

Chapter 5

A Melt Processable Semicrystalline Polyimide Structural Adhesive based on 1,3-bis (4-aminophenoxy) benzene and 3,3', 4,4'-biphenyltetracarboxylic dianhydride.

Abstract:

Introducing crystallinity in polyimides offers the advantage of increased solvent resistance and retention of mechanical properties above the glass transition temperature (T_g). This work examines the thermal stability, semicrystalline morphology and adhesive properties of a new polyimide based on 1,3-bis (4-aminophenoxy) benzene (TPER diamine) and 3,3', 4,4'-biphenyltetracarboxylic dianhydride (BPDA). The polymer has a T_g of ca. 210°C and a T_m of 395°C. Polarized light microscopy was used to evaluate the morphology and spherulitic growth rates from the melt for $M_n=15,000$ daltons and $M_n=30,000$ daltons molecular weight polymer. Lap-shear specimens were made using Ti-6Al-4V alloy coupons using a melt process. Three surface treatments: gritblasting, chromic acid anodization and sodium hydroxide etch were evaluated and it was found that macroroughness provided by gritblasting was sufficient in providing a strong interface. The bonding conditions were optimized with respect to bonding temperature, bonding time and pressure and adhesive bonds made using the optimized conditions displayed a bondline thickness of ca. 2-3 mils. High room temperature lap-shear strengths of more than 6000psi were obtained and the fracture surface investigation using the SEM revealed a very rough and plastically deformed surface. Durability studies on lap-shear specimens were conducted for aging and testing temperatures of ambient, 177°C and 232°C. Significant stability was observed for all these aging and testing temperatures for a period up to seven weeks. The bond strengths were affected by testing temperatures rather than the aging conditions for the duration of the study. The influence of various solvents on

the lap-shear strengths was investigated by immersing the specimens in these solvents for 9 days. None of the solvents had any major effect on the strength of lap-shear specimens.

5.1 Introduction

Aromatic polyimides exhibit good thermal stability, chemical and radiation resistance and have been shown to be promising as high temperature structural adhesives^{1-2,9-10,17-18}. Polyimides are reaction products of diamines and dianhydrides and the final properties such as tensile strength, toughness, modulus and upper use temperature are dependent on the selection of the starting monomers. These aromatic based polyimide materials generally display high glass transition temperatures in the range of 200°C to 400°C or higher, which greatly depends on the stiffness of the backbone chain. However, most polyimides are amorphous in nature and this often leaves them susceptible to attack by different solvents. Thus, introduction of crystallinity in polyimides offers the advantage of increased resistance to solvents and enhanced radiation resistance. The presence of crystallinity can also lead to partial retention of properties much above the glass transition temperature thus effectively increasing the upper use temperature substantially. This makes semicrystalline polyimides very attractive and efforts have continued to develop such materials in various laboratories²⁻⁶. One successful way of introducing crystallinity in the polyimides has been the introduction of flexible aliphatic units in the chain backbone⁷. Although this introduces the crystallinity, it can greatly lower the glass transition temperature thereby often limiting the upper use temperature. Other attempts utilizing a change in the backbone structure have yielded semicrystalline polyimides with glass transitions in excess of 200°C and melting temperatures in the range of 400°C² respectively. However, to process such polyimides, it involves utilizing temperatures in excess of 400°C that often leads to the degradation of the material. Hence, most of the structural polyimide adhesives suffer from the drawback that they are often processed by casting the polyamic acid precursor onto a glass scrim cloth before use in the bonding process. This often involves elaborate adhesive tape/scrim cloth preparation, with the

imidization reaction taking place during this step⁸⁻¹⁰. Sometimes, successive coatings of polyamic acid are applied and the imidization step repeated several times to obtain the desired thickness⁸⁻¹⁰. Also, this often leads to the entrapment of reaction volatiles in the adhesive tape which are finally released during the bonding step. In order to reduce the high financial and environmental costs of such a process, there has been considerable interest in thermoplastic polyimides which are amenable to melt processing^{2, 3,5-7}. Melt processing is advantageous from both the economical and environmental standpoint and offers considerable savings on processing time which makes it very attractive for large scale industrial processes.

The high temperature stability of these materials is usually examined by dynamic or isothermal thermogravimetric analysis which detects the weight loss as either a function of increasing temperature or as a function of time at a given temperature. It has been shown that melt processing of even thermogravimetrically stable polyimides has an adverse effect on the recrystallization ability of these materials². Recrystallization has been shown to decrease substantially with increased temperature and time in the melt; while in most cases it was not possible to attain any crystallinity in the polyimide once it was taken to melt temperatures. Thus, efforts have continued to develop such semicrystalline polyimides that display sufficient thermal and recrystallization stability. Out of the relatively few such polyimides investigated in the literature, many have been characterized in laboratories at Virginia Tech². One such new polyimide developed here is based on 1,3-bis (4-aminophenoxy) benzene (TPER diamine or 1,3(4) APB) and 3,3', 4,4'-biphenyltetracarboxylic dianhydride (BPDA). The polymer has a T_g of ca. 210°C and a T_m of 395°C. This material has shown excellent thermal and recrystallization stability and very fast crystallization kinetics². The polyimide maintained its recrystallization ability after exposure to melt temperatures of 430°C and melt times of 30 minutes, with essentially no changes in the melting temperature and the heat of melting. These characteristics have made this polyimide an attractive candidate for melt processing.

This paper deals with the adhesive properties of this melt processable semicrystalline polyimide with surface treated Ti-6Al-4V alloy coupons using lap-shear test geometry. Although the lap-shear geometry suffers from various drawbacks such as

presence of a bending moment, peel stresses and non-uniform shear stresses along the adhesive layer²⁶, this test serves as a useful tool for evaluating the ultimate strengths of various adhesives and also affords easy comparison with other similar studies in the literature. This test was thus selected for evaluating the adhesive properties of TPER-BPDA-PA. The first steps in the adhesion study were the selection of an appropriate molecular weight polyimide to be bonded and the evaluation of several common surface treatments. Polyimides inherently show a very high melt viscosity due to their rigid aromatic backbone. This has been one of their major drawbacks and efforts have continued to lower the viscosity to improve processability. Wetting of the substrate and good interfacial contact is critical in obtaining a strong and durable interface. The earlier characterization studies with this polyimide involved primarily the use of $M_n = 30,000$ daltons (30K) material. This molecular weight version displayed very high viscosity of the order of 10,000 Pa.s and hence there was a need to lower the viscosity. It was found that lowering the number average molecular weight to 15,000-daltons (15K) decreased the viscosity substantially while still producing films that were creasable. This lower molecular weight allowed the use of lower bonding pressure of ca.100 psi that is in the range of traditional processing equipment, e.g. autoclaves.

Suitable surface preparation is essential in any adhesive work and the presence of a robust interface is necessary for making a strong and durable bond. In this regard much work has been presented in literature with the applicability of various surface treatments for Ti-6Al-4V alloy substrates. The surface treatments generally involve the removal of weak boundary layers and the creation of new surfaces that are chemically and mechanically compatible with the adhesive. Traditional processes like chromic acid anodization (CAA), sodium hydroxide anodization (SHA) and silane coupling agents have been used to form a stable oxide layer on the surface¹¹⁻¹³. Some studies have dealt with the effect of the surface morphology of this oxide layer on bond strength and durability. In this regard the surface treatments have been generally divided into three groups by Venables et al^{14,15}.

These are :

Group I: surface treatments which result in no microroughness ($<0.1 \mu\text{m}$) or macroroughness ($>1 \mu\text{m}$)

Group II: surface treatments that result in a large degree of macroroughness. Sandblasting used in this work falls in this category.

Group III: surface treatments that produce a microporous oxide with little or no macroroughness. The chromic acid anodization and sodium hydroxide etch fall in this category although the latter also results in some amount of macroroughness. The presence of microroughness has been advocated for attaining better bonds and much of these arguments are based on increased mechanical interlocking that this microroughness may provide^{13, 14}. Although these oxides have been shown to be effective for moderately harsh environments like 60°C and 95% relative humidity, they result in very low bond strengths if exposed to temperatures higher than 300°C ¹⁴⁻¹⁶. In the present work three such common treatments were selected and evaluated.

The presence of a suitable and strong interface is often indicated by the mode of failure of the adhesive specimen. In this regard, a cohesive failure, i.e. failure in the adhesive, is the desired objective and is a sign of a strong interface. However, once such an interface has been obtained, the strength of the adhesive bond is primarily dependent on the properties of the polymeric adhesive. For a semicrystalline polymer such as the one used in this work, the polymer properties like modulus, yield strength and toughness may significantly depend on the degree of crystallinity and the crystalline morphology. The way the crystalline content is arranged is affected by factors like thermal history, strain in the melt at the time of crystallization, presence of nucleating agents and the molecular weight of the polymer. Crystallization of an unstrained melt, however, typically promotes a crystalline morphology that is usually spherulitic, the spherulites themselves being composed of outward radiating lamellae originating from a centralized nucleation point. The degree of crystallinity within a spherulite may vary significantly for different polymers and also the size and the number of such spherulitic moieties may vary considerably. These factors influence the morphology and the overall degree of crystallinity and are strongly dependent on the structure of the polymer chain, molecular weight and the thermal history. In the present work the semicrystalline morphology was investigated by

optical microscopy as a function of various crystallization temperatures. The effect of crystallization temperature on the subsequent morphology will be discussed. The information gained from this portion of the study was utilized in the development of an optimum thermal cycle for forming the adhesive bonds. The other factors considered in the optimization procedure were bonding temperature, time and pressure.

After optimizing the bonding conditions, the next step was to study the durability of these lap-shear bonds when exposed to high temperatures. High temperature structural adhesives are often required to sustain temperatures of ca. 177°C for a long duration of time^{17, 18}. In addition, the studies dealing with high temperature adhesives often have utilized testing temperatures of ambient, 204°C and 232°C⁸⁻¹⁰. For this study, aging temperatures of ambient, 177°C and 232°C and aging times of 1, 3 and 7 weeks (~1200 hours) were selected. While the material in any such high temperature environment may repeatedly encounter these high temperatures, the failure may be initiated at some different temperature due to various reasons. Thus in this study, all the samples which were aged at room temperature, 177°C and 232°C were also tested at each of these aforementioned temperatures. Finally, the effect of various common solvents on the lap-shear strength will also be presented.

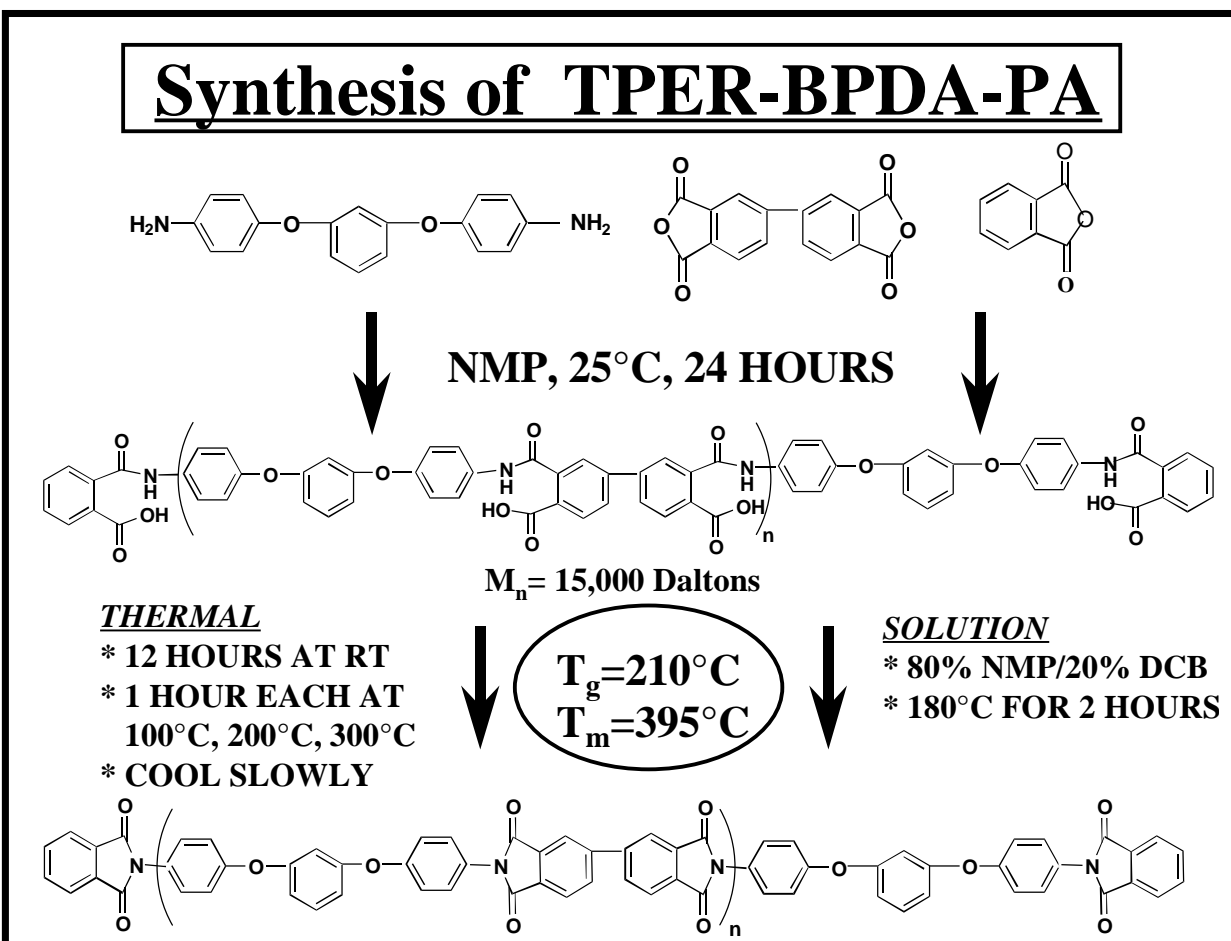
5.2 Experimental

5.2.1 Synthesis

1,3-bis (4-aminophenoxy) benzene (TPER diamine) was supplied by Ken-Seika and was recrystallized from toluene before use. 3,3', 4,4'-biphenyltetracarboxylic dianhydride (BPDA) was supplied by the Occidental Chemical Corporation and was dried at 120°C prior to use. The endcapper phthalic anhydride (PA) was obtained from Aldrich and sublimed prior to use. N-methylpyrrolidinone (NMP) and 1,2-dichlorobenzene (DCB) were obtained from Fisher and vacuum distilled after drying over P₂O₅ before use.

Polymer samples were synthesized with a number average molecular weights 15,000 (15K) and 30,000-(30K) daltons by controlling monomer and endcapper concentration. The monomer concentration was calculated using the Carothers equation. The reaction vessel was a three neck round bottom flask equipped with a mechanical stirrer, nitrogen inlet and a drying tube. Sufficient NMP was added to achieve a 10% solids concentration and the solution was allowed to stir for 24 hours, to afford a homogenous poly(amic acid) solution as shown in Scheme I. A stepwise thermal imidization procedure was utilized which has been used successfully in the past². The first step was the casting of the poly(amic acid) precursor on the pyrex glass plates. It was important in this work to obtain films with uniform thickness as the initial film thickness and the bonding pressure served as the controlling factors in obtaining the desired final bondline thickness. To achieve the desired uniform thickness of the final films (~2mils for 15K and ~3mils for the 30K) and also to prevent any resin flow out of the glass plates, careful control was exercised on leveling the glass plates. This was done by using aluminum base plates equipped with three screws at the corners. The problem of resin overflow was particularly encountered for the 15K resin as the temperature was raised due to the decreased poly(amic acid) viscosity. These plates were placed in the vacuum oven overnight until smooth non tacky films were obtained. Thermal imidization was achieved by raising the temperature to 100°C, 200°C and 300°C and holding at each of these temperatures for 1 hour. The time to go from one temperature to the next was ca. one hour each at the fastest heating rate available with the oven. After the completion of the cycle, the plates were allowed to cool down to room temperature before being removed from the oven. The films were carefully stripped off the glass plates in hot water and stored in a dessicator before use. For preparing the lap-shear specimens the film was carefully cut into pieces having the dimension of 2.54 cm × 1.27 cm and the thickness of was measured using the micrometer before use.

Synthesis of TPER-BPDA-PA



Scheme 5.1 Scheme followed for the synthesis of TPER-BPDA-PA.

5.2.2 Characterization:

Thermogravimetric (TGA) studies utilized a Seiko TG/DTA and all experiments were carried in either a nitrogen or air atmosphere. The temperature was calibrated using indium and zinc standards and the dynamic experiments utilized a heating rate of 10°C/min. The isothermal experiments were performed for a duration of 1000 minutes and the final weight loss reported.

The DSC experiments were conducted with a Seiko DSC 220C on 6-8 mg of sample under a nitrogen purge and a heating rate of 10°C/min unless otherwise specified. Indium, tin and zinc were used to calibrate the temperature and the heat flow. The DSC curves shown in the paper have been normalized to a 1mg-sample mass.

Rheological experiments were carried out on a Bohlin VOR Rheometer using a 12mm diameter parallel plate fixture. The temperature was controlled with a Bohlin HTC using nitrogen as the heating gas. The samples for this test were prepared by pressing together several of the imidized films at room temperature. The fluids torque measuring head was used with a 96 g-cm torque bar. Testing was done using the oscillation mode with a frequency of 0.1 Hz and a strain of 2%. The data was collected from 395°C and the rate of heating was approximately 3°C/min.

Polarized optical microscopy was carried out on a Zeiss optical microscope equipped with a Linkam 600 hot stage and 35mm camera. The hot stage was calibrated using indium, tin and zinc. The same imidized film, which was used for the adhesive work, was also utilized for doing the optical microscopy. The film (~2 mils) was sandwiched between two glass slides and a nitrogen purge was maintained inside the hot stage. The sample was taken to 430°C and kept there for 20 minutes before being quenched to a specific crystallization temperature or cooled to room temperature. The quenching was achieved by using a separate nitrogen source.

For fracture surface analysis of the lap-shear specimens, the overlap area was cut and sputter coated with a layer of gold of ca. 100Å using a Bio-Rad E5400 high resolution

sputter coater. A Cambridge instrument stereoscan model 200SEM was used to analyze the surface structure.

Lap-shear tests were conducted in accordance with ASTM D1002. Ti-6Al-4V alloy was purchased from 'President Titanium Inc.' in the form of 2.54 cm × 10.16 cm × × 0.3175-cm coupons. The strips of the polyimide film were cut into 2.54 cm × 1.27 cm pieces after which these were stacked up and carefully placed between the two titanium adherends. For all the bonding purposes the total thickness of the film utilized was 6 mils. Because of this relatively thin bondline thickness, it was important to match the titanium coupons very carefully. Five to six lap-shear specimens were made in a single run of the hot press. The thickness of all the titanium coupons was measured using calipers and the coupons were matched to less than 0.01mm before use. The hot press used was equipped with four thermocouples in the platens. The necessary rate of cooling could be achieved by utilizing water as a coolant. An Instron universal testing machine equipped with a 25,000 lbf. (11,325 kgf) load cell was utilized for breaking the lap-shear specimens.

5.2.3 Surface treatment:

In order to make a strong interface, three different surface treatments were initially evaluated. These were standard sandblasting, chromic acid anodization (CAA) and a sodium hydroxide etch. The coupons utilizing the standard sandblasting were washed in water, dried in an oven and subsequently wiped with acetone. The chromic acid anodization consisted of scrubbing with a crocus cloth to promote a mirror like finish and a water break free surface. The coupons were subsequently soaked in a Isoprep 177 solution (75 g/l) supplied by Boeing for 10 minutes at room temperature with stirring. The coupons were rinsed in de-ionized water and soaked in an acid solution consisting of fuming nitric acid (151 ml), de-ionized water (114 ml) and HF (10.9 ml) for 1.5 minutes. The coupons were rinsed again with de-ionized water and checked for water break free surface. If water did not spread on the surface then the coupons were soaked again in the

acid solution. The anodization was carried out at room temperature in a solution consisting of 45-g/l chromic acid solution for 20 minutes using 5 volts and 1.25 amp/ft². The desired current density was achieved using 48-52% HF solution. The coupons were rinsed with de-ionized water and dried at 50°C for 1 hour. These coupons were stored in a desiccator and bonded within 72 hours of anodization. For the sodium hydroxide etch, the solution was prepared by dissolving Turco 5578 (supplied by Boeing) in deionized water. The coupons were abraded and washed with acetone; subsequently the coupons were immersed in Turco 5578 solution (37.6 g/l) at 70-80°C for 5 minutes. The coupons were rinsed in de-ionized water for 5 minutes at room temperature and immersed in a second Turco solution (360g/l) at 80-100°C for 10 minutes. The coupons were then soaked in deionized water at 60-70°C for 5 minutes and subsequently dried in an oven.

5.3 Results and Discussion

5.3.1 Thermal Stability:

Thermogravimetric analysis has been the traditional method to evaluate the thermal stability of most high temperature polyimides. This technique relies on detecting the loss in sample weight due to emission of volatiles and degradation products as a function of varying temperature or time. Figure 5.1 shows the temperature scans of TPER-BPDA-PA (15K) in air and in nitrogen. The 5% weight loss temperatures in air and nitrogen are 572°C and 564°C respectively. Also, isothermal scans of 15K material at 430°C in air and nitrogen for a duration of more than 16 hours were performed to assess the weight loss characteristics at this melt processing temperature. The 5% weight loss time in air was 372 minutes while there was only 2.4% weight loss in nitrogen after 1000 minutes. These values compare well with other semicrystalline polyimides like New-TPI². However, earlier studies in this laboratory have shown that a thermogravimetric experiment is not the best means to evaluate all the facets of thermal stability of these semicrystalline thermoplastic polyimides if they are to be candidates as melt processable materials. Crosslinking and chain-branching reactions may occur above the melting temperature of the polymer without any significant weight loss. These reactions can adversely affect the recrystallization ability of the polyimide and indeed this seems to be the case for most semicrystalline polyimides investigated in the literature and in this laboratory¹.

Figure 5.2 shows the DSC rescans of TPER-BPDA-PA (15K) after heating the polymer to melt temperatures of 430°C for 1 min, cooling to below the glass transition at a rate of 200°C/min, and then again heating to 430°C at 10°C/min. This was repeated several times although only the initial and the subsequent four rescans are reported here. It is observed that the DSC melting point and $\Delta H_{\text{melting}}$ remain relatively unaffected after repeated exposures to a melt temperature of 430°C. Also, as shown earlier², this polyimide crystallizes during the cooling scan as is indicated by the absence of any

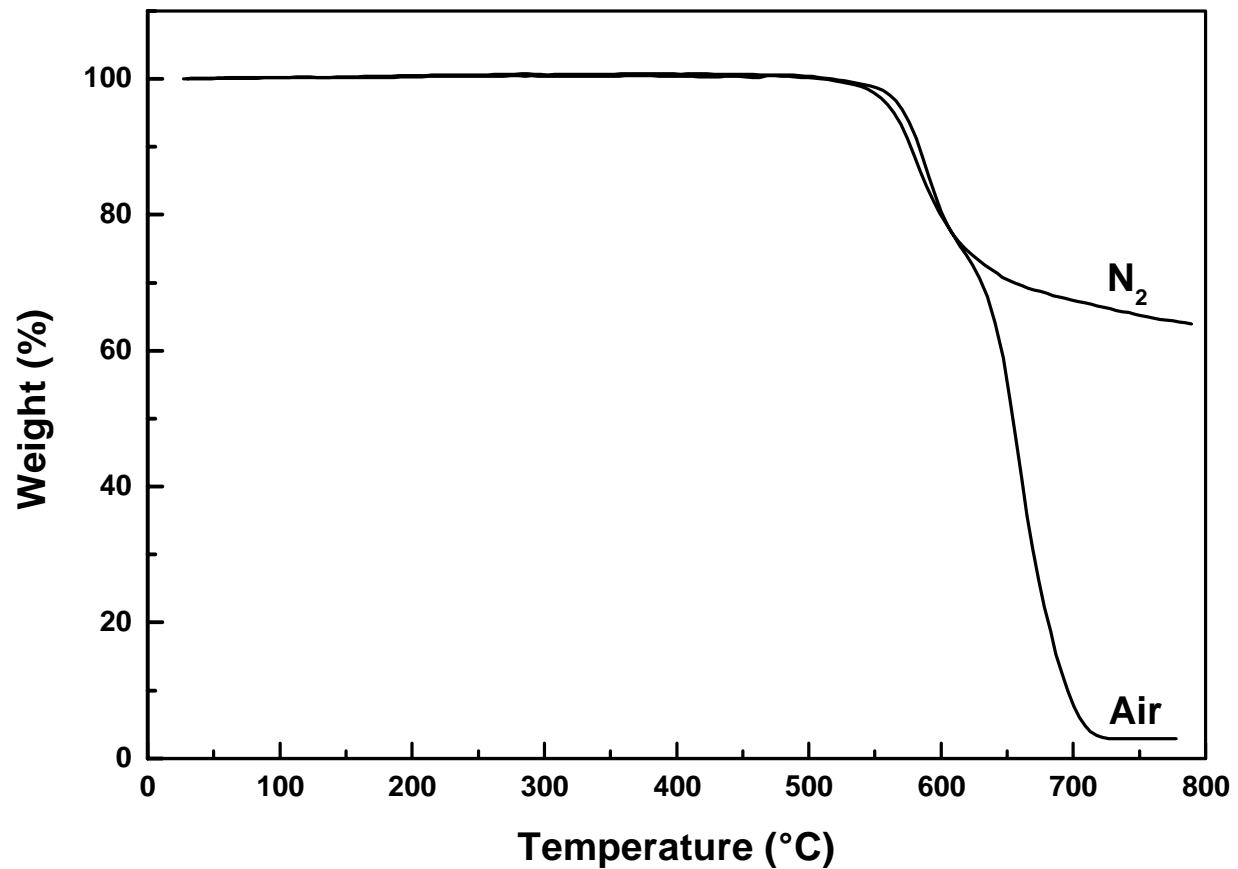


Figure 5.1 Percentage weight loss as a function of increasing temperature in nitrogen and air for TPER-BPDA-PA (15K) when heated at 10°C/minute.

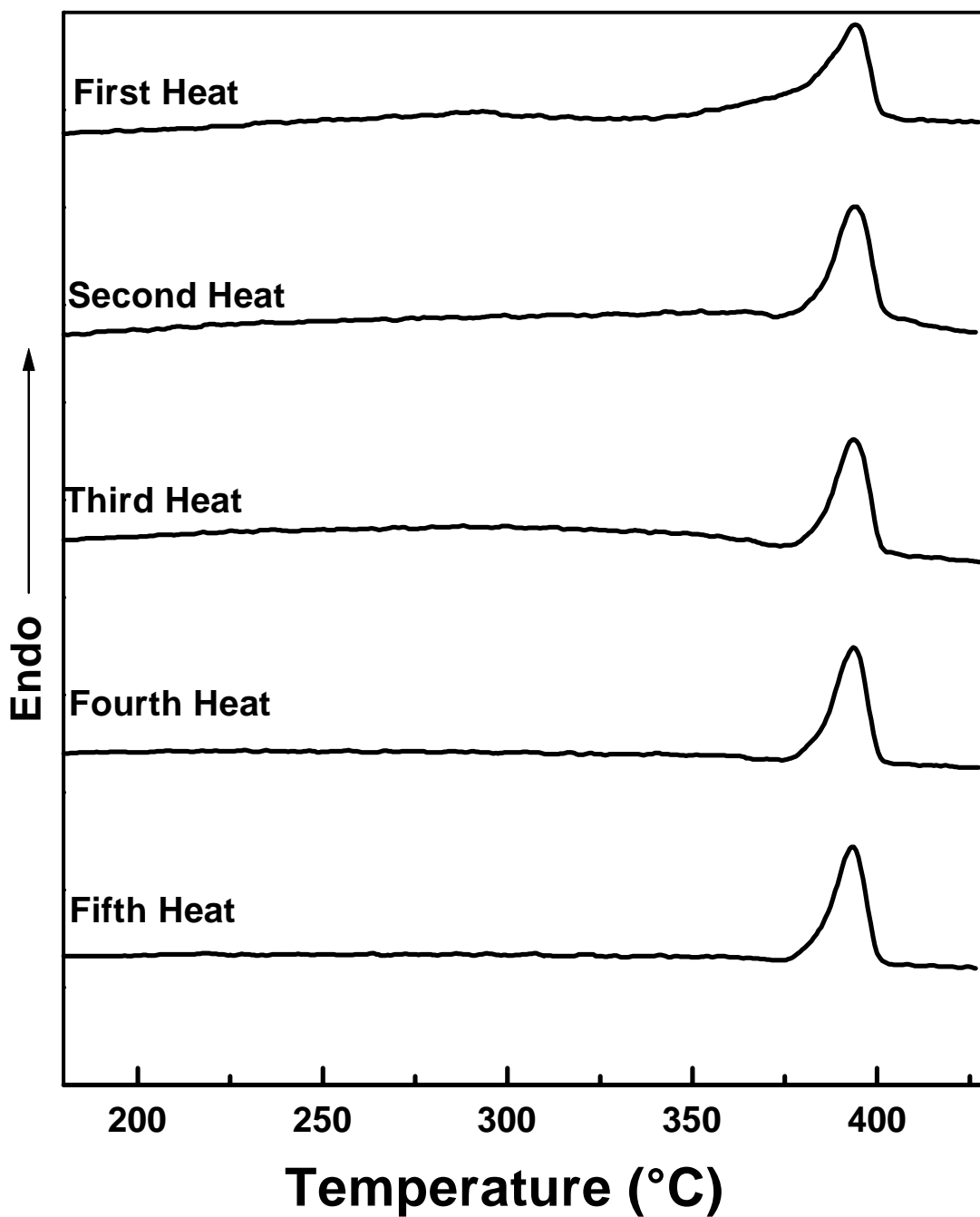


Figure 5.2 Consecutive DSC heating scans for TPER-BPDA-PA ($M_n=15,000$ daltons) after heating to 430°C at 10°C/min, holding for 1 min, quenching to 150°C and reheating at 10°C/min.

significant crystallization exotherm during the heating scan. This indicates the fast crystallization kinetics of the system even after repeated exposures to relatively harsh melt conditions in excess of 400°C. Also, at 430°C this behavior is maintained for 30 min, though for longer duration some effect on the recrystallizability of the material from melt conditions begin to be noted². The reduction in molecular weight from $M_n=30,000$ to $M_n=15,000$ does not affect the recrystallization stability of the material. The $\Delta H_{\text{melting}}$ for the 15K material is 39.6 J/g and for 30K material is 24.5 J/g which indicates the higher amount of crystallinity present in the lower molecular weight sample as might be expected.

5.3.2 Melt Rheology

Melt viscosity is an important property for any hot-melt thermoplastic adhesive application. Lower viscosity is required of the adhesive for enhancing the spreadability and for ease of applicability¹⁹. Often, this requires using the lower molecular weight versions of the polymer or the use of suitable diluents¹⁹. It is well known, however, that molecular weight also affects the mechanical properties of the polymer. At molecular weights below the entanglement molecular weight (M_e) the mechanical properties are generally poor but there is a substantial improvement in the properties as the molecular weight is increased beyond this critical value. The viscosity on the other hand increases with an increase in the molecular weight ($\eta \propto MW^1$ below M_e and $\eta \propto MW^{3.4}$ above M_e). In this regard, most hot-melt adhesives like ethylene-vinyl acetate copolymers, polyvinyl acetates, polyethylene and polyesters can be used above their entanglement molecular weight and yet afford low viscosity. However, this problem is especially significant for rigid chain polymers like aromatic polyimides (like the one used in this work) which often show very high melt viscosity above their entanglement molecular weights. Figure 5.3 shows the viscosity of $M_n=30,000$ daltons TPER-BPDA-PA as a function of increasing temperature. Although the material shows significant thermal stability with the viscosity essentially constant up to 450°C, the viscosity is too high to allow easy spreading at pressures of 100-200 psi, which are common for many structural adhesives. Bonding pressures lower than 300 psi are necessary in order to use the polymer as a structural

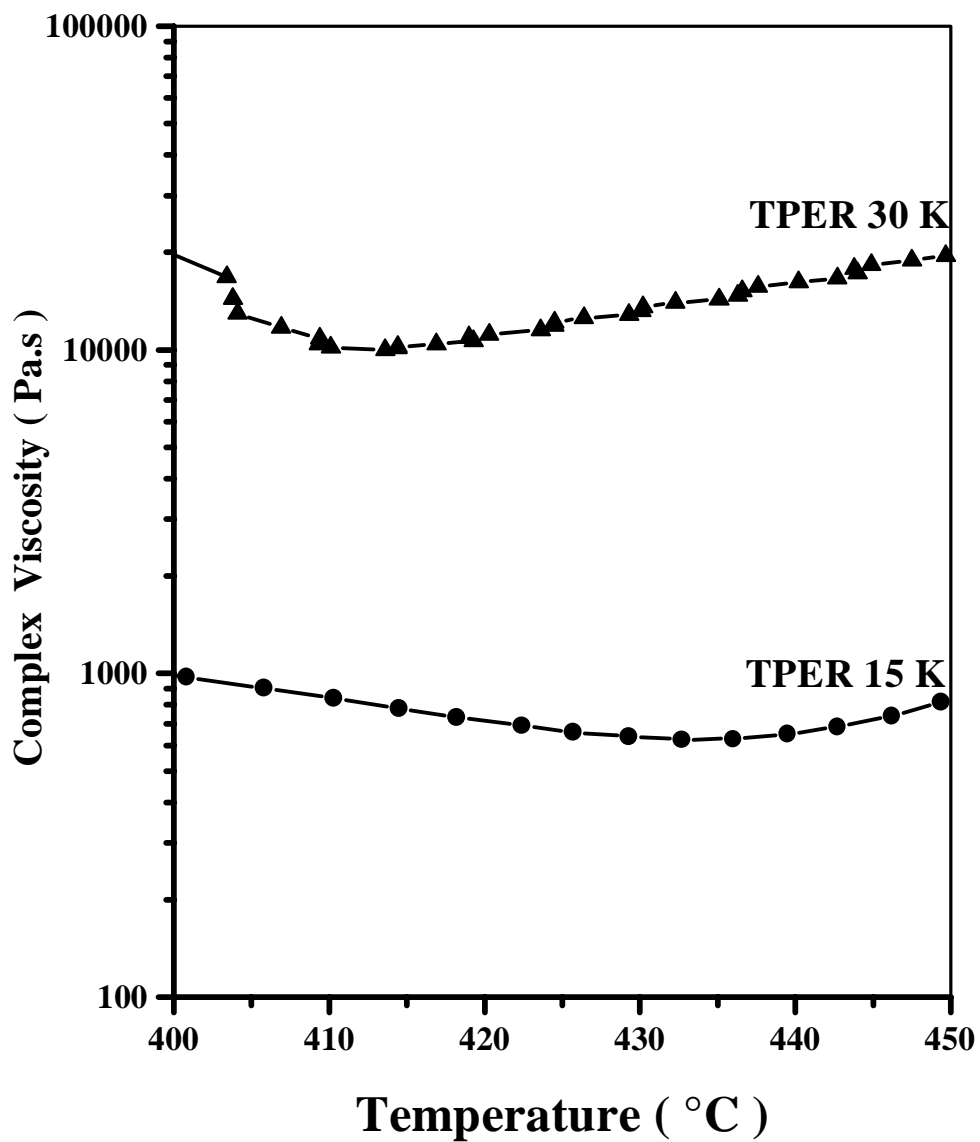


Figure 5.3 Complex viscosity as a function of increasing temperature for TPER-BPDA-PA (30K) and TPER-BPDA-PA (15K).

adhesive in large scale industrial processes^{9, 10}. Hence, the molecular weight was decreased to $M_n=15,000$ daltons (15K) which resulted in a large drop in viscosity by almost an order of magnitude. As stated earlier, the film with this molecular weight was still creasable although the elongation at break in a tensile test was reduced from ca. 140% for the 30K film to ca. 22% for the 15K film at the same strain rate for testing. The polymer with lower molecular weight of 12K and 10K was also prepared but was extremely brittle and lacked any structural integrity for a tensile test. It is clear from Figure 5.3 that the 15K version of the polymer also displayed very good thermal stability with much lower viscosity at temperatures almost 55°C above the DSC melting temperature. The reason for this thermal stability is use of full endcapping of the polymer chains by phthalic anhydride as discussed elsewhere². Hence, the 15K material was selected and the data presented in this paper will focus on the use of only this molecular weight polymer.

5.3.3 Morphology of TPER-BPDA-PA:

The initial cast and thermally imidized film was semicrystalline and showed a fine grainy morphology indicating very small superstructure (Figure 5.4). Recall that this initial film undergoes a complex thermal history where the polyamic acid is converted to polyimide when exposed to temperatures of 100°C, 200°C and 300°C for one hour each. The solvent present during these imidization steps influences the formation of the observed spherulites that melt at approximately 400°C. With respect to the melt crystallization, the two important parameters controlling the final amount of crystallization and morphology are the nucleation density and the spherulitic growth rate. Both these factors are highly dependent on the amount of undercooling and the crystallization temperature. The nucleation density generally increases with increasing amount of undercooling when cooling from the melt²¹. Also, it is well known that for melt

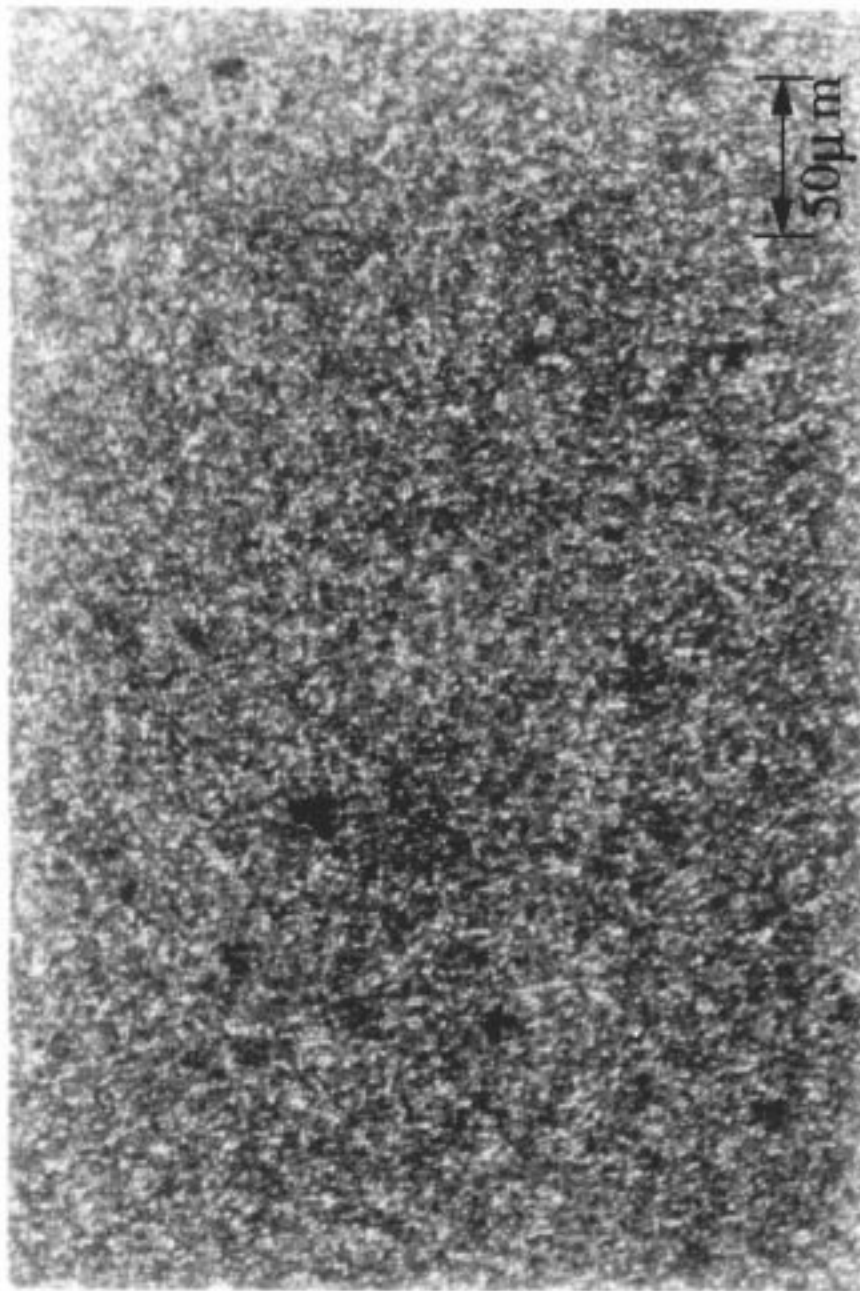


Figure 5.4 Polarized optical micrograph of the initial TPER-BPDA-PA film.

crystallization, a number of nuclei may survive above the DSC melting point²⁰ and influence the final crystallization morphology during the cooling step. For the rigid chain polyimide studied here, the melt temperature and melt times are important parameters influencing the number of nuclei surviving the melt conditions. For these rigid chain polyimides, sufficient nuclei may be present well above the DSC melting temperature that then may aid in the subsequent crystallization on cooling. However, for the results presented here, the samples were exposed for 20 minutes at melt temperatures of 420°C or 430°C. These melt conditions used for the microscopy study corresponded with the conditions used for bonding the lap-shear specimens as will be discussed later. These melt conditions should be sufficient to remove the effect of previous thermal history to a large extent though some nuclei may still survive.

For any semicrystalline polymer, the growth rate of spherulites increases with increasing amount of undercooling till a certain temperature at which these spherulitic moieties show a maximum in growth rate. Below the peak growth rate temperature, the rate of diffusive transport of the chain molecules determines the growth rate and above this peak temperature, the rate of surface nucleation at the growth front of a spherulite (nucleation control) is more important in determining the growth rate. The higher molecular weight sample obviously has much more entanglements for a given polymer chain and thus higher viscosity. Hence the growth rate for higher molecular weight species are significantly lower at any crystallization temperature. Figure 5.5 shows the spherulitic morphologies (15K) observed at different crystallization temperatures after being in the melt for 20 minutes at 430°C. The time at the isothermal crystallization temperature at which these micrographs were taken is also indicated. It is evident that the resulting morphology is very sensitive to the crystallization temperature. At an isothermal crystallization temperature of 355°C, large spherulites are observed which is due to a low nucleation density at this temperature. Also the radial growth rate of the spherulites is quite low as is illustrated in Figure 5.6 which shows the growth rates of spherulites as a function of crystallization temperature. As the crystallization temperature is decreased to 345°C, the nucleation density increases significantly and there is substantial increase in the spherulitic growth rate. In Figure 5.5, the third micrograph shows the semicrystalline

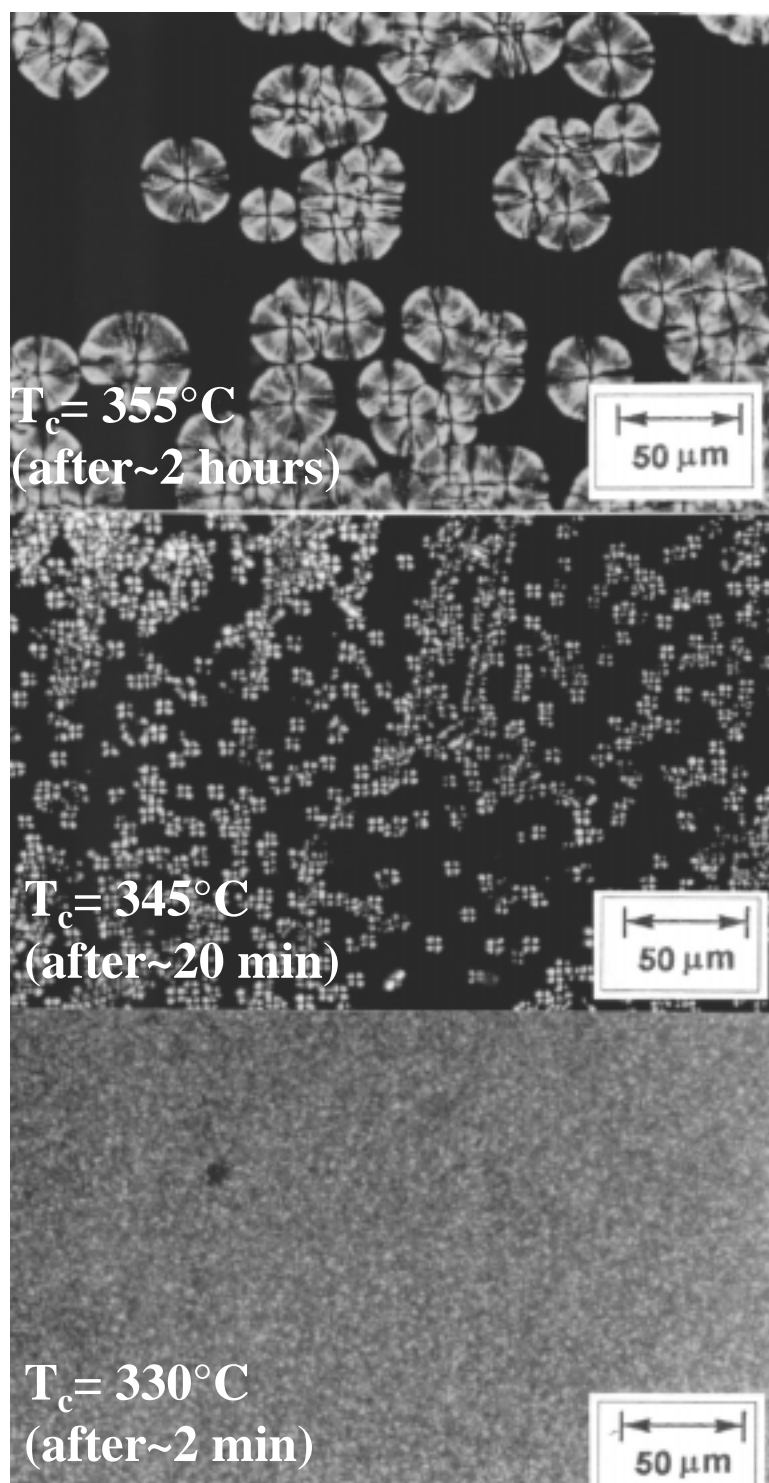


Figure 5.5 Polarized optical micrograph of TPER-BPDA-PA (15K) after heating at 430°C for 20 minutes and subsequent quenching to various crystallization temperatures.

morphology observed for a crystallization temperature of 330°C. In this case there is a large increase in the nucleation density as is indicated by the fine grainy pattern obtained. The size of the crystalline moieties is too small to observe by optical microscopy. The space filling times shown with the respective micrographs are an indication of the difference in the crystallization kinetics with various crystallization temperatures. While it takes only 2 minutes at 330°C to totally fill the volume with small spherulites, it takes ca. 2 hours at 355°C! The induction time at which the first crystallites are observed also decreases from ca. 90 seconds at 330°C to ca. 12 minutes at 355°C. Similar behavior is observed for the 30K TPER-BPDA-PA, although in this case the fine morphology appears at 340°C, also within 2 minutes. The effect of crystallization temperature on the kinetics of crystallization is even more pronounced for the 30K polymer as it shows significantly lower radial growth rates at higher crystallization temperatures as shown in Figure 5.6. The growth rates observed for both the molecular weights are not high compared to growth rates observed for other semicrystalline polymers²¹. Thus it is clear that the increase in nucleation density at temperatures below 340°C is responsible for the fast crystallization kinetics of the system. Also, it was not possible to quench the sample to an amorphous state even after taking it out directly from the hot stage after 430°C, 20 minutes into liquid nitrogen or dry ice and acetone. The fine morphology was obtained regardless of how fast the sample was cooled. For the same reason growth rates could not be observed on the lower temperature side of the crystallization window, where they may be expected to decrease with increasing undercooling.

Few semicrystalline polymers are processed at these high melt temperatures of 420°C and 430°C and thus any crosslinking that may take place at these conditions is of concern. However, if any such reactions are occurring at these conditions then the relative amount of these reactions will be greater at 430°C than at 420°C. Figure 5.6 also shows the growth rates for two different melt treatments of 430°C and 420°C for 20 minutes. Any significant amount of crosslinking or chain branching taking place by raising the temperature to 430°C will reflect in lower growth rates observed at the same crystallization temperature. It is clear that for the melt time utilized, this increase in melt temperature does not influence the spherulitic growth rates for either 30K or the 15K

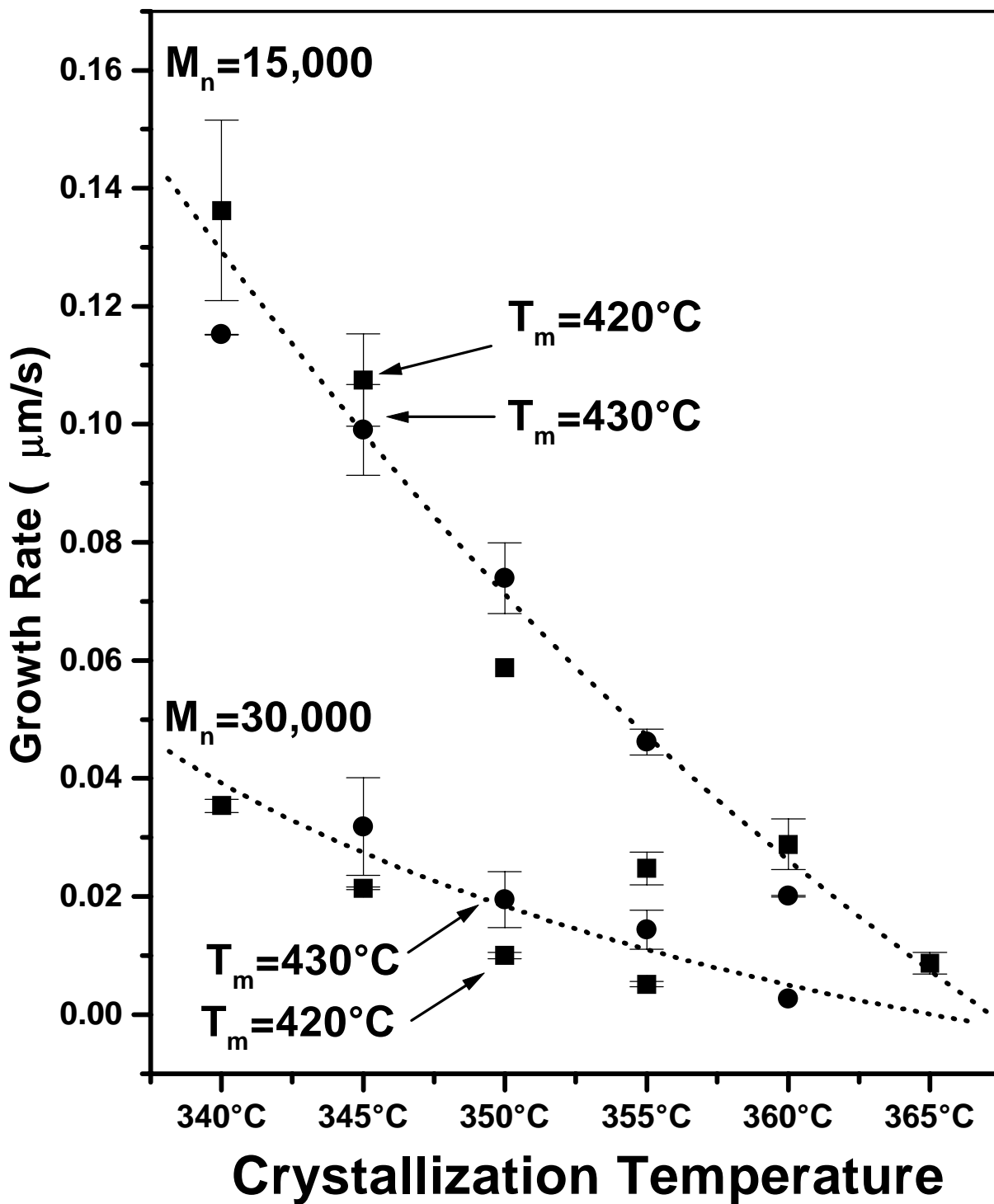


Figure 5.6 Growth rate of spherulites as a function of crystallization temperature for TPER-BPDA-PA (both 15K and 30K molecular weights) after 20 minutes in melt at (■)420°C and (●) 430°C.

molecular weight. These results thus reinforce the earlier conclusions based on the DSC study about the thermal stability of TPER-BPDA-PA.

It is well known that smaller spherulites result in significantly better mechanical properties than larger spherulites²¹ (other factors like molecular weight, degree of crystallinity etc being constant). Sharples et al.²² showed that the yield stress of a specific nylon 66 increases from 72 MPa to 98 MPa as the average spherulite size was varied from 50 μ m to 3 μ m. Friedrich et al.²³ studied the fracture stress and fracture strain of semicrystalline polypropylene at -40°C for samples with coarse and fine spherulitic morphology. The fracture stress was found to increase from 34 MPa to 64 MPa while the fracture strain increased from 1.5% to 6.5% as the morphology varied from coarse to fine spherulitic. This is not surprising, as the fracture path for a fine spherulitic will be much more tortuous than for the sample with coarse spherulites. Also, depending upon the molecular weight of the polymer, the fine spherulitic microstructure will possess much larger amounts of interspherulitic linkages than the sample with coarse spherulitic microstructure thus providing increased toughness. In fact, specimens displaying large spherulitic structure often show brittle fracture. Thus it is clear that for the polymer used in this study, fine spherulitic superstructure observed at 330°C and at lower temperatures needs to be promoted to attain higher lap-shear strengths. The thermal cycle for preparing the adhesive specimens thus was designed in such a way that the rapid cooling to temperatures in the vicinity of 330° took place. In this regard some adhesive specimens were intentionally made with thin films and unmatched adherends so that it became possible to study the unbonded film with the optical microscope. For any adhesive specimens using slow cooling rates, some coarse spherulites may form although much of the polymer did still consist of the fine structure. Although, any such coarse structure was not observed in any of the samples prepared in such a way, the effect of these few large spherulites will be relatively small as compared to the presence of solely large spherulites.

Also, sometimes transcrystallinity is observed in many polymer samples in the presence of a foreign surface such as a metal like titanium alloy used in this work. This morphology can develop due to the presence of small amounts of strain at the polymer-metal interface leading to high nucleation density. Another explanation for such an effect

results from the heat transfer difference between a surface layer and the bulk polymer resulting in the cooling of the surface layer, thereby resulting in increased nucleation density. This results in the formation of large amounts of outwardly radiating crystalline lamellae from the foreign surface. Such an effect, if present, may alter the properties of the interface significantly. In this regard several experiments were conducted using the titanium alloy coil which was grit blasted in a fashion similar to that used for adhesive specimens and the 15K TPER-BPDA-PA film. Various optical microscopy experiments conducted at different isothermal crystallization temperatures and at various cooling rates from the melt gave no evidence of any transcrystallization on the metal surface. Thus transcrystallization was ruled out for any of the adhesive specimens presented in this work.

5.3.4 Surface Preparation:

Much work has been done evaluating the durability and strength provided by chromic acid anodization (CAA) and sodium hydroxide etching (SH) as surface treatments¹¹⁻¹⁵ for Ti-6Al-4V alloy. Venables^{14, 15} and coworkers found excellent results with CAA and SH surface treatments with respect to the durability of adhesive joints when using liquid resins and attributed this to penetration of the microporous oxide layers by the liquid resin. Other workers^{11, 13} have also advocated the use of surface treatments producing large amounts of microroughness to improve the durability of adhesive joints although most work in this regard has been done with liquid resins, thermosets or low viscosity amorphous polymers. In this work, three such common surface treatments-CAA, SH and sandblasting were evaluated for bonding the Ti-6Al-4V alloy coupons with TPER-BPDA-PA. For evaluating these surface treatments, the titanium alloy coupons were bonded at conditions of 420°C, 20 minutes and a pressure of 300 psi. The highest lap-shear strength was obtained for the sandblasted specimens (2500-psi) whereas the chromic acid anodization gave the lowest values (500-psi). The lap-shear strengths of bonds using the sodium hydroxide etch as surface treatment fell between the two values

(1500-psi). Also, perhaps more important than the absolute values of these lap-shear strengths obtained was the fact that chromic acid anodization and sodium hydroxide etch always gave 100% adhesive failure (by visual inspection) whereas sandblasting gave cohesive failures. These results were not surprising and support the earlier studies done with regards to the high temperature instability of the chromic acid and sodium hydroxide treatments. Clearfield et al.^{11, 12} have showed the lack of stability of the oxide metal interface at temperatures approaching 300°C. They found that dissociation of oxide followed by the dissolution of oxygen into the alloy led to the formation of an embrittled zone on the surface. It is clear, that in the present case, macroroughness provided by the sandblasting technique was sufficient in giving a strong interface. However, for the CAA and SH surface treatments, significant degradation of the oxide layer will already take place before the adhesive melts at ca. 400°C. Also, it is unlikely that microroughness present in the chromic acid and sodium hydroxide treatments will provide a significant amount of interlocking as the bonding pressure used in this work (100 psi) will be insufficient to force the high viscosity polymer melt into the nanometer sized pores provided by these treatments. The slightly higher values obtained by the SH treatment may be due to the presence of a substantial amount of macroroughness often present for this treatment.

Hence, sandblasting was selected as the surface treatment for this adhesive study. The lap-shear strengths obtained on bonds exposed to 232°C for 7 weeks (presented later in the paper) and cohesive failures of specimens in these cases show the long term high temperature stability of these treatments. Also, the high strengths and cohesive failures of samples exposed to various solvents (for up to 9 days) point to the durability of this surface treatment in the present case.

5.3.5 Optimization of Bonding Process:

It is well known that for any hot melt adhesive application there are at least three important parameters that will affect the degree of spreading and thus these need to be properly controlled in order to attain good adhesion¹⁹. These are the melt temperature, the bonding pressure and the bonding time. These conditions were optimized in this study to obtain high lap-shear strengths. Lower molecular weights and higher temperatures have been proven to increase the ease of spreading significantly by lowering the viscosity of the polymer melt. Wightman et al.²⁴ showed that the wetting of the metal by polystyrene increased significantly as the temperature was increased. Figure 5.7 shows the lap-shear strengths when the bonding temperature was varied from 420°C to 430°C while the bonding time and pressure were kept constant at 20 minutes and 300 psi respectively. Temperatures higher than 430°C were not selected as recrystallizability of the material begins to decrease at 440°C. The lap-shear strength improved significantly over this range from 4000 psi to ca. 6600 psi and thus 430°C was selected as the bonding temperature. The next step was to vary the bonding time keeping the bonding temperature and bonding pressure constant. It was found that the average lap-shear strengths increased from 6000 to 6600 psi when bonding time was increased from 10 to 20 minutes (Figure 5.8) though the average values are well within the range of error for the two cases. However, the specimens bonded for 30 minutes showed reduced strengths (3500 psi). Thus 20 minutes was selected as the bonding time which is relatively low compared to times required for bonding with other high temperature adhesives. Also, for hot melt adhesives, the high viscosity results in low interfacial contact area due to the presence of voids and air at the substrate surface. Thus increasing the bonding pressure helps in increasing the interfacial contact area. In this regard, bonding pressures of 100-300 psi are common when using high temperature polymeric adhesives^{8, 9,10}. Four different bonding pressures were tried for this study: 100, 200, 300, 500 psi. As shown in Figure 5.9, the average bond strengths obtained were within the error bars associated with the lap-shear tests. Thus it was found

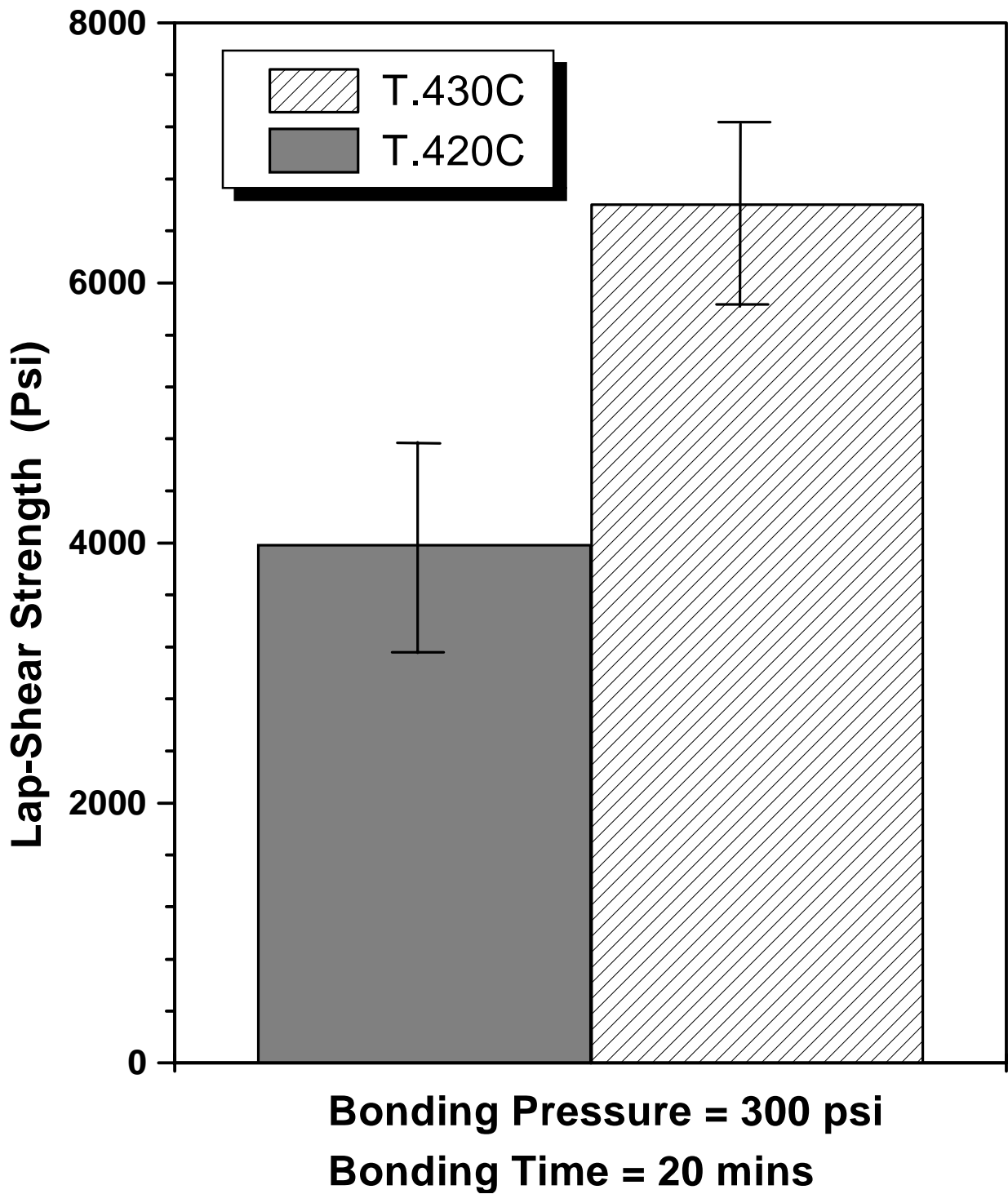


Figure 5.7 Lap-shear strengths as a function of bonding temperature (420°C and 430°C). Bonding pressure and bonding time were kept constant at 300 psi and 20 minutes respectively.

that a pressure of 100 psi, which is also within the range of traditional autoclaves was sufficient to attain good bond strengths. Pressures lower than 100 psi were not tried due to the limitations of the hot press. Also as discussed earlier, the cooling step was designed such that the fine spherulitic superstructure was developed. This was accomplished by cooling at $\sim 20^{\circ}\text{C}/\text{min}$ to 340°C , holding at that temperature for 5 minutes followed by slow cooling. This cooling cycle was followed for all the results presented in this paper. The overall thermal cycle thus is shown in Figure 5.10 whereas Figure 5.11 lists the bonding conditions that were tried and those that were finally selected.

The average lap-shear strengths obtained at the optimized conditions are of the order of 8400 psi (which compare favorably with the highest values reported for other polyimide adhesives) while some individual specimens showed lap-shear strengths as high as 9800 psi. In fact, significant bending of the 3.175-mm thick titanium alloy coupons was observed for some of these specimens. This makes this material a strong candidate as a structural adhesive for areas demanding high strengths at high temperatures. The fracture surface of the broken lap-shear samples was analyzed using SEM and a representative micrograph is shown in Figure 5.12. It is evident that the polymer provides a very rough and plastically deformed fracture surface. Similar features were observed on both sides of the fractured lap-shear specimens. This kind of rough fracture surface is uncommon for most high performance thermosetting adhesives and likely is responsible for the high strengths obtained for this material.

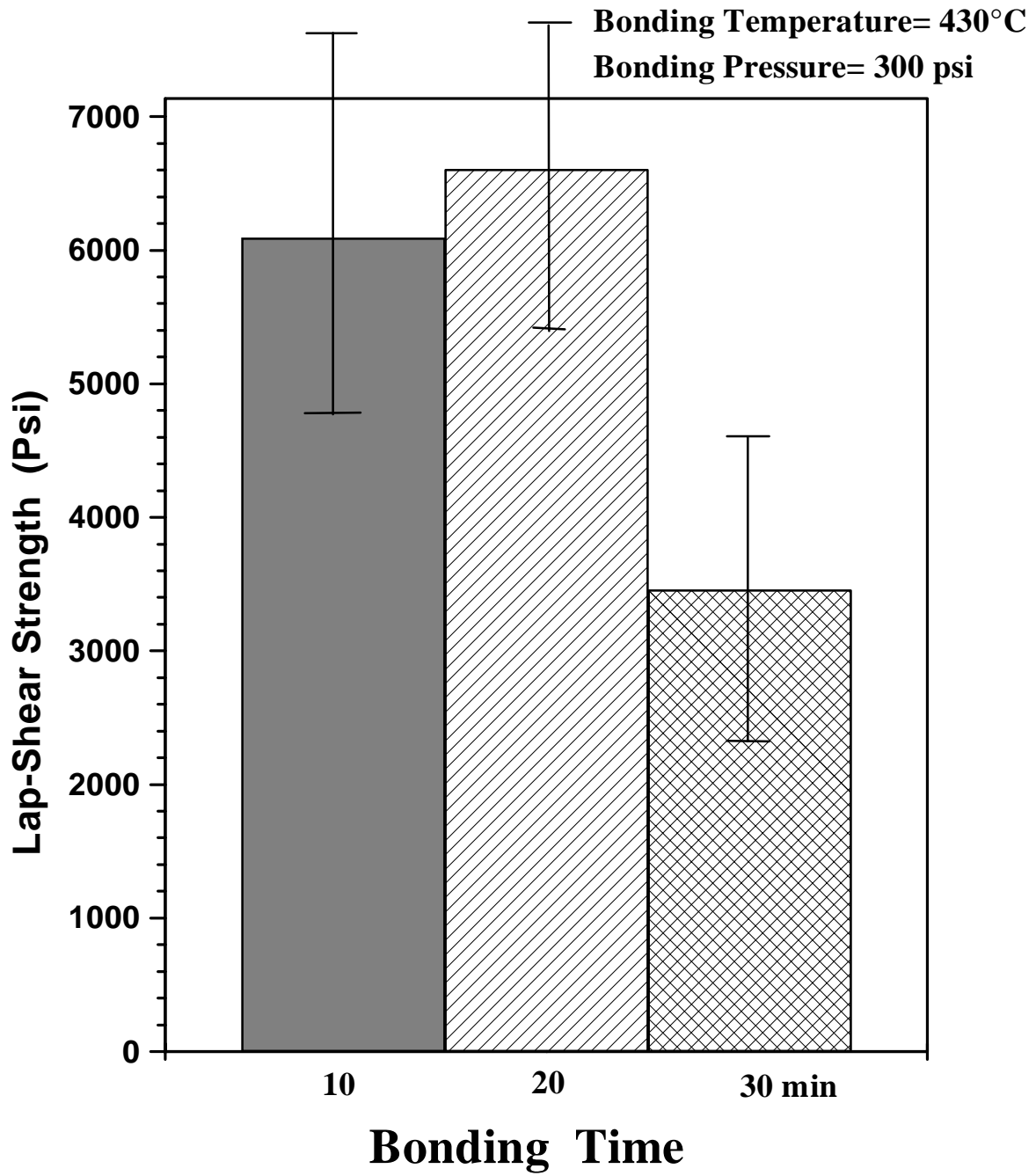


Figure 5.8 Lap-shear strengths as a function of bonding time (10, 20 and 30 minutes). Bonding pressure and bonding temperature were kept constant at 300 psi and 430°C respectively.

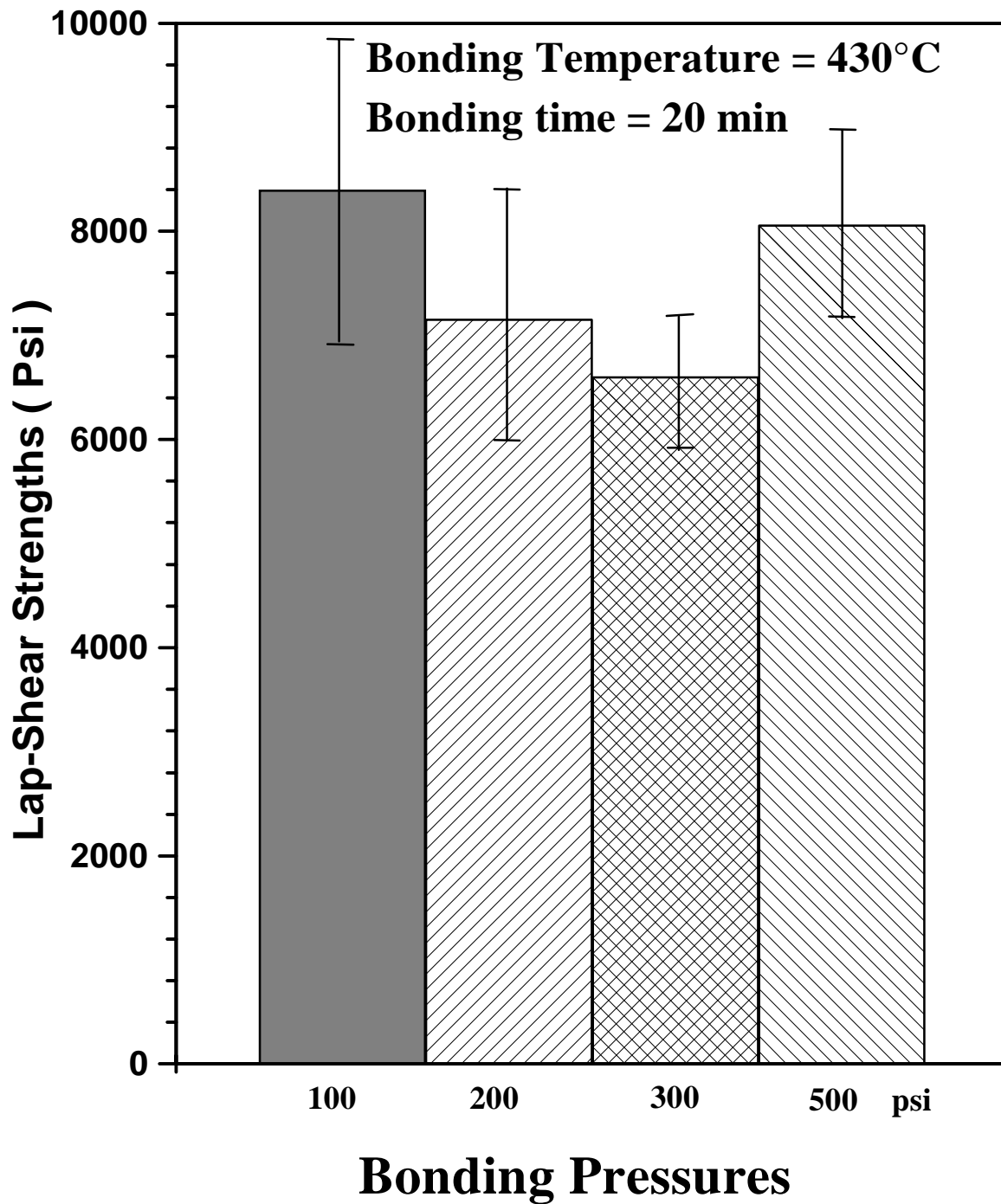
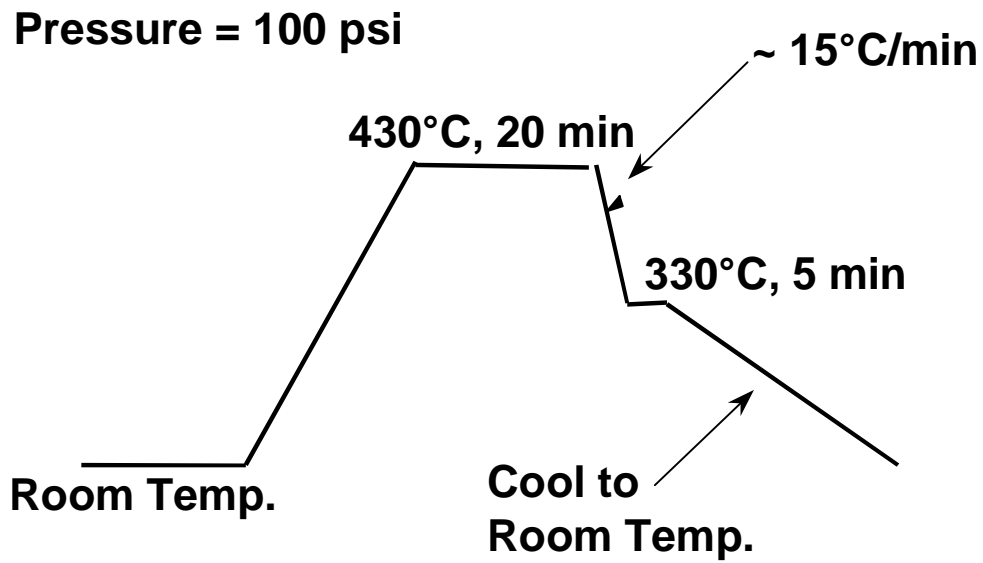


Figure 5.9 Lap-shear strengths as a function of bonding pressure (100, 200, 300 and 500 psi). Bonding temperature and bonding time were kept constant at 430°C and 20 minutes respectively.



Thermal Cycle for TPER-BPDA-PA Lap-Shear Specimen Preparation

Figure 5.10 Thermal cycle followed for preparing lap-shear specimens.

Optimization of the Bonding Process

1. Surface Preparation:

Chromic Acid Anodization

Gritblasting

Turco 5578

2. Bonding Temperature:

420°C

430°C

3. Bonding Pressure:

100 psi

200 psi

300 psi

500 psi

4. Bonding Time:

10 min

20 min

30 min

Figure 5.11 Scheme illustrating the conditions tried and finally selected for optimization of the bonding process.

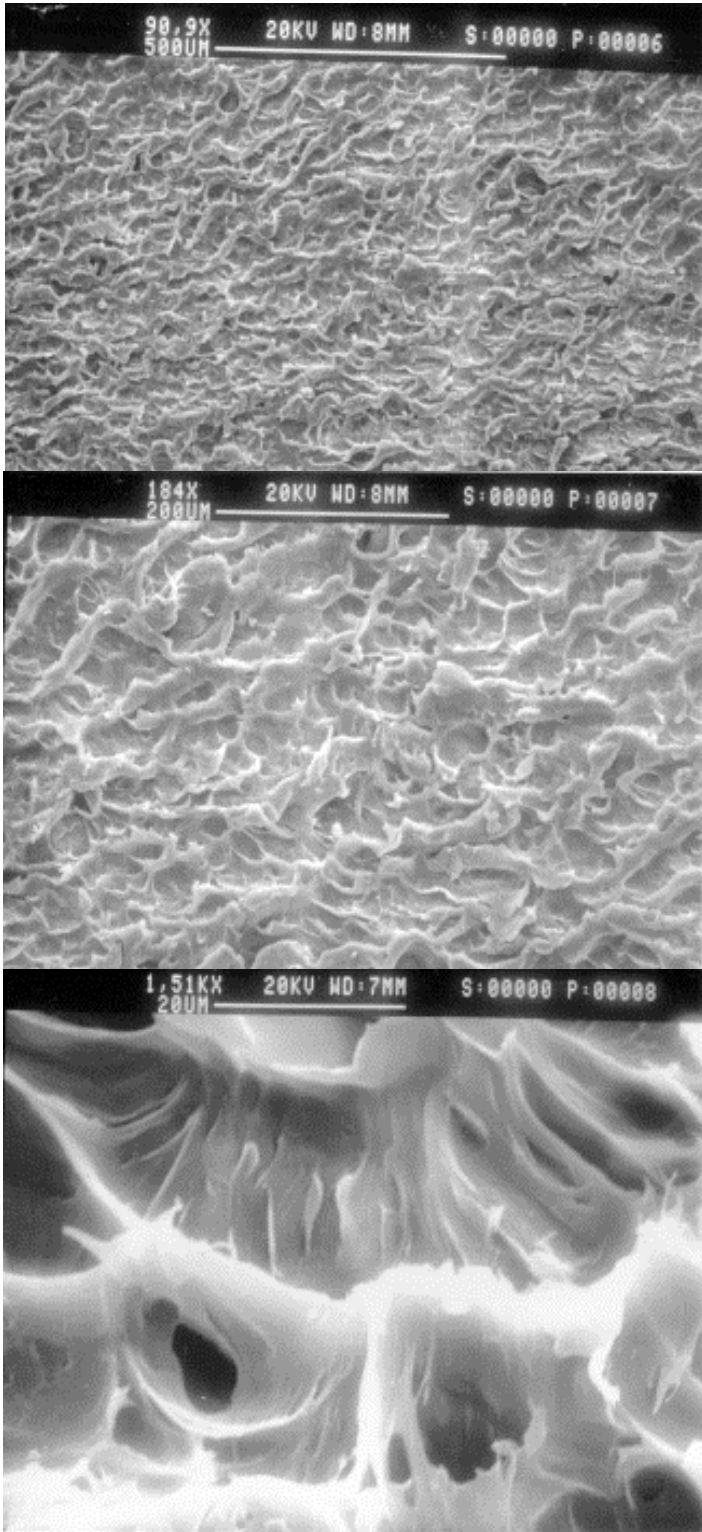


Figure 5.12 SEM micrographs of the fracture surface of the lap-shear specimens.

5.3.6 Durability Studies on Lap-Shear Bonds

Considerable work has been done by workers at NASA^{8-10, 17,18} with respect to durability of lap-shear bonds when exposed to high temperatures for extended periods of times. In this regard, testing of bonds exposed for long times at 177°C, 204°C and 232°C has been done while in a few studies lap-shears have been tested at these temperatures after extended periods of aging. Nonetheless, it is sufficient to say that for any material being used in such high temperature environments, degradation of the polymeric adhesive or the interface may lead to failure at the use temperature or some other higher or lower temperatures that the adhesive may experience. Also, thermal stresses may build up due to difference in the thermal expansion coefficient between the adhesive and the adherend leading to failure of the adhesive bond. Thus while aging temperature and time are important variables of interest, the importance of testing temperature cannot be ignored. In this study results are presented for specimens aged at temperatures of ambient, 177°C and 232°C for a period of 1, 3 and 7 weeks. In addition all the specimens aged at these conditions were also tested at temperatures of ambient, 177°C and 232°C. Figure 5.13 shows the overall aging and testing scheme followed in this study. For each test, 4-5 specimens were used. It is important to point out that while 177°C is 33°C below the glass transition, the aging and testing temperature of 232°C is 22°C above the glass transition of the polymeric adhesive. In this regard the presence of crystallinity and the nature of crystalline morphology becomes important in maintaining sufficient strength above the glass transition. Figure 5.14, 5.15 and 5.16 present the results obtained for different aging temperatures as a function of aging time and three testing temperatures. It is clear that for any given aging and testing temperature the specimens maintain their strengths (within the range of error) with varying aging times. Also it is evident that the

Aging Study of Lap-Shear Bonds

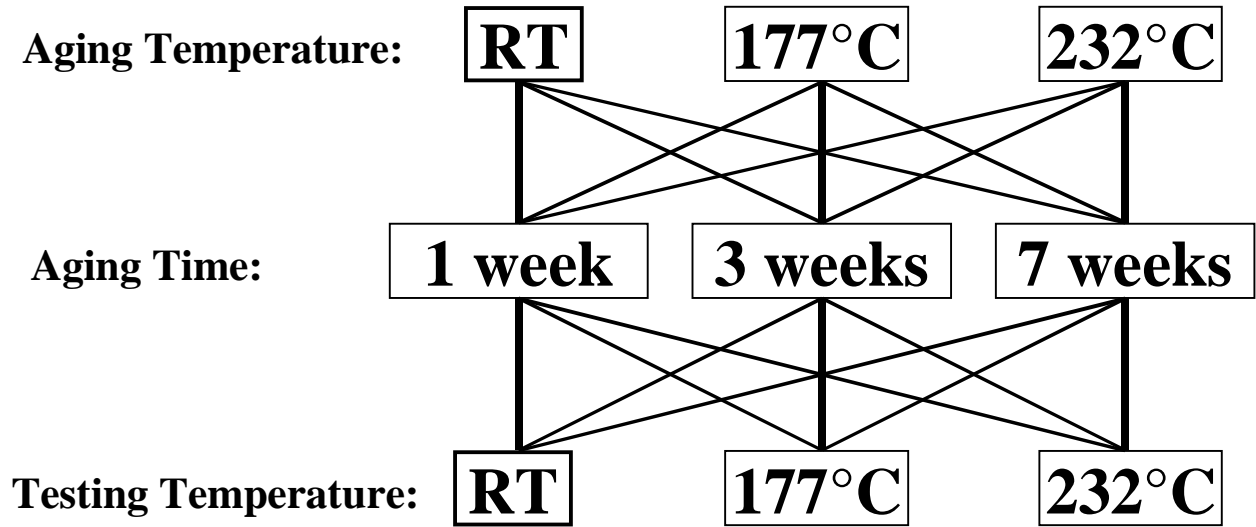


Figure 5.13 Scheme followed in the aging study of the lap-shear bonds.

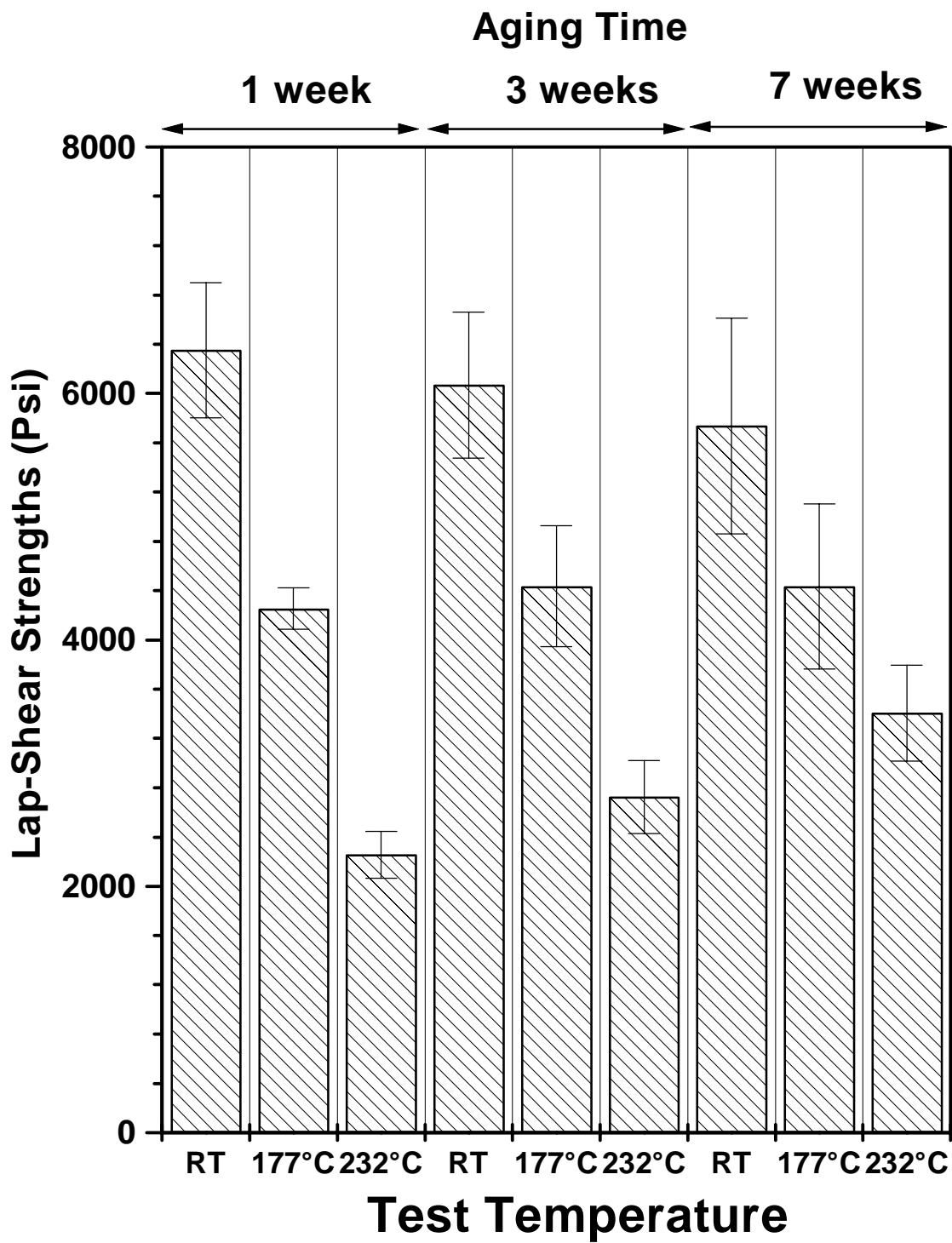


Figure 5.14 Lap-shear strengths after aging at room temperature for a period of 1,3 and 7 weeks and testing at ambient, 177°C and 232°C.

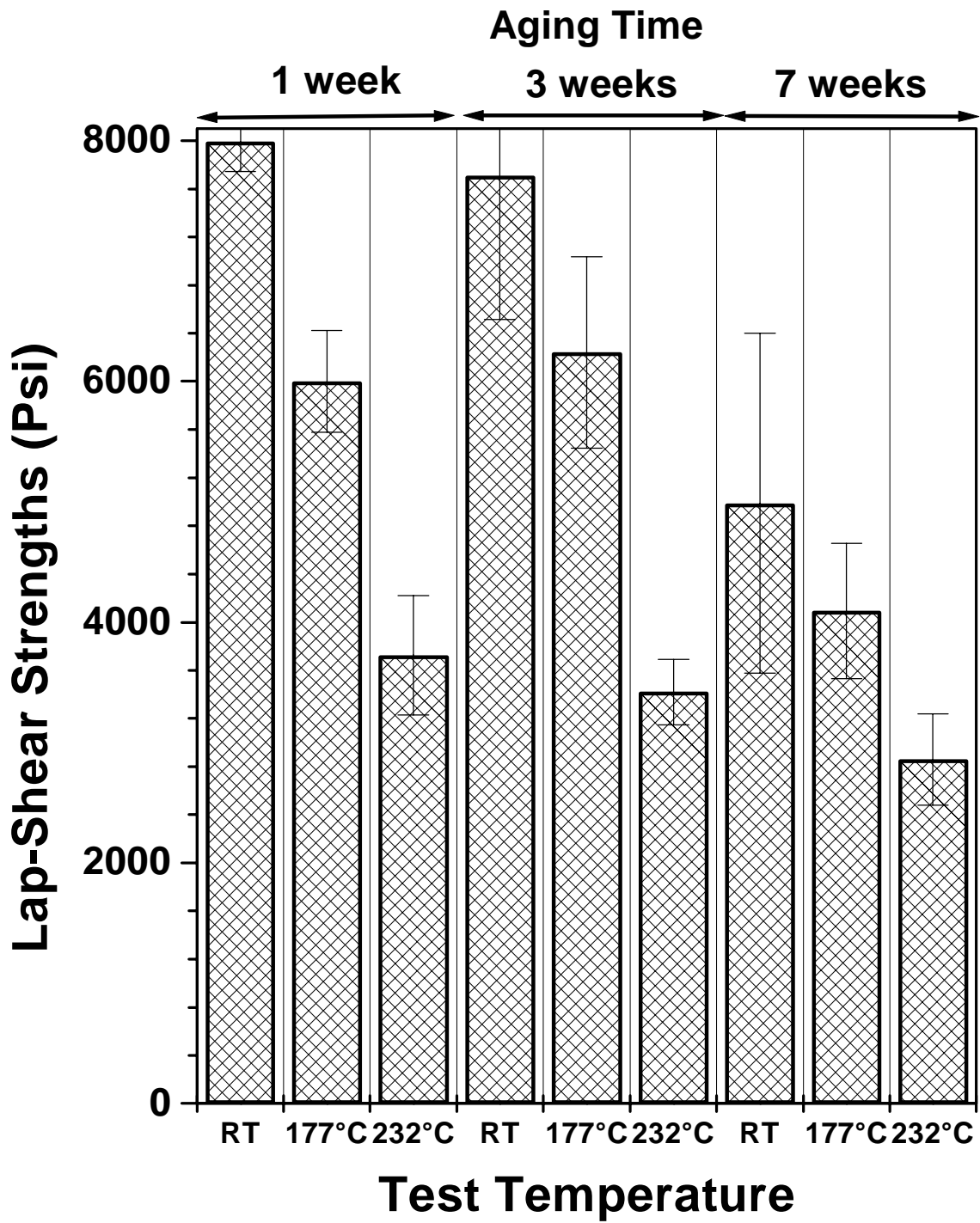


Figure 5.15 Lap-shear strengths after aging at 177°C for a period of 1,3 and 7 weeks and testing at ambient, 177°C and 232°C.

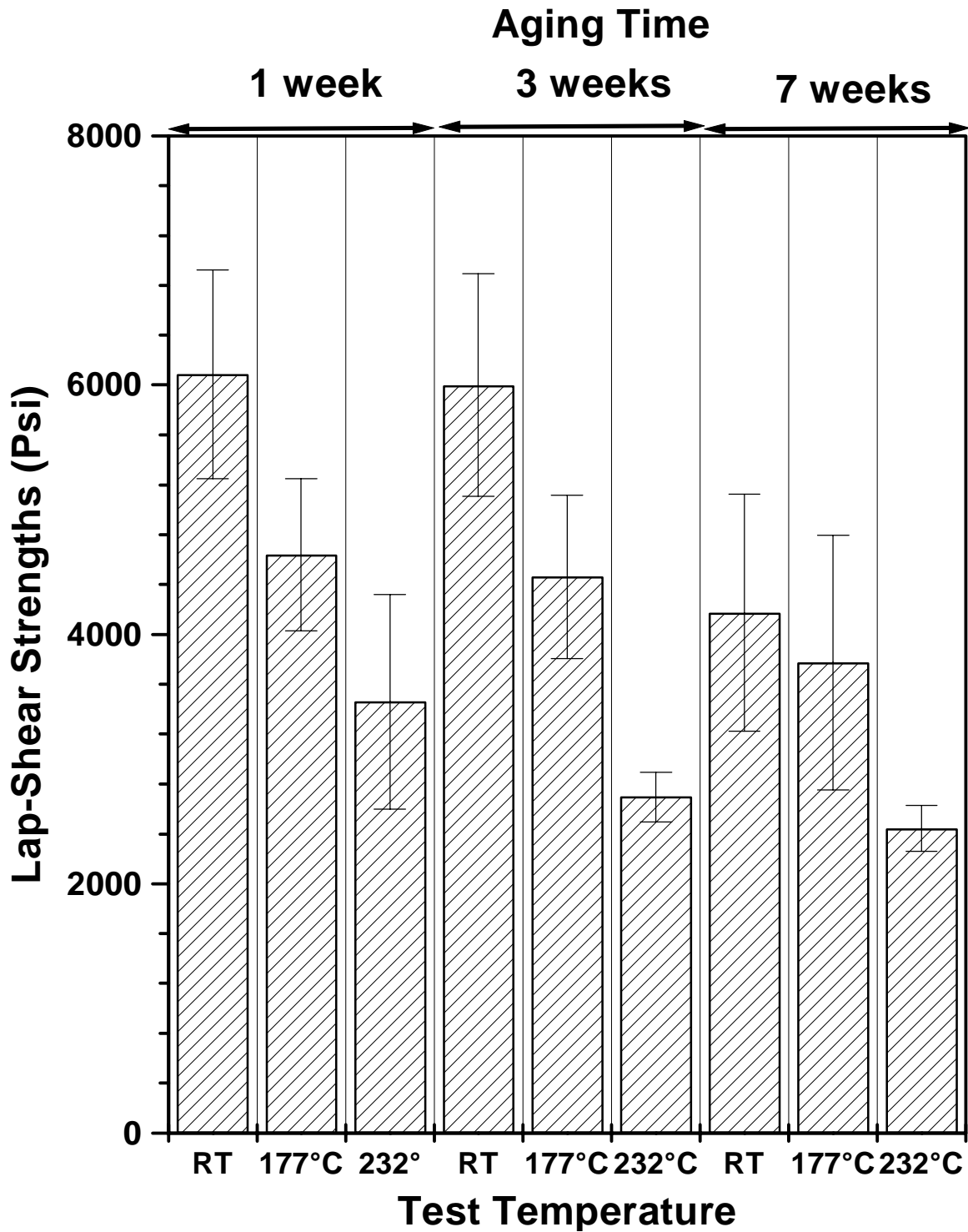


Figure 5.16 Lap-shear strengths after aging at 232°C for a period of 1,3 and 7 weeks and testing at ambient, 177°C and 232°C.

Aging Temperature/Time

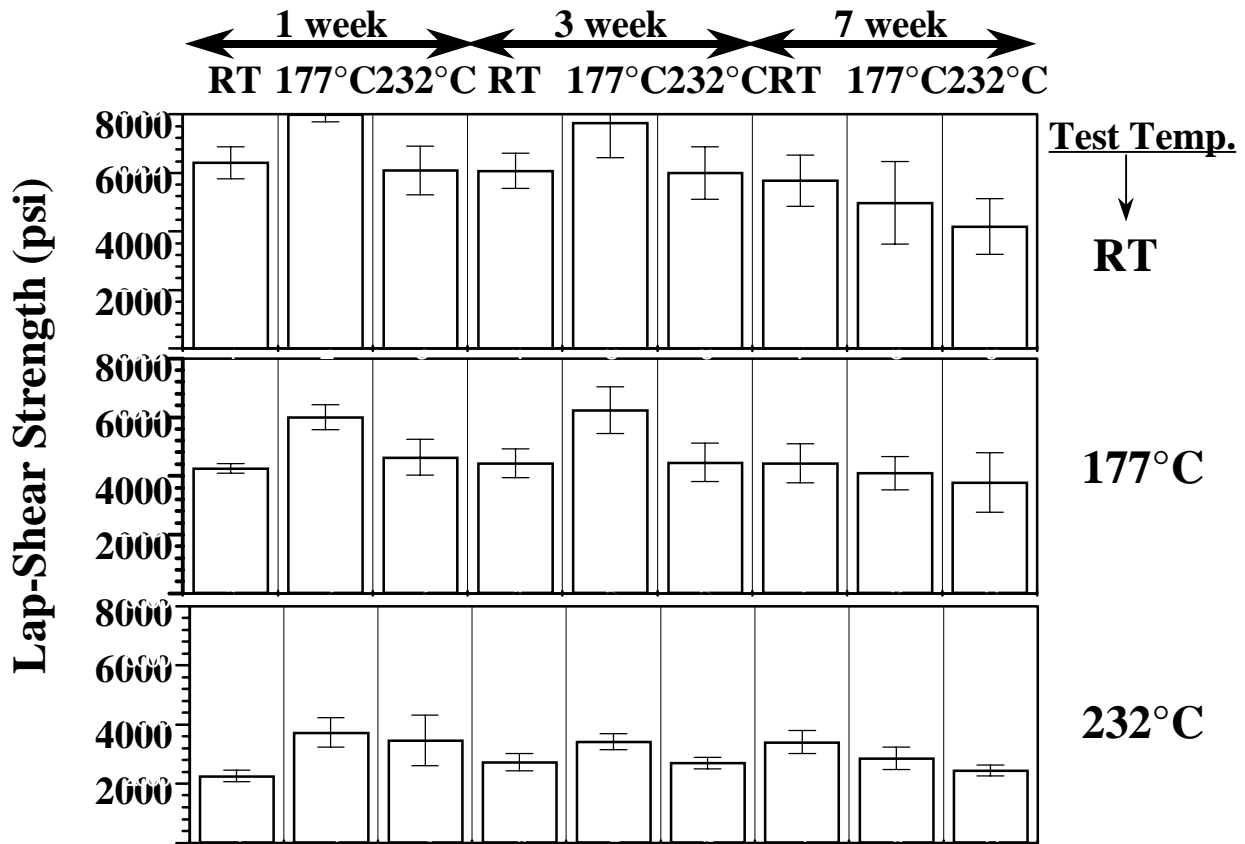


Figure 5.17 Lap-shear strengths shown as function of test temperature for various aging times and aging temperatures.

testing temperature and not the aging temperature affects the lap-shear strengths obtained. The strengths always decrease with increasing test temperature as would be expected. Figure 5.17 presents all the data in a slightly different form which makes it clear that the bond strengths are a function of test temperature and remain relatively unaffected by aging temperature or time for up to seven weeks. While the strengths vary between 6000-8000psi for an ambient test, they are between 4000-6000 psi for at 177°C. Also, interestingly the material shows good bond strengths of 2500-4000 psi for test temperatures of 232°C. These values compare favorably with some of the highest values reported at these temperatures for some other polyimides by workers at NASA⁸⁻¹⁰. The semicrystalline nature of the polymer is thus clearly advantageous in this regard. These results make this material a strong candidate for any high temperature and high service environment needed for advanced aerospace applications and further long-term aging studies are continuing.

5.3.7 Effect of various solvents:

The lap-shears were tested against various solvents which the adhesive may encounter when used as a structural adhesive. These solvents were selected on the basis of similar studies done by others^{8-10, 17,18} so as to compare the performance of this adhesive with other such studies. Figure 5.18 shows the effect of methyl ethyl ketone, toluene, hydraulic fluid, jet fuel, antifreeze and acetone on adhesive bonds made with TPER-BPDA-PA. Values after the 72-hour water boil tests are also presented. Some of the best results in the literature using similar solvents are presented for comparison though the duration of testing for these specimens was significantly shorter than that used in this study. It is evident that the common solvents do not seem to have any effect on the lap-shear strengths of TPER-BPDA-PA while similar solvents had a significant effect on the thermoplastics LARC-8515²⁵ and LARC-TPI¹⁰. The failure mode was 100% cohesive for TPER-BPDA-PA indicating the stability of interface when exposed to these various

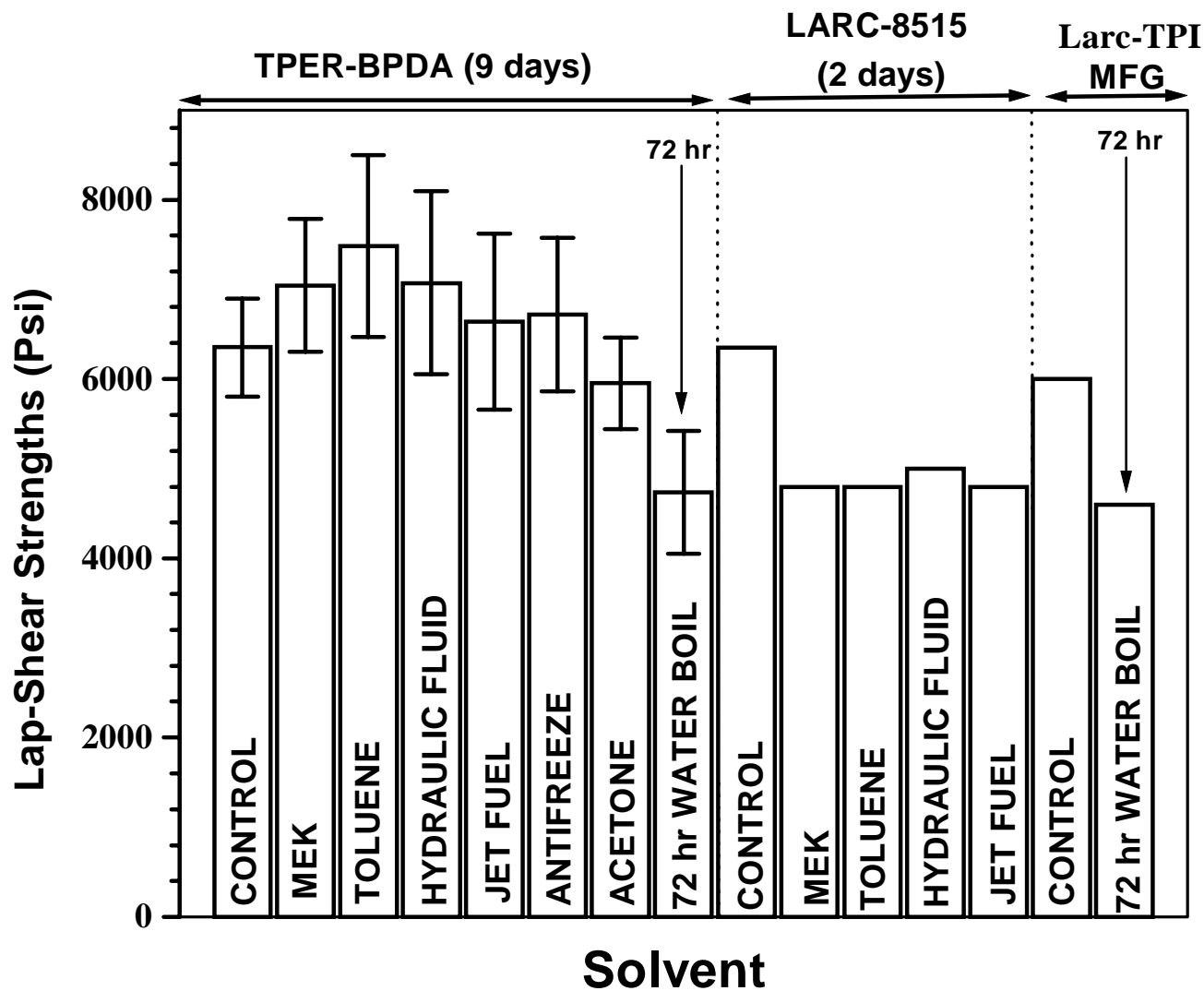


Figure 5.18 Lap-shear strengths of TPER-BPDA-PA (15K) after exposure to different solvents for a period of nine days. Values from other similar studies in literature are also shown for comparison.

solvents. It is important to point out that both LARC-8515 and LARC-TPI were completely amorphous and thus susceptible to some degree of solvent attack. The presence of crystallinity thus seems to greatly aid the solvent resistance of TPER-BPDA-PA significantly. It is likely that sometimes the effect of solvents on the interface may not become evident in lap-shear test geometry while a wedge test geometry may give contrasting results. Thus, wedge tests were also conducted for these solvents and the results are presented in chapter 7.

5.4 Conclusions

The crystalline morphology was studied for a new semicrystalline polyimide, TPER-BPDA-PA-PA and it was found that the final morphology was very sensitive to the crystallization temperature. The nucleation density increased at ca.330°C leading to the formation of fine grainy spherulitic morphology. Also, the spherulitic growth rates were significantly higher for the 15K material compared to the 30K system although the increase in nucleation density also occurred for the latter at ca.340°C. The melt conditions did not affect the spherulitic growth rates for either molecular weight reinforcing the results from the earlier studies indicating the exceptional thermal stability of this polymer.

Three surface treatments were evaluated with simple sandblasting giving the best results. The chromic acid anodization and sodium hydroxide etch gave interfacial failures while sandblasting always gave cohesive failures. The lap-shear strengths were greatly affected by the bonding conditions with a temperature of 430°C for 20 minutes at a pressure of 100psi giving the best results. The fracture surface was rough and showed large amounts of plastic deformation. The overall cycle time for preparing the adhesive specimen was considerably lower due to the melt processability, simple surface treatment needed and reduced bonding time.

The high temperature durability studies were conducted at three different temperatures of ambient, 177°C and 232°C and it was found that the strengths remained relatively unaffected for up to 7 weeks for a given test temperature. For any given set of aging conditions the strengths decreased as the testing temperature was increased from ambient to 177°C to 232°C. Lap-shear strengths in the range of 6000-8400 psi were obtained for ambient testing while strengths were in the range of 4000-6000 psi for test temperature of 177°C. Also, testing above the glass transition at 232°C gave reasonable strengths of approximately 2500-4000 psi owing to the presence of crystallinity. Finally, common solvents did not seem to affect the lap-shear strengths of TPER-BPDA-PA lap-shear adhesive specimens.

5.5 Acknowledgments

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References:

1. Hergenrother, P.M., Stenzenberger, H.D. and Wilson, D. 'Polyimides', Blackie & Son Ltd, London, 1990.
2. Srinivas, S., Caputo, F.E., Graham, M., Gardner, S., Davis, R.M., McGrath, J.E. and Wilkes, G.L. *Macromolecules*, 1997, **30**, 1012.
3. Kreuz, J.A., Hsiao, B.S., Renner, C.A. and Goff, D.L. *Macromolecules* 1995, **28**, 6926.
4. Wang, Y.D., Cakmak, M. and Harris, F.W. *J. Appl. Polym. Sc.* 1995, **56**, 837.
5. Bandom, D.K. and Wilkes, G.L. *Polymer* 1994, **35**, 5672.
6. Hsiao, B.S., Kreuz, J.A. and Cheng, S.Z.D. *Macromolecules* 1996, **29**, 135.

7. Heberer, D.P., Cheng, S.Z.D., Barley, J.S., Lien, S.H.S., Bryant, R.G. and Harris, F.W. *Macromolecules* 1991, **24**, 1890.
8. Progar, D.J. and Dezern, J.F. *J. Adhes. Sci. Technol.* 1989, **3**, 305.
9. Progar, D.J. and Clair, T.L. *J. Adhesion* 1989, **30**, 185.
10. Progar, D.J. and Clair, T.L. *J. Adhes. Sci. Technol* 1994, **8**, 67.
11. Clearfield, H.M., Shaffer, D.K., Vandoren, S.L. and Ahearn, J.S. *J. Adhesion* 1989, **29**, 81.
12. Clearfield, H.M., Cote, G.O., Olver, K.A., Shaffer, D.K. and Ahearn, J.S. *Surface and Interface analysis* 1988, **11**, 34.
13. Dezfuly, M. A., Vlachos, C. and Andrews, E.H. *J. Mater. Sci.* 1984, **19**, 3626.
14. Venables, J.D., McNamara, D.K., Chen, J.M. and Sun, T.S. *Appl. Surf. Sci.* 1979, **3**, 88.
15. Davis, G.D., Sun, T.S., Ahearn, J.S. and Venables, J.D. *J. Mater. Sci.* 1982, **17**, 1807.
16. Kennedy, A.C., Kohler, R. and Poole, P. *Int. J. Adhes. And Adhesives* 1983, **3**, 133.
17. Progar, D.J. and Clair, T.L. *J. Adhesion* 1987, **21**, 35.
18. Progar, D.J. *J. Adhes. Sci. Technol.* 1987, **1**, 135.
19. Gauthier, M.M. pg. 80, Vol 3, 'Engineered Materials Handbook, Adhesives and Sealants' ASM International, 1995, Materials Park, Ohio.
20. Lee, Y. and Porter, R.S. *Macromolecules* 1988, **21**, 2770.
21. Krevelen, V. in Ch 19, Crystallization and Recrystallization, in the book 'Physical Properties of Polymers', Elsevier, 1990, London.
22. Sharples, A. 'Introduction to polymer crystallization', Edw. Arnold, 1966, London.
23. Friedrich, K. and Karsch, U.A. 'The influence of Molecular Weight on Crazing and Fracture in Polypropylene', in Proc. 27th Int. Symp. on Macromolecules, Vol 2, 1981, 1035.
24. Wightman J.P., Department of Chemistry, Virginia Tech, (private communication).
25. Jensen, B.J., Hou, T.H. and Wilkinson, S.P. 40th Int. SAMPE Symp., May 8-11, 1995, 1072.
26. Adams, R.D. pg 325, Vol 3, 'Engineered Materials Handbook, Adhesives and Sealants', ASM International, 1995, Materials Park, Ohio.