Chapter 3 Experimental

3.1 Materials

3.1.1 R-410 Adhesive Laminate

The adhesive laminate utilized in this study is supplied commercially by Rogers Corp. as R/Flex 410. It consists of a *lightly crosslinked amorphous polyamide* which is partially-cured ("B-staged") into sheets of various thicknesses ranging from 0.5mils to 10mils, prior to arrival from Rogers Corp. The adhesive is based upon poly-(ε-caprolactam) cured with low levels of Epon 828™ as demonstrated by a SS-NMR scan given in Appendix I. The T_g of the final-cured material measured by DSC was found to be approximately 32°C (Figure 3-1) using a *Perkin-Elmer* DSC-2 at a heating rate of 10°C/min. This product is typically used in flexible laminate circuit applications. Typical properties of this material are a tensile strength of 34,000 psi, elongation to break of 65%, dielectric constant of 3.2 (1Mhz), and an excellent flex life.

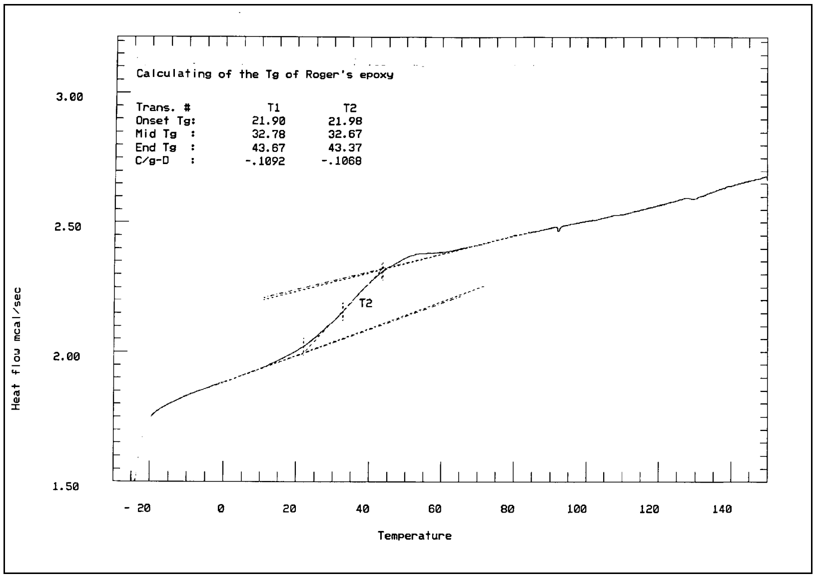

Figure 3-1. DSC Thermogram of R/flex 410 Adhesive

3.1.2 Penetrants

The low molecular weight species utilized in this study consists of linear architectures of two chemical types of penetrants. The first chemical-type is a nonpolar, aliphatic material made up of the n-alkane homologous series from hexane (C6) to heptadecane (C17). These materials are 99.9+% pure and are purchased from Aldrich. Some of their physical properties are given in Table 3-1.

The second chemical-type consists of a homologous series of small molecular weight linear esters ranging from methyl acetate (C3) to isopropyl myristate (C17). This series given in Table 3-2 covers the same molecular weight range as the n-alkanes, but now with the addition of an ester functionality. These materials are 99.9+% pure and are purchased from Aldrich. Other physical properties are given in Table 3-2.

A special note should be made of one of the ester species in Table 3-2. Isodecyl pelargonate (Emery 2911) is a synthetic lubricant/plasticizer supplied by Emery Chemicals (99.9+%). It is formed from the esterification of isodecyl alcohol and pelargonic acid and has the empirical structure: $(CH_3)_2CH(CH_2)_6OCO(CH_2)_6CH_3$.

Table 3-1. Alkane Penetrants

PENETRANT	Solubility Parameter	Molecular Weight	Molar Volume
	($MPa^{0.5}$)	(gram/mole)	(cm^3/mole)
Hexane	14.8	86.17	130.50
Heptane	15.2	100.20	147.40
Nonane	15.6	128.25	179.70
Decane	15.8	142.28	195.95
Undecane	16.0	156.30	212.47
Tridecane	16.4	184.35	244.92
Pentadecane	16.8	212.41	277.69
Hexadecane	17.0	226.43	294.07
Heptadecane	17.2	240.46	309.50

Table 3-2. Ester Penetrants

PENETRANT	Solubility Parameter	Molecular Weight	Molar Volume
	($MPa^{0.5}$)	(gram/mole)	(cm^3/mole)
Methyl Acetate	19.4	74.07	79.86
Ethyl Propionate	17.9	102.12	115.45
Propyl Butyrate	17.2	130.19	149.97
Ethyl Heptanoate	17.0	158.24	183.09
Ethyl Nonanoate	16.9	186.30	216.24
Ethyl Undecanoate*	16.7	214.35	249.53
Ethyl Myristate*	16.6	256.43	299.22
Isodecyl Pelargonate*	16.4	270.46	314.56
Isopropyl Myristate*	16.5	270.46	318.19

* Solubility parameter calculated using Hansen's method

3.2 Adhesive Preparation

R/flex 410 was supplied as a "B-staged" sheet and was fully cured through the following treatment using a *Fisher Scientific Isotemp Forced Draft Programmable Oven (Model 838F)*:

1) Heated from 25°C to 100°C at 5°C/min
2) Held isothermally at 100°C for 1 hour
3) Heated from 100°C to 150°C at 5°C/min
4) Held isothermally at 150°C for 3 hours

Samples were removed promptly from the oven and allowed to cool to room temperature. The samples were stored in a dessicator before and after curing. Before each experiment, the samples were held at 85°C for 1 hour to erase any thermal history that may have developed. This temperature was selected due to the fact that it is also the highest test temperature utilized for experiments. Completeness of cure was monitored via *differential scanning calorimetry* and *dielectric thermal analysis*.

3.3 FTIR-ATR Spectroscopy

Analysis of adhesive films was done using *Fourier transform analysis* on a *Nicolet 800 FTIR* system. A globular IR source and a Germanium on KBr substrate beamsplitter were used to investigate the Mid-IR range (4000 cm^{-1} to 400 cm^{-1}). The resolution used for the IR analysis was $4cm^{-1}$. Mirror velocity, aperture settings, and signal gain were set to 20, 300, and 2, respectively. A TGS (tellurium-germanium-selenide) room-temperature IR detector was used in the setup. Every absorbance spectrum was created by averaging a total of 64 scans.

A *SpectraTech horizontal attenuated total reflectance* (H-ATR) attachment was utilized in conjunction with the Nicolet 800 FTIR to collect IR absorbance spectra of the R/flex 410 adhesive as a function of penetrant exposure. A ZnSe ATR flatplate with an angle of incidence set to 45^o, was used to study the laminate films.

ATR adhesive samples were prepared using the same curing cycle described above. The R/flex 410 adhesive films of 0.5 mil and 1.5 mil thicknesses were cured directly onto the ZnSe crystals with only a slight pressure of approximately 10 psi to insure good contact. Films were later removed using a soaking procedure with acetone and carefully peeled off to prevent scratching of the crystal surface.

Kinetic data have been collected using a setup that will be described in detail later. They were analyzed using programs written specifically for these diffusion experiments on the Nicolet 800 FTIR system. These programs are listed in Appendix A.

The analysis was carried out in the temperature range from 25^{o}C to 85^{o}C. Temperature control was maintained using an *Omega CN900A temperature controller* in conjunction with a 120V *variable autotransformer* and a temperature-controlled oven from a *Hewlett-Packard 5890 Series II Gas Chromatograph.*

3.4 Dynamic Solvent Mass Uptake

The dynamic solvent uptake measurements consisted of placing a piece of the adhesive film into a solvent, and periodically removing the specimen from the solvent and weighing it using a *Mettler AE200 balance* (+/- 0.0003 g). The samples were placed in scintillation vials (total volume of 20 ml) with the selected solvent and stored isothermally in a *Hewlett-Packard 5890 Series II G.C. oven* during the entire time of the experiment. Before each weight measurement, the surface of the sample was carefully wiped to eliminate any excess solvent. When the measurements were completed, the sample was promptly put back into its scintillation vial. The entire weighing process took place in about 15-20 seconds.

Dimensions of the samples used are rectangular geometries of approximately 1.0 x 0.5 x 0.020 inches (2.54 x 1.27 x 0.05 cm). Thicknesses of the samples were measured at intervals throughout the solvent uptake experiments using a *Mitutoyo micrometer* (+/- 0.0001 in.) to monitor dimension changes as a function of exposure time. The entire thickness measurement process took place in about 10 seconds.

3.5 Dynamic Mechanical Analysis

All dynamic mechanical analysis experiments have been performed using a *Polymer Laboratories Mark II Instrument* in a *shear* geometry. A schematic of the actual "sandwich" testing geometry is shown in Figure 3-2 and Figure 3-3. The shear studs are circular in geometry and approximately 13 mm in diameter. The center shear plate connected to the drive shaft is "T-shaped" and oscillates forwards and backwards a total of 40 microns peak-to-peak resulting in approximately 1.262 % strain in the shear samples. Each test required two circular samples each about 0.56 mm thick and 7 mm in diameter. These samples were cut out from "B-staged" sheets using a die with a 7 mm inside diameter, prior to curing and testing.

Dynamic experiments were performed in a step-isothermal mode over a temperature range of –55°C to 280°C with 3°C step intervals and a 0.5 min isothermal time. At each isothermal step, a series of 8 frequencies (0.1, 0.3, 1, 3, 10, 30, 50, and 100 Hz) were tested using the shear geometry. Locking screw clamps and adjustment screws were tightened with torque wrench settings of 30 and 25 cN*m, respectively.

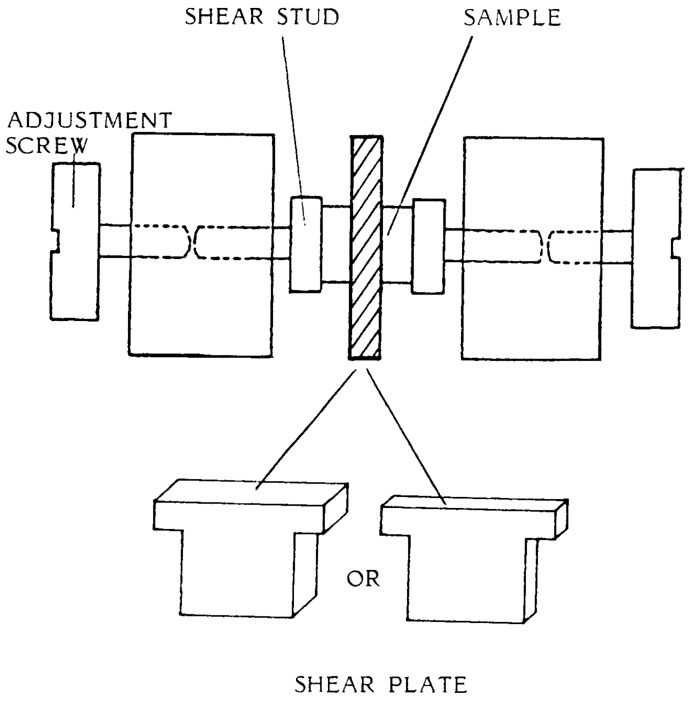

Figure 3-2. Schematic of shear “sandwich” geometry

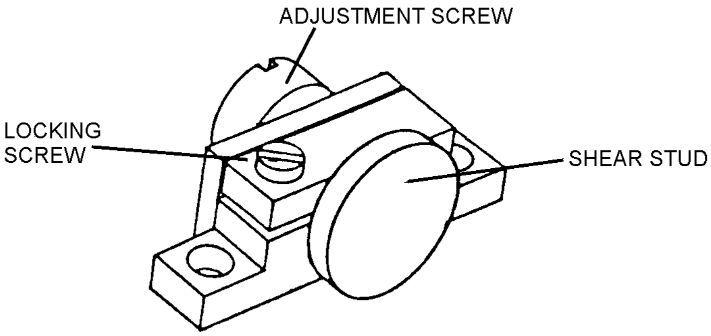

Figure 3-3. Schematic of shear stud

3.6 Density Evaluation

Polymer density was determined at room temperature using a *Micromeritics Accupyc 1330 gas displacement pycnometer* (± 0.005 g/cm^3). A 1 cm^3 sample cup was utilized with a helium purge. The sample enclosure was purged 5 times during which 5 readings are averaged to yield an experimental value for the volume of the polymer sample. The mass was previously weighed on a *Denver Instruments Microbalance* (±0.0001 g). A total of 5 different experimental runs were completed to yield an average polymer density of 1.121 (std.dev. 0.001) g/cm^3 at 23^{o}C. Details of the evaluation of polymer density via pycnometry are given in Appendix B.

Polymer density as a function of temperature was evaluated optically using an *Olympus BH-2 optical microscope* in conjunction with a *Linkam THM 600 hot stage*. Polymer samples were placed onto a quartz disc and inserted into the temperature-controlled environment. Test temperatures ranged from 20°C to 170°C in 5-10°C increments and allowed to equilibrate for at least 10 minutes at each isothermal step. The experiment was repeated during the cooling process to insure reversibility of the process. Dimensional changes in the x and y directions were calculated using an *Olympus CUE Micro300 video caliper* (± 0.5 µm). This experiment was repeated twice to evaluate linear expansion coefficients for both the x and y axes. Assuming isotropic behavior, the linear expansion was converted into a volume expansion for each axes and temperature. These values were then averaged to yield a volume expansion term for each temperature of interest. Evaluation of these terms is given in Appendix C.

3.7 Stress-Strain Measurements

Mechanical evaluation of stress-strain behavior was done using an *Instron 5500R Materials Tester* in conjunction with an extensiometer. The load cell has a 200 lb. maximum load and samples were held in place using two pneumatic clamps. Sample were cut out prior to curing from a 20mil (~0.50mm) thick sheet of “B-staged” adhesive using an ASTM Type IV D638 die whose gauge length and width were 10 in. and 0.25 in., respectively. Test temperatures were maintained using an *Instron model 3116 furnace* attachment.

Evaluation of crosslink density of the adhesive film was done using five test specimens. The test temperature was 150°C, and the film was held isothermally for approximately 15 minutes prior to testing. A crosshead speed of 10 mm/min was used for all experiments and samples were elongated to 40% elongation. Stress relaxation was allowed to occur for approximately 25 minutes until an equilibrium stress was obtained. Equilibrium engineering stress (σ_o) and strain (ε) values for each of the specimen were utilized to calculate the molecular weight between crosslinks (M_c) and crosslink density (N_v) based upon theories of rubber elasticity. Average values obtained for these parameters were M_c = 6887 g/mole of network chains (std.dev. 739) and N_v = $9.17e^{19}$ crosslinks/cm^3 (std.dev. $9.89e^{18}$). The values and details on the calculation of these parameters are given in Chapter 5.