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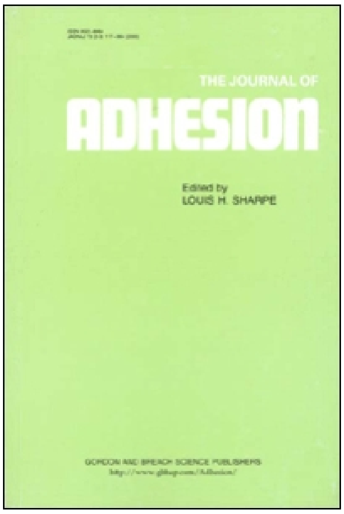

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The Influence of Curing Agent Content on the Mechanical and Adhesive Properties of Dicyandiamide Cured Epoxy Systems

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The Influence of Curing Agent Content on the Mechanical and Adhesive Properties of Dicyandiamide Cured Epoxy Systems*

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Mechanical and adhesive properties were evaluated for an elastomer-modified model epoxy system cured with varying amounts of dicyandiamide (Dicy). The modulus and bulk fracture toughness values were found to be independent of Dicy content, whereas the adhesive performance was shown to be greatly influenced. For increases in Dicy content, single lap shear (SLS) failure values increased, while quasi-static double cantilever beam (DCB) performance was decreased. These adhesion test results are discussed in a comparative fashion. Preliminary x-ray photoelectron spectroscopy (XPS) surface evaluations are presented to discuss the drastic changes in DCB performance. It is postulated that in these model adhesive systems the Dicy variations produce significant chemical changes only in the epoxy/steel interphase region.

KEY WORDS Epoxy; dicyandiamide; steel; adhesion; DCB; SLS; interphase; XPS.

INTRODUCTION

Dicyandiamide (Dicy), a widely-used, latent curing agent in heat-cured epoxy adhesives, has been utilized since the 1950's when epoxy resins were first commercially introduced.[1,2] Since that time, a great deal of effort has been exerted towards deciphering the reaction mechanisms. Unfortunately, this complex scheme still remains to be established and, to complicate this issue, Dicy is often used in conjunction with a urea-based accelerator. These reactions have gone essentially unanalyzed.[1,3–9]

Much effort has been focused, as well, on determining the effects of reaction conditions on the bulk mechanical properties of Dicy/epoxy systems.[6,10–13] It is

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[*] One of a Collection of papers honoring James P. Wightman, who received the 13th Adhesive and Sealant Council Award at the ASC's 1993 Fall Convention in St. Louis, Missouri, USA, in October 1993.

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understood that even though these systems are widely used in industry, they are complex and not well understood. Small changes in the reaction conditions can result in drastic changes in the mechanical performance. In a recent study by Ennis and coworkers, it was shown that even an open *vs.* closed curing configuration could alter the mechanism of cure, and thus the properties of the cured material, due to the production of volatile gaseous byproducts by the resin.[9]

Unfortunately, due to the complex nature of this system, little work has been focused directly on determining how these small changes influence adhesive performance in bonded systems. One area of particular interest deals with what types of changes take place at an adhesive/substrate interphase *vs.* those in the bulk of the material. In this study, that aspect of adhesive performance for Dicy/epoxy systems is evaluated. The interphase has long intrigued Professor James P. Wightman and his students, and their research has advanced our knowledge in this field.[14–16] It seems appropriate to dedicate this article to him.

Bulk mechanical measurements were conducted to provide background information for comparison with adhesive tests (to allow subtraction of bulk mechanical property changes from those in bonded specimens). Adhesive tests were carried out utilizing both fracture and traditional test geometries, the DCB and SLS tests, respectively. Preliminary XPS failure surface studies were conducted on the failed fracture specimens, as well, to demonstrate that chemical changes, responsible for the changes in bonded joint performance, occur at the epoxy/steel interphase region.

EXPERIMENTAL

Adhesive Components and Preparation

Three model epoxy systems with various amounts of curing agent were used as the adhesives for this study. The model epoxy systems were composed of a liquid bisphenol A-type resin, a curing agent, a curing accelerator, a filler, and an epoxy-terminated toughener. The compositions are shown in Table I. The epoxy resin used was D.E.R. 331, a "standard", low molecular weight, liquid bisphenol A-type resin available from The Dow Chemical Company. The curing agent used was dicyandiamide. It is a latent, solid curing agent, which, when milled into liquid epoxy resins, provides one-package

TABLE I
Model Epoxy formulations (Components in Wt. %)

Formulaion	A	B	C
D.E.R. 331	69.1	69.1	69.1
DICY	2.5	4.1	6.2
PDMU	1.6	1.6	1.6
M-5 SILICA	4.9	4.9	4.9
KELPOXY G272	20.3	20.3	20.3
Amine Hydrogen/ Epoxy Group Ratio	0.30	0.47	0.70

stability for up to six months at ambient temperatures. 3-phenyl-1,1 dimethyl urea, or PDMU, was used as an accelerator to reduce cure times. The use of 2-3 parts of PDMU per hundred of resin reduces the curing temperatures of such systems from 177°C to about 121°C. A filler was used to suspend the Dicy evenly throughout the adhesive, thus producing a more homogeneous final product. The filler used was M-5 SILICA which is a slightly acidic, hydrophilic fumed silica produced by the Cabot Corporation. A toughener was added, Kelpoxy G272-100, a concentrate of an epoxy-terminated elastomeric copolymer designed by Reichhold Chemicals as an additive or modifier to toughen epoxies, epoxy novolacs, and PVC plastisols. Epoxy resin blends containing Kelpoxy exhibit elastomer particles of 0.01–10 micron diameter which impede the propagation of cracks. The epoxide equivalent weight of Kelpoxy is approximately 340 g/eq.

The epoxy resins were prepared as follows: The D.E.R. 331, Dicy and PDMU were placed in a 1-gallon Ross mixing pot. The mixing speed was set at approximately 18 r.p.m. until the Dicy and PDMU were mixed into the resin. The speed was then increased to about 72 r.p.m. and a vacuum was employed to 28 inches Hg. After 15 minutes, the fumed silica was added. The mixer was started at a low speed, and increased to a setting of 100 r.p.m. after the silica was "wet". With the vacuum on, mixing was continued for 15 minutes. The Kelpoxy was then added and mixed with the resin for 5 minutes or until all air bubbles were removed.

Tensile Tests

Tensile specimens were used to determine the modulus of the bulk polymers. ASTM D-638 type IV test specimens were cast in silicone rubber molds, sandwiched between steel plates to mimic the cure of a bonded system, and cured at 170°C for 90 minutes. To remove small defects and produce more uniform samples, the samples were hand-polished with 600-grit sandpaper and stored in a desiccator prior to testing. A Lab VIEW program was written to conduct the testing in accordance with ASTM D 638 on a screw-driven Instron 4505 test frame. The testing temperature was 22°C, and the relative humidity was approximately 20%. A 1/2-inch (1.27 cm) extensometer and a constant crosshead displacement rate of 1 mm/min was used. The Young's modulus was determined from the slope of the initial linear portion of the stress-strain curves.

Single Edge Notched Bend Tests

Single-edge-notch bend (SENB) specimens were used to determine the plane-strain fracture toughness, K_{Ic}, of the bulk polymers. 6.2 mm × 7.4 mm × 51 mm specimens were cut from a plate of the polymer which had been cast in an aluminum mold. The mold was sprayed with a release agent prior to use. These samples were also cured at 170°C for 90 minutes. The specimens were pre-cracked with a razor blade to obtain sharp starter cracks. A LabVIEW program was written to conduct the testing on a screw-driven Instron 4505 test frame. A constant crosshead displacement rate of 1 mm/min was used for these tests, and the K_{Ic} calculations were carried out in accordance with ASTM D5045.

Single Lap Shear Tests

In order to be able to make comparisons between fracture mechanics results and test geometries which are typically used in industry, single lap shear (SLS) joints were also prepared and axially tested according to ASTM D1002-72. The single lap shear coupons were prepared using 2.54 × 25.4 × 101.6 mm 1010 cold-rolled steel coupons, with an acetone wipe surface pretreatment, and 0.254 mm glass beads as spacers to control the bond thickness. 0.1 wt.% glass beads were blended with the epoxy resin in a plastic bag, and the resin was applied over a 322.58 mm^2 area at one end of each coupon. The coupons were then pushed together and lightly clamped, and the excess adhesive wiped from the sample. Curing was carried out in an oven for 90 minutes at 170°C. Testing was conducted on an MTS model 810 servo-hydraulic testing system at a constant displacement rate of 12.7 mm/minute and tensile strengths were taken from computer generated data files.

DCB Specimen Fabrication Procedure

Double cantilever beam specimens were made by bonding 6.4 mm × 25.4 mm × 184 mm coupons of 1018 steel. After receiving an acetone wipe, Teflon tabs and appropriate-sized wire strips (to control bond thickness) were taped onto one steel adherend. The Teflon tabs also helped control the bond thickness of the panels and, after being removed once the cure process was complete, providing a "void" in the specimens to aid in developing starter cracks. Heat resistant tape was used to hold the Teflon in place, and it also helped to produce the sharp starter cracks. After the wire and Teflon were in place, the adhesive was poured onto the surface of the steel and smoothed to the desired thickness (0.80 mm) with a clean spatula. Finally, the second adherend was placed on top of the steel plate containing the Teflon, wire, and adhesive. The resulting specimen was then placed in a preheated, programmable hot press and maintained at a temperature of 170°C and a pressure of 33 kPa (4.8 psi) for a period of 90 minutes. After curing, the samples were removed from the press while still hot and allowed to cool slowly to room temperature. The resulting bonded specimens were then drilled, tapped, and polished as necessary to conduct a given testing procedure. A schematic of the DCB specimen, with the deformed geometry inset, is shown in Figure 1.

Between the surface cleansing process, an acetone wipe, and the panel bonding process (less than one hour), no special storage of the prepared panels was used. Also, there was no apparent surface corrosion of the steel panels prior to the cleaning process and oil was not visually observed on the panel surfaces.

As with all fracture tests, a sharp starter crack is essential to obtain valid and repeatable results. Therefore, sharp precracks were produced by driving a wedge into the specimens. A clamp was placed approximately 15 mm from the end of the adhesive layer in order to prevent the starter crack from propagating too far down the specimen when the wedge was introduced.

(Quasi-)Static DCB Testing Procedure

Static DCB tests were used to determine the initiation (G_c) and arrest (G_a) strain energy release rates in the bonded joints as a function of curing agent content. The initiation

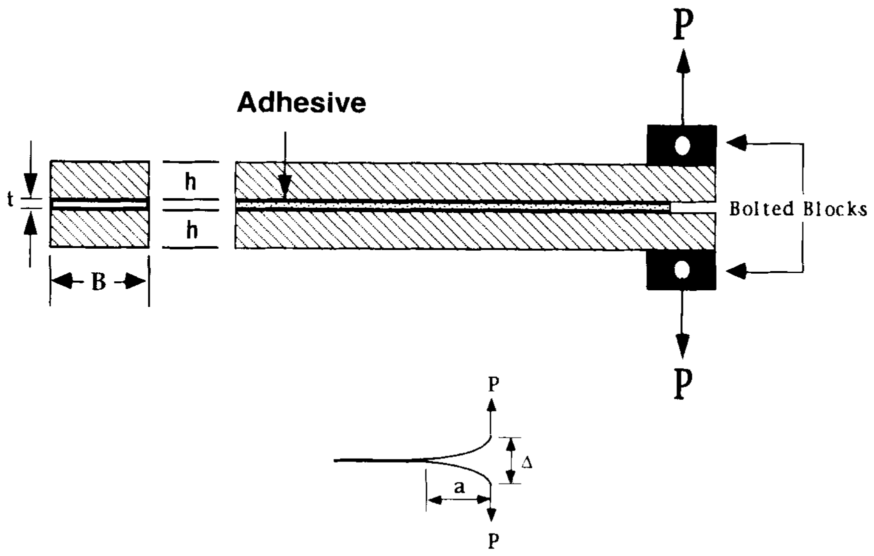

FIGURE 1 Schematic of the DCB specimen (deformed specimen inset).

(or critical) strain energy release rate is the loading level at which crack growth begins while the arrest strain energy release rate defines the loading level at which crack growth stops or arrests itself. These adhesive systems also displayed a rate-dependent interfacial failure process which allowed for a maximum strain energy release rate loading ($G_{\max}$) to be achieved that was sometimes much higher than either the initiation or arrest loading levels. The following testing procedure has been described elsewhere, but will be summarized below to facilitate understanding of the process.[17,18]

All static DCB tests were carried out at a constant crosshead displacement rate of 1 mm/min on a screw-driven Instron 4505 testing frame which was controlled through its GPIB interface using LabVIEW software. After bolting end-blocks to the DCB specimens, they were attached to the load frame using self-aligning pin connections and the crosshead was set in motion. As the specimen was loaded using displacement control, a microscope and either the load-deflection or the load-time curve (which appear as real-time plots on the LabVIEW program used to control the tests) were used to detect critical events taking place in the specimen. For example, when either curve deviated from linearity upon loading, the crack had begun to grow and the critical fracture energy, G_c, had been reached. This observation was confirmed visually using the movable microscope. Now, due to the rate-dependent interfacial failure of these adhesive systems, the loading value continued to increase. When the load reached a maximum and began to decrease rapidly, the specimen had achieved a maximum loading level for this loading cycle, $G_{\max}$. Note that the existence of a maximum in G is not guaranteed and does not necessarily correspond to a maximum in P. However, it has been confirmed that the two occur almost simultaneously for these particular adhesive systems with $G_{\max}$ lagging $P_{\max}$ slightly (less than 3 seconds).[18]

Shortly after $P_{\max}$ had been detected (about 5 sec), the crosshead motion was stopped to allow the crack growth to continue "naturally" until it reached near-equilibrium conditions. The term near-equilibrium is used because the crack was not always allowed to stop completely. The criterion used to establish a reasonable arrest loading level was that the load decreased by less than 1 N/min and no crack growth was observable. This component of the testing procedure was necessary to speed up the static DCB tests. If a test was allowed to continue until the loading level was at complete equilibrium, it may have taken an hour or more for each loading cycle, and this was not feasible. Therefore, this procedure was used to approximate the arrest fracture energy, G_a. Error induced by this testing strategy was found to be negligible. Once G_a was determined, the specimen was unloaded to make sure plastic deformation of the adherends had not occurred. If plastic deformation had occurred, the P-Δ curves would not have returned to the origin, but instead would have intersected the deflection-axis to the right of the origin. Finally, this load-hold-unload procedure was repeated until the specimen was fully fractured.

During the testing process described above, microscopically determined crack length values were periodically attached to the load and deflection data sets when there was sufficient confidence in the readings. The data collected were later used to compute the relevant strain energy release rates. The equations and details of the calculations are outlined elsewhere.[17,18]

XPS Failure Surface Evaluations (of DCB Specimens)

X-ray photoelectron spectroscopy (XPS) studies were conducted to quantify the failure surfaces of the DCB specimens. Since the specimens *appeared* to fail in an interfacial manner, with the exception of a small area at the end of each specimen, the two arms of the broken DCB specimens will be denoted as the "metal" and "adhesive" sides corresponding to their appearances. A sample of the 1018 steel was also cut from a pretreated plate, prior to bonding, to provide background information. This will be denoted as "steel".

The samples were analyzed using a PHI Perkin-Elmer 5400 XPS. Initial scans were carried out over a range of 0.0 to 1100.0 ev, at a take-off angle of 45°, using a magnesium anode as the x-ray source. After obtaining the initial spectra, narrow scans in the carbon 1s, oxygen 1s, nitrogen 1s, silicon 2p, and iron 2p energy regions, were conducted. Atomic percent compositions were calculated using peak areas and experimentally-determined sensitivity factors.

RESULTS

Mechanical Tests

From the tensile and bulk fracture tests, it was demonstrated that for these cured model epoxy systems, changes in Dicy content over a range of 2.5 to 6.2 percent by weight did not result in significant changes in the bulk material properties. The modulus values,

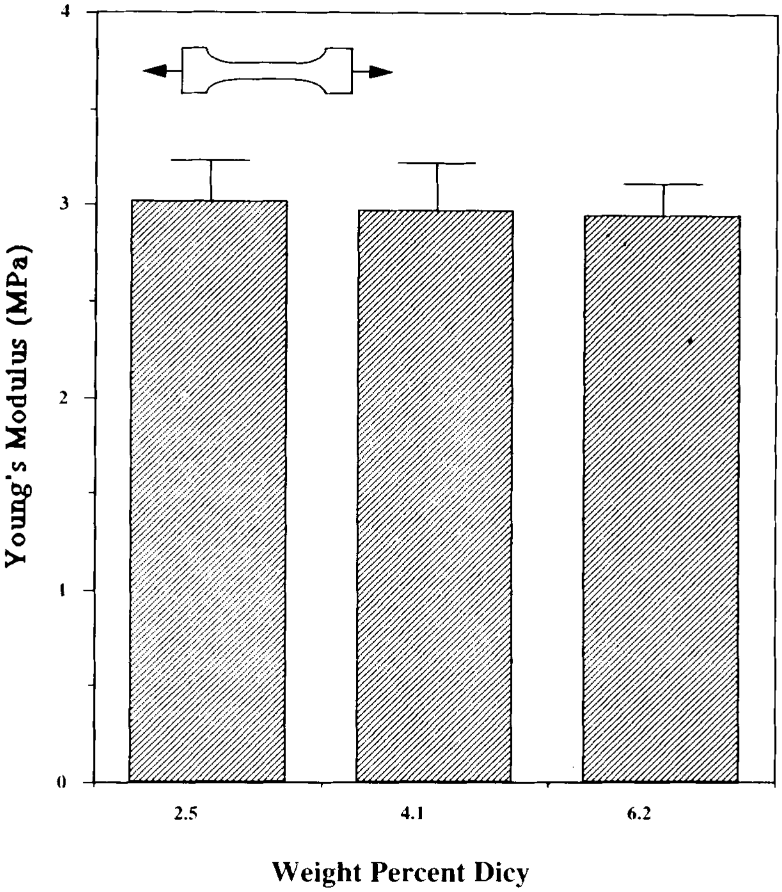

FIGURE 2 Young's modulus as a function of Dicy content.

shown in Figure 2, along with the K_{Ic} values shown in Figure 3, were not statistically different from one formulation to another.

The adhesive tests, however, showed an appreciable dependence on Dicy content. As the Dicy content was increased from 2.5 to 6.2 percent by weight, the SLS strength increased from 4490 ± 404 psi to 5789 ± 168 psi (see Figure 4). The $G_{Ic,Ia}$ values from the DCB tests, given in Figure 5, showed an even more pronounced change, decreasing from 749 ± 66 J/m^2 to 198 ± 45 J/m^2.

In light of the bulk *vs.* adhesive test results, the influence of Dicy content was concluded to be most highly pronounced in the epoxy/steel interphase region. Were chemical changes significant in the bulk, the modulus and K_{Ic} values would have shown some variability. The fact that the differences are only apparent in the bonded specimens shows these effects are confined to the interphase (since these systems fail at the interphase as shown by XPS).

It was found that there were differences in the trends demonstrated by the SLS and DCB tests. Since both methods give reproducible results with a low percentage of error,

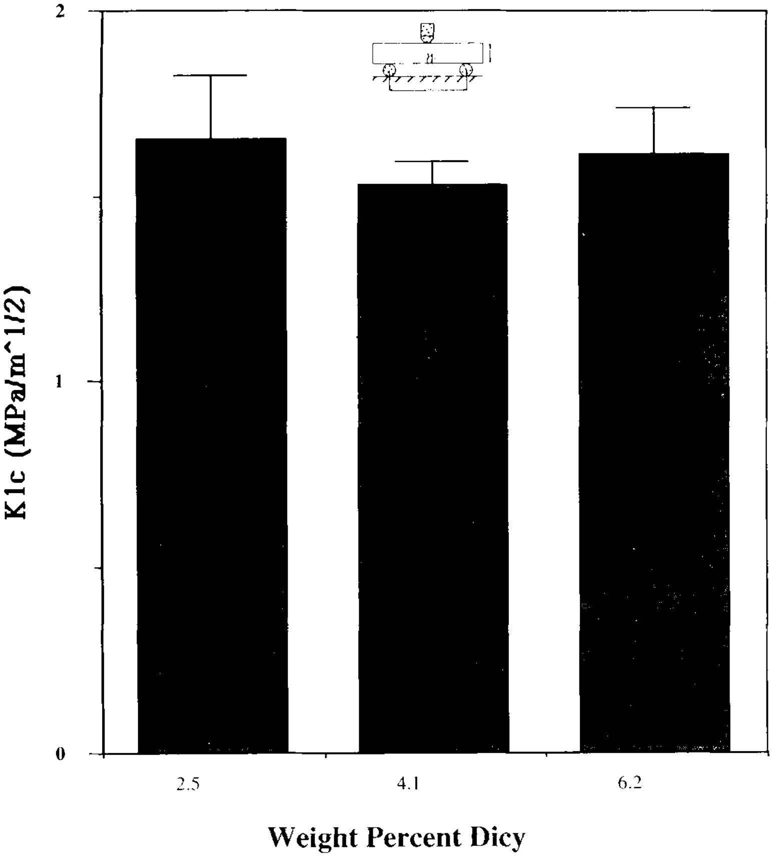

FIGURE 3 Critical fracture toughness values for the bulk adhesives, K_{Ic}.

they are not believed to be incorrect. In fact, if one considers what each test measures, the results can be explained. The SLS test, although considered a shear test, actually measures failure due to transverse tensile stresses.[19] Thus, if the ASTM analysis procedure is used, the stronger adhesives *appear* to be weaker.[20,21] This was indeed the case for our SLS tests, and therefore it can be inferred that the SLS and DCB results are within reason, but measure different mechanistic features of failure.

XPS Surface Studies

The surface analysis results are generally consistent with the visual observation that interfacial failure occurred in the region of the interface for all of the systems tested. This conclusion is based on the fact that a high concentration of iron, in the range equivalent to that for the non-bonded metal ("steel" in Table II), appears on the metal failure surface. However, one anomaly which should be pointed out is the presence of nitrogen on the metal failure surface. This nitrogen was not present on the steel prior to bonding,

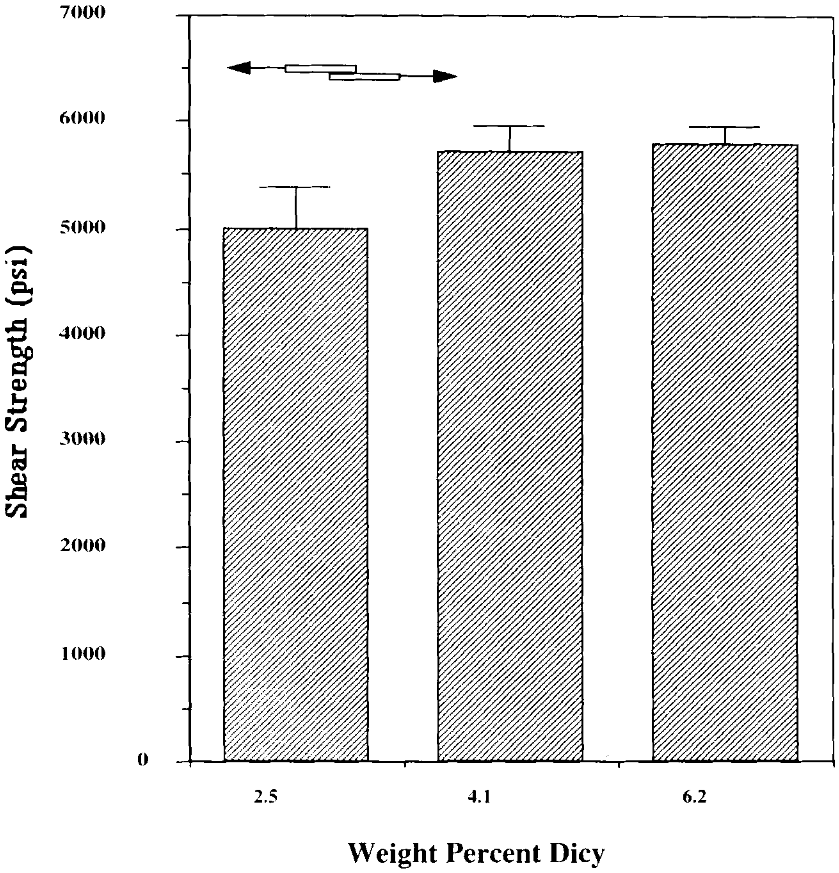

FIGURE 4 Single lap shear strength as a function of Dicy content.

TABLE II
Surface Compositions (At.%) for the DCB Metal Side Failures

Specimen	A	B	C	Steel
Carbon	50.0	54.6	53.1	51.7
Oxygen	38.2	34.4	31.7	37.5
Nitrogen	1.2	1.9	6.7	< 0.2
Iron	10.6	9.2	8.6	10.3
Silicon	< 0.2	< 0.2	< 0.2	< 0.2

and suggests an interaction of curing agent with the adherends, or a migration or sedimentation to the interphase (an interaction of Dicy with metal adherends has been previously reported by other researchers, however not in the case of cold rolled steel).[22,23]

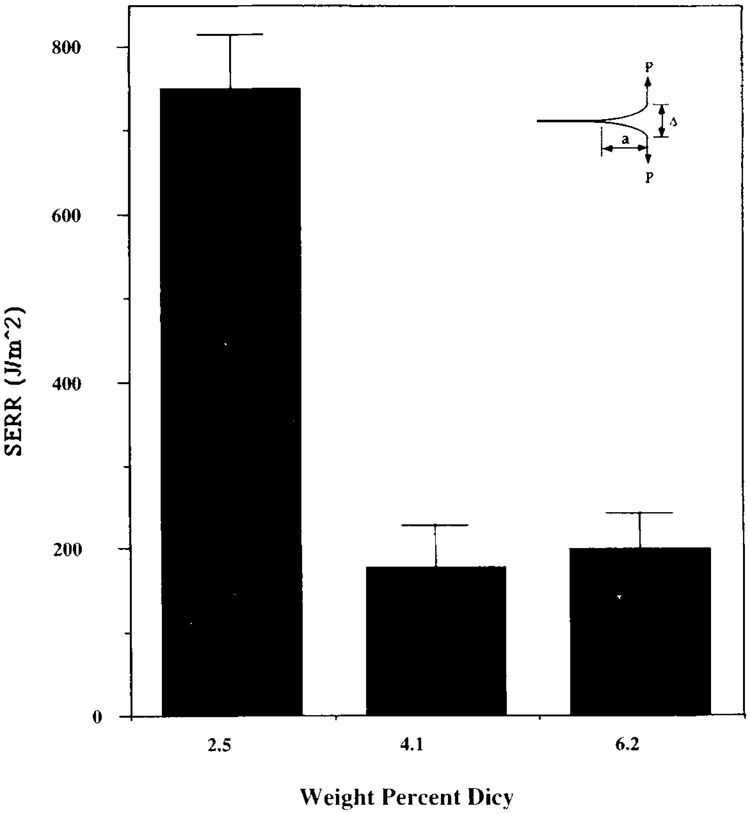

FIGURE 5 Critical (and arrest) strain energy release rates as a function of Dicy content.

The O1s photopeaks demonstrate quite clearly a variation of interphase chemistry in the failure regions. An overlay of these curves is shown in Figure 6. If it is reasoned, at least qualitatively, that cured epoxy is characterized by the O—H component, these curves demonstrate the following; For lower amounts of Dicy, a more complete Dicy/epoxy cure occurs in the vicinity of the steel adherend. As the Dicy content is increased, migration or sedimentation greatly increases the content of Dicy near the steel surface. The result is a brittle, Dicy-rich interphase with a low concentration of epoxy. This is demonstrated by the decrease in the O1s photopeak at 533.5 ev and the simultaneous increase in the failure surface nitrogen (seen in Table II). These findings would agree, as well, with decreased bonded specimen performance (but not decreased bulk performance) for the systems.

As mentioned in the Abstract, the surface evaluations are not intended to be quantitative at this time. Future work, including multiple surface evaluation techniques, will be used to define specifically the chemical changes at the interphase. Rather, they are used only qualitatively to demonstrate that there are variations in the interphase chemistry due to variations in the curing agent content.

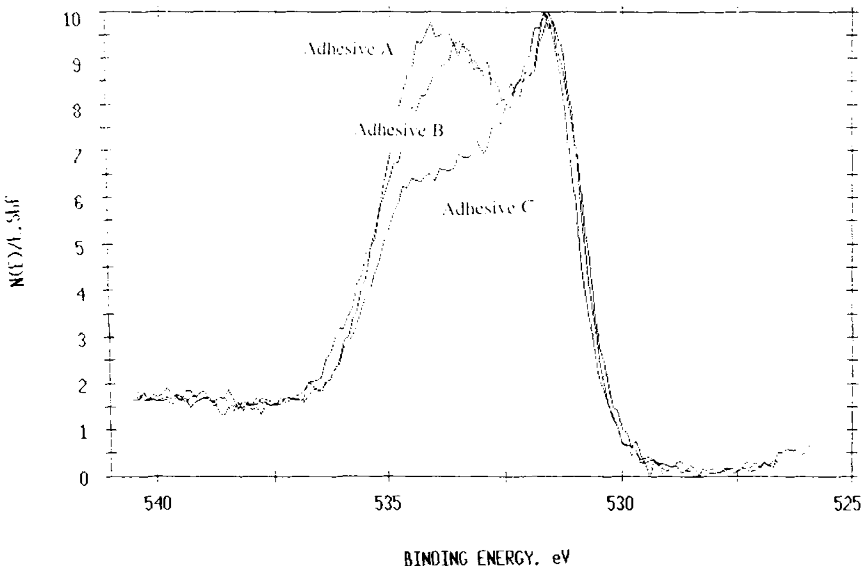

FIGURE 6 Overlay of O1s photopeaks from the failed DCB specimens (metal side of failure).

CONCLUSIONS

In the cured, simple, model epoxy systems used in this study, changes in Dicy content were found to have no effect on the bulk material properties. However, a pronounced effect on the adhesive performance was noted. Considering what these measurements show, and utilizing XPS to evaluate the failure surfaces, it is believed that migration or sedimentation of Dicy occurs during the cure process. This leaves the materials essentially the same in the bulk, but drastically different at the adhesive/adherend interphase.

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