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PHYSICAL AGING AND SOLVENT EFFECTS ON THE FRACTURE OF LaRC-TPI ADHESIVES

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When amorphous materials are quenched below their glass transition temperature, excess enthalpy is trapped in the glassy material because the viscosity is too great to allow the material to remain in volumetric equilibrium. Over time, this excess free volume is reduced as the material slowly approaches its equilibrium configuration. This process, known as physical aging, leads to substantial changes in the constitutive behavior of polymers, as has been widely discussed in the literature [1]. Less is known about the effects of this physical aging process on fracture and fatigue properties of aged materials [2]. The original goal of the summer was to investigate the effects of physical aging on the fracture and fatigue behavior of LaRC-TPI, a thermoplastic polyimide developed at NASA-Langley. Preliminary results are reported, although a lack of equipment availability prevented completion of this task. In the process of making specimens, the current LaRC-TPI, produced by Mitsui Toatsu, was observed to be extremely susceptible to environmental stress cracking [3]. A study of the unique failure patterns resulting from this degradation process in bonded joints was conducted and is also reported herein.

The first step in studying physical aging was to identify the aging kinetics for the LaRC-TPI material system. Specimens were subjected to short aging times, and loaded to measure the momentary creep compliance response, as shown in Fig. 1. This testing was conducted at VPI because of a lack of suitable equipment at NASA. These creep compliance curves were shifted in log time space to form the smooth master curve as indicated. Collecting data at several different temperatures allowed us to establish preliminary aging kinetics for this polymer, as illustrated in Fig. 2. These results seem quite consistent with those reported in the literature [1].

Fracture and fatigue testing of aged specimens was planned for neat polymer samples (notched 3-point bend, ASTM E-399) and bonded joints with titanium adherends (double cantilever beams (DCB)). Specimens were fabricated and subjected to aging times of 1, 10, 100, and 1000 hours at 350°F and 400°F. These temperatures were selected to simulate anticipated skin temperatures for the HSCT. Testing of these specimens was not completed, although plans are being made to complete the testing in the near future. Additional specimens continue to be aged in order to achieve 10,000 hour of aging time.

Although previous LaRC-TPI materials do not show susceptibility to environmental stress cracking, the Mitsui Toatsu versions of this material system have been end-capped at a carefully controlled molecular weight in order to optimize processing. Apparently the reduced molecular weight has resulted in a material which is highly susceptible to a variety of organic solvents including acetone, diglyme, methyl ethyl ketone, and toluene [3]. In the presence of these solvents, the molecular entanglements are no longer sufficient to maintain structural integrity. The combination of even

small stresses and any of these solvents results in profuse cracking. When the polymer film is constrained by an adherend, as when used as an adhesive or coating, very interesting cracking patterns result, as shown in Fig. 3. The polymer is under residual in-plane tensile stresses from the cool-down process. The solvent weakens the material and allow "mud cracking" to occur to relieve these stresses. Of particular interest are the curious spiral fracture patterns which spiral inward over time, as shown in Fig. 4. Although a recent reference to spiral cracks growing outward from an inclusion has been found [4], the phenomenon we have observed does not appear to have been reported in the literature. A number of interesting micrographs and video tapes of this failure process have been obtained.

Slightly bent films of the Mitsui Toatsu LaRC-TPI exposed to solvent immediately fracture, suggesting the tremendous drop in strength of these materials because of the environmental stress cracking phenomenon. If the solvent is allowed to dry, however, the strength returns, perhaps to original levels in the free films which have not sustained any damage. Since bonded joints exposed to even small amounts of solvent will crack profusely, we were interested to measure the effects of prior solvent exposure on bonded joint strength. DCB specimens were tested in accordance with ASTM D-3433 in order to obtain the propagation and arrest values of the material's strain energy release rates. The crack length was corrected using modified beam theory, and good correlation was observed with theoretical compliance, as shown in Fig. 5. Typical results for the critical strain energy release rates, as a function of crack length are illustrated in Fig. 6. A summary of the propagation (by 5% offset/maximum load method) and arrest values are given in Fig. 7 for several different exposures. It is seen that while the strength is significantly reduced when liquid solvent is present, there appears to be no substantial strength reduction in joints which have been exposed to solvents and then dried. This is somewhat astonishing in light of the severe damage which is present in the exposed specimens. A possible explanation is recognized by realizing that all of the observed damage cracks are nearly perpendicular to the bond plane. Since the DCB specimen is a mode I test, these cracks are not aligned with the mechanically induced fracture surfaces. The highly fragmented adhesive layer lacks continuity, so can no longer be under plane strain loading conditions. The relieved constraint and the crack stopping ability of the individual adhesive prisms seems to result in no substantial strength reduction if all of the solvent has been removed. The long term durability of these damaged joints would be of great concern, however. Of particular interest would be to determine if solvent induced cracks in these materials can be used as an accelerated characterization technique to predict damage states which result over time without solvents.

Finally, a special loading technique was developed in order to assist in pre-cracking notched 3 point bend fracture specimens [5]. By making use of the concept of the kern for a cross-section, an eccentric compressive load is applied to the specimen to allow a crack to be tapped into the specimen without severing the sample. By making the load eccentric, the large compressive stresses at the notch root are eliminated, and a more favorable stress field is induced to permit pre-cracking of the specimens in order to utilize them as fracture specimens.

1) L C E Struik, *Physical Aging in Amorphous Polymers and Other Materials*, Elsevier, 1978.

3) J P Berry, *Journal of Polymer Science: Part A*, 2 (2), 1964, p 4069.

4) L B Freund and K S Kim, "Spiral Cracking around a Strained Cylindrical Inclusion in a Brittle Material and Implications for VIAS in Integrated Circuits", *Materials Research Journal*, 1991.

5) J G Williams and M J Cawood, "European Group on Fracture: K_c and G_c Methods for Polymers", *Polymer Testing*, 9, 1990, p15-26.

2) G Allen, D C W Morely and T Williams, "The Impact Strength of Polycarbonate", *Journal of Material Science*, 8, 1973, 1449-1452.

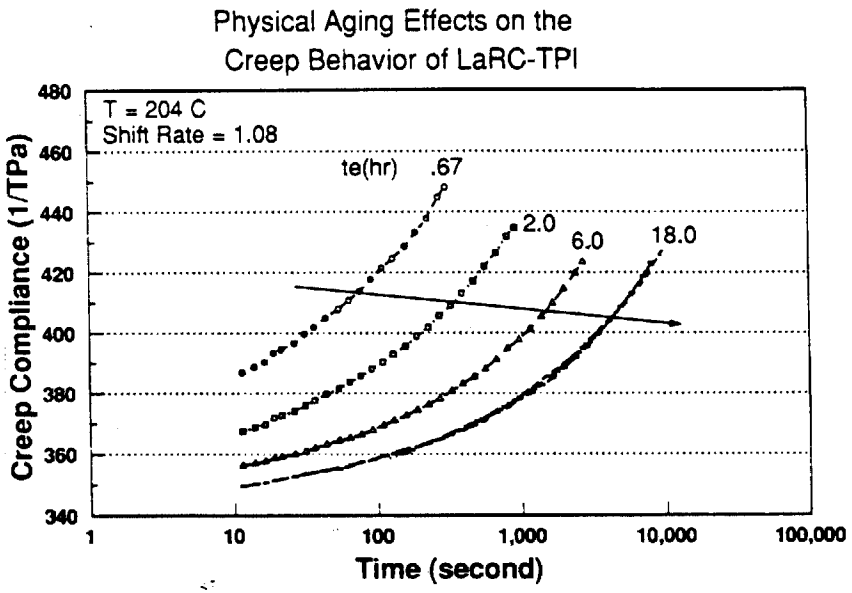

Figure 1. The effect of aging time on the creep compliance of LaRC-TPI at 204°C.

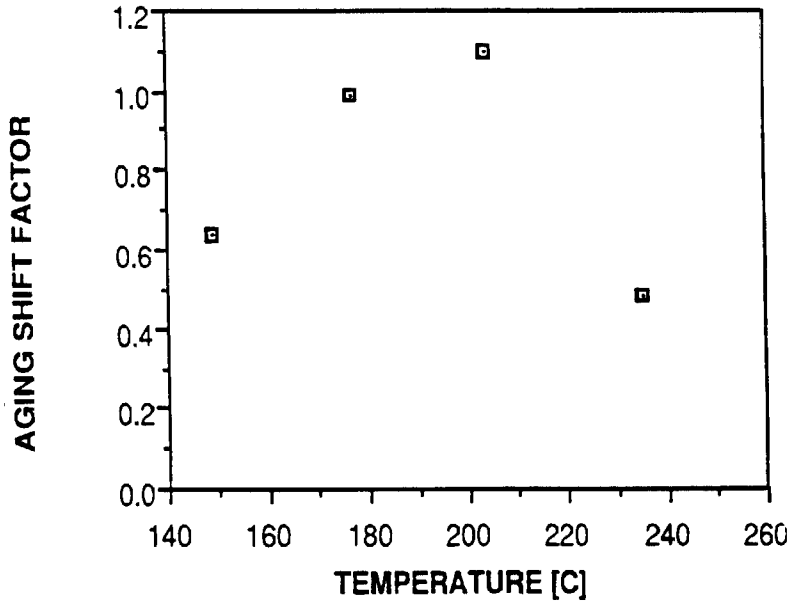

Figure 2. Preliminary physical aging kinetics for LaRC-TPI at several temperatures.

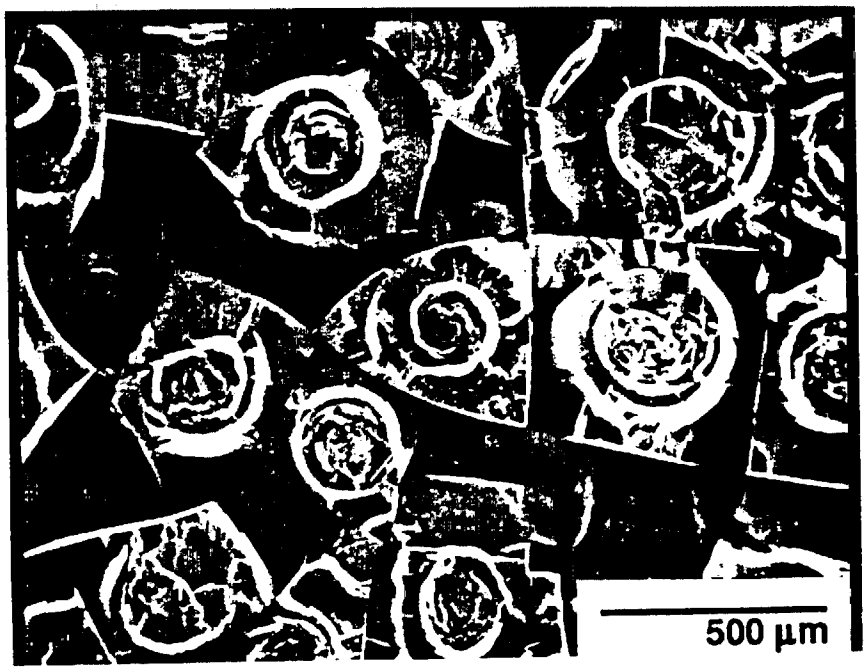

Figure 3. LaRC-TPI adhesive exposed to diglyme, showing fragmented adhesive layer.

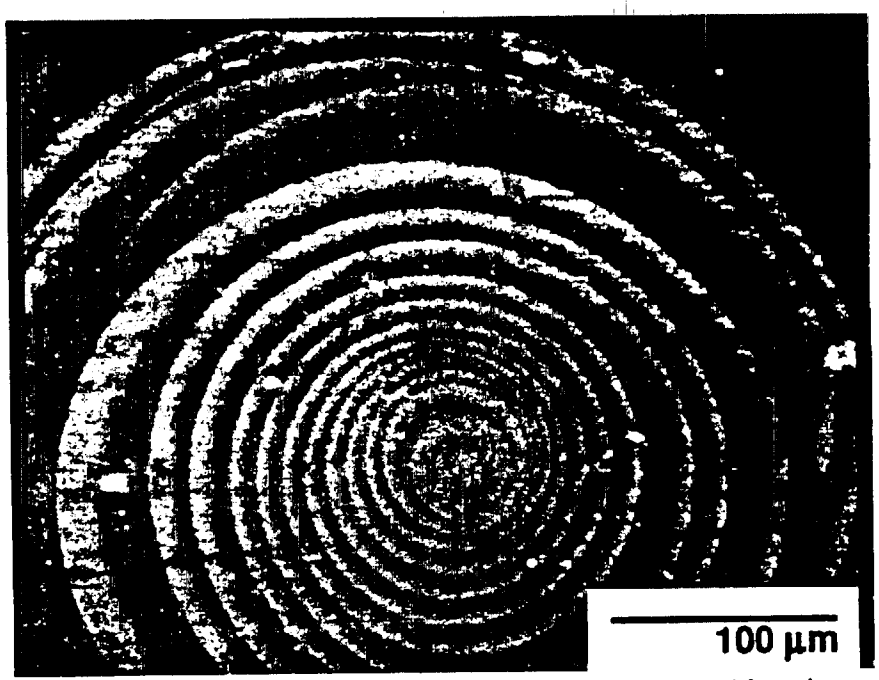

Figure 4a. Subsurface spiral cracks on a LaRC-TPI adhesive layer removed from glass.

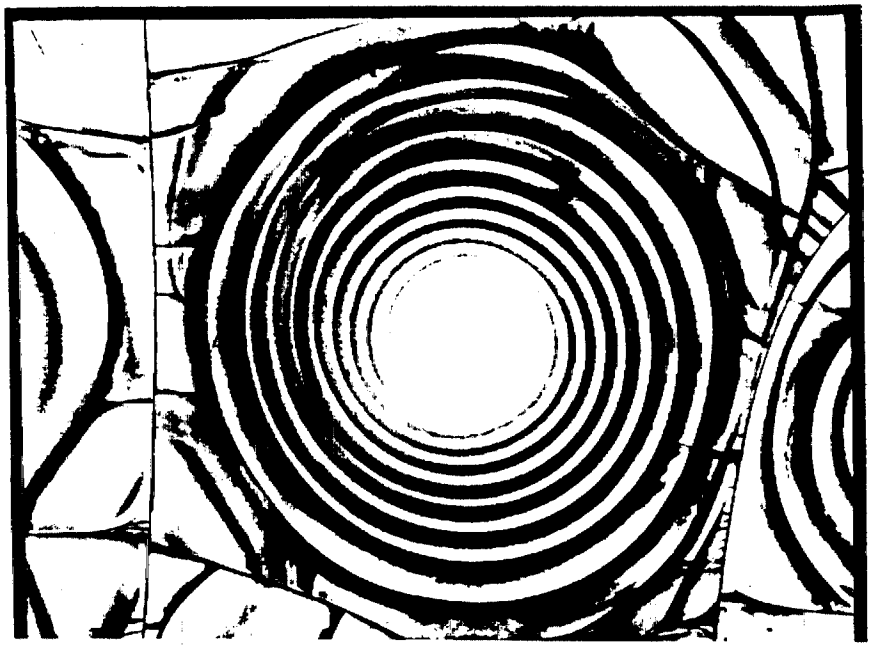

Figure 4b. Spiral crack in a LaRC-TPI adhesive bonded between glass slides.

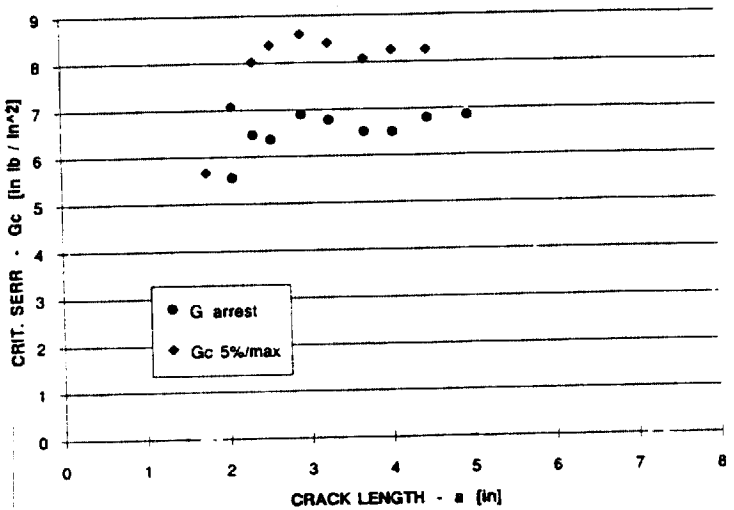

Figure 6. Typical strain energy release rates for a titanium / LaRC-TPI DCB specimen.

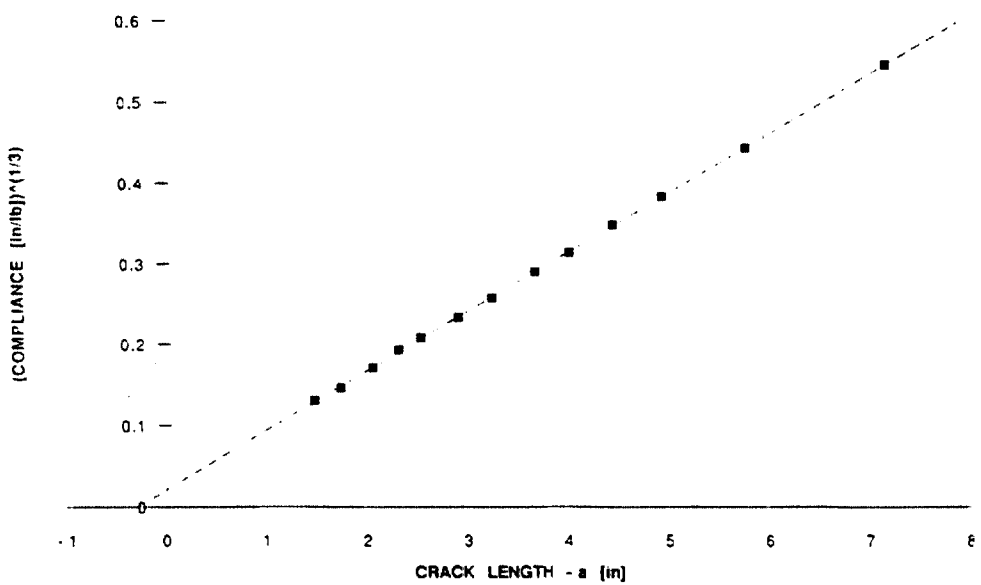

Figure 5. Effective crack length determination by modified beam theory.

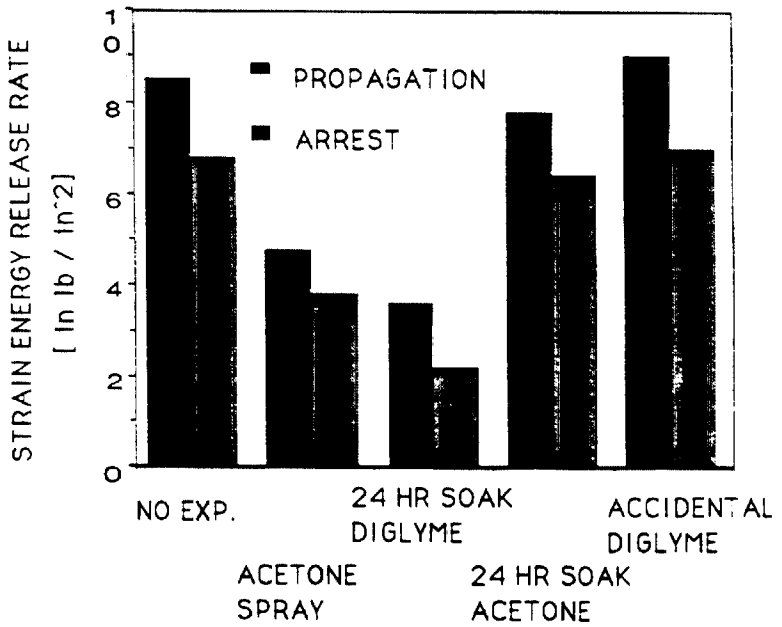

Figure 7. The effect of exposure on the fracture resistance of Ti / TPI DCB specimens.