

Chapter 4

Polyimides as Adhesives: -Literature review

4.1 Introduction

Much like the subject of polymer crystallization, the field of adhesion is vast and thus it is impossible to even remotely cover the area in a review of this size. The material presented therefore is intended to cover a few selected topics that are more relevant to the author's research. The selection of topics is therefore guided by the author's choice.

To quote R.C. Patrick¹, "adhesion is the phenomenon of causing two materials to be held together, while an adhesive is the material utilized in carrying out this phenomenon". This simple definition avoids much debate and confusion that has surrounded the exact meaning of the word adhesion. This fascinating field, however, has come a long way since man first realized that the blood caused his hair to cling together quite glutinously. Specifically, major strides have been made in the second half of this century, and these have enabled a more fundamental understanding of the subject. Notably, major interest has risen in the past decade or so regarding the use of various adhesives for military, aerospace and microelectronic and applications². In this regard, aromatic polyimides and related polymers have been of significant importance. Specifically, these materials possess a broad array of superior properties like excellent thermal stability, solvent resistance, good mechanical properties, radiation resistance, low thermal expansion, wear resistance, hydrolytic stability, low dielectric constant and high breakdown voltage³. This broad range of attractive properties in these high performance polymers has made them excellent candidates as adhesives.

4.2 Theories of adhesion

The definition of the word “adhesion” depends on whether the viewpoint is macroscopic or microscopic. However, it is important to realize an intimate contact between the adherend and the adhesive is necessary for the adhesion forces to be operative⁴. The various theories of adhesion essentially differ in qualifying the nature of these inherent adhesion forces. None of these widely prevalent theories, however, is successful in satisfactorily explaining the entire existing adhesion phenomenon. These theories are briefly addressed here to highlight the essential concepts on which they are based.

4.2.1 Mechanical interlocking

This theory postulates that the adhesion is achieved as a consequence of flowing of an adhesive into a rough surface and the resulting ‘interlocking’⁵. Thus this mechanical anchoring between the adhesive and the adherend prevents the removal of adhesive from the substrate. However, it is important to realize the degree of roughness that is being considered and the spreading of the adhesive that is achieved. It is meaningful to remember that the increase in roughness also results in availability of more area for intimate contact. The various surface treatments themselves have been divided by Venables et al^{6,7}. on the basis of roughness produced (i.e. pore size on the surface of the adherend) as:

- Group I: Surface treatments that produce no micro-roughness (pore size < 0.1 μm) or macro-roughness (pore size > 0.1 μm).
- Group II: Surface treatments that result in a large degree of macro-roughness.
- Group III: Surface treatments that result in a large degree of micro-roughness due to a porous oxide layer, with little or no macro-roughness produced.

4.2.2 Molecular interdiffusion

This theory proposed by Voyutskii⁸ and Vakula^{9,10} states that the polymer-polymer adhesion results from interdiffusion of polymer molecules across the interface.

This can be viewed as a molecular interlock enabled adhesion. The theory was proposed to account for the experimental results dealing with adhesion between dissimilar polymers when satisfactory explanations could not be reached by applying other existing theories. The theory accounted for effects of contact time, influence of time and temperature on bonding rate, and the influences of polymer molecular weight and polymer structure. Additionally, these models take into account the motion of the entire chain across the interface¹¹. While diffusion applies well for cases of self-adhesion or autohesion, its sole use to provide satisfactory explanation for polymer-polymer adhesion is questionable. High molecular weight thermoplastic polymers that often display very high melt viscosity may not diffuse easily within the time frame of most bonding operations.

4.2.3 Electronic theory

This theory is based on the argument that the electrostatic forces arising from the junction potentials between the contacting adhesive and substrate will contribute significantly towards the forces required to rupture the bonds. This theory was proposed by Derjaguin et al.^{12,13} who proposed the formation of an electrical double layer due to electron transfer during contact. This theory has invited some controversy as many workers have questioned the practical significance of the amount of forces involved¹⁴. While this concept may be useful to explain some specific instances of adhesion, substantial doubts have been cast regarding its overall utility. These include improved adhesion strengths with lowering of temperature for a large variety of systems (lower temperatures will favor smaller charge densities and hence poorer electrostatic forces) and negligible changes in adhesion performance with gross variations in the electronic character of the adhesives¹⁵.

4.2.4 Adsorption theory

This widely credited and much investigated theory is due to Sharpe and Schonhorn¹⁶. According to this theory, in the event of intimate contact between the adhesive and the adherend, the adhesive strength arises as a result of interatomic and

intermolecular forces at the interface. The forces between the adhesive and the adherend are usually grouped into two categories (1) primary forces and (2) secondary forces. Primary forces include ionic (600-1100 kJ/mole), covalent (60-700 kJ/mole) and metallic bonds (110-350 kJ/mole). Secondary bonds may include Van der Waals forces (0.02-40 kJ/mole), hydrogen bonds (10-40 kJ/mole), Lewis acid-base interactions (up to 80 kJ/mole), dipole-dipole and dipole-induced dipole (up to 20 kJ/mole) interactions. In this regard, introduction of chemical bonding between the adhesive and the adherend will obviously improve the adhesion strengths¹⁷. This can be done by in-situ reactions at the surface, by applying proper surface treatments, or by using various coupling agents.

4.3 Adhesion aspects of the present work

The study of adhesion can be broadly divided into the areas of “Surface Science”, “Mechanistic Studies” and “Material Properties”. Each of these aspects is extremely important and focuses on different but interrelated concepts in addressing the general phenomenon of adhesion. Without indulging in the task of describing details of the each of these sciences, the review will address the specific topics that are directly relevant to this research work. In this regard, the various features of the titanium adherend and the various surface treatments practiced for high performance adhesives will be discussed. Following this, the most widely used adhesion test, lap-shear test will be addressed with regards to the mechanics involved in this test. Some aspects of shear-lag approach due to Volkersen¹⁸ and effect of bending moments and peel stresses due to Goland and Reissner¹⁹ will also be discussed. The review of important material properties with respect to the semicrystalline adhesives will then be given with emphasis on crystalline morphology and bonding variables. Lastly, the techniques and the results from studies dealing with specifically the high performance and high temperature polyimide adhesives will be reviewed.

4.4 Titanium as an adherend

Titanium has a high strength to weight ratio, possesses excellent corrosion resistance and displays superb toughness relative to steel and aluminum and is able to retain its mechanical properties until very high temperatures²⁰. These properties have made titanium the metal of choice for applications like aerospace structural applications, landing gears, blades of gas turbines, nuclear power plants and prosthetic implants²¹. The high cost of this metal, however, limits its uses. Titanium possesses two different crystalline phases: the ' α -phase' which is hexagonal closed packed form and the ' β -phase' that is a body centered cubic form²². The β -phase is favored to form when temperatures exceed 882.5° and it shows lower strength to weight ratios and increased sensitivity to corrosion. On the positive side, β -phase metals show good hot and cold strength and are easily formed. ' α -Phase' alloys though showing poorer forming characteristics are stronger, tougher and resistant to environmental corrosion. Ti-6Al-4V is an α - β alloy having been developed to optimize the desirable properties of both phases^{23,24}. Aluminum stabilizes the α -phase and raises the $\alpha \rightarrow \beta$ conversion temperature while the vanadium stabilizes the β phase and raises the $\beta \rightarrow \alpha$ temperature. The comparison of Ti-6Al-4V with various other metals is illustrated in the Table 4.1 below²⁵.

Table 4.1 Some selected properties of different metals²⁵

Metal	E' [GPa]	σ_y [Mpa]	σ_{max} [Mpa]	K _{Ic} [Mpa m ^{1/2}]
Aluminum	70	40	200	100
Copper	120	60	400	To
Nickel	210	70	400	350
Ti-6Al-4V	110	900	1000	120
Al Alloys	70	100-380	250-480	23-40
Carbon Steel	210	250	420	140
Stainless Steel (304)	195	240	365	200

Surface treatment of the titanium-alloy is critical in improving the initial strength and long term durability of the adhesive joint. These surface treatments are utilized to remove the contaminants comprising the weak boundary layer and for creation of a stable adherend surface which may be *chemically* and *mechanically* compatible with the adhesive²³. For optimizing the durability of the adhesive joints, the surface treatments that enhance surface wettability and introduce macro- and to a greater degree micro-roughness are favored. In this regard, the chemical and morphological stability of the various surface treatments is especially important. The detailed procedures for various surface treatments have been extensively reviewed²³. Of the variety of surface treatments, three popular surface treatments utilized in this work are (1) grit blasting (2) TURCO 5578 and (3) chromic acid anodization (CAA). While grit blasting falls in the category of mechanical treatments, the TURCO 5578 treatment is chemical, and CAA falls under the category of anodization based treatments. The resulting surface morphology from these surface treatments differs in the nature of roughness and chemical composition of the oxide formed on the surface²⁶. The grit blasting involves high-speed alumina grit particles of micron level sizes hitting the surface at high speeds and thereby introducing macro-roughness (Group II) on the surface. The CAA treatment is perhaps the most popular of all surface treatments for titanium and it leads to the formation of a chemically durable and porous layer of amorphous TiO₂. The large degree of micro-roughness resulting from this treatment makes it a Group III type surface treatment. The increased surface area due to the micro-roughness and the generally observed durability of the oxide layer have been widely advocated to enhance both the physical and chemical bonding with the adhesive²⁷. The details of this involved surface treatment are described in several references and need to be followed very precisely in order to reproduce the experimental results^{26,28}. The morphology of the CAA treated surfaces is shown in Figure 4.1 and resembles a honeycomb-like structure with cell diameters of 30-40 nm and a wall thickness of 5-10 nm²⁶. The depth of the oxide layer depends on the concentration of the solution and the anodization voltage used and varies from 40 to 140 nm²³. The aqueous environment and high temperature durability of the CAA treatment is albeit a suspect. Regarding the effect of aqueous environments Clearfield et al.²³ have shown the

lack of stability of the oxide layer at temperatures approaching 300°C. Figure 4.1 shows the morphological transformation of the surface after a 3 hour moisture exposure at 300°C and shows that the originally present honeycomb structure has disappeared²⁶. These severe morphological changes that may occur on exposure to such conditions can destabilize the adhesive interface and thus have been advocated to cause a loss of bond strength or failure. With respect to the effect of dry and high temperature environments it has been observed that the treated surfaces maintained the honeycomb morphology even after exposure to air at 330°C for 1200 hours or vacuum at 400°C for 165 hours. However, bonds formed by these treatments failed under minimum force. The XPS studied revealed that the failure occurred in the oxide/metal interface. It has been proposed that development of microcracks takes place and leads to formation of an embrittled zone at the surface²³. While the exact causes of the failure of CAA treatment on exposures to high temperatures is not yet certain, it is important to state that similar results have been obtained in the present research work. Chromic acid anodization was briefly tried out in this research work as it is the most widely used treatment for titanium alloys. However, very weak adhesion and clear interfacial failures were obtained in this case (results are discussed in chapter 5). The bonding temperature utilized for the hot melt polyimide adhesive exceeded 400°C and thus could have been contributed to the failure of this surface treatment. Another important treatment for titanium adherends is TURCO 5578. The treatment is based on the sodium hydroxide etch and is has been discussed in detail by Filbey²⁹. The treatment produces a micro-rough surface with formation of an oxide layer on the surface.

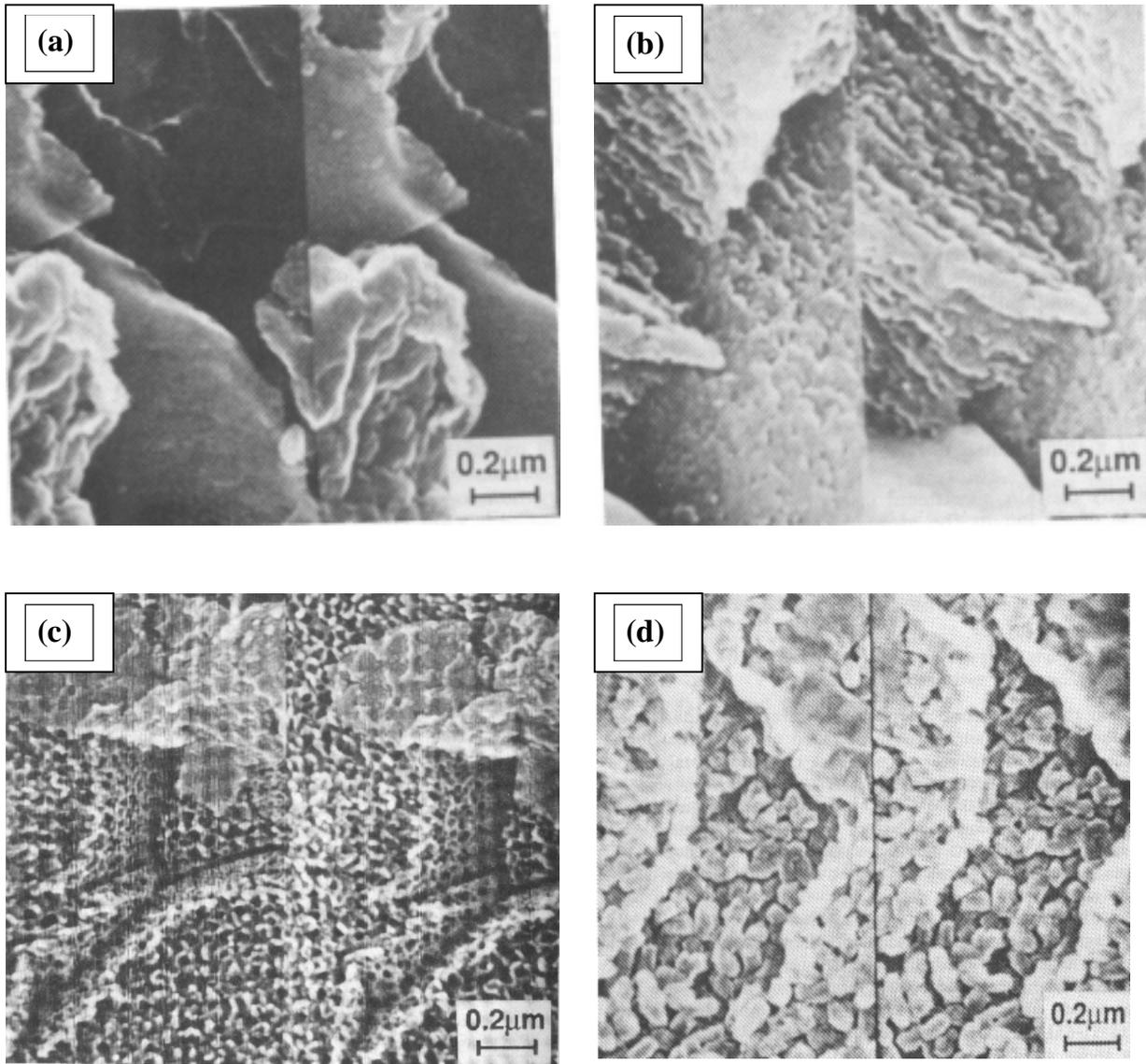


Figure 4.1 The surface morphology of the Ti-6Al-4V after various surface treatments²³ (a) gritblasting (b) TURCO 5578 sodium hydroxide etch (c) chromic acid treatment (d) chromic acid treated samples after exposure to water vapor at 300°C.

4.5 Some aspects of various adhesion tests

Before an adhesive is put into its final use, detailed analysis regarding design, testing and durability of the actual bonded structures needs to be conducted. This is especially true of structural adhesives where bond failures during actual use can have devastating consequences. However, during development of new adhesives such as the one attempted in the present work, standardized tests need to be conducted in order to compare and evaluate the various adhesion parameters. Probably the most important criteria for the new adhesive to be tested relate to (1) strength (2) fracture toughness and (3) solvent resistance of the bonded joints. The most widely used tests to characterize these phenomenon are the lap-shear test for strength comparisons, the double cantilever beam test to test the fracture toughness of the adhesive joints and the wedge test to evaluate the solvent resistance. Thus these three tests were conducted in the present study to characterize the polyimide used in this study as an adhesive. Once the material has been evaluated with these initial tests, subsequent testing methodology can be designed with respect to the proposed use. In the current section, the lap-shear test, which was the primary adhesion test used, is discussed.

4.6 Lap-shear test

This test is an ASTM standard (D1002) and is the most widely used adhesion test. The test gives the apparent average shear strength and is not intended for designing actual bonded structures or obtaining true shear strength of the adhesive. However, it is a sufficient comparative test and is especially useful due to its simple geometry³⁰. The average shear strength is given as:

$$\tau_m = P/bl \quad \{4.1\}$$

where τ_m is the apparent average shear strength, P is the applied load and b & l are the joint width and length respectively. While the geometry of the test is simple and a reason for its popularity, from a mechanistic viewpoint the lap-shear joint is a very complex loaded structure. The stress distributions within the sample are effected by several

factors such as (1) adherend modulus and thickness, (2) adhesive modulus and thickness, (3) bond overlap (4) other factors like presence of spew, shear moduli of adhesive etc^{31,32,33}. It is important to recognize these factors before testing as they can have a significant influence on the bond strengths obtained. Volkersen¹⁸ proposed a shear lag model to account for the non-uniform shear stress distribution along the bondline. The major assumptions of the model are that the adhesive deforms only in shear and the adherends only in tension. The equation that he derived for shear stress distribution along any point 'x' along the bondline is given by:

$$\tau(x) = \frac{P\omega}{2\sinh(\omega l/2)} \cosh(\omega x) + \frac{P\omega}{2\cosh(\omega l/2)} \sinh(\omega x) \left[\frac{E_2 t_2 - E_1 t_1}{E_2 t_2 + E_1 t_1} \right] \dots\dots\dots \{4.2\}$$

$$\text{where } \omega = \sqrt{\frac{G}{h} \left[\frac{E_2 t_2 + E_1 t_1}{E_2 t_2 E_1 t_1} \right]}$$

where:

h = Adhesive thickness

t = Adherend thickness

E = Young's modulus of the adherends

G = Shear modulus of the adhesive

l = Length of the overlap

P = Force per unit width

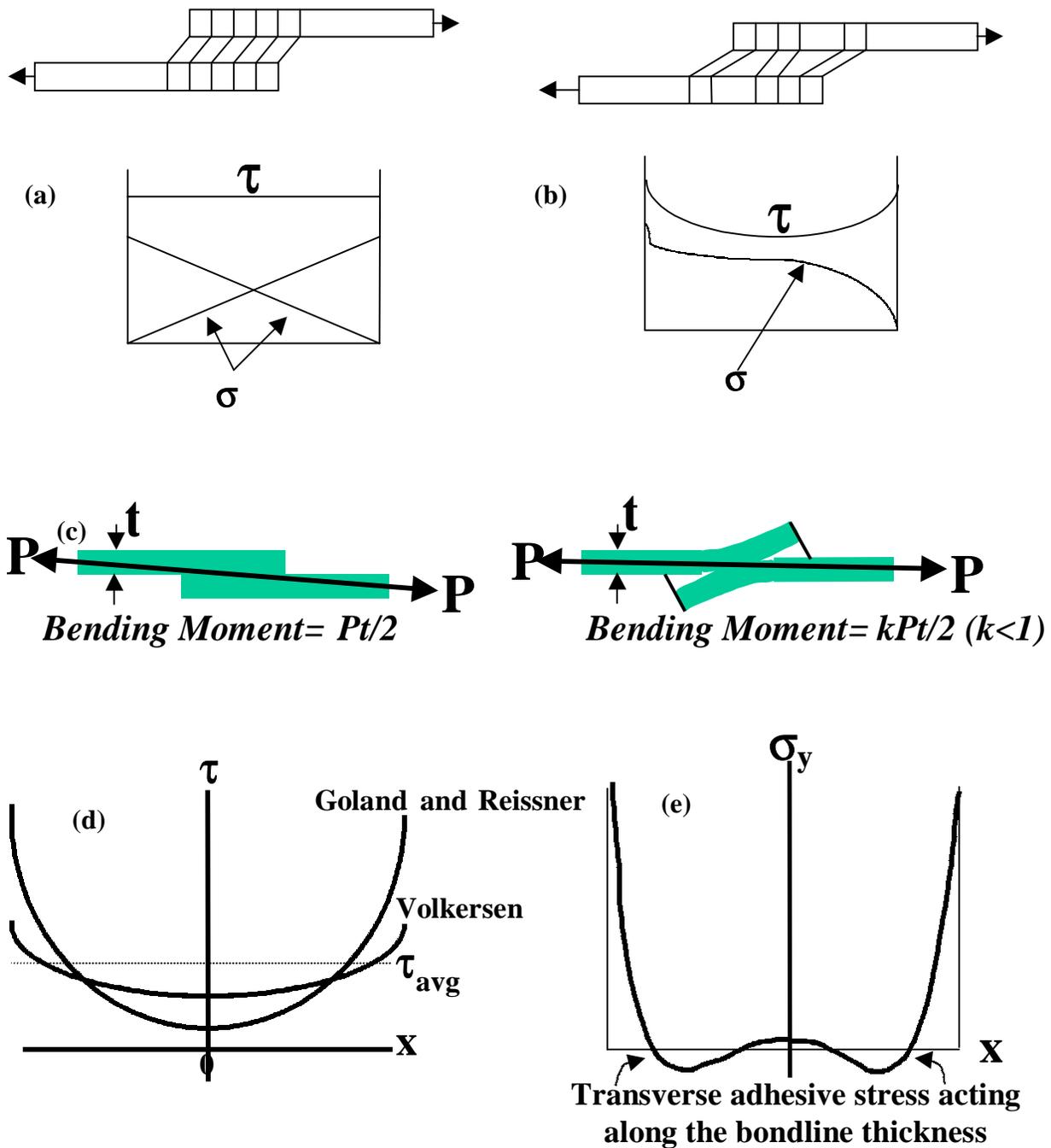


Figure 4.2 Shear strain (& shear stress) in the bond-line and tensile stress on the adherends as given (a) ideally & (b) predicted by Volkersen's analysis¹⁸. (c) effect of bending moment, which acts along the bondline to give a peel stress, thereby reducing joint strengths. (d) shear strength profile as given by various analysis (e) peel stresses along the bondline as calculated by Goland-Reissner analysis¹⁹.

Volkersen's shear lag approach also assumes that the adhesive and the adherend are *linearly elastic*. Figure 4.2 illustrates the shear stress profile for the adhesive and tensile stress profile for the adherend in the idealized case and with respect to Volkersen's approach. When proper account of the various joint parameters is taken, it is found that the adherend tensile stress decreases progressively from the loaded end to that on the unloaded end with the rate of change of the adherend stress being primarily dependent upon the adherend stiffness. The shear strain and shear stress in the adhesive are at the maximum at the ends and a minimum in the center. Also, dissimilar adherends will lead to a asymmetric shear stress distribution.

However, Volkersen ignored the bending moments in the sample due to non-linear load application. Any bending of the adherends changes the direction of the load line and in the adhesive deformation no longer is proportional to the applied load. Goland and Reissner¹⁹ took this fact into account and introduced a bending moment factor 'k' which relates the bending moment in the adherend end (M_0) to the applied load as:

$$M_0 = \frac{kPt}{2} \quad \{4.3\}$$

where 't' is the adherend thickness. While $k=1$ for no bending, it assumes a value less than one as the overlap area rotates and brings the load line closer to the center of the adherends. Goland and Reissner predicted a more non-uniform shear stress profile in the bondline than that predicted by Volkersen. One important aspect of Goland and Reissner analysis is that it predicts the excessive adhesive shear strains at the edges due to the elastic bending of the adherends. These excessive strains may lead to failure of the adhesive bond. In addition, the analysis predicts a 'peel stress' acting on the adhesive layer, σ_y which can be given as³⁴:

$$\sigma_y = \frac{\sigma^2}{C^2 R_3} \left[\left(R_2 \lambda^2 \frac{k}{2} - \lambda k' \cosh \lambda \cos \lambda \right) \cosh \frac{\lambda x}{C} \cos \frac{\lambda x}{C} + \left(R_1 \lambda^2 \frac{k}{2} - \lambda k' \sinh \lambda \sin \lambda \right) \sinh \frac{\lambda x}{C} \sin \frac{\lambda x}{C} \right] \quad \{4.4\}$$

where:

σ = mean tensile stress in the adherends

t = adherend thickness

x = position along the glue line

$$C=l/2$$

$$\lambda=C/t(6E_3t/Et_3)^{1/4}$$

$$k'=k(C/t)[3(1-\nu^2)\sigma/E]^{1/2}$$

$$R_1= \sinh\lambda \cos\lambda + \cosh\lambda \sin\lambda$$

$$R_2= \sinh\lambda \cos\lambda - \cosh\lambda \sin\lambda$$

$$R_3= (\sinh 2\lambda + \sin 2\lambda)/2$$

ν = Poisson's ratio

The shear and peel stresses are assumed to be constant along the bond thickness. The peel test itself is non-uniform and varies along the bond overlap, the maximum being at the edges. As predicted by Goland and Reissner, the value of the bending moment factor 'k' does not go to zero but approaches 0.2 towards the middle of the bondline. The analysis by Hart-Smith, however, predicts this value will fall to zero, implying negligible peel stress towards the middle^{31,35}. It is thus important to recognize that peel forces affect the bond strength values critically in lap-shear joints and often the failure can be attributed to these effects. Secondly, increasing the length of the overlap or increasing the shear modulus of the adhesive increases the non-uniformity of the shear stress profile. Increasing the modulus of the adherend, thickness of the adherends and the bondline thickness increase the uniformity of the shear stress distribution. These factors need to be kept in mind before any direct comparisons of the lap-shear strengths are made of results from different laboratories.

While most of the above quantitative relationships are based on elastic deformation of adhesive, an elastic-plastic model is often more appropriate in describing the fracture behavior of many viscoelastic adhesives. The large magnitude of fracture energy for some materials is attributed to their ability to undergo localized deformation in a relatively large region around the crack tip. The stress concentration is therefore reduced and the crack is blunted. The reduction in stress concentration can be related to the radius of the deformation zone. In this regard, the bond thickness if too small can limit the radius of the deformation zone and thus limit the toughness³⁶. The crack tip deformation process is viscoelastic in nature and the usual loading rate dependence and temperature dependence are thus introduced. Increasing the temperature or decreasing the loading rate increases the size of the deformation zone and thus the optimum bond thickness³⁷.

4.7 Crystallization aspects in adhesion

While crystalline polymers like polyethylene and polypropylene are widely used as hot melt adhesives, the amount of research work studying the effect of polymer crystallization on adhesion is surprisingly scarce. Only a few authors have looked at the effect of crystallinity and crystalline morphology on the adhesive performance (this may be in large part due to the widely prevalent misconception that crystallinity always promotes brittleness and loss of toughness). In fact, despite extensive literature search, this author was not able to come across a single study that addresses the effect of crystallinity on the solvent resistance of the adhesive interfaces.

With respect to the effect of crystallinity on adhesion, two features become important, (1) the effect due to strengthening/weakening of the bulk of the adhesive and (2) the effect on the adhesive interface. With regards to the first factor, Packham et al.³⁸ studied polyethylene adhesion to copper using the peel test. It was found that quenched samples gave higher peel strengths and a rougher fracture surface morphology than the samples that were slow cooled. Earlier Fan³⁹ and Tordella⁴⁰ had achieved similar results where they found extensively drawn polymer at the substrate for quenched samples. However, the failure was cohesive for all cases and thus it was proposed that the higher fracture energy values obtained for quenched samples were not due to the inhibition of weak boundary layer at the surface. Although the spherulitic sizes were not obtained the results may in part be due to smaller spherulitic sizes and reduced percentage crystallinity. Love et al.⁴¹ showed that faster cooling rates gave stronger adhesion between PCTFE and glass due to greater ductility and higher fracture energy of the adhesive. The peel test specimens showed that slower cooling rates gave more percentage crystallinity as more time was available for the polymer to crystallize. However, this increase in crystallinity resulted in lower adhesion strengths and an interfacial mode of failure (as observed visually).

The second factor deals with the effect of crystalline morphology on the adhesive interface. In this regard, the effect of transcristallinity at the substrate becomes

important in effecting the adhesion strength. Schonhorn^{42,43} has shown that the critical surface tension of wetting increases with transcrystallinity for polyethylene from 31mJ/m² to 69.6mJ/m². The increase in wettability will improve adhesion and thus will lead to higher joint strengths. Additionally, the presence of low molecular weight chains and impurities at the spherulitic boundaries has been widely documented. These regions will generally possess lower strength and have been proposed to constitute a weak boundary layer at the surface⁴⁴. The elimination of this weak boundary layer in theory can be achieved by introducing transcrystallinity or decreasing spherulitic sizes. However, Tordella⁴⁵ and Nakao⁴⁶ using peel tests on aluminum-polyethylene joints have shown that the peel strengths were unaffected by the presence or absence of transcrystalline regions. Nakao obtained similar results⁴⁷ for Nylon 12-steel joints where adhesive failures were obtained regardless of the presence or absence of transcrystallinity. Detailed systematic studies on these aspects for different adhesives and different bond types, however, have not been conducted to make firm conclusions. This may be area of potential research for workers dealing with semicrystalline hot-melt adhesives.

4.8 Polyimides as high performance adhesives

The bulk of the adhesive work dealing with high performance polyimides has come from workers at NASA^{48,49,50}. The method of choice has been the lap shear test on which the effect of the following variables has been studied:

- (1) effect of conditions utilized during tape making
- (2) effect of bonding time, bonding temperature and bonding pressure⁵¹
- (3) effect of aging time and aging temperature on room temperature lap-shear strengths⁵²
- (4) some results studying the effect of high testing temperature on lap-shear strengths
- (5) few results studying the effect of a limited number of solvents & boiling water on lap-shear strengths⁵³.
- (6) effect of surface treatments.

All the studies to date dealing with polyimide adhesion studies involve the preparation of an adhesive tape and subsequent bonding steps. While many polyimide systems have been thermosetting in origin, the use of this process for thermoplastic polyimides is due to unavailability of melt processable resins and the lack of thermal stability of the polymers above their high melting points. Secondly, as discussed before, the crystallization ability of the past polyimides rapidly deteriorates once taken to melt temperatures. Hence in order to preserve crystallinity which often occurs in the thermoplastic systems during the imidization process, the solvent route is preferred. The adhesive tape serves as:

- (1) a carrier of adhesive
- (2) for bondline control
- (3) the escape channel for solvent and volatile reaction products
- (4) may serve as additional reinforcement

The adhesive tape preparation is laborious and a procedure is presented from a study of Progar et al.⁴⁹ to illustrate the various steps usually involved:

- (a) brush coating of 0.1 mm thick 112 E-glass cloth with 7.5 wt.% DMAc poly (amic acid) solution
- (b) drying of glass cloth in forced air oven at 100°C for 0.5 hour
- (c) priming the scrim cloth with A-1110 finish (γ -aminopropylsilane) and drying for 0.5 hour.
- (d) second coating of 7.5-wt.% DMAc solution is applied.
- (e) placing the tape in forced air oven and conducting the thermal imidization cycle (in their case 1 hour each at 100, 150 and 175°C.
- (f) subsequent applications of 15 wt.% DMAc solution and repeating the thermal imidization cycle.
- (g) repeating step (f) till the desired tape thickness is achieved.

It is obvious that the adhesive tape preparation procedure is very involved, takes a long time and involves repeated handling of dangerous solvents. The repeat imidization steps are necessary due to the thickness effects on imidization discussed in Chapter I.

Various polyimides, which were described earlier in Chapter 3, were tested in accordance with the steps described earlier and using the lap-shear geometry. Jensen et al.⁵⁴ while evaluating LaRC-8515 found that higher bonding pressures produced thinner bondlines and higher strengths. While the strengths were in the range of ca. 6400 psi for bonding pressures of 150 psi (1h at 371°C), they dropped to 5000-5500 psi when the pressure was lowered to 75psi and 5700psi for bond pressure of 84 psi. For samples bonded at 84psi, the strengths decreased with testing temperature with the value of 4310 psi obtained at 177°C. For samples exposed to a variety of solvents for period as long as 2 days, the strengths were found to be in the range of 3380-4700 psi. Progar et al.⁵² found that for different copolymer grades of LaRC-TPI and pasajell treated surfaces, the lap-shear strengths were 4680-4860 psi at RT and dropped to 4180-4450 psi at 177°C. Progar and St. Clair et al.⁵⁰ conducted studies on amorphous grades of LaRC-TPI and found that bonding pressures could be decreased significantly (to 15 psi) by increasing the bonding temperature. Bonding temperatures 20°C in excess of the glass transition only required a 100psi bond pressure while at 350°C (90°C above the glass transition) only very low bonding pressures of 15psi were needed. Average lap-shear strengths as high as 5780psi were obtained at room temperature while at 204°C, various samples were in the range of ca. 3000-4000psi. Solvent resistance of these systems was not reported in this paper. In 1994, St. Clair et al.⁵² again conducted adhesive evaluations on newly developed grades of LaRC-TPI manufactured by Mitsui Toatsu Chemicals, Inc. While the materials could be bonded at temperatures in the range of 343-371°C at low pressures of 15 psi, the materials were amorphous in character. The optimized strengths at room temperature were in the range of 3000-6000 psi and 2000-3000 psi at elevated temperatures. While the strengths were reported to decrease by about 2000 psi after a 72 hour water boil, resistance to solvents was not reported in that paper. Hergenrother et al.⁵³ reported average lap shear strengths for an amorphous polyimide as high as 7850 psi with cohesive failure (the polyimide was based on BTDA dianhydride and 1,3-bis(2,3-aminophenoxy) ethyl ether). The strengths dropped to ca. 4100 psi when tested at 121°C (no aging). The water 72-hour water boil strengths were in the range of 3000-3600 psi. In 1991, Progar and St.Clair⁵⁰ reported the effect of bisimide additives on the strengths of LaRC-TPI bonds. The additives were added to lower the melt viscosity without lowering

the T_g . While some lowering of the bonding pressures was achieved, the elevated temperature strengths dropped. It was found that the additives were not affective in lowering the melt viscosity of LaRC-TPI.

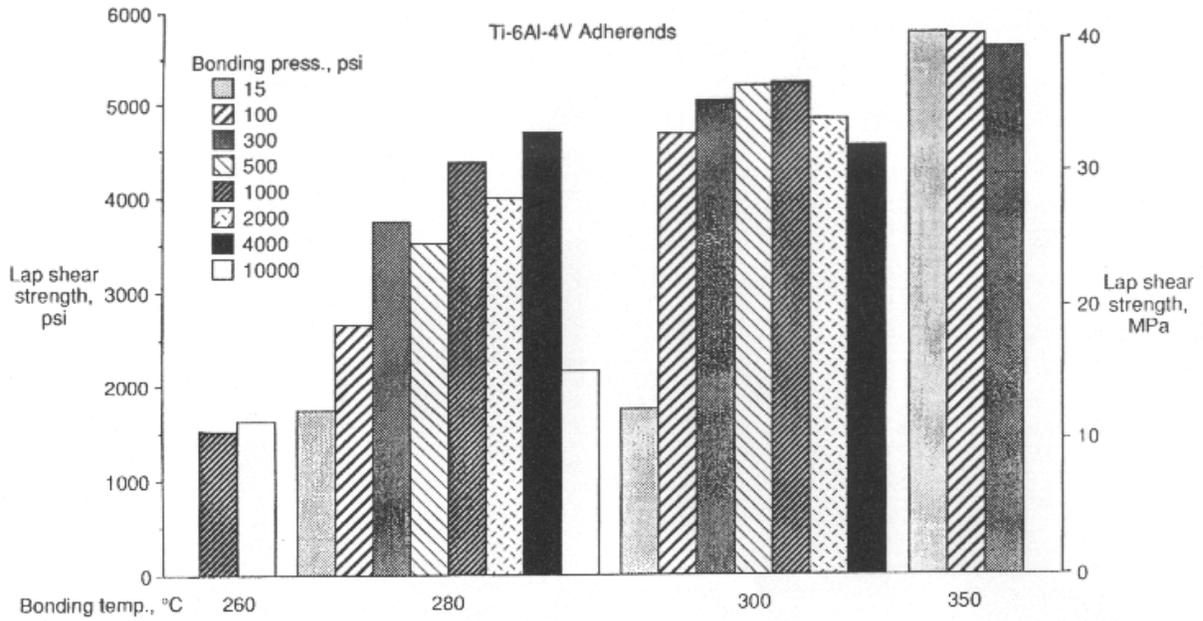


Figure 4.3 Room temperature lap-shear strength of the LaRC-TPI-am adhesive for various bonding temperatures and pressures⁴⁹.

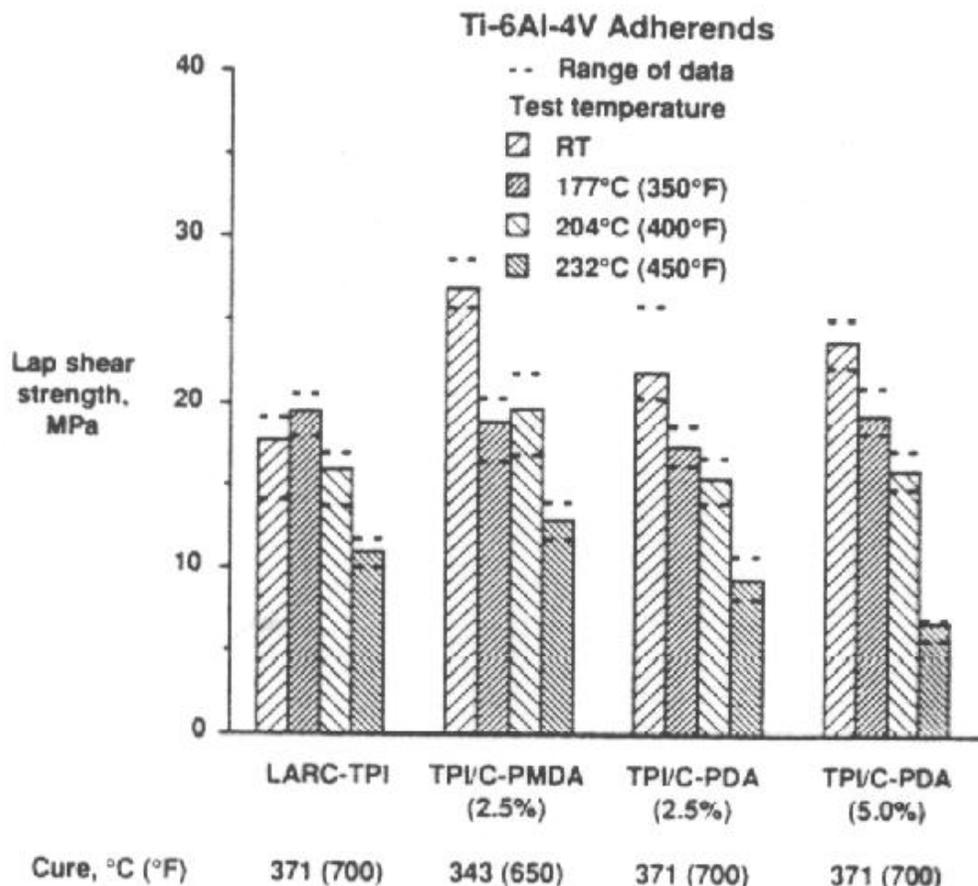


Figure 4.4 Lap-shear strengths for LaRC-TPI and effect of adding various additives (to change the melt viscosity) when bonded at 50 psi⁵⁰.

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