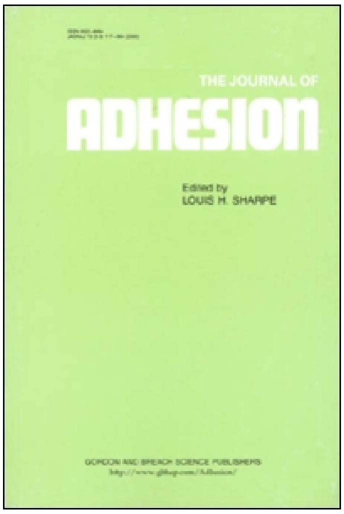

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Spiral Tunneling Cracks Induced by Environmental Stress Cracking in LaRC™-TPI Adhesives

David A. Dillard[a]; Jeffrey A. Hinkley[b]; W. Steven Johnson[b]; Terry L. St. Clair[b]
[a] Engineering Science and Mechanics Department, Virginia Polytechnic Institute and State University, Blacksburg, VA, USA [b] Materials Division, NASA-Langley, Hampton, VA, USA

To cite this Article Dillard, David A. , Hinkley, Jeffrey A. , Johnson, W. Steven and Clair, Terry L. St.(1994) 'Spiral Tunneling Cracks Induced by Environmental Stress Cracking in LaRC™-TPI Adhesives', The Journal of Adhesion, 44: 1, 51 — 67

To link to this Article: DOI: 10.1080/00218469408026616

URL: http://dx.doi.org/10.1080/00218469408026616

J. Adhesion, 1994, Vol. 44, pp. 51–67
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Spiral Tunneling Cracks Induced by Environmental Stress Cracking in LARC™-TPI Adhesives

DAVID A. DILLARD

Engineering Science and Mechanics Department, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

JEFFREY A. HINKLEY, W. STEVEN JOHNSON and TERRY L. ST. CLAIR

Materials Division, NASA-Langley, Hampton, VA 23686, USA

(Received December 1, 1992; in final form August 24, 1993)

Some currently-available formulations of LaRC™-TPI, a thermoplastic polyimide originally developed at NASA-Langley, were found to be highly susceptible to environmental stress cracking when exposed to solvents such as acetone, toluene, diglyme and methyl ethyl ketone. The combination of stress and solvent led to rapid cracking in films and adhesive layers of this material system. Residual cool-down stresses induced when the LaRC-TPI is used as an adhesive or coating led, in the presence of a solvent, to dense "mud crack" patterns which relieve a portion of the stored energy. Because these through-the-thickness cracks are not able to relieve the stored energy in the vicinity of the adherends, additional fractures in the form of curious spiral tunnel cracks initiated and grew inward within each adhesive fragment. Micrographs of the spiral fractures are given, along with a qualitative explanation for the failure process as observed in adhesives and coatings.

KEY WORDS spiral cracks; adhesives; coatings; LaRC-TPI; polyimide; environmental stress cracking; residual stresses; tunnel cracks.

INTRODUCTION

Polymeric materials are being used for an ever-increasing number of applications which depend on very high performance in terms of service temperature, applied stress levels, and environmental exposure. An increasing number of designs depend on fiber-reinforced polymers and adhesives for structural integrity. Improvements in polymer synthesis, processing, and design are leading to further inroads of these material systems into areas which have typically been dominated by metals and ceramics.

The first-generation high-performance polymer systems were typically based on thermoset chemistry which takes advantage of chemical crosslinks to result in polymer networks which are resistant to time, temperature, stress, and environment. Some recent applications have utilized thermoplastic systems which offer improved toughness, reduced processing time, improved storage capability, and the potential for recycling. The increased molecular mobility of these systems results in greatly improved toughness over most monolithic thermoset systems, eliminating the need for toughening particles, etc. Adding stiff rings to the backbone increases the energy required for molecular motion, and can lead to very high glass transition temperatures (*e.g.*, LaRC-TPI $T_g = 240°C$). Whereas thermoset polymers normally cannot be dissolved, thermoplastics are susceptible to dissolution in the proper solvents. Semicrystalline thermoplastics are quite resistant to being dissolved in solvents because the crystalline structure acts like physical crosslinks to prevent dissolution. Even thermoplastic systems which are completely amorphous may be made quite resistant to many solvents by adjusting the backbone stiffness, molecular weight, and molecular attractions to solvents of concern.

In addition to solvation concerns, certain thermoplastics may be susceptible to the phenomenon of environmental stress cracking or crazing in the presence of certain solvents.[1, 2, 3] Common examples include polyethylene in the presence of detergents (Igepal®) or n-propanol,[4] polycarbonate exposed to ethanol[5] or acetone, and poly(methyl methacrylate) (PMMA) exposed to ethanol or methanol.[6] This phenomenon results in crazes and/or cracks at applied strain energy release rates which are much smaller than normally needed to produce fracture of the polymer. Environmental stress cracking has been of major concern to the polyethylene pipe and container industries, for example.

The present paper outlines some observations made in dealing with the environmental stress cracking susceptibility of current formulations of a thermoplastic polyimide, LaRC-TPI. This material was originally developed at NASA-Langley,[7, 8, 9] and is now produced and sold by Mitsui Toatsu in several different grades. Two lower molecular weight grades have exhibited extensive environmental stress cracking in the presence of solvents such as acetone, toluene, methyl ethyl ketone (MEK), and diglyme. A higher molecular weight formulation of LaRC-TPI was found to be very resistant to these solvents. Apparently, in an effort to improve processability, the molecular weights have been reduced to a point that the lower molecular weight versions of LaRC-TPI are quite susceptible to environmental stress cracking. When these grades are used as adhesives to bond titanium or glass panels, solvent exposure results in very unusual failure patterns. Details will be presented about how the residual thermal stresses in the adhesive, coupled with a solvent, led to tunneling cracks in a random "mud crack" pattern throughout the adhesive layer. Within each cell, spiral cracks were observed to initiate and propagate inward for a number of revolutions. Similar behavior has been reported for several polymeric coatings[10] and nickel coatings.[11] Freund and Kim[12] have recently analyzed outward-growing spirals in ceramics containing cylindrical metal inclusions. A qualitative interpretation of the spiral cracks which we have observed is presented herein, and a more extensive analysis of the curious fracture event is underway using crack path selection techniques similar to those discussed in Refs. 12 and 13.

MATERIALS AND SPECIMEN PREPARATION

The results in this paper are based on observations of four LaRC-TPI systems obtained through Mitsui Toatsu: 1), a high molecular weight version designated low flow grade (LFG) which was obtained in cast sheet form; 2), LFG powder; 3), an extruded film of the medium flow grade (MFG) stock; and 4), a 50/50 blend of medium flow grade and high flow grade (HFG) pellets. The LFG sheets and LFG films compression molded from powder were both unaffected by solvents, so hereafter both are referred to as LFG material. Lots 3 and 4 will be referred to as MFG and HFG/MFG, respectively. The properties for the components are given in Table I.

The MFG extruded film was tested in the extruded form, with a thickness that varied across the width from 50 μm (0.002 inch) to 300 μm (0.012 inch). Some of these films were also used to bond glass plates for visual observation of the cracking phenomena. The HFG/MFG blend pellets were compression molded into glass fiber scrim cloth supported films with a nominal thickness of 350 μm (0.014 in). These scrimmed films were then used directly for cracking studies or were used as adhesives to bond titanium or glass plates. The LFG film was only tested in its free-standing sheet form.

Before bonding, titanium (Ti-6Al-4V) panels of 2.5 mm (0.10 in) thickness were grit blasted, treated with Pasa Gel® (American Cyanomid) 107, and primed with a dilute poly (amic acid)/diglyme solution. Following a 30-minute drying time at ambient conditions, the panels were placed in an oven, heated to 100°C and held for 15 minutes, heated to 165°C and held for 15 minutes, allowed to cool gradually, placed in plastic bags, and stored in a desiccator. Glass plates of 6.4 mm (1/4 in) thickness and microscope slides with a thick- ness of 1 mm were prepared by cleaning with methanol, brushing lightly with the poly(amic acid) diglyme solution, and subjecting to the same imidization cure cycle.

Bonded joints were prepared by placing LaRC-TPI films between the titanium adherends and processing in a hot press. The 150 mm by 200 mm ("6 × 8") titanium plates were bonded over a 150 mm by 150 mm ("6 × 6") area in a 40 kN (10,000 pound) press. The temperature was measured by a thermocouple welded to one of the adherends. Insulation was applied around the panels to improve temperature uniformity. The plates were heated to 357°C (675°F) at a rate of 6°C (11.8°F) per minute and held for 1 hour at the 375°C temperature. Throughout the press cycle, a pressure of 100 kPa (15 psi) was applied in order to simulate vacuum bag technology. Panels were then allowed to cool gradually in the press. A small amount of compressed air was directed onto the press, resulting in a cool down time of approximately 3 hours. The titanium

TABLE I
Physical properties of LaRC™-TPI 1500 (Data supplied by Mitsui Toatsu Chemicals, Inc.)

	HFG	MFG	LFG
Inherent viscosity of polyimide η_{in}, dL/g (0.5 wt.% in p-Cl-phenol/phenol 95/5%)	0.37–0.38	0.45–0.46	0.61–0.62
Glass transition temperature (by differential scanning calorimetry (DSC)) T_g, °C	236	240	245
M_n (by low angle laser light scattering (LALLS))	21,700	26,200	—
M_w, (by gel permeation chromatography (GPC))	66,400	77,100	—
Relative flow at 380°C (flow through a short 1 mm capillary normalized to HFG)	1.0	0.2	0.06

panels were then cut with a diamond saw and stored in a desiccator until testing. Of the six panels made, all but one were relatively free of entrapped voids. The glass plates were bonded in a similar manner, although, for microscopy purposes, a vacuum press was used to fabricate most of these bonded joints in order to minimize further the occurrence of voids.

EXPERIMENTAL OBSERVATIONS

The first indication that the currently-available forms of LaRC-TPI would be susceptible to stress corrosion cracking occurred when cleaning the titanium bonded plates with diglyme. Kapton® tape had been wrapped around the panels prior to bonding in order to help hold the adhesive films in place and maintain plate alignment during the bonding process. We were advised to use diglyme in order to remove the mastic left over after the bonding was completed. On several panels a distinct cracking sound was heard when diglyme was applied to the surfaces of the titanium plate for cleaning. Apparently, enough diglyme was able to wick into the edge and voids present in the LaRC-TPI near the edge of the panels to begin the degradation process. As will be discussed later, this residual amount of diglyme apparently continued cracking the panels for considerable distances away from the edges, as revealed when specimens were examined after failure.

Free Film Experiments

While cleaning a scrimmed HFG/MFG film with acetone in preparation for bonding, profuse cracking was also observed. Several small pieces of the scrimmed HFG/MFG materials were taped to a rigid plate and several drops of the following solvents were applied: methanol, propanol, acetone, diglyme, MEK, toluene. Acetone resulted in immediate cracking in a mud crack pattern. Diglyme acted more slowly, requiring several minutes to produce the extremely dense fracture pattern. Toluene and MEK produced results which were similar to acetone. Neither of the two alcohols produced any perceptible amount of cracking in these panels. The only stress applied to these panels was the residual thermal stress and the stress induced by flattening these curved adhesive layers against a rigid substrate. The mechanically induced stresses were estimated to be on the order of 30 MPa (4.5 ksi).

Further tests were conducted on free films of the HFG/MFG material. In the absence of a solvent, the films would break only if bent sharply. Neither acetone nor diglyme produced any visible damage in unstressed films. However, bending films slightly and applying a drop of solvent resulted in cracking. In the case of acetone, there was an immediate failure of the film and an audible cracking sound. As mentioned earlier, diglyme seemed to act more slowly, but produced more overall damage. When a slightly-bent film was subjected to diglyme, it slowly deteriorated. Cracks formed, bifurcated, and continued to grow. Numerous crazes were obvious for a considerable distance away from the crack tip.

We also observed that initial flaws in bent films would propagate in the presence of acetone vapor, although at a much-reduced rate relative to the liquid. (Cracking in gaseous environments has been reviewed by Brown[14]). Bent films of LaRC-TPI showed no cracking in a 50/50 acetone/water mixture. It is presumed that the acetone molecules have such an affinity for water that they are effectively surrounded by water molecules, preventing attack of the polymer. We had hoped that titrated mixtures would allow us to slow the growth rate to simplify observation, although this does not seem possible with the acetone/water mixture.

Several films of both forms of the LFG material were bent and exposed to solvents. No cracking could be produced. The LFG material appears to be quite resistant to environmental stress cracking, at least in the time scale of our investigations.

Titanium Bond Observations

The bonded titanium panels were sliced into 200 mm by 25 mm (8" × 1") double cantilever beam (DCB) test coupons, and loaded to failure in the course of our studies. We had originally believed that the small amount of cracking which we had heard while wiping the titanium bonded joints with diglyme would, at most, result in a minor amount of fracture very near the edges of the panel. Upon microscopic examination of the fracture surfaces, however, very drastic failure features were observed even well into the panel. Specimens from one panel all exhibited anomalous cracking, suggesting that the solvent had been able to migrate 75 mm to the center of the panel. The anomalous fracture patterns consisted of a highly-fragmented adhesive layer with each fragment capped by curious spiral patterns as shown in Figure 1. The spacing roughly corresponds with the scrim cloth pattern, and we first thought that the patterns were associated with the presence of the scrim. As seen in the following micrographs, however, the characteristic patterns form even in the absence of the scrim. The

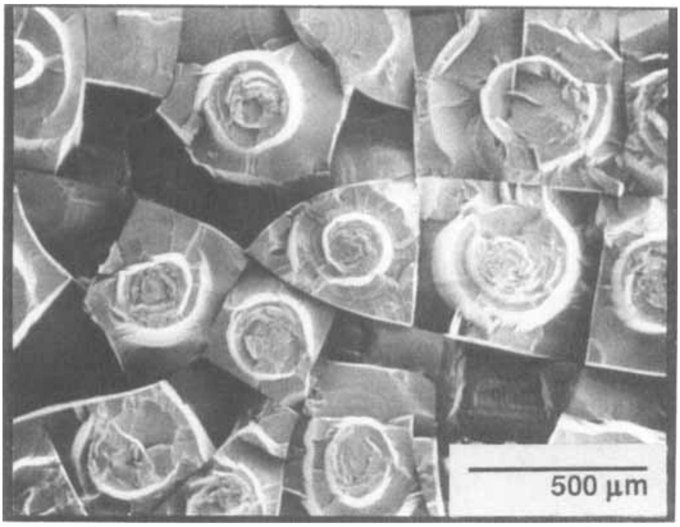

FIGURE 1 Typical failure surface of a DCB specimen bonded with scrimmed HFG/MFG adhesive film and exposed to diglyme. This illustrates the features on the tops of prisms which were pulled away from an adherend.

mechanics of the fragmentation process dictate that the characteristic crack density happened to correspond with the scrim spacing by coincidence. The presence of the scrim weakens the material slightly, and the cracks tended to form through the scrim yarns.

Photomicrographs of adhesive which had spewed from the scrim cloth region and bonded to both adherends provide some of the clearest illustrations of the fracture phenomenon. In Figure 2, we observe that this adhesive region has broken into a large number of cells because of cracks which have tunneled throughout the adhesive layer. The combination of these cells resembles a honeycomb structure. Even more curious is that each of these cells displays spiral failure rings. When loaded to failure in an opening mode, mechanical separation tends to take place very close to the interface on one of the adherends. This failure locus may be at alternate adherends for adjacent cells, so the failure process then involves cells sliding past one another along the pre-existing tunnel crack faces. One can observe that the sides of each cell are very straight and smooth, representing a very glassy failure process as shown in Figure 3. The smooth sides and geometric cross section of each of these elements resemble prisms. This term will be used throughout the remainder of the paper to refer to these individual fragments. The typical diameter of the prisms is 0.5 mm (0.02 in). This is about twice the adhesive layer thickness, which was 0.25 mm.

Bonded Glass Plate Observations

By using optical and scanning electron microscopy of fracture surfaces, and watching fractures occur (in real time and using video recordings) in the LaRC-TPI bonded

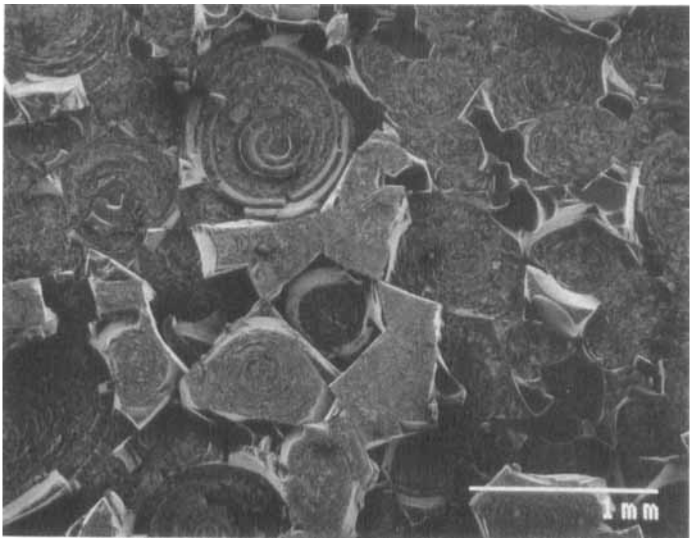

FIGURE 2 Typical failure surface of a DCB specimen bonded with HFG/MFG adhesive film and exposed to diglyme. The majority of the prisms have been pulled away with the other adherend, leaving behind the spiral patterns in the polymer layer remaining on the adherend.

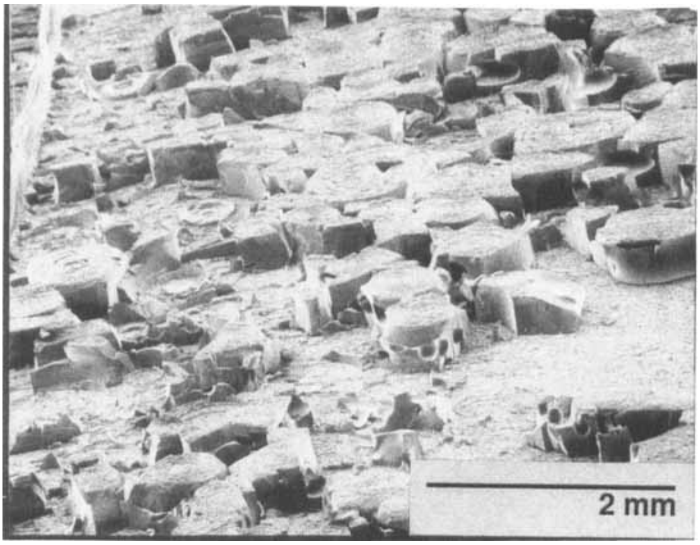

FIGURE 3 Grazing angle (60°) view of prisms, showing smooth glassy prism faces.

between glass plates, we were able to postulate the following fracture scenario. The initial failure process is one of quite rapid tunnel crack extension in a somewhat random fashion. This cracking results in the characteristic "mud crack" pattern seen in Figures 1–3. Visual observations and inspection of polished cross-sections indicate that each crack extends throughout the adhesive layer thickness to within close proximity of the interface. The cracks are not likely to propagate all the way to the interface for theoretical reasons[15] and because we see no evidence of any debonding of the LaRC-TPI from the adherends. SEM micrographs of LaRC-TPI films de-adhered from glass adherends by a water soak also fail to exhibit any flaws rupturing the surface. Because the strain energy release rate will decrease as a crack approaches a relatively rigid adherend, each crack would be expected to stop just short of the interface.

The next event seems to be a further breakdown of the random cells which were initially produced. In many cases, this results in a long cell being broken into two or more parts, and protruding corners of the irregularly-shaped cells being broken off. It appears that the high stresses which develop in the vicinity of the projecting corners are the precursor to the spiral cracking patterns. As the corners begin to split off, the flaws seem to curve away from the boundaries, as seen in optical micrographs of flaws growing in a MFG adhesive between two microscope slides (see Figure 4). These highly-stressed corner regions thus spawn the precursors for spiral cracks. In most cases, only one to five spiral cracks propagate, although we have evidence that, in some cases at least, numerous cracks are initiated, as seen in Figure 5. The spiral cracks continue to grow slowly; one crack was clocked at one revolution in 15 minutes. The spiral often continues until it approaches the center of the prism, as seen in a typical pattern showing two spirals in Figure 6. These patterns are quite ubiquitous, as illustrated by Figure 7. There seems to be no preference for counterclockwise *versus*

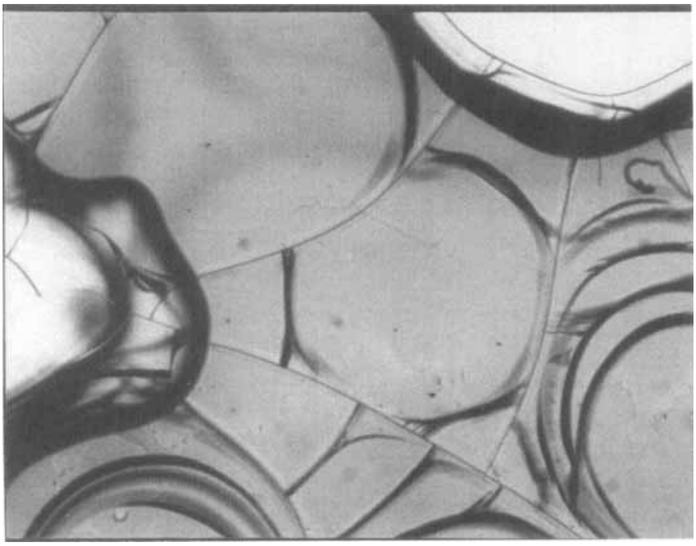

FIGURE 4 Fracture of protruding corners serve as precursors which initiate spiral crack growth.

clockwise spiral growth, although, within any given cell, the spirals tended to grow in the same direction. The precursor cracks seen in Figure 5 are an exception to this, although if they are allowed to continue growing, one direction will prevail, as we never observed intersection of counter-rotating spirals.

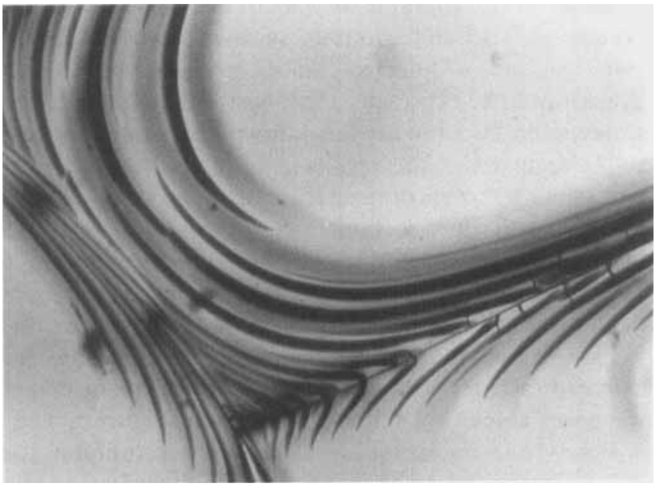

FIGURE 5 Multiple precursors emanate from the highly-stressed corner region, and begin parallel flaw growth.

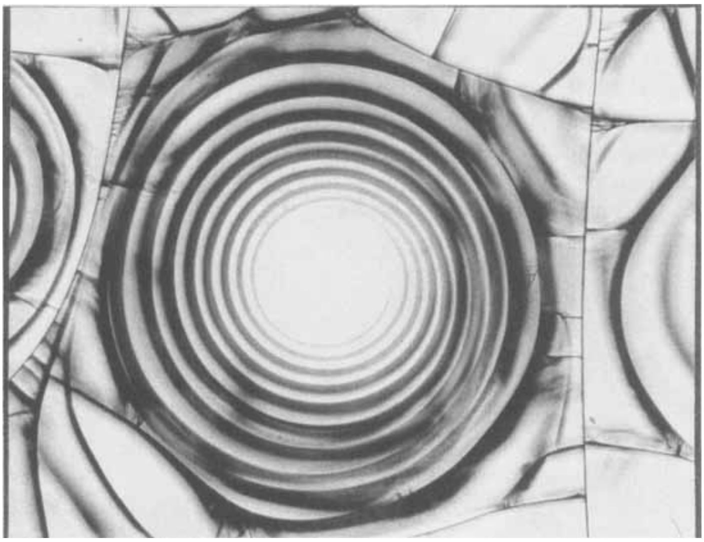

FIGURE 6 Typical spiral pattern formed by two flaws growing near one interface.

By using an optical microscope, and focusing at different depths within the LaRC-TPI layer, we were able to recognize that the spiral cracks occur very close to the interface. As was the case with the "mud cracks", it is unlikely that the spiral cracks proceed all the way to the interface, but they are limited to the vicinity of the adherend. By focusing near the upper interface and then near the lower interface, different spiral

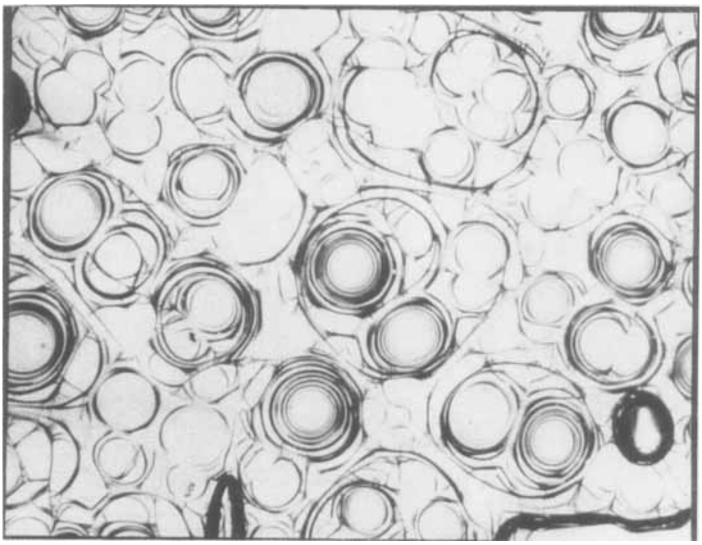

FIGURE 7 Ubiquitous cell and spiral flaw patterns resulting when MFG film bonding two glass slides was exposed to diglyme.

patterns were observed. Their growths were apparently independent of one another. No spiral patterns were visible at intermediate depths. Although the spiral patterns definitely originate and propagate near an interface, over time they may extend towards the midplane of the adhesive layer. Another interesting feature of the spiral patterns is the flare angle exhibited by each spiral crack. A close-up of one of the prisms shown in Figure 1 is shown in Figure 8, clearly illustrating the flared spirals. Similar features will be seen upon close examination of Figures 1–3, and they are indirectly implied in the broadened cracks as seen through the optical microscope in Figures 4–6.

Titanium Joint Strength

In spite of the extensive crack patterns seen in the previous micrographs, the bonded specimens still retain considerable strength. In fact, the critical strain energy release rate of double cantilever beam (DCB) specimens with no exposure and those which had been soaked in acetone for 24 hours were essentially the same, approximately 1.4 kJ/m^2 (8 lb/in) propagation and 1.2 kJ/m^2 (6.8 lb/in) arrest, as measured according to ASTM D-3433 and Ref. 16, even though the exposed specimen was riddled with cracks. It is suspected that the mud cracks and spiral cracks relieve the triaxial constraint which would be present in the absence of such cracks. Because these cracks are nominally perpendicular to the bond plane, they do not substantially weaken the adhesive for opening mode loading, and the discrete prisms and cracks may act as crack stoppers. A close-up of Figure 2 is shown in Figure 9, illustrating the features of the final failure surface after mechanical separation. The failure locus proceeds through the adhesive near the interface, although a considerable amount of polymer is left on the adherend surface. The flared spiral patterns are obvious, and the smooth surfaces provide

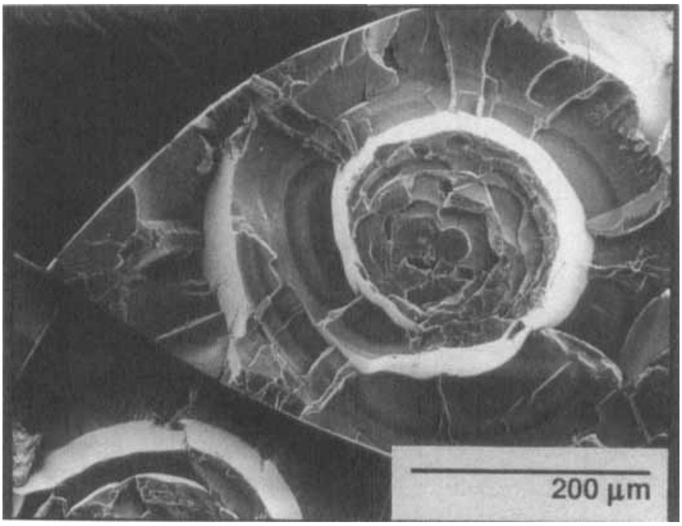

FIGURE 8 A single prism showing the outward-flared spiral pattern.

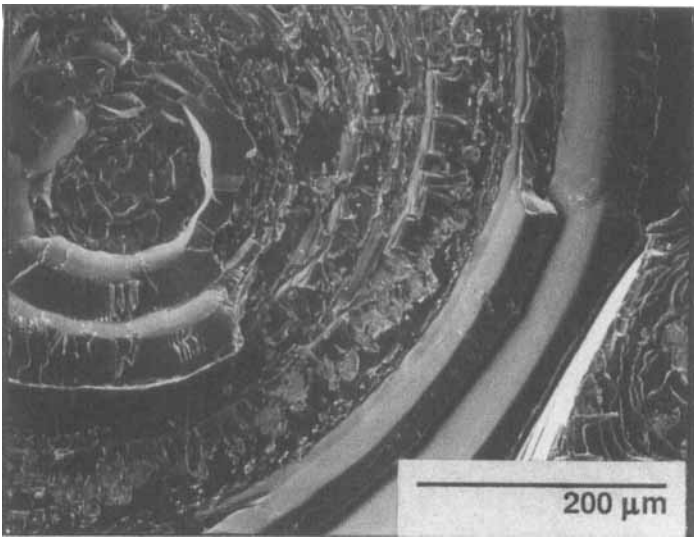

FIGURE 9 Close-up of one quadrant of the polymer remaining on a titanium adherend after the prism has been pulled away, showing the glassy surfaces of the flared spirals.

evidence of the brittle failure which allowed the spiral cracks to propagate in the presence of the solvent. Referring to Figures 1–3, one sees that the failure locus within a given prism is always near the interface, although different prisms may break at either the upper or lower adherend. For specimens which have not been exposed to solvent, the failure locus is always a torturous ductile failure along the midplane of the scrim cloth (as seen in Figure 10), presumably because the scrim yarns slightly weaken the adhesive and also were the site of residual air bubbles.

DISCUSSION

While a number of parameters affect the environmental stress cracking susceptibility of a given polymer/solvent system, molecular weight is known to be of major importance.[4] Low molecular weight systems are especially susceptible to environmental stress cracking, presumably because the solvent enables the short molecular chains to disentangle in the highly-stressed regions at the tip of a loaded crack.[17] Crack growth rates have been shown to vary as the inverse of the molecular weight raised to powers of 20 or more.[4] It has also been noted that the entire molecular weight distribution of polydisperse polymers is of importance.[4] Depending on the degree of strength reduction and the kinetics of the degradation process, a given polymer may be unacceptable for applications in which exposure to detrimental solvents will occur. As indicated earlier, both of the lower molecular weight versions of LaRC-TPI were found to be

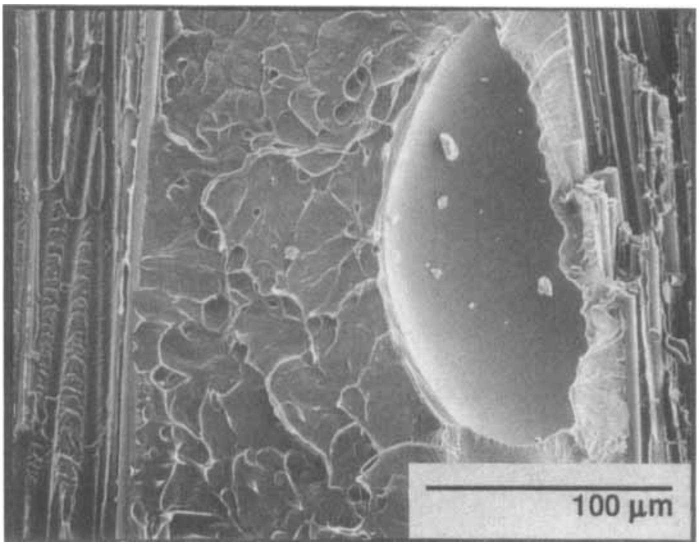

FIGURE 10 Typical failure of a HFG/MFG film used for a DCB specimen which has not been exposed to a solvent. The failure occurs through the scrim cloth plane, and passes through a trapped air bubble, but the material shows considerable ductility.

susceptible to environmental stress cracking, although the higher molecular weight version (LFG) did not exhibit any susceptibility. Our perception is that the low molecular weight versions, which are desirable from a processing standpoint, are not resistant to environmental stress cracking, presumably because the shorter molecular chains are able to disentangle when stressed in the presence of an appropriate solvent. A wide angle X-ray (WAXS) scan of material pulverized in diglyme failed to detect crystallinity, suggesting that the brittleness was not due to crystallite formation.

Mechanics of the Failure Process

Relying heavily on microscopy of failed surfaces, and real time optical microscope observation of the failure process, we have been able to determine the chronology of the failure process. The mechanics necessary to explain the phenomenon in a precise manner are under investigation. For our present purposes, we simply present a preliminary description of the mechanics involved.

Through-the-thickness Cracks We begin with an understanding of the residual stress state in the adhesive layer. With the exception of regions affected by edge effects, the nominal stress state in the adhesive is equal biaxial tension in the plane of the bond. The magnitude of these stresses has been estimated at 30 MPa (4 ksi). The initial through-the-thickness or mud crack patterns are similar to those widely observed in a variety of cracking problems.[18] The random pattern is expected because the biaxial stresses are equal to one another. As mentioned earlier, experimental evidence and the mechanics of cracks approaching relatively rigid adherends both suggest that these mud cracks do not penetrate to the interface, but that they do exist throughout most of the adhesive thickness. As these cracks propagate in the vicinity of other cracks, each growing crack was observed to turn in order to intersect an existing crack at a right angle. This cracking process occurred relatively quickly, and extended considerable distances into the adhesive bond.

We observed that the mud cracks form until some characteristic flaw spacing is achieved, as has been reported in other nonhomogeneous systems.[19] In the systems which we have observed, this characteristic spacing is on the same order as the adhesive or coating thickness. For adhesives, the prism dimension is roughly twice the adhesive layer thickness, whereas, for coatings, the dimensions are somewhat larger as might be expected from a simple shear lag model of a single substrate geometry. While the stress state in these fragments remains one of biaxial in-plane tension, the size has become small enough that there is not sufficient energy available to propagate more of the through-thickness flaws. Within each of the prisms, the in-plane stress is relieved in the midplane area (especially near the prism faces), but the residual stresses near the stiff adherends remain nearly as high as they were initially if there is no significant debonding from the adherends. In addition, large shear stresses are expected near the interfaces. These shear stresses will have a maximum value near the prism faces (and especially the corners) and will decrease to zero as one approaches the center of the prism. This highly nonuniform stress field leads to the growth of flared spiral flaws in the adherend vicinity, as illustrated schematically in Figure 11. (Slight compressive stresses normal to the bond may be expected to occur in newly-formed prisms because of the Poisson coupling, but these stresses are relieved as mud cracks form in the

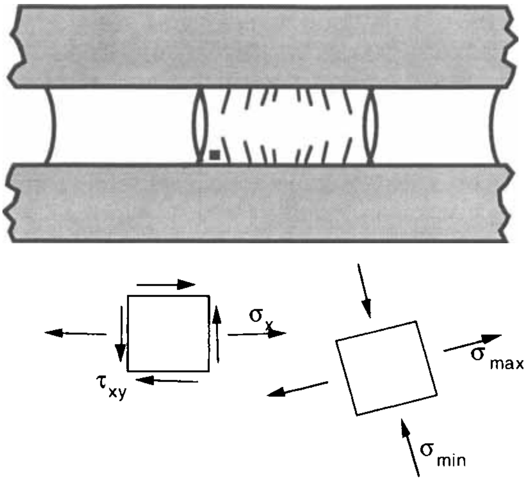

FIGURE 11 A schematic cross-section showing spiral flaw position and orientation. The expected stress state and principal stress state for the dark element near the adherend/mud crack intersection is also illustrated.

adjacent adhesive. These compressive stresses are not believed to play a significant role in the spiral fracture process.)

Spiral Cracks We begin our discussion of spiral crack growth by recognizing that cracks do curve in order to continue to propagate in a manner which will relieve stored energy in a favored manner. A fracture mechanics postulate known as the principle of local symmetry has been employed, for example, to predict curved crack trajectories.[12,20] This principle states that in isotropic, homogeneous material, a crack will grow in such a way that the Mode II crack intensity factor is zero. This is supported by the observation (especially in brittle materials) that flaws will turn to grow such that their growth direction is perpendicular to the largest principal stress. In a state of equal biaxial tension, a crack could run in any direction if it is not influenced by a boundary or another crack. When the flaw is growing in the presence of another crack, it will want to run either parallel or perpendicular to this existing flaw. Either direction will satisfy the local symmetry principle. Thus, in our specimens, the mud cracks have been observed to intersect existing cracks at right angles, whereas the spiral flaws always run parallel to one another.

There are perhaps several ways by which the surface regions of the adhesive layer could fail in order to relieve the residual stresses. One might speculate that a random mud crack pattern could occur on a smaller scale than the through-thickness flaws. We have not observed this pattern, and suspect that it is not energetically favored because it is inefficient in terms of the amount of flaw surface generated in order to relieve stored energy. A second method would be for a series of parallel cracks to grow, as has been occasionally observed, and as was beginning to develop in the prisms illustrated in Figure 5. While this is a possible configuration, it is not stable in the confines of an adhesive fragment. As these parallel cracks approach a boundary, they all begin to curve. Some cracks are apparently "squeezed out" in the curve, and fewer cracks emerge to continue. From the ubiquitous nature of the spiral cracks, it appears that this is the thermodynamically-favored growth pattern. Since a growing crack only sees the close cracks, several spiral flaw may grow simultaneously, as is illustrated by the two flaws shown growing in Figure 6.

Of particular interest is why the spacing between the spirals is so uniform. The reasons for this are not clearly understood, especially when we consider how uniformly spaced the spiral cracks are even in very irregular cells. It is obvious that for the spiral crack to veer outward and intersect the prism face would not be favored from an available energy standpoint. But it is less obvious why the crack does not veer inward and split the end of the prism. It would appear that such splitting would greatly reduce the amount of stored energy. There is some indication that this does happen in certain instances, although the split is apparently a through-the-thickness crack, but they are quite rare from our observations. Figure 12 shows a cell which apparently had several spiral cracks growing in it before the cell was split. Spiral cracks then began to grow within the smaller cellular regions. This prism splitting is not common once the spiral patterns have commenced, and we conjecture that for a crack to veer inward would not be favored because it would violate the principle of local symmetry. Thus, each spiral crack is constrained to move in a spiral track whose distance from the previous crack is controlled by the stress state in the material. Similar principles are believed to govern the regularly-spaced secondary flaws initiating near the interface in cross-ply composites.[21,22] We have observed that the distance between adjacent spirals does decrease as one approaches the center of the prism,

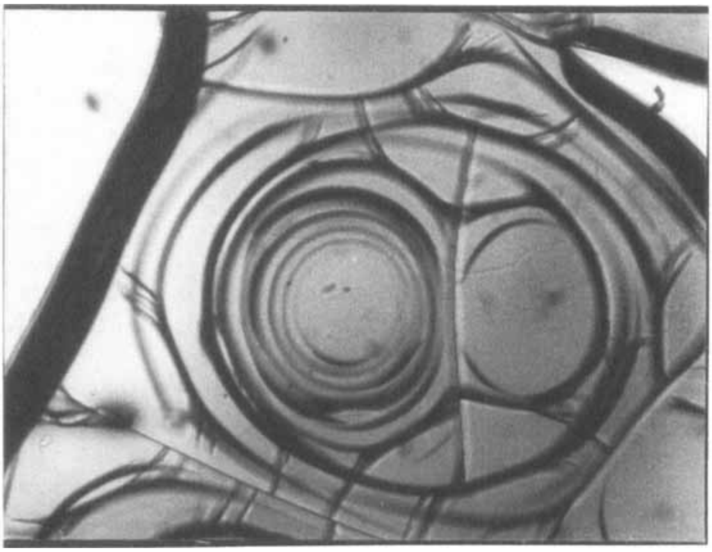

FIGURE 12 Spiral cracks were interrupted when a prism split in two, and new spiral flaws were initiated within the new prisms.

although the mechanics for this are not under- stood at this point. A logarithmic spiral was proposed by MacNulty,[10] although this was not justified from a rigorous mechanics perspective.

Where air bubbles are present, one gets a unique opportunity to investigate the behavior of thin adhesive layers with a free surface (*i.e.*, coatings). These regions are found to crack profusely as seen in the region which is restrained by both adherends. Frequently, the cracks lie very close to the meniscus of the bubble, indicating a stress concentration which undoubtedly is present in the regions. Although a few instances of the precursor to spirals has been seen within these regions, there appears to be less likelihood for spirals to form in these thin layers which are attached to only one surface. Spiral cracks were observed forming in very low molecular weight phenylethy- nyl-terminated polyarylene ether which had been dried in the bottom of a beaker. The spirals were not as complete as seen in the LaRC-TPI adhesive layers, but they do suggest that the residual stresses induced by either one (coating) or two (adhesive) substrates will give rise to the spiral patterns. Thus, we believe that if the critical strain energy release rate is low enough, spiral cracks may be a common fracture phenomenon.

Although we do not have quantitative measurements for the amount of solvent necessary to cause the extensive mud crack and spiral crack networks, we have observed that a tremendous amount of crack area, and large penetration depths, are possible with only a drop or two of solvent. This process may proceed with liquid which continuously wicks to the confined crack tip region. The slower growth of the spiral cracks may be consistent with vapor-induced cracking, or may simply reflect the smaller available energy release rate for the spiral cracks.

CONCLUSIONS

Currently-available formulations of LaRC-TPI thermoplastic polyimide have been found to be susceptible to environmental stress cracking in the presence of solvents such as acetone, MEK, toluene, and diglyme. The low molecular weight fractions of these formulations, which have been optimized to provide acceptable processability, appear to be responsible for the problem. A higher molecular weight formulation of the LaRC-TPI did not appear to be susceptible to environmental stress cracking in the time scale of our observations. Modifications to material systems will likely need to be made in order to improve the solvent resistance of the commercially-available materials. Mitsui Toatsu has reported that extracting low molecular weight material from LaRC-TPI with toluene results in greatly reduced susceptibility to solvent cracking.

By significantly reducing the critical strain energy release rate for crack propagation, the presence of solvents in materials susceptible to environmental stress cracking can lead to very peculiar fracture patterns. For bonded joints utilizing the currently-available TPI materials, random cracking is induced which subdivides the adhesive layer into a number of prisms which are perpendicular to the bond plane. The prism sides are found to be very smooth and glassy. The ends of each prism (*i.e.* near the adherend interfaces) are further fractured through a curious spiral crack formation, each crack spiraling inward toward the center of the prism. These spiral patterns were very uniform in spacing and were ubiquitous across the entire specimen and in all bonded specimens exposed to these solvents. Of particular interest is the transition from the through-the-thickness "mud cracks", which tend to intersect other crack planes at right angles, to the spiral cracks which steer away from other cracks in order to produce the intricate spiral patterns.

The curious spiral patterns seen in the LaRC-TPI in the presence of a solvent have also been witnessed in other low molecular weight materials, even without solvent exposure. We believe that the spiral fracture patterns are energetically favored in situations where biaxial residual stresses are imposed on an adhesive by the adherends, or on a coating by the substrate. Spiral cracks are likely to occur under these loading conditions if the critical strain energy release rate is low enough. The decrease in critical strain energy release rate for environmental stress cracking susceptible materials exposed to solvents give rise to ubiquitous and profuse spiral cracking patterns. Although this process results in a tremendous amount of damage to the material, the damage observed in our specimens did not significantly reduce the Mode I toughness under static loading conditions. A further understanding of this process could give better insights into fracture behavior in general. A quantitative study of the spiral crack process is currently underway.

Acknowledgements

The principal author is grateful to the NASA/ASEE program for funding his visit at NASA-Langley during the summer of 1992 and to the National Science Foundation's High Performance Adhesives and Composites Science and Technology Center at Virginia Tech under contract DMR 9120004 for allowing completion of the work. The authors are also grateful to Don Progar for assistance with preparing samples, Carol Kalil for assisting with the SEM photomicrographs, Dennis Working for conducting the x-ray analysis, Brian Jensen for sharing information about spiral fracture patterns in polyarylene ether, and Paul Hergenrother for helpful comments.

References

1. R. P. Kambour, *J. Polym. Sci.: Macromolecular Review* **7**, 1973, 1.
2. E. J. Kramer, *Developments in Polymer Fracture*, E. H. Andrews, Ed. (Applied Science Publishers, London, 1979).
3. A. Lustiger, "Environmental Stress Cracking: the Phenomenon and its Utility", *in Failure of Plastics*, W. Brostow and R. D. Corneliussen, Eds. (Hanser Publishers, Munich, 1986).
4. H. Okamoto and Y. Ohde, "Environmental Stress Failure: an Irreversible Thermodynamics Approach", *in Failure of Plastics*, W. Brostow and R. D. Corneliussen, Eds. (Hanser Publishers, Munich, 1986).
5. S. P. Petrie, A. T. Dibenedetto, and J. Miltz, *Polym. Eng. Sci.* **20**, 385 (1980).
6. J. G. Williams, *Fracture Mechanics of Polymers* (Ellis Horwood Ltd., Sussex, 1984).
7. D. J. Progar, V. L. Bell, and T. L. St. Clair, "Polyimide Adhesives", U.S. Patent 4,065,345, (Dec. 1977).
8. A. K. St. Clair and T. L. St. Clair, *26th Nat. SAMPE Symp.* **26**, 165 (1981).
9. D. J. Progar, and T. L. St. Clair, *36th Int. SAMPE Symp. and Exhib.* **36**, 1755 (1991).
10. B. J. MacNulty, *J. Mater. Sci.* **6**, 1070 (1971).
11. M. Monev, S. Rahskov, and R. Kaischev, *Surface Technology* **17**, 315 (1982).
12. L. B. Freund and K. S. Kim, *Materials Research Society Symposium Proceedings* **226**, 291 (1991).
13. N. A. Fleck, J. W. Hutchinson, and Z. Suo, *Int. J. Solids and Structures* **27**, 1683 (1991).
14. N. Brown, "Mechanical Behavior in Gaseous Environments", in *Failure of Plastics*, W. Brostow and R. D. Corneliussen, Eds. (Hanser Publishers, Munich, 1986).
15. J. L. Beuth, *Int. J. Solids and Structures* **29**, 1657 (1992).
16. B. Blackman, J. P. Dear, A. J. Kinloch, and S. Osiyemi, *J. Mater. Sci. Letts.* **10**, 253–256 (1991).
17. J. P. Berry, *J. Polym. Sci.* (*Part A*) **2**, 4069 (1964).
18. J. W. Hutchinson and Z. Suo, *Advances in Applied Mechanics* **29**, 64–187 (1991)
19. K. L. Reifsnider and A. Highsmith, in *Materials, Experimentation, and Design in Fatigue*, F. Sherratt and J. Sturgeon, Eds. (Westbury House, Guilford, Surrey, 1981), pp. 246–260.
20. H. Horri and S. Nemat-Nasser, in *1982 Advances in Aerospace Structures and Materials* (American Society of Mechanical Engineers, Phoenix, 1982), p. 75.
21. S. Hu, J. S. Bark, J. A. Nairn, *Composites Science & Technology*, **47**, 321–329 (1993).
22. G. P. Fang, R. A. Schapery, and Y. Weitsman, *Eng. Fract. Mech.* **33**, 619 (1989).