proton, labeled *A* in the anhydride structure. The region at 7.4 ppm in PEPA (Fig. 15) is due to the 3 protons, labeled *D*, on the phenyl group. The intensity of the 3 protons *D* in PEPA is three times greater than the intensity of the *A* proton, and therefore 1/3 of this intensity is equivalent to the intensity of the *A* proton. The peak in the region of 8.3 ppm in 6FDA (Fig. 16) is due to the 2 protons (doublet), designated "*a*"on the 6FDA unit. For the phenylethynyl end-capped oligomer, PE-6F-PDA (Fig. 17), broadening of the peaks occurs, as well as a shift in the peaks due to these protons. The peaks at 8.05 ppm is due to 2 protons designated *a* on each 6FDA unit, and to 2 protons, designated *a′*on the PEPA end caps, one for each end cap. The peak at 7.39 ppm is assigned to six protons on the phenyl group of the PEPA end caps (3 each), designated b (Fig. 17). To determine the intensity of peaks at 8.05 ppm due to the *a* protons of the 6FDA unit, the contribution due to the *a′* protons of the end caps must be subtracted from the total intensity at 8.05 ppm. Since these signals between *a* and *a′*overlap, the specific this is not possible without contribution from *a* and *a′* can not be determined directly. However, since the intensity of the 2 protons a' is equivalent to the intensity of the six protons b in the oligomer, then the intensity of a' is equivalent to 1/3 the intensity of the b protons (Equation 1),

$$\underset{8.05}{I_{a'}} = {}^{2}/_{6}\,\underset{7.39}{I_{b}} \qquad 1$$

therefore, the intensity of 6FDA protons, $\underset{8.05}{I_{a}}$ can be determined by subtraction of $\underset{8.05}{I_{a'}}$ from the total intensity $\underset{8.05}{I_{a,a'}}$ as shown in (Equation 2),

$$\underset{8.05}{I_{a}} = \underset{8.05}{I_{a,a'}} - {}^{2}/_{6}\,\underset{7.39}{I_{b}} \qquad 2$$

However, the number of a' protons (end groups) is fixed at 2 and is independent of molecular weight or n; therefore the ratio of the total number of protons a (intensity) to the number of protons at a'(intensity) is a measure of the number of n repeat units (Equation 3).

$$n = \frac{\underset{8.05}{I_{a,a'}}}{\underset{8.05}{I_{a'}}} = \frac{\underset{8.05}{I_{a,a'}} - {}^{2}/_{6}\,\underset{7.39}{I_{b}}}{{}^{2}/_{6}\,\underset{7.39}{I_{b}}} \qquad 3$$

Therefore, the molecular weight M_n, can be calculated using the value of n, as follows:

Molecular Weight (M_n) = (n x Mw of each repeat unit) + molecular weight of End-Cap EC-1 + molecular weight of End-Cap EC-2

The experimental values of M_n for both of the co-oligomides measured agree with the calculated molecular weights, M_n. The data are shown in Table 8.

Table 8. M_n as determined by ^{1}H-NMR

Oligomer	M_n Calc.	M_n by ^{1}H-NMR	η intrinsic viscosity
6F-PDA-4K (80p/20m)	4000	3970	0.142
6F-PDA-7K (80p/20m)	7000	6780	0.197

The intrinsic viscosity values are also in the range expected of co-oligomides with these molecular weights.

2.5 Adhesive Test Results

Based on the thermal and viscosity data, several oligomer and oligomer/reactive diluent blend systems were selected for adhesive measurements (Table 9).

Table 9. Oligomide and Oligomides/ Reactive Blend Compositions Evaluated as Adhesives

Oligomide or Oligomide/Blend Joint Designation	Adhesive Composition
PE-PI-1	PE-6F-PDA-4K (80*p*/20*m*)
PE-PI-2	PE-6F-PDA-4K (80*p*/20*m*) blend with PEPA-3,4′-ODA (90/10 blend)
PE-PI-3	PE-6F-PDA-4K (80*p*/20*m*) blend with PEPA 3,4′-ODA (80/20 blend)
PE-PI-4	PE-6F-PDA-4K (70*p*/30*m*)
PE-PI-5	PE-6F-PDA-4K (70*p*/30*m*) blend with PEPA-3,4′-ODA (90/10 blend)
PE-PI-6	PE-6F-PDA-4K (70*p*/30*m*) blend with PEPA-3,4′-ODA (80/20 blend)
PE-PI-7	PE-6F-PDA-4K (80*p*/20*m*) blend with PE-6F-*m*-PDA (80/20 blend)
PE-PI-8	PE-3F-PDA-4K (80*p*/20*m*)
PE-PI-9	PE-3F-PDA-4K (80*p*/20*m*) blend with PE-3F-*m*-PDA (80/20 blend)

Titanium (Ti-6 Al-4V) to titanium test lap shear points were fabricated as described in the experimental section. Five joints were made for each adhesive composition. The raw data for these tests are shown in the experimental section of this report. The average test result of the 5 joints are tabulated in Table 10, along with the bonding conditions, the glass transition temperature and the failure mode. The oligomide PE-6F-PDA-4K (70*p*/30*m*) (PEPI-4 joint system) exhibited the highest tensile lap shear strength, 3582 psi of all systems investigated, while joint system PE-PI-3 containing a 80/20 mole % blend of PE-6F-PDA-4K (80*p*/20*m*) with PEPA-3,4′-ODA also exhibiting good tensile lap shear strength, 3378 psi. It is not clear why PE-6F-PDA-4K (70*p*/30*m*) blended with PEPA-3,4′-ODA at 10 or 20 mole % blend or PE-6F-PDA-4K (80*p*/20*m*) blended with 10 mole % PEPA-3,4′-ODA yielded lower adhesive strengths (2530-2810 psi) than the systems mentioned above with almost similar compositions.

Table 10. Tensile Lap Shear Strength Data of PE-PI Titanium/Titanium Adhesive Joints

Joint Adhesive Designation	Adhesive Tg°C[1]	Bonding Conditions			Tensile Shear Strength	Failure Mode
		Temp °C	Pressure MPa (psi)	Time (hrs.)	Mpa (Psi)	
PE-PI-1	365	370	48	1	17.5(2545)	2
PE-PI-2	366	370	48	1	19.0(2765)	2
PE-PI-3	365	370	14.7	1	23.2(3378)	2
PE-PI-4	371	370	14.7	1	24.6(3583)	2
PE-PI-5	371	370	14.7	1	19.3(2810)	2
PE-PI-6	360	370	14.7	1	17.4(2530)	2
PE-PI-7	366	370	14.7	1	16.4 (2392)	2
PE-PI-7	366	370	14.7	1	20.6 (2998)	3
PE-PI-8	346	370	14.7	1	18.8(2740)	2
PE-PI-9	354	370	14.7	1	15.6(2273)	2

1. From G′, G″ crossover in rheology measurements
2. Cohesive between primer and scrim cloth
3. Adhesive failure between titanium and adhesive (without scrim cloth)

Titanium to titanium joints containing PE-3F-PDA-4K and a 80/20 blend of this oligomer with the reactive diluent PE-3F-*m*-PDA also exhibited low adhesive strengths despite the fact that the blend composition also exhibited the lowest complex minimum melt viscosity of all systems investigated.

Adhesion of the PE-6F-PDA-4K and PE-3F-PDA-4K oligomides and blends of these oligomides with PEPA-3,4′-ODA or bisimides PE-6F-*m*-PDA or PE-3F-*m*-PDA to the titanium surface is excellent in all cases. This is based on the fact that all joints failed cohesively at the interface between the primer and scrim cloth. No failure occurred at the titanium to primer interface region. The exception to this is when no scrim cloth was used. This is to be discussed below. Therefore, the weak link in all tests is the interfacial region between the primer and glass scrim cloth. It can be hypothesized that the glass scrim cloth compromises the adhesion between the primed titanium surface and the PE-6F-PDA-4K or PE-3F-PDA-4K blended adhesives. In a few cases, failure occurred between the glass scrim cloth and primer crossover through the scrim cloth.

The results clearly demonstrated that phenylethynyl end-capped oligomides with low viscosity can be utilized as adhesives in titanium to titanium joints. Moreover, the results demonstrated that good adhesives strengths can be attained for joints, fabricated at low pressure (14.7 psi) (under vacuum) at 370^{0}C for 1 hour.

In joint system PE-PI-7 (Table 9) two of the 5 joints were fabricated without scrim cloth. In these two cases, one sample without scrim cloth failed at 3297 psi, while the average of the two joints failed at 2998 psi. The joints with scrim failed at 2392 psi (average). This clearly shows that adhesion to the titanium surface is better than it is to the primer-scrim interface.

Optical micrograph of the surfaces of titanium coupons after treatment with pasa jell 107 and then primed with oligomide are shown in Figure 19a and b respectively, for comparison with failed joint surfaces. Optical micrographs of joints (PE-PI-2) which failed at the primer-glass scrim cloth interface are shown in Figures 20a and 20b respectively. Optical micrographs of joints (PE-PI-7) which contained no glass scrim cloth failed at the titanium-adhesive interface region are shown in Figures 21a and 21b. These micrographs show that bonded specimens containing glass scrim cloth between both titanium adherents fail cohesively at the primer/glass scrim cloth interface (Fig. 20a and 20b). A replica of the glass scrim cloth is clearly shown on the failed primer surface of Fig. 20a. The titanium joints which contained no glass scrim cloth failed mostly at the titanium adhesive interface region, indicated by the adhesive residue (dark areas) on the free titanium surface (light regions) in Fig. 21a.

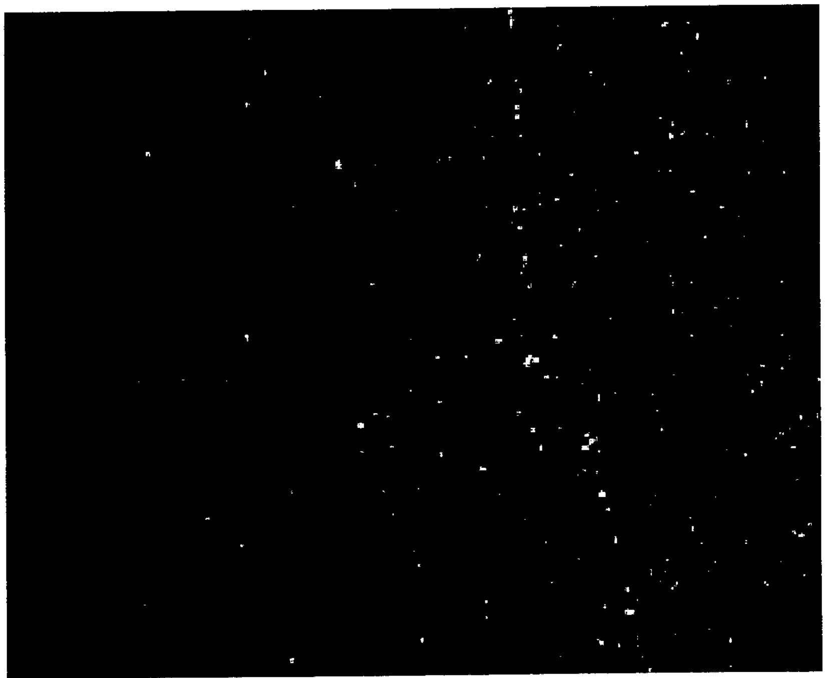


Figure 19a. Optical micrograph of Pasa-Jell 107 treated titanium surface before bonding, showing grainy surface (3.5x)

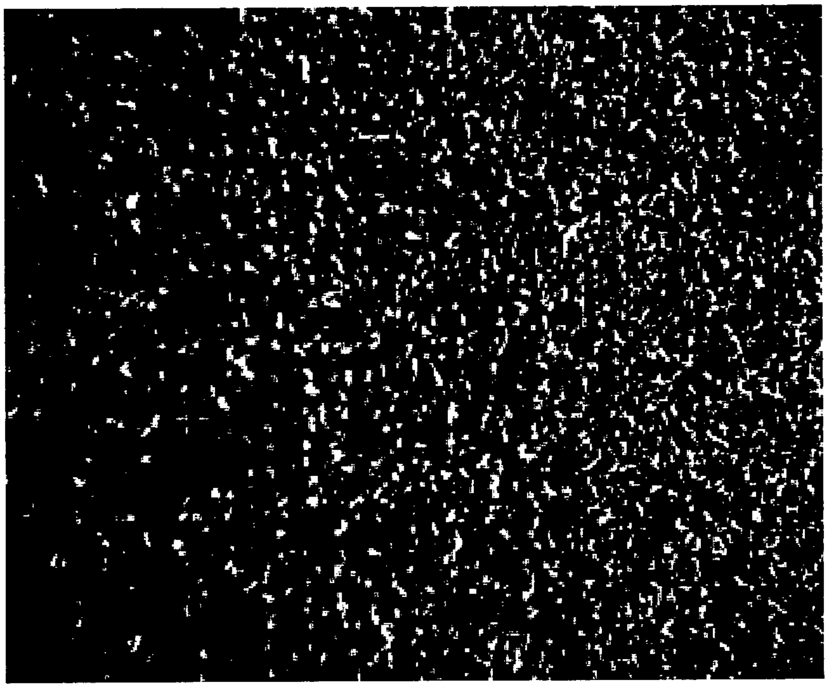


Figure 19b. Optical micrograph of Oligomide Primer over Pasa-Jell treated titanium surface before bonding (3.5x)

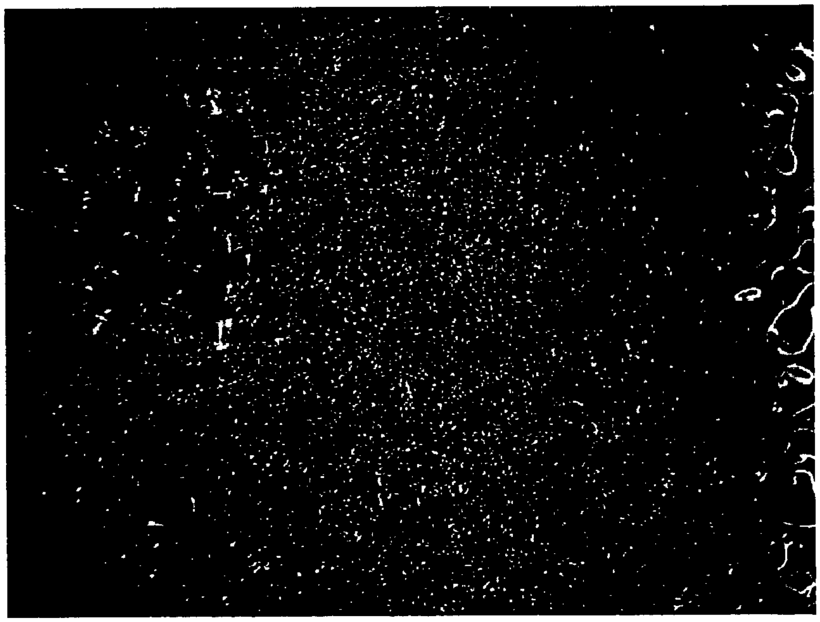


Figure 20a. Optical micrograph of failed primer interface surface (joint PE-PI-2) showing scrim cloth replica (2.3 x Mag)

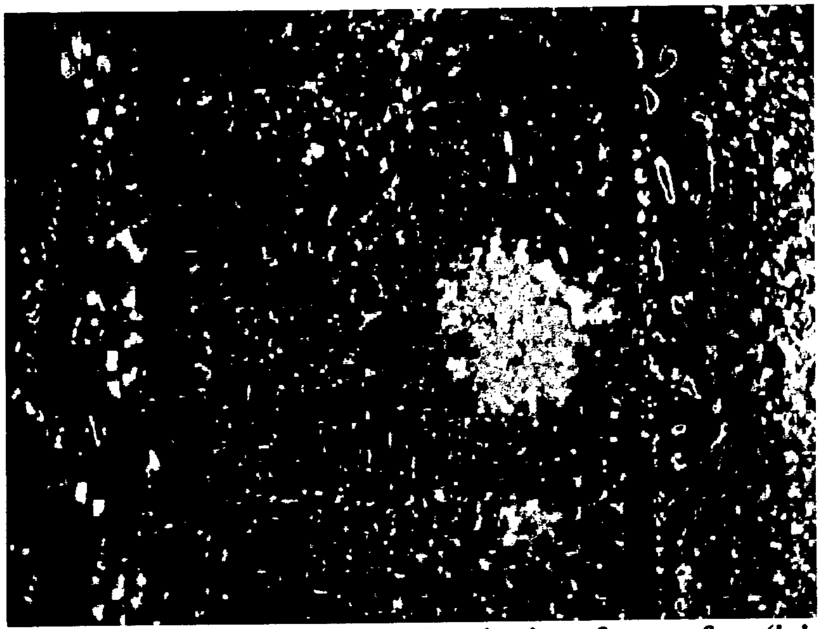


Figure 20b. Optical micrograph of failed scrim-interface surface (joint PE-PI-2) (2.3 x Mag)

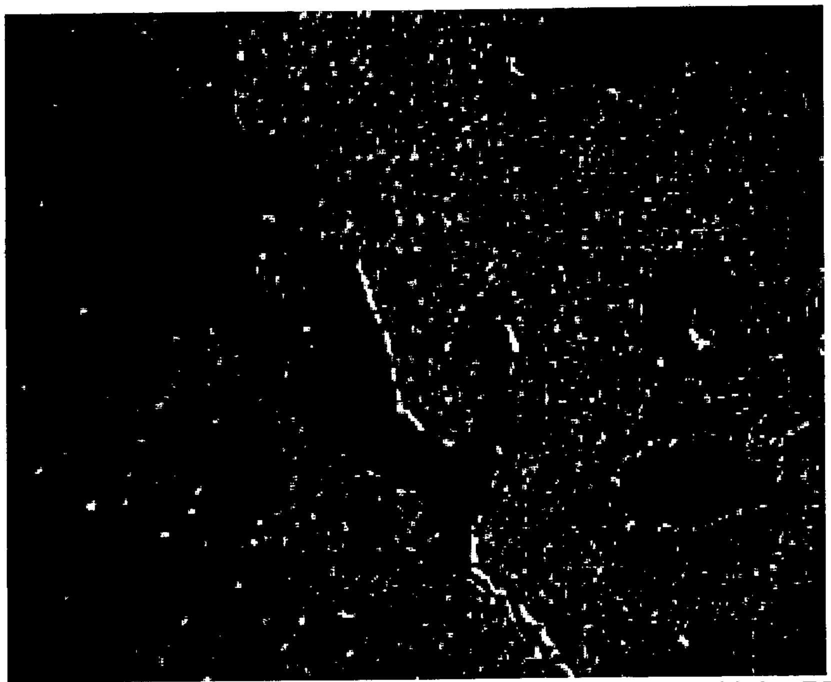


Figure 21a. Optical micrograph of failed titanium surface region of joint PE-PI-7 without glass scrim cloth , showing titanium surface and residual adhesive (dark areas) on surface (3.5x)

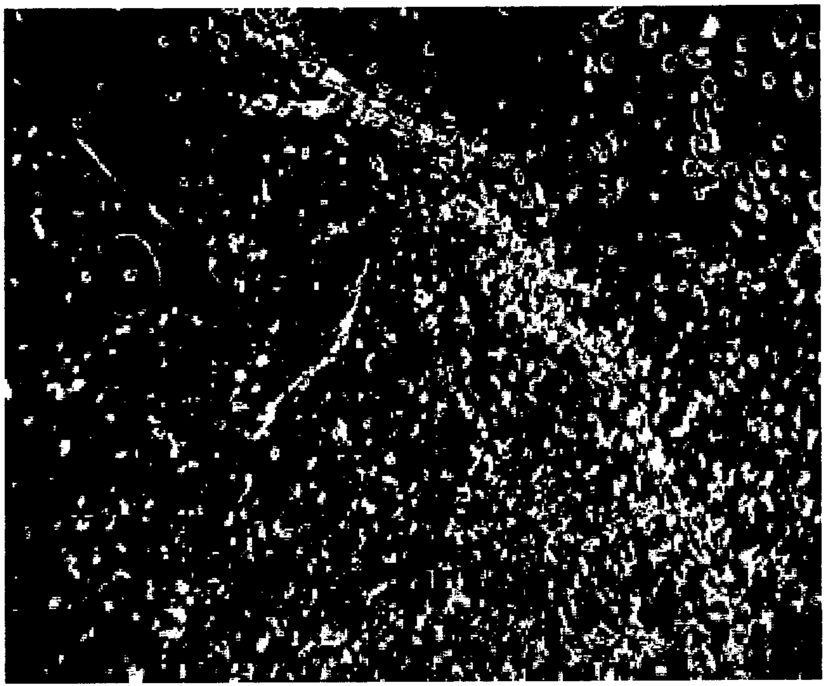
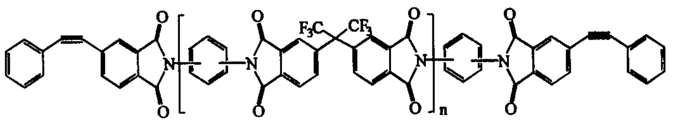


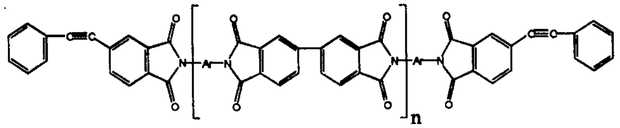
Figure 21b. Optical micrograph of failed adhesive region of joint PE-PI-7 without glass scrim cloth, showing adhesive on surface (3.5 x)

A comparison of tensile lap shear strengths of the best in this series with literature data is shown in Table 11. The conditions of joint fabrication, test temperature and Tg's are also listed. The data suggest that co-polyimide PE-6F-PDA-4K (70*p*/30*m*) with a 70/30 para/meta diamine mole ratio exhibits superior room temperature adhesive bond strength relative to all para PE-6F-p-PDA adhesive bond (3583 psi vs 2681 psi) for similar molecular weight levels, 4200, and at less stringent bonding conditions. The PETI-5 adhesive bond strength is superior to the 6F-PDA data in all cases, but the Tg of this material system (Tg, 270^{0}C) is too low for 300 and 350^{0}C applications. Therefore, the PE-6F-PDA para/meta compositions look promising for this application.

Table 11. Comparison of Tensile Lap Shear Strengths



PE-6F-PDA's



LaRC PETI-5 Ar = 3,4′-ODA (.85)
APB (.15)

	Bonding Conditions					
	Temp. (°C)	Pressure (psi)	Time (hr.)	Test Temp (°C)	Shear Strength MPa (psi)	T_g (°C)
PE-6F-PDA-4K (70*p*/30*m*)[1]	370	14.7	1	23	24.6 (3583)	371
PE-6F-PDA-4K (70p/30m) with PEPA-3,4′-ODA (90/10 blend)[2]	370	14.7	1	23	19.3 (2810)	374
PE-6F-p-PDA[3]						
3200	365	50	6	23	3.51 (552)	379
4200	365	50	6	23	18.5 (2681)	365
7000	365	50	6	23	7.59 (1,100)	365
7000	365	400	6	23	17.0 (2,469)	365
PETI-5[4] 5000	350	100	1	23	49.0 (7,100)	270

1. mole % para and meta phenylene diamine in co-oligomide
2. mole % oligomide and reactive diluent
3. Ref. 2, A.J. Johnson et. Al., Polymer 35(2) 4865-4973 (1994)
4. Ref. 3, J.W. Connell et. Al., SAMPE Tech. Conf., 28, 14-18 (1996)

3.0 Experimental

3.1 Materials

4,4′-(2,2,2-Trifluoro-1-phenylethylidene) diphthalic anhydride (3FDA) was prepared according to a published technique[1]. 3,4′-Oxydianiline (3,4′-ODA), Wakugama Seika Koygo, Ent., mp 84⁰C was recrystallized from 2/1 absolute ethanol/water and dried at 60⁰C for 10 hrs prior to use. 4-Phenylethynylphthalic anhydride (4-PEPA, Imitec Corp., m.p. 152⁰C) was purified by recrystallization in acetic anhydride prior to use. 1,4-phenylenediamine (p-PDA, Aldrich, m.p. 143-145⁰C) was used as received. 1-methyl-2-pyrrolidinone (NMP, Fisher) was distilled from calcium hydride under reduced pressure and stored under calcium hydride. 1,3-Phenylene diamine (*m*-PDA) and methanol was purchased from Aldrich and used as received. 4,4′-hexafluroisopropylidene dipthalic anhydride (6FDA) was purchased from Hoesch Celanese and recrystallized from acetic anhydride. Acetic anhydride and glacial acetic acid were both purchased from Fisher and used as received.

3.2 Experimental Materials Synthesized

3.2.1 Synthesis of Phenylethynyl end-capped 6FDA/PDA (*p/m*) co-oligomides

Synthesis Procedure

A general procedure was applied for the synthesis of all the oligomers. The PE 6F-PDA (*p/m*) co-oligomides were synthesized according to Figure 22.

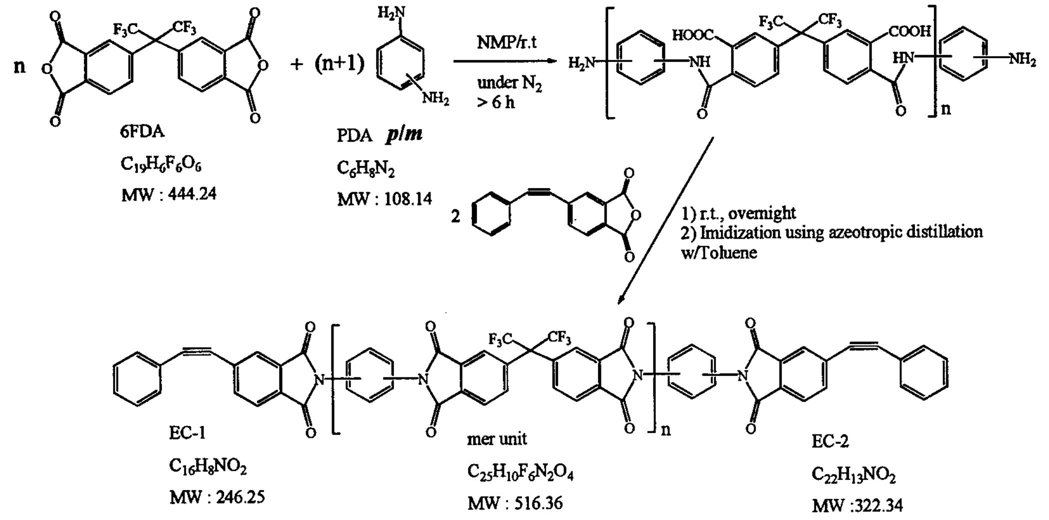


Figure 22. Reaction scheme for PE-6F-PDA oligomides showing molecular weights of monomers and oligomer units

The stoichiometry for 6F-PDA (*p/m*) with M_n 4,000 and 7,000 and para-/meta-phenylenediamine ratios 80/20 and 70/30 are listed in Tables 12 and 13 respectively. Details of the molecular weights for the monomers, repeat unit, and end-cap of the oligomer are shown in Tables 12, 13 and Figure 22 respectively. Procedure for the synthesis of PE-6F-PDA-4K (80/20) (M_n of 4,000), molar ratio of 80/20 for *p*-PDA to *m*-PDA. A mixture of p-phenylene diamine (*p*-PDA, 5.95 g, 36.70 mmol) and m-phenylene diamine (*m*-PDA, 0.99 g, 9.17 mmol) was added to a 250 mL round bottomed flask equipped with a magnetic stir bar. 100 mL of *N*-methyl pyrolidinone (NMP) was added and the solution was stirred at room temperature and nitrogen atmosphere to obtain a clear solution. 6FDA (7.71 g, 39.87 mmol) was then added, and the reaction mixture was stirred at room temperature under nitrogen atmosphere for a minimum of 6 hour, to yield an ambered colored solution. PEPA (8.93 g, 12.00 mmol) was then added and the reaction mixture was stirred overnight at room temperature under nitrogen atmosphere. Toluene (60 mL) was added to the solution and a Dean Stark trap and condenser were equipped to the reaction flask. The reaction mixture was heated to reflux using an oil bath. During the reaction, small samples were collected, precipitated in methanol and analyzed by FT-IR to determine the degree of imidization. After complete imidzation into methanol, the reaction mizture was continuously heated to remove most of the toluene. The hot reaction mixture was added to approximately 20 times volume (1 L) of methanol in a high speed blender. An off-white colored precipitate was collected by suction filtration and thoroughly rinsed with methanol. The collected precipitate was dried in a vacuum oven at 130°C overnight. The final product (22.30 g, 93% yield) was obtained as a fine off-white colored powder.

Table 12. Stoichiometry for the Synthesis of PE-6F-PDA (80*p*/20*m*) with M_n 4000 and 7000

	M_n of 6FPI	**6FDA**	**PDA**		**PEPA**	**Theo Yield (g)**	**H_2O (loss)**
			***p*- (80)**	***m*- (20)**			
Mw		**444.24**	**108.14**	**108.14**	**248.23**		**18.02**
n = 6.645	**4,000**						
mmol		6.645	6.116	1.529	2		15.29
grams		2.952	0.661	0.165	0.496	3.998	0.276
3X-Scale-up		**8.856**	**1.983**	**0.495**	**1.488**	**11.994**	**0.828**
n = 12.455							
mmol	**7,000**	12.455	10.764	2.691	2		26.91
grams		5.533	1.164	0.291	0.496	7.000	0.485
2X-Scale-up		**11.066**	**2.328**	**0.582**	**0.992**	**14.000**	**0.970**

Calculation formula:
$n = M_w$ (6FPI – EC1 – EC2) / M_w mer unit
6FDA = n mmol; PDA = n + 1 mmol, PEPA = 2 mmol; H_2O = 2n + 2 mmol
Theoretical yield = Mass[(6FDA + *p*-PDA + *o*-PDA + PEPA) – H_2O]

Table 13. Stoichiometry for the Synthesis of PE-6F-PDA (70*p*/30*m*) with M_n 4000 and 7000

	M_n of 6FPI	**6FDA**	**PDA**		**PEPA**	**Theo Yield (g)**	**H_2O (loss)**
			***p*- (70)**	***m*- (30)**			
M_w		**444.24**	**108.14**	**108.14**	**248.23**		**18.02**
n = 6.645	**4,000**						
mmol		6.645	5.352	2.294	2		15.29
grams		2.952	0.578	0.245	0.496	3.998	0.276
3X-Scale-up		**8.856**	**1.735**	**0.743**	**1.488**	**11.994**	**0.828**
n = 12.455							
mmol	**7,000**	12.455	9.419	4.037	2		26.91
grams		5.533	1.019	0.437	0.496	7.000	0.485
2X-Scale-up		**11.066**	**2.037**	**0.873**	**0.992**	**14.000**	**0.970**

Calculation formula:
$n = M_w$ (6FPI – EC1 – EC2) / M_w mer unit
6FDA = n mmol; PDA = n + 1 mmol, PEPA = 2 mmol; H_2O = 2n + 2 mmol
Theoretical yield = Mass[(6FDA + *p*-PDA + *o*-PDA + PEPA) – H_2O]

3.2.2. Synthesis of PEPA-3,4′-ODA Reactive Diluent (Fig. 23).

To a three-neck, 200 mL round bottom flask equipped with nitrogen inlet, condenser, and Teflon coated magnetic stir bar was added 2.402 g (0.012 mol) 3,4′-ODA, 6.454 g (0.026 mol) PEPA, 2.65 g (0.026 mol) acetic anhydride, and 50 ml glacial acetic acid. The mixture was heated and maintained at reflux for five hours under a nitrogen blanket. The reaction was then cooled, the precipitated product was filtered and then air dried. The crude product was recrystallized from acetic anhydride, washed with copious amounts of methanol and dried in vacuo at 200^{0}C for 16 hours. The light yellow powder was obtained with an 89% yield (10.23 g). Elemental analysis for $C_{44}H_{24}O_5BN_2$: Calc. C = 80.0%, H = 3.6%, N = 4.3%. Found: C = 79.46%, H = 3.99%, N = 4.31%. FT-IR: 2213 cm^{-1} (C≡C), 1775 and 1717 cm^{-1} (C=O), 1379 cm^{-1} (C-N). M.p. (DSC) 297^{0}C (sharp).

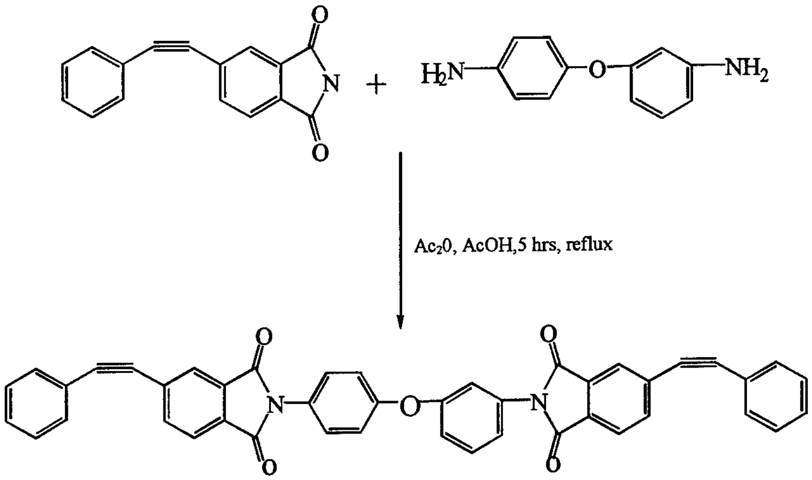


Figure 23. Synthesis of 3,4′-Bis[(phenylethynyl)phthalimido]diphenyl ether (PEPA-3,4′-ODA)

3.2.3 Synthesis of PE-6F-*m*-PDA Reactive Diluent

This material was synthesized in the same manner as used to prepare the PE-6F-PDA-4K oligomides described in Section 3.2.1. The reaction Scheme is shown in Figure 24.

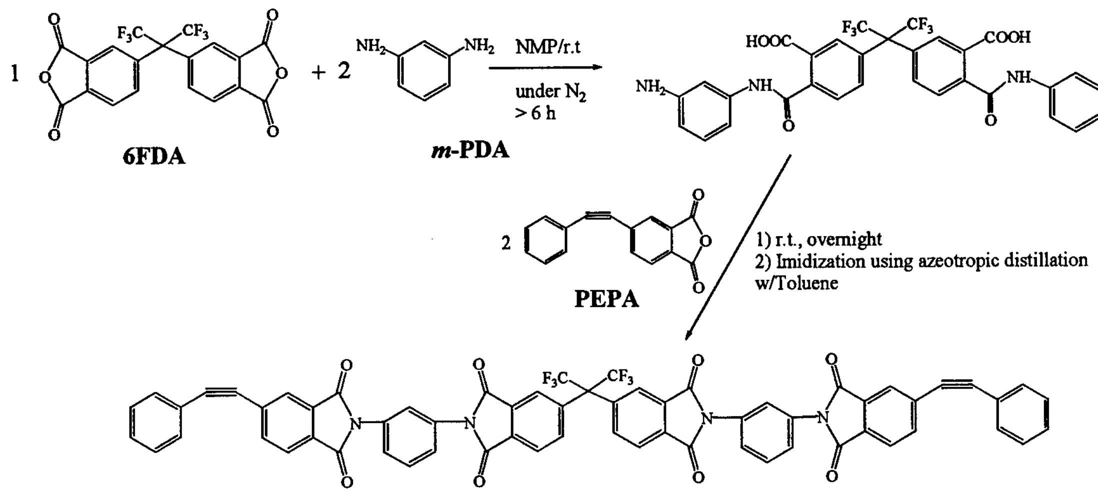


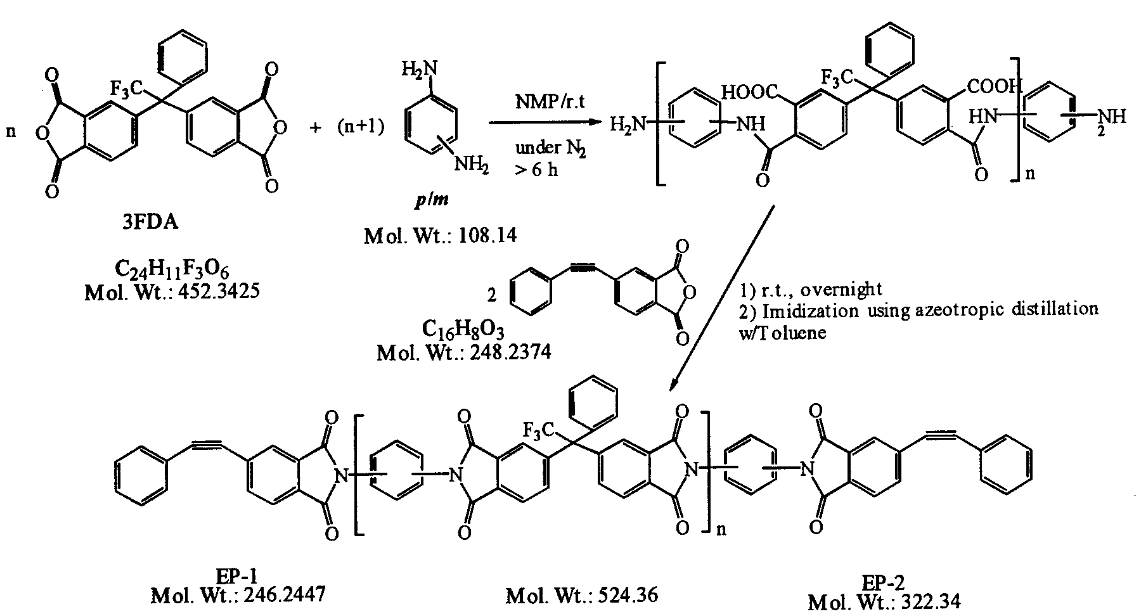
Figure 24. Synthesis of *N,N′*- bis [*N″N‴*-1,3-phenylenephenylethynylphthalimido)]-4,4′-hexafluoroisopropylidenediphthalimide (PE-6F-*m*PDA)

Preparation of PE-6F-*m*-PDA reactive diluent

To a 250 ml 3-meck round bottom flask, about 50 ml of 1-methyl-2-pyrolidinone (NMP) was added and a gentle stream of N_2 was passed through the solution for 30 min. 1,3-Phenylenediamine (*m*-PDA, 2.16g, 20.0 mmol) was added to dissolve followed by the addition of 6FDA (4.44g. 10.0 mmol). The solution was left stirred at room temperature under N_2 atmosphere overnight. PEPA (4.96g, 20.0 mmol) was then added and the solution was stirred at room temperature under N_2 atmosphere overnight. About 60ml of toluene was then added to the solution and the flask was equipped with a Dean Stark trap and condenser. The reaction mixture was heated to reflux using an oil bath. During the azeotropic distillation, water was drained occasionally. The reaction progress was monitored by FT-IR by analyzing the precipitate obtained by adding a small amount of reaction mixture to methanol. After FT-IR of the sample showed complete imidization, the reaction mixture was further heated to remove most of the toluene. The remaining reaction solution (while hot) was added dropwise to 1000 ml methanol in a high speed blender. The precipitate was collected by suction filtration followed by extensive rinsing using methanol. The solid was then dried in a vacuum oven at ca. 130°C overnight. The final product (10.30g, 95% yield) was obtained as light yellow colored powder.

3.2.4 Synthesis of PE-3F-PDA-4K (80*p*/20*m*) Co-oligomide

The stoichiometry for a 4.0g and 16.0g run is listed in Table 14 and the reactive scheme is shown in Figure 25.



Calculation formula:
n = (Mn of 3FPI – EC-1 – EC-2)/Mer unit
3FDA = n mmol; PDA = n + 1 mmol, PEPA = 2 mmol; H_2O = 2n + 2 mmol
Theoretical yield = Mass [(3FDA + *p*-PDA + *m*-PDA + PEPA) – H_2O]

Figure 25. PE-3F-PDA-4K (80p/20m) Co-oligomide Reaction Scheme

Table 14 Stochiometry for PE-3F-PDA-4K Synthesis

	M_n of 3F oligomer	3FDA	Phenylenediamine (PDA)		PEPA	Theo. Yield	H_2O (loss)
			para- (80%)	*meta-* (20%)			
MW		452.34	108.14	108.14	248.23		18.02
***n*=6.544**	4,000						
Mmol		6.544	6.035	1.509	2		15.09
Grams		2.96	0.653	0.163	0.496	4.00	0.272
4× Scale up		11.84	2.612	0.652	1.984	16.00	1.088

The oligomer was prepared using the standard procedure. To a dried 150mL three –neck flask was added the appropriate amount of NMP to eventually yield 20% (w/v) solution. Argon was bubbled through the solvent for 15 minutes. Next, the appropriate amount of diamine was added and stirred using a magnetic stir-bar until completely dissolved. At this point, 3FDA was added as a solid and the resultant solution stirred at room temperature for 24 hours. The PEPA end-capper was then added and the solution was left to stir for an additional 24 hours. Approximately 17 mL of toluene was added to the solution and heated to reflux. The oligomer was then imidized by azeotropic distillation using toluene. The solution was maintained at reflux conditions until the theoretical amount of water was collected in the Dean-Stark trap. The solution was then precipitated into a 20× excess of warm methanol in a high speed laboratory blender. The precipitate was filtered and washed with a copious amount of warm methanol. The oligomer was then dried in vacuo at 125°C for 18 hours to yield 14.6g (91.2%) of PE-PDA 80p/20m 4K. An infrared spectrum is shown in Fig. 26 and a TGA curve is shown in Fig. 29.

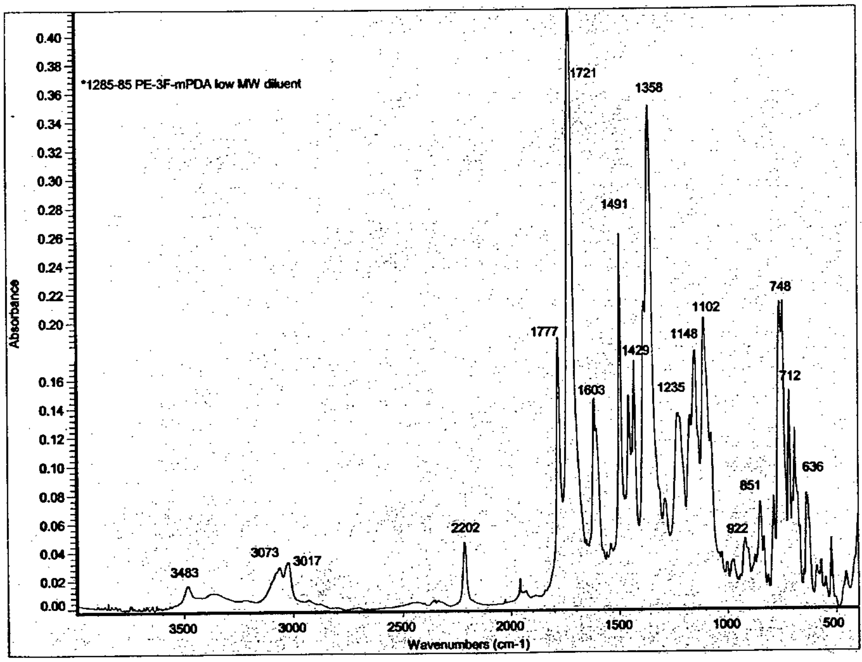
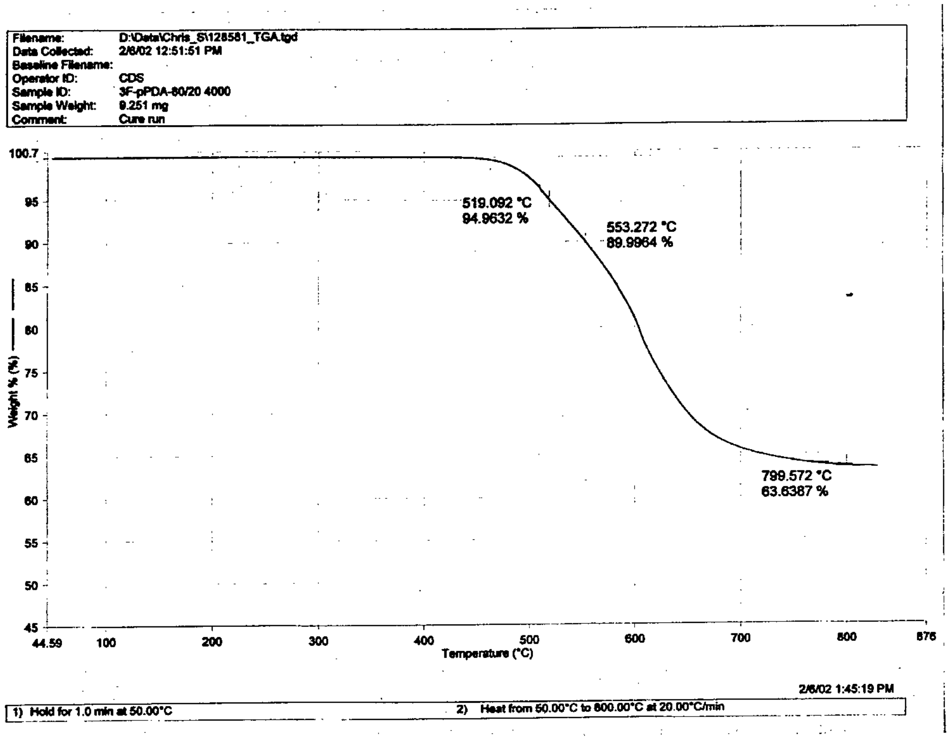


Figure 26. FT-IR of PE-3F-PDA 4K (80*p*/20*m*), thin film cast from chloroform



Filename: D:\Data\Chris_S\128581_TGA.tgd
Data Collected: 2/6/02 12:51:51 PM
Baseline Filename:
Operator ID: CDS
Sample ID: 3F-pPDA-80/20 4000
Sample Weight: 9.251 mg
Comment: Cure run

1) Hold for 1.0 min at 50.00°C
2) Heat from 50.00°C to 800.00°C at 20.00°C/min

Figure 27. Dynamic TGA (20^0C min^{-1} in N_2) of PE-3F-PDA 4K (80*p*/20*m*)

3.2.5 Synthesis of PE-3F-*m*PDA Reactive Diluent

The stoichiometry for the synthesis of this compound is shown in Table 15. The reaction scheme is shown in Figure 28. The compound was synthesized using the same procedure described above for PE-3F-PDA-4K 80*p*/20*m*. The product was obtained in a yield of 87.3% (9.55g). An infrared spectrum of this material is shown in Figure 29. The glass transition temperature as determined from DSC is shown in Figure 30.

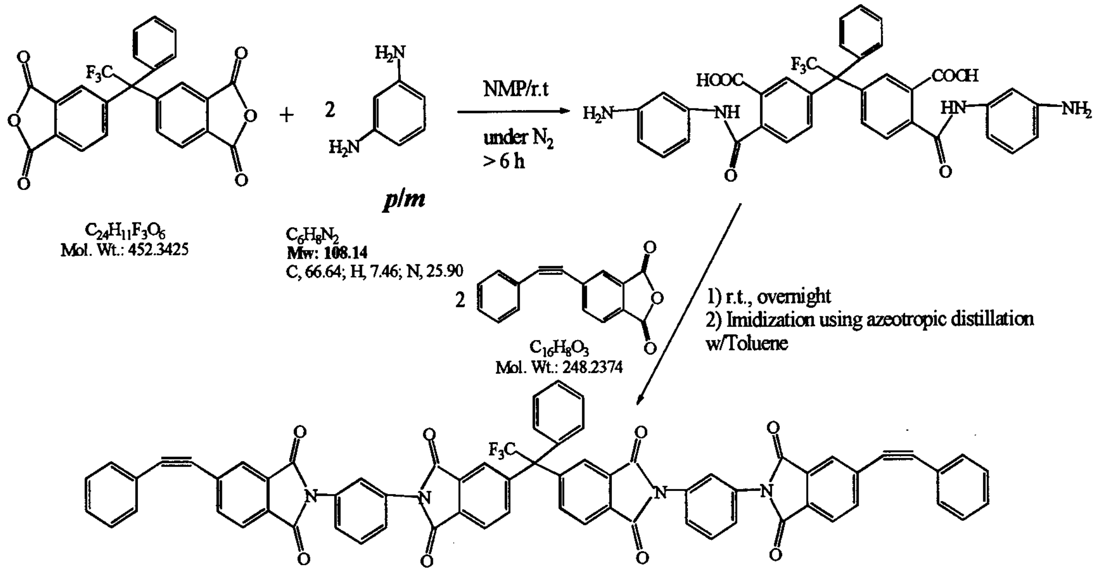


Figure 28. Reaction Scheme for PE-3F-*m*-PDA reactive diluent synthesis

Table 15. Stoichiometry of PE-3F-*m*-PDA synthesis

	3FDA	*m*-PDA	PEPA	Diluent	H_2O loss
Mw	452.34	108.14	248.23	1,093	18.02
mmol	1	2	2	1	4
Amount	0.452	0.216	0.496	1.093	0.072
10X sale	**4.520g**	**2.160g**	**4.960g**	**10.93g**	**0.72g**

Calculation formula:
3FDA = 1 mmol; *m*-PDA = 2 mmol, PEPA = 2 mmol; H_2O = 4 mmol

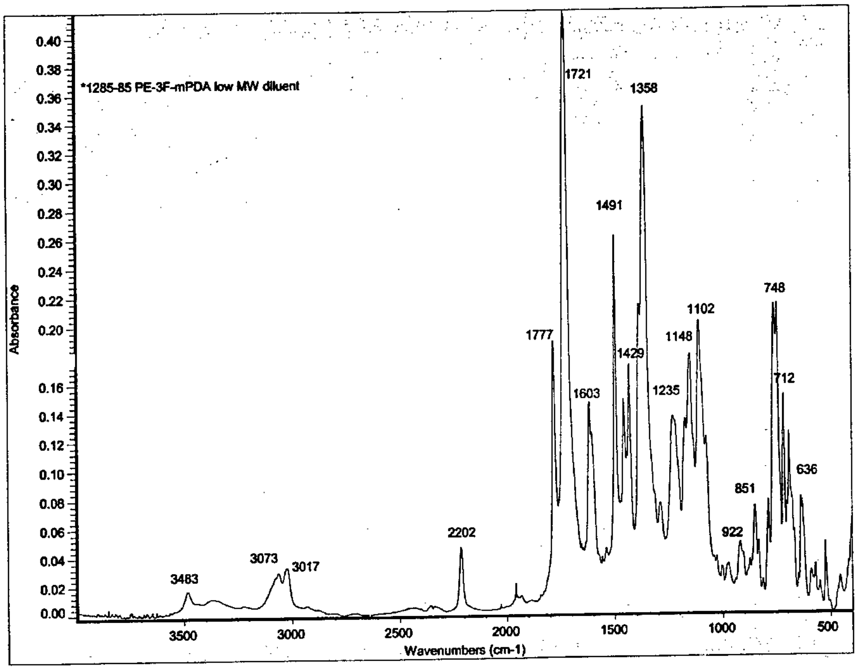


Figure 29. FT-IR of PE-3F-*m*-PDA diluent , thin film cast from chloroform

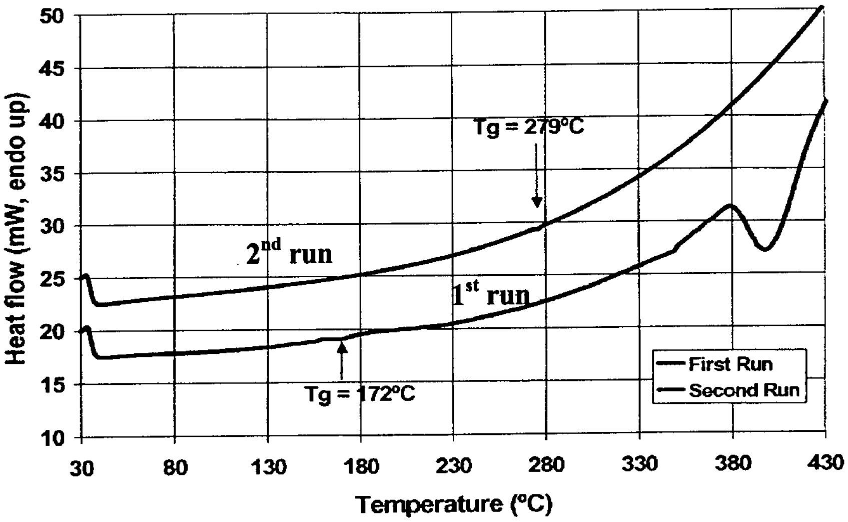


Figure 30. Tg of PE-3F-m-PDA diluent

3.2.6 Preparation of PE-6F-PDA-4K and –7K (p/m) / Reactive Diluent Blends

The stoichiometries of the PE-6F-PDA (p/m)/reactive diluent blends are listed in Tables 16 and 17. A general procedure was applied for the preparation of all the oligomers blends.

Procedure for the preparation of 6F-PDA-4K (80*p*/20*m*) and 3,4′-PEPA-ODA blend (PE-6F-PDA-4K(80/20)/PEPA-ODA at blend molar ratio of 90:10 is given as an example.

A mixture of 6F-PDA-4K (80*p*/20*m*) (4.910 g, 1.23 mmol) and PEPA-3,4′-ODA (0.090 g, 0.136 mmol) was dissolved in 25 ml of NMP assisted by heating. A homogeneous solution was obtained. This hot solution was added to 20 times its volume (500 mL) of methanol. An off white colored precipitate was obtained and collected by suction filtration followed by a thorough methanol rinse. The final product was dried in a vacuum oven overnight at 130 °C. Final product was obtained as fine off white colored powder, 4.74 g, 95% yield.

Table 16. Blending of Polyimide 6-FPI's and PEPA-ODA

6FPI's	6FPI	Reactive diluent (Mw = 660.67)	Pseudo-Mw of blend	Total amount
7,000 (80-20)	90 mole% 4.948 g	10 mole% 0.052 g	6,366.067	5.000 g
7,000 (80-20)	80 mole% 4.885 g	20 mole% 0.115 g	5,732.134	5.000 g
7,000 (70-30)	90 mole% 4.948 g	10 mole% 0.052 g	6,366.067	5.000 g
7,000 (70-30)	80 mole% 4.885 g	20 mole% 0.115 g	5,732.134	5.000 g
4,000 (80-20)	90 mole% 4.910 g	10 mole% 0.090 g	3,666.067	5.000 g
4,000 (80-20)	80 mole% 4.802 g	20 mole% 0.198 g	3,332.134	5.000 g
4,000 (70-30)	90 mole% 4.910 g	10 mole% 0.090 g	3,666.067	5.000 g
4,000 (70-30)	80 mole% 4.802 g	20 mole% 0.198 g	3,332.134	5.000 g

Table 17. Stoichiometry of Polyimide 6-FPI's and Reactive Diluent (PE-6F-*m*-PDA) Blends

FPI's	FPI	Reactive diluent (Mw = 660.67)	Pseudo-Mw of blend	Total amount
7,000 (80-20)	90 mole% 4.948 g	10 mole% 0.052 g	6,366.067	5.000 g
7,000 (80-20)	80 mole% 4.885 g	20 mole% 0.115 g	5,732.134	5.000 g
7,000 (70-30)	90 mole% 4.948 g	10 mole% 0.052 g	6,366.067	5.000 g
7,000 (70-30)	80 mole% 4.885 g	20 mole% 0.115 g	5,732.134	5.000 g
4,000 (80-20)	90 mole% 4.910 g	10 mole% 0.090 g	3,666.067	5.000 g
4,000 (80-20)	80 mole% 4.802 g	20 mole% 0.198 g	3,332.134	5.000 g
4,000 (70-30)	90 mole% 4.910 g	10 mole% 0.090 g	3,666.067	5.000 g
4,000 (70-30)	80 mole% 4.802 g	20 mole% 0.198 g	3,332.134	5.000 g

4.0 Characterization

4.1 Differential Scanning Calorimetry (DSC)

DSC of the imide oligomers was performed by a Perkin-Elmer DSC 7 Series analysis system at a heating rate of 20°C min^{-1} under nitrogen atmosphere at a flow rate of 20 cm^3 min^{-1}. The glass transition temperature (T_g) was taken at the inflection point of the heat flow versus temperature curve.

4.2 Thermogravimetric Analysis (TGA)

TGA of cured imide film specimens was performed by a Perkin-Elmer TGA 7 Series analysis system at a heating rate of 20°C min^{-1} under nitrogen and oxygen atmosphere at a flow rate of 20 cm^3 min^{-1}.

4.3 Infrared Spectroscopy (IR)

IR spectra of the imide oligomers and cured oligomers were taken using a Nicolet Magna 560 FT-IR system, on films deposited on KBr.

4.4 Intrinsic Viscosity

Intrinsic viscosities $[\eta]_{NMP}^{25}$ were obtained by dissolving the imide oligomer powder in NMP at a concentration of 0.5% (w/v) and measuring the elution time using a Ubbelohde viscometer in a thermostatted 25°C water bath.

4.5 Complex Viscosity

Rheological measurements were conducted on a Rheometric Scientific ARES mechanical spectrometer. Sample specimen discs, 2.54 cm in diameter and ~ 1.5 mm thick, were prepared by press molding the imide powder at room temperature. The compacted resin disc was subsequently loaded in the rheometer fixture equipped with 2.54 cm diameter parallel plates. The lower plate was oscillated at a fixed strain of 5% and a fixed angular frequency of 10 rad s^{-1} while the upper plate was attached to a transducer which recorded the resultant torque. Autotension was used which was set at 50 g (compression) with a sensitivity set at 10 g. The initial temperature, 200°C was set and the parallel plates and sample were equilibrated at this temperature for 20 minutes. Complex viscosity (η^*) as a function of temperature was measured from 200°C to 390°C at a rate of 4°C min^{-1}, but only the data between 300°C and 390°C are plotted because this is within the viscosity/temperature range of the minimum viscosity.

4.6 Proton Nuclear Magnetic Resonance (^{1}H-NMR) Spectroscopy

High resolution solution nuclear magnetic resonance (NMR) spectra were acquired using a Bruker DMX 500 MHz NMR spectrometer. The solution samples of the co-oligomides were prepared in deuterated chloroform ($CDCl_3$). Solution samples of 6FDA, *p*- and *m*-phenylenediamine, and PEPA-3,4′-ODA were prepared in deuterated chloroform ($CDCl_3$).

4.7 Molecular Weight Determination

The number average molecular weights of the co-oligomides were determined by proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy. The ^{1}H-NMR spectra of PEPA, 6FDA, and the PE-6F-PDA(p/m) co-oligomer are shown in Figures 14, 15, and 16, respectively. The spectra were run in $CDCl_3$. Chemical shifts for quantitation are assigned as follows:

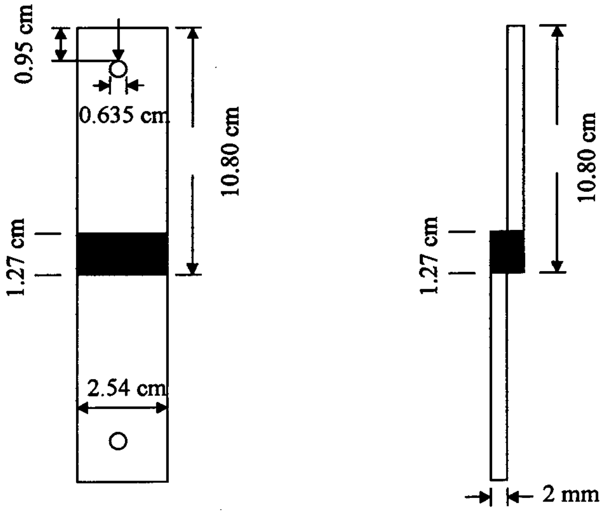
at 8.05 ppm: 2 ^{1}H fom 6FDA and 2 ^{1}H from PEPA, and
at 7.39 ppm: 6 ^{1}H from PEPA

$$n = \frac{\underset{8.05}{I_a} - {}^{2}/_{6}\,\underset{7.39}{I_b}}{{}^{2}/_{6}\,\underset{7.39}{I_b}}$$

where n = the number of repeat units, or moles of 6FDA.

4.8 Preparation of Lap Shear Joint Coupons

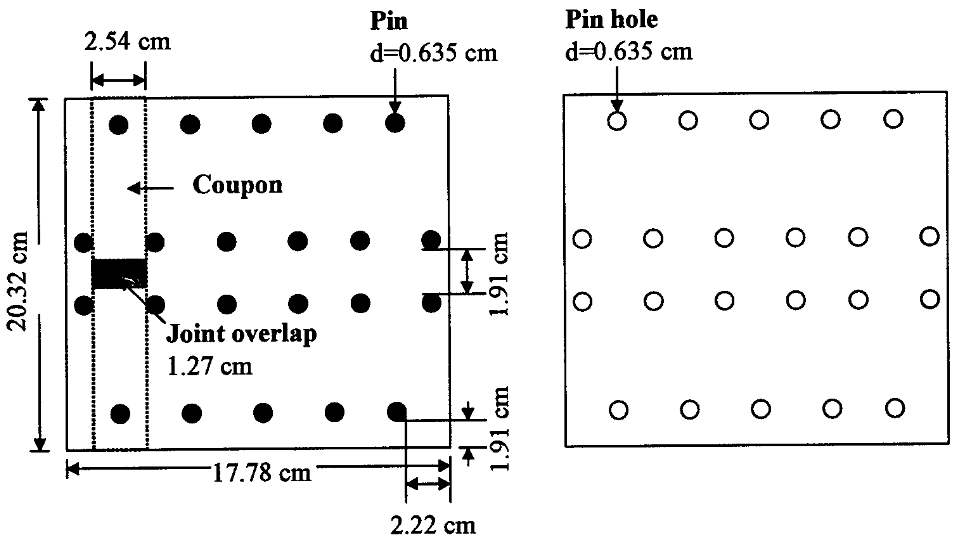
The lap shear joint coupon was made from Ti-6Al-4V titanium. The shape and dimensions of the coupon is shown in Figure 31. The pin hole is designed for placement of ¼" pin to testing in the tensile mode.



Top View **Cross section**

Figure 31. Lap shear joint coupon

The lap shear joint fixture was manufactured using stainless steel. Its shape and dimensions are shown in Figure 32 and Figure 33. The fixture is capable of hosting five joint specimens at the same time.



Base Fixture (plate) **Cover Fixture (plate)**

Figure 32. top view of the lap shear joint fixture

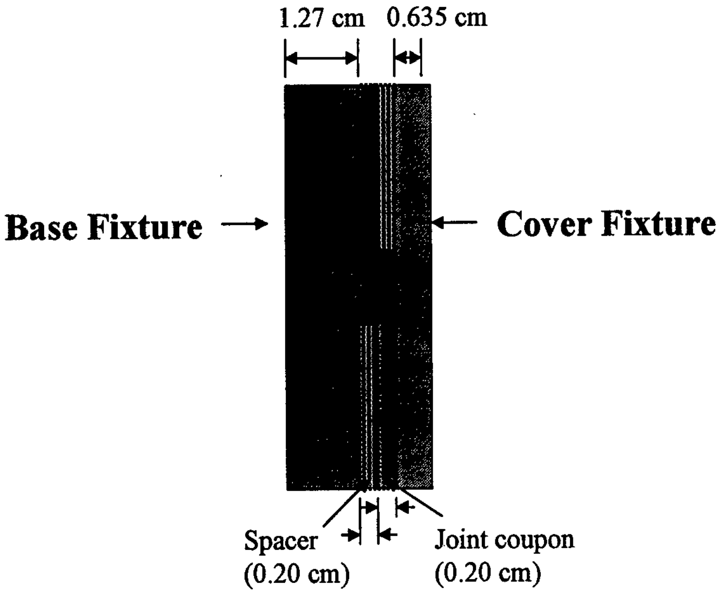


Figure 33. cross-sectional view of the lap shear joint fixture

4.9 Pretreatment of Titanium Coupon

The titanium alloy coupons (T1-6-Al-4V) were treated as outlined below before being bonded.

1. The coupon surface was cleaned using water, acetone, and methyl ethyl ketone, successively and air-dried.
2. The coupons were dry-blasted using fine grit of 250 aluminum oxide coated abrasives followed immediately by soaking in aqueous NaOH solution (13 g/250 ml water, i.e., 5.0% by weight) at ca. 70 °C for 5 min.
3. The coupons were then rinsed thoroughly by running tap water and dried in air at room temperature.
4. Semaco Pasa-Jell 107 (PRC-Desoto® International, Inc.) was applied on the surface of the above treated coupons and allowed to interact with the surface for 15 min before complete removal using running tap water.
5. The coupons were allowed to air dry.
6. Immediately the coupons were primed by painting an oligomer (or blend) solution in NMP at concentration of 30% by weight using an oil-based paint brush. The painted coupons were allowed to stand at room temperature for 1 hour before being vacuum-dried overnight at 130 °C. For joints PE-PI-8, PE-PI-9 and PE-PI-10, the primed surfaces were treated at 180^{0}C for 1 hour.
7. The coupons were later coated with more oligomer (or blend) by applying ca. 0.5 ml of 30%wt solution (in NMP) directly on the surface and spread to cover the overlap area completely, followed by drying at 130 °C overnight in a vacuum oven. This process was repeated three times in order to deposit sufficient material for bond formation. For joints PE-PI-8, PE-PI-9 and PE-PI-10, the coated coupons were dried at 180^{0}C for 1 hour.

4.10 Preparation of impregnated scrim cloth (112E glass)

112E Glass scrim cloth (A1100 finish) was used. The cloth was coated with a solution of oligomer (or blend) at a concentration of 30%wt using an oil-based paint brush. The painted cloth was placed on a Teflon® sheet and dried at 130 °C overnight in a vacuum oven. This cycle was repeated two or three times in order to deposit appreciable amount of material. The cloth was then cut into pieces with dimensions of 1.91 × 3.18 cm for bonding of the titanium to titanium test joints. For joints PE-PI-8, and PE-PI-9, the coated scrim cloth was treated at 180^0C for 1 hr. For joint PE-PI-10, the uncoated scrim cloth was placed on the second coat of adhesive on the titanium coupon and heat treated at 180^0C/1 hr.

4.11 Preparation of Lap Shear Joints

The coated coupons and impregnated cloth were placed between the coated surfaces of paired coupons in the specimen joint fixture (Figure 32). It was then placed in a stainless steel bag (30.48 x 45.72 cm) fitted with a connector to a vacuum pump. The bag was sealed tight using a rubber sealant, parallel bars and clamps. The bag was placed in a cold Tetrahedron press, (model MTP.8) and evacuated to less than 0.1mm Hg. The pressure was closed to within 0.25cm

(0.1