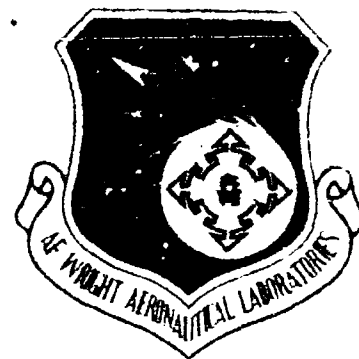


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## LOW MOISTURE ABSORPTION ADHESIVES

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December 1982

Final Report for Period August 1980 through September 1982

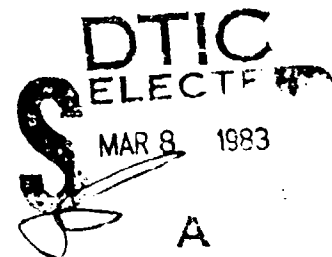
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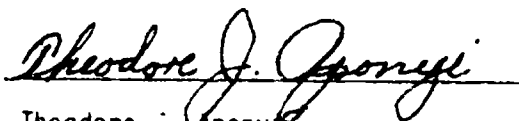


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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A broad spectrum of<br>commercially available ABA block copolymers used for thermoplastics were<br>found to be compatible with vinyl cured thermoset compositions. These<br>hydrophobic compositions showed excellent resistance to moisture as<br>adhesives. Modest shear strength with high peel and good shear strength with<br>modest peel were obtained suggesting that two types of adhesives will be the<br>result of continued efforts with this new class of low odor, structural<br>acrylates. |                                      |   |

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## FOREWORD

This final technical report was prepared by Acurex Corporation, Aerotherm Division, Mountain View, California 94042, under USAF Contract No. F33615-80-C-5071, "Low Moisture-Absorption Adhesives." This development effort was administered under the Direction of the Nonmetallic Materials Division, Air Force Wright-Aeronautical Laboratories (AFWAL/MLBC), Air Force Systems Command, Wright-Patterson Air Force Base, Ohio 45433 with Mr. T. J. Aponyi (AFWAL/MLBC) as Project Monitor.

The work reported herein was initiated under Program Element 62102F, Project 2419, "Nonmetallic Materials," Task 02, "Structural Adhesives and Adhesive Bonding" and Work Unit Number 24190212.

The effort at Aerotherm was conducted within the Materials Department under the direction of Mr. R. M. Washburn. Mr. C. B. Delano was the Principal Investigator. Mr. A. H. McLeod and Mr. C. J. Kiskiras provided technical support and guidance.



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## SECTION 1

### INTRODUCTION

#### 1.1 STATEMENT OF THE PROBLEM

There are many commercially available tough structural adhesives which cure at 121°C (250°F) and provide excellent bonded joint strength properties over a temperature range of -54° to 93°C (-65° to 200°F). However, the available structural adhesives are adversely affected by moisture, especially at elevated temperatures, and the bonded joint strength is seriously reduced. Reduced bond strength has led to discarding and/or major repair of aircraft components and major problems with portable shelters in the field.

Prior to the development of methods to stabilize aluminum against moisture attack, failure occurred at both the metal surface and within the wet adhesive. With the development of the phosphoric acid anodize surface treatment and corrosion-inhibiting primers, the aluminum has been sufficiently stabilized against moisture attack so that the adhesive can be considered to be the weak link in the moisture durability of bonded structures. With the development of new moisture-resistant adhesive systems, the wet service life of bonded components can be greatly extended.

In general, the service life or durability is related to adhesive properties as follows:

- Durability is directly proportional to  $T_g$
- Peel is inversely proportional to the  $T_g$

- Peel is inversely proportional to durability

Adhesives which exhibit high peel strength are obtained readily from resins which have Tg's near room temperature. However, adhesives with low Tg's, unless they are completely hydrocarbon (hydrophobic), as in the case of some tackifiers, have poor environmental durability. Progress is being made in the development of hydrocarbon-like hot melt adhesives for better moisture durability, but these systems do not have the required 93°C (200°F) mechanical properties.

The development of more moisture-resistant 93°C (200°F) performing adhesives must address high Tg attainment while maintaining low temperature peel strength. Extensive investigations have been carried out to study the effects of sorbed moisture on the mechanical properties of cured resins. The diffusion rates have been quantitatively defined using Fick's second law for materials, and the quantitative effects of the moisture on the mechanical properties have been determined. The most serious gross effect is moisture plasticization of polymer causing serious degradation of adhesive properties at moderately elevated temperatures. Banks and Ellis (Reference 1), investigating the effects of water in an epoxy resin, demonstrated that the critical factor which determines the Tg of the completely cured resin is not the average residence time of the water molecules in the resin, but the average persistence time of the interhydroxy hydrogen bonds. Thus, the role of absorbed water was demonstrated to be a catalyst in the breaking of hydrogen bonds; small amounts of water have a large effect because water molecules readily migrate from one group to another group.

There are also many examples of the serious consequences associated with moisture absorption during the processing of green (uncured) epoxy

formulations. Absorbed moisture in the green state can cause a number of deleterious effects:

- Serious void formation during processing
- Water can react with an epoxide, especially in the presence of an amine to form glycols which act as plasticizers
- Moisture can cause the degradation of the anodize

The development of low moisture-absorption 121°C (250°F) curing resins with low glass transition temperatures typified by FM-73 ( $T_g \sim 82^\circ\text{C}$ ) is known technology. The unsaturated polyesters are an example. Glass transition temperatures of thermoset resins as high as 149°C (300°F) can be obtained with 121°C (250°F) cure. However, high  $T_g$ , high peel strength adhesives are not available today.

#### 1.2 PROGRAM OBJECTIVES

The major objectives of the program are to:

- Develop low moisture-absorbing adhesives which cure at 121°C (250°F) and retain mechanical integrity at 93°C (200°F) in a humid environment
- Develop a low-creep reinforced film adhesive for bonding aircraft structures
- Develop a paste and a film adhesive for bonding portable structures

#### 1.3 APPROACH

Initial program target properties for superior moisture-resistant adhesive systems for use in aircraft and portable shelters are given in Table 1. The dry adhesive properties given in Table 1 are best met with

TABLE 1. TARGET ADHESIVE PROPERTIES

| Adhesive Type<br>Adherends |  | Aircraft<br>2024-T3, Bare   | Shelter<br>6061-T6, Bare    |
|----------------------------|--|-----------------------------|-----------------------------|
| Property                   | Test Condition   |                             |                             |
| 1. Tensile shear           | Room temperature   | 38 MPa (5,500 psi)          | 38 MPa (5,500 psi)          |
| 2. Tensile shear           | -54°C (-65°F), 30 min exposure   | 30 MPa (4,300 psi)          | 25 MPa (3,600 psi)          |
| 3. Tensile shear           | 93°C (200°F), dry, 30 min exposure   | 26 MPa (3,800 psi)          | 25 MPa (3,600 psi)          |
| 4. Tensile shear           | 93°C (200°F), dry, 500 hr exposure   | 21 MPa (3,000 psi)          | 17 MPa (2,500 psi)          |
| 5. Tensile shear           | 93°C (200°F), wet, 15 min exposure after 14 days at 93°C and 95 to 100 percent R.H.              | 25 MPa (3,600 psi)          | 24 MPa (3,500 psi)          |
| 6. Bell peel               | -54°C (-65°F), 30 min exposure   | 3.5 kN/m (20 pli) minimum   | 7.0 kN/m (40 pli) minimum   |
| 7. Bell peel               | Room temperature   | 4.4 kN/m (25 pli) minimum   | 8.9 kN/m (50 pli) minimum   |
| 8. Wedge crack extension   | Room temperature, 30 days  | 1.8 cm (0.7 in.) maximum    | 1.8 cm (0.7 in.) maximum    |
| 9. Wedge crack extension   | 93°C (200°F) at 95 to 100 percent R.H. after 14 days at 93°C and 95 to 100 percent R.H., 30 days | 2.5 cm (1.0 in.) maximum    | 2.5 cm (1.0 in.) maximum    |
| 10. Tensile stress rupture | R.T. at 40 percent R.T. Str., 500 hr   | 0.03 cm (0.015 in.) maximum | 0.08 cm (0.03 in.) maximum  |
|                            | 93°C (200°F) at 40 percent 93°C Str., 500 hr   | 0.06 cm (0.025 in.) maximum | 0.13 cm (0.05 in.) maximum  |
|                            | 93°C (200°F) at 95 to 100 percent R.H. at 40 percent of 5., 500 hr                               | 0.10 cm (0.04 in.) maximum  | 0.17 cm (0.065 in.) maximum |

ductile\* adhesives typified by FM-73. These adhesives exemplify a type of interpenetrating network (IPN) rubber-toughened epoxy. The wet aged adhesive requirements in Table 1 are not met by known adhesives.

Discussions reviewing the initial program goal(s) and target properties were held at the Materials Laboratory on October 31, 1980. As a result of these discussions, Acurex undertook a review of available adhesives systems for both aircraft and shelter applications. This review led to identification of new 93°C (200°F) performing ductile adhesive products designed to give improved moisture durability performance. However, 121°C (250°F) performance capability was not indicated for these epoxy systems and further availability of low-cost products for use in shelters was questionable. As a consequence, the basic goals of the program remain excellent. Moisture insensitivity improvements over available adhesives will lead to improved moisture durability properties. Further development of an adhesive with a wet Tg in excess of 121°C (250°F) will lead to improvement over equivalent available systems in time-dependent properties (e.g., creep, wedge crack, etc.). Thus:

- Aircraft Adhesives -- Continue efforts toward development of more moisture-resistant FM-73-type ductile adhesives. Target minimum Tg of 121°C (250°F) after 14-day water boil. The 121°C (250°F) cure requirement differentiates such a product from FM-300, 400-type products. The 14-day water-boiled Tg of FM-73 was found to be only 66°C (151°F). The 93°C (200°F) lap shear strength<sup>†</sup> of FM-73 was

---

\*Ductile adhesives derive their name from fracture toughness testing. Ductile, as opposed to brittle, fracture is observed. Ductile fracture gives very high resistance to crack propagation.

<sup>†</sup>2024-T3 bare phosphoric acid anodized aluminum adherends with BR 127 primer

found to be reduced from 25 MPa (3,700 psi) to 1 MPa (200 psi) by 14-day water boil treatment.

- Shelter Adhesives -- Continue efforts toward development of more moisture-resistant shelter adhesives with particular focus on paste systems for field repair. As with aircraft adhesives discussed above, the 14-day water-boiled  $T_g$  is to be  $121^{\circ}\text{C}$  ( $250^{\circ}\text{F}$ ). The 14-day water-boiled  $T_g$  of XA-180 was found to be only  $92^{\circ}\text{C}$  ( $198^{\circ}\text{F}$ ).

Acurex attended the ASTM shelter adhesive workshop in Concord, California, in January of 1981. Of particular note with regard to field repair of shelters is that EA 934 is the "backbone" of both Air Force and Army shelter field repair. Since this product contains asbestos, it was scheduled for phase-out. EA 934 is a brittle system. Peel testing should be incorporated into repair adhesive specifications, since repaired, installed shelters may be moved and again be subjected to handling damage illustrating a need for ductile adhesives. If present program efforts resulted in development of a shelter repair ductile adhesive which would match the performance of heat-cured systems, the contribution to field repair would be significant.

The ductility of FM-73 led to yielding of the aluminum during tensile testing in the bond area on the PABST program, as sketched in Figure 1 (Reference 2). This type of failure is not obtained with brittle adhesive systems and represents a very damage-resistant, fail-safe bondline.

The ductile adhesives obtain their increased properties from a particular type of failure, "crazing," which occurs at test temperatures below the  $T_g$  of the adhesive. Since  $93^{\circ}\text{C}$  ( $200^{\circ}\text{F}$ ) performing adhesives require that the  $T_g$  of the material be above room temperature, the adhesive will be brittle at  $-54^{\circ}\text{C}$  ( $-65^{\circ}\text{F}$ ) and have no significant peel strength unless crazing occurs.

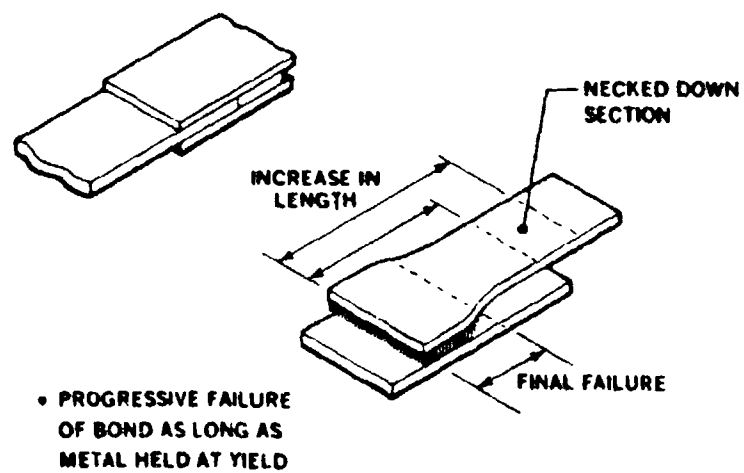


Figure 1. Yielding of Aluminum with FM-73 Adhesive



The IPN approach to ductile adhesives provides the specific advantage of minimal matrix shear modulus loss, which provides good creep resistance while concurrently increasing the peel strength of the adhesive. The influence discrete rubber particles have on resins has been reviewed by Kambour (Reference 3). Due to the creation of multiple fractures, the fracture surface work is increased as shown in Figure 2 (Reference 4).

As developed above, the Acurex approach focused on the development of rubber-toughened thermosets. The first efforts consisted of selection of moisture-resistant 93°C (250°F) curing high-Tg resins. Selection criteria included Tg shift and final Tg determination after 14-day water boil and ability to be cured at 93°C (250°F). These resins were then investigated for IPN formation (rubber toughening), using improvements made in adhesive properties (peel strength) to suggest indirectly that rubber toughening had occurred.

Further, our approach focused on use of ABA block copolymers where the A portions of the block were matrix resin compatible and the B portion was the incompatible rubber. Familiar examples of ABA-type prepolymers used to rubber-toughen thermosets are B.F. Goodrich's CTRN, ATRN, CTB series of low-molecular butadiene-acrylonitrile prepolymers. They are functional or reactive prepolymers. Prereaction of the functional prepolymers with 1,000 to 2,000 molecular weight epoxies such as Shell's EPON 1004 results in the formation of true triblocks. Two methods of rubber particle formation are given in Figure 3. Acurex planned to use Method 2 for IPN formation.

As will be developed in the next section, we did not form our own ABA block copolymers to prepare the IPN's since the selected, most moisture-resistant matrix system was found to be compatible with a large number of commercially available ABA block copolymers. This unexpected development led

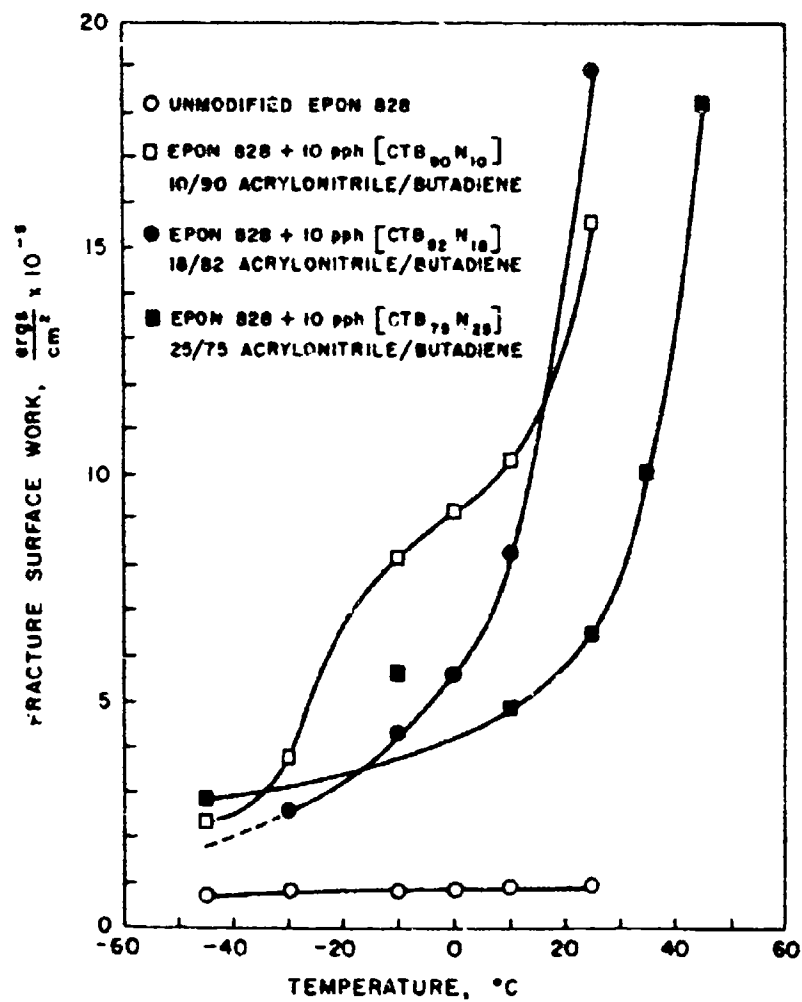


Figure 2. Fracture Surface Work Versus Test Temperature for EPON 828 Cured with 5 pph Curing Agent D

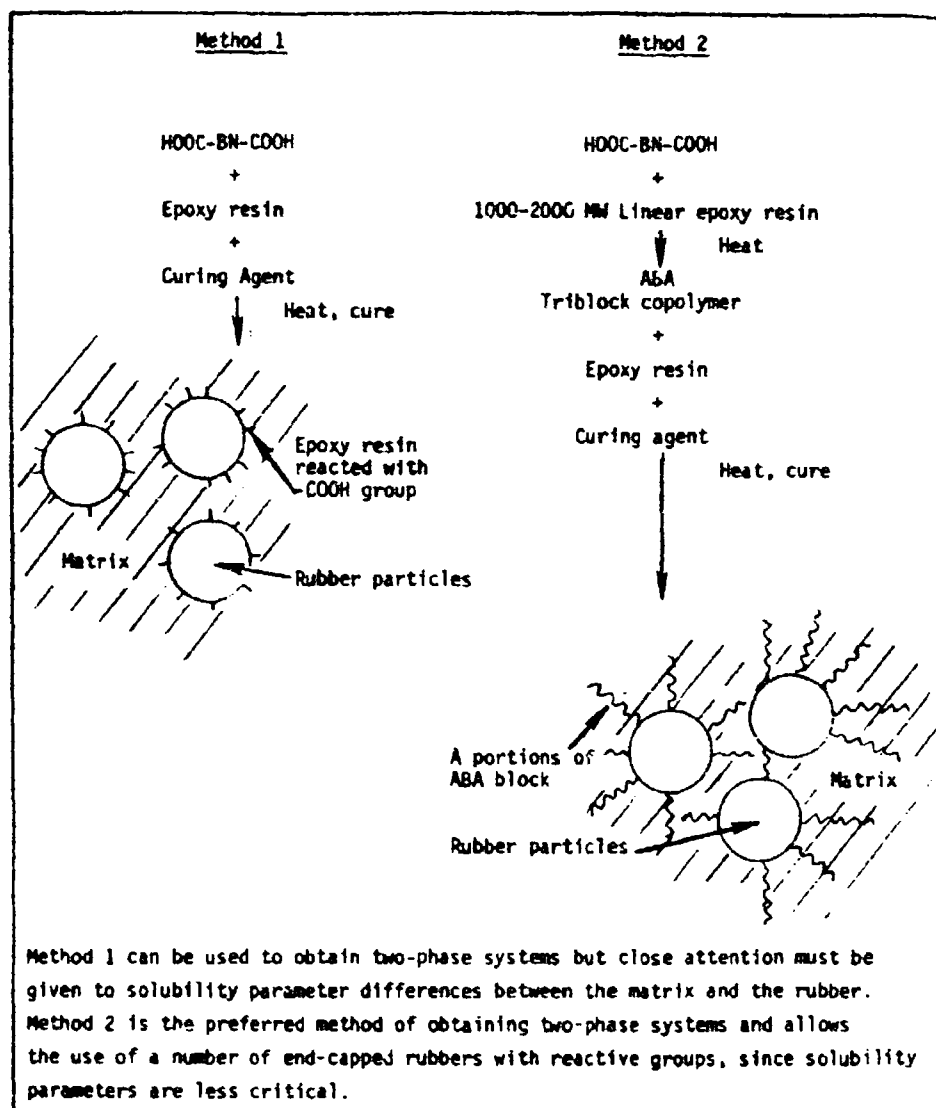


Figure 3. Two Methods Which Yield Rubber-Toughened Thermoset Materials

to major program efforts to identify an available ABA block copolymer(s) which would give the sought adhesive properties.

As will be evident to those skilled in impact acrylic and epoxy technology, much remains to be investigated before the extremely moisture-resistant vinyl cured compositions indicated from program efforts will be optimum.

## SECTION 2

### TECHNICAL DISCUSSION

#### 2.1 MOISTURE RESISTANCE OF CANDIDATE RESINS

Epoxy, cyanate and acrylate resins were obtained from commercial sources or synthesized by Acurex. They were polymerized and screened for ability to provide a distortion temperature under 3.1 MPa (450 psi) compressive load (DTUL) of 121°C (250°F) after 14-day water boil. Several candidates passed this screening test.

##### 2.1.1 Epoxy Resins

Table 2 gives the initial dry, 24-hr and 14-day water boil results on neat resin castings of the XA-180 and FM-73 adhesives, as well as several epoxy systems investigated as candidate matrices for rubber toughening efforts. The 14-day water-boil DTUL's of the XA-180 and FM-73 systems suggest that these systems will show sensitivity to moisture at 93°C (200°F). The moisture weight gains of both adhesive systems are high for epoxy resins, and the redry weights indicate some weight loss of some component of the resin systems by extraction during water boil. Neither of the systems cracked upon redry.

The Epon 828 and the DEN 438 systems cured with isophorone diamine (IPDA) demonstrated the performance required for rubber toughening, namely, 14-day water-boil DTUL in excess of 121°C (250°F). Their moisture weight gains were less than 3 percent and both castings showed no change upon redry.

TABLE 2. DRY AND WET BULK RESIN DATA ON AVAILABLE ADHESIVES AND CANDIDATE EPOXY RESINS

| Resin System <sup>b</sup>   | Code | Dry Properties   |              | 24 Hour Water Boil Properties |                |                      |   |    | Dried Sample Condition |
|---|------|------------------|--------------|-------------------------------|----------------|----------------------|---|----|------------------------|
|   |      | Hardness, Barcol | Dry DTUL, °C | DTUL, °C                      | DTUL Shift, °C | Weight Gain, Percent | Sample Weight <sup>a</sup> After Redry, Percent |    |                        |
| XA-180 (JM)<br>FM 73 (Cyanamide)<br>EPON 828/IPDA<br>DEN 438/IPDA<br>ROGE (Helox 69)/IPDA<br>DGA/IPDA | D5   | 0                | 92           | 82                            | 10             | 5.75                 | 98.81   | OK |                        |
|   | D4   | 0                | 82           | 70                            | 12             | 4.12                 | 98.15   |    |                        |
|   | D13  | 35               | 150          | 133                           | 17             | 1.74                 | 100.07  |    |                        |
|   | D11  | 36               | 160          | 150                           | 10             | 1.83                 | 99.93   |    |                        |
|   | D9   | 38               | 108          | 76                            | 32             | 3.17                 | 100.10  |    |                        |
|   | D7   | 51               | 127          | 109                           | 18             | 1.79                 | 99.97   |    |                        |
| Resin System  | Code |                  |              | 14 Day Water Boil Properties  |                |                      |   |    | Dried Sample Condition |
|   |      |                  |              | DTUL, °C                      | DTUL Shift, °C | Weight Gain, Percent | Sample Weight <sup>a</sup> After Redry, Percent |    |                        |
| XA-180 (JM)<br>FM 73 (Cyanamide)<br>EPON 828/IPDA<br>DEN 438/IPDA<br>ROGE (Helox 69)/IPDA<br>DGA/IPDA | D5   |                  |              | 87                            | 5              | 16.28                | 96.25   | OK |                        |
|   | D4   |                  |              | 66                            | 16             | 12.65                | 97.52   |    |                        |
|   | D13  |                  |              | 131                           | 19             | 2.49                 | 100.68  |    |                        |
|   | D11  |                  |              | 141                           | 19             | 2.92                 | 100.61  |    |                        |
|   | D9   |                  |              | 89                            | 19             | 5.04                 | 101.49  |    |                        |
|   | D7   |                  |              | 105                           | 22             | 3.29                 | 101.04  |    |                        |

<sup>a</sup>Two hour at 121°C redry  
bXA-180 and FM 73 were cured per manufacturer's specification and the  
IPDA cured epoxy resins were cured through 1 hr at 150°C

The resorcinoldiglycidyl ether (RDGE) and diglycidylaniline (DGA) systems cured with isophorone diamine did not meet the target 121°C (250°F) DTUL performance after 14-day water boil. The RDGE system had high moisture gain, whereas the DGA system was somewhat less. Due to the slow reactivity of the DGA system, it should not be eliminated from future considerations; however, prognosis for amine or DICY cures to provide a wet DTUL of 121°C (250°F) is poor and other curatives need to be investigated.

Figure 4 shows the initial dry DTUL curves for the systems investigated. The relationship between DTUL and glass transition temperature obtained from expansion coefficient was investigated and the DTUL was found to be typically 6° to 22°C below the T<sub>g</sub> (DTUL was taken as the intercept of nonsoftening to softening behavior under the 3.1 MPa load). Good wet expansion T<sub>g</sub> traces could not be obtained on the XA-180 or FM-73 systems, possibly due to the loss of moisture leading to sample contraction during test. Wet DTUL curves under load, however, showed curves typical of those shown in Figure 4.

#### 2.1.2 Cyanates

A small quantity of 2,2'-dicyanato-3,3',5,5'-tetramethyldiphenylmethane, (2,2'-DCTMDM), was prepared, staged, and cured into castings. The structure and water-boil properties of this system are given in Table 3. As expected, the system provided the target 14-day water-boiled DTUL in excess of 121°C (250°F) and had a weight gain of less than 1.5 percent.

#### 2.1.3 Acrylates

Three acrylate systems were proposed for investigation as matrices for rubber-toughened adhesives. The condensation of 2-hydroxymethylmethacrylate with isophorone diisocyanate and PAPI was carried out. The PAPI product, after standing for several days, gelled and, due to this apparent instability,

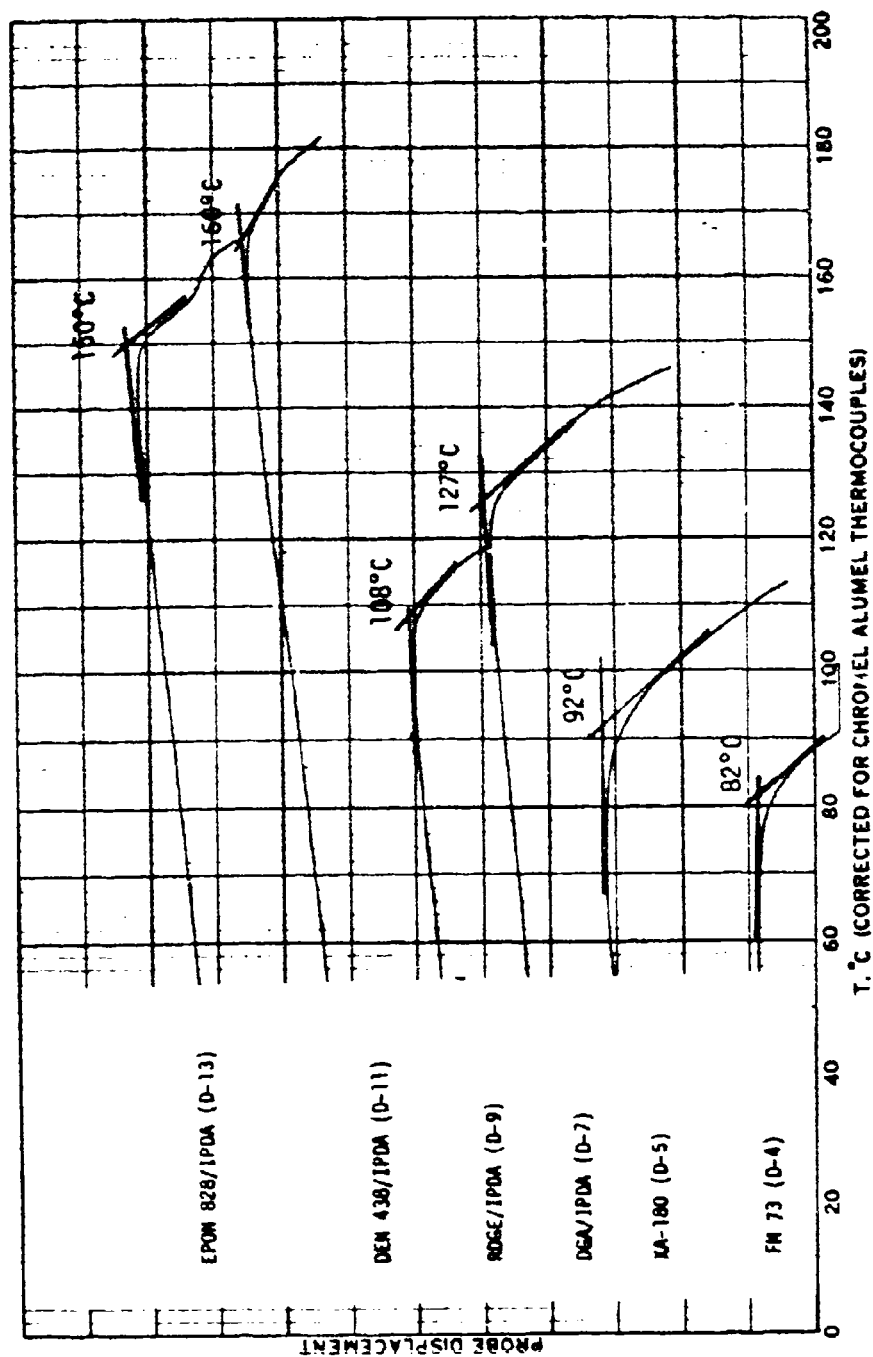


Figure 4. Initial Dry DTIL Curves on Available Adhesives and Epoxy Resins



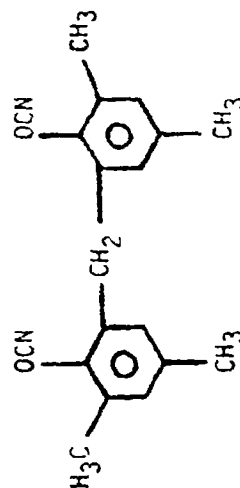
TABLE 3. DRY AND WET BULK RESIN DATA ON THE CYANATE RESIN CANDIDATE

| Resin System             | Sample Condition  | DTUL <sup>a</sup><br>°C | DTUL Shift<br>°C | Weight Gain<br>Percent | Sample Weight<br>After Redry,<br>Percent | Dried<br>Sample<br>Condition |
|--------------------------|-------------------|-------------------------|------------------|------------------------|--|------------------------------|
| 2,2'-DCTMDM <sup>b</sup> | Initial dry       | 153                     | --               | --                     | --                                       | --                           |
| 2,2'-DCTMDM <sup>c</sup> | " "               | 157                     | --               | --                     | --                                       | --                           |
| 2,2'-DCTMDM <sup>b</sup> | 24 Hr Water Boil  | 138                     | 15               | 0.80                   | 100.19                                   | Cracked                      |
| 2,2'-DCTMDM <sup>c</sup> | " " "             | 138                     | 19               | 0.79                   | 100.25                                   | OK                           |
| 2,2'-DCTMDM <sup>b</sup> | 14 Day Water Boil | 144                     | 5                | 1.40                   | 100.35                                   | Cracked                      |
| 2,2'-DCTMDM <sup>c</sup> | " " "             | 145                     | 12               | 1.23                   | 100.38                                   | OK                           |

<sup>a</sup>DTUL onset (curve variation from linear glassy expansion curve)

<sup>b</sup>Catalyst: 0.5 phr zinc stearate catalyst

<sup>c</sup>Catalyst: 5 Percent of 10 percent solution of zinc stearate in 2,4-dimethylanhenyl cyanate



2,2'-Dicyanato-3,3',5,5'-tetramethyldiphenylmethane (2,2'-DCTMDM)

was eliminated from further consideration. Epocryl 12 from Shell and Diacryl 101 from Akzo Chemie were also included in the screening effort. Castings were prepared, boiled for 24 hr and for 14 days and the neat resin properties determined. The structures of the three resins used to prepare the neat resin castings are given in Figure 5 and the results of the water boil testing are provided in Table 4.

All three resin systems provided the target performance of a DTUL of 121°C (250°F) after 14-day water boil. Twenty-four-hour water boil was remarkably equivalent to 14-day water boil properties in the observed DTUL shift. This apparently is due to the nature of the DTUL test where surface properties of the resin cube are measured. The cube's surface is saturated with water (near its equilibrium moisture content) after both 24-hr and 14-day tests even though the cube's interior is not. Moisture weight gain properties, however, continued to increase through the 14-day test. The same trends can be noted for both the previously discussed epoxy and cyanate resins. The Diacryl 101 showed no Tg loss after 24-hr water boil or 14-day water boil, even though both samples gained weight. It was concluded that the Diacryl 101 has excellent potential to become a major ingredient in a moisture-resistant adhesive formulation (or composite matrix resin formulation) which can be cured by an addition method.

The small weight loss measured upon redry of the Diacryl 101 samples after water boil may be monomer extraction; however, it is more likely that the weight loss is from catalyst residues or other nonreactive species in the Diacryl monomer.

Since candidates from all three resin systems passed our initial screening test, they became candidates for rubber toughening efforts. As discussed in the next section, a selection of the candidates that held the most promise relevant to overall program goals was required.

Room Temperature  
Lap Shear Strength, MPa (psi)<sup>a</sup>

|   | Dry,<br>Initial | After<br>24 Hour<br>Water Boil |
|---|-----------------|--------------------------------|
| $\text{CH}_2 = \text{C}(\text{CH}_3) - \text{C}(=\text{O}) - \text{O} - \text{CH}_2\text{CH}(\text{OH})\text{CH}_2 - \text{O} - \text{CH}_2\text{CH}(\text{OH})\text{CH}_2 - \text{O} - \text{C}(\text{CH}_3)_2 - \text{C}_6\text{H}_4 - \text{C}(\text{CH}_3)_2 - \text{C}_6\text{H}_4 - \text{O} - \text{CH}_2\text{CH}(\text{OH})\text{CH}_2 - \text{O} - \text{C}(\text{CH}_3)_2 - \text{C}(=\text{O}) - \text{CH}_2$ | 9.3 (1354)      | 7.0 (1405)                     |
| Isocalized Structure of Epocryl 12 (Shell)  |                 |                                |
| $\text{CH}_2 = \text{C}(\text{CH}_3) - \text{C}(=\text{O}) - \text{O} - \text{CH}_2\text{CH}_2\text{O} - \text{C}(=\text{O}) - \text{NH} - \text{C}(\text{CH}_3)_2 - \text{C}_6\text{H}_4 - \text{C}(\text{CH}_3)_2 - \text{C}_6\text{H}_4 - \text{O} - \text{CH}_2\text{CH}_2\text{O} - \text{C}(=\text{O}) - \text{CH}_2$   | 10.1 (1467)     | 10.1 (1460)                    |
| Isophorone Urethane Methacrylate  |                 |                                |
| $\text{CH}_2 = \text{C}(\text{CH}_3) - \text{C}(=\text{O}) - \text{O} - \text{CH}_2\text{CH}_2\text{O} - \text{C}(=\text{O}) - \text{NH} - \text{C}(\text{CH}_3)_2 - \text{C}_6\text{H}_4 - \text{C}(\text{CH}_3)_2 - \text{C}_6\text{H}_4 - \text{O} - \text{CH}_2\text{CH}_2\text{O} - \text{C}(=\text{O}) - \text{CH}_2$   | No data         |                                |

Diacryl 101 (Akzo Chemie)

<sup>a</sup>From Reference 5

Figure 5. Acrylate Monomer Structures

TABLE 4. DRY AND WET BULK RESIN DATA ON METHACRYLATE SYSTEMS

| Resin System <sup>a</sup> | Code | Dry Properties      |          |                  | 24 Hour Water Boil Properties |                |                      |                               |                        |          | 14 Day Water Boil Properties |                      |                               |                        |
|---------------------------|------|---------------------|----------|------------------|-------------------------------|----------------|----------------------|-------------------------------|------------------------|----------|------------------------------|----------------------|-------------------------------|------------------------|
|                           |      | Final Cure Temp, °C | DTUL, °C | Hardness, Barcol | DTUL, °C                      | DTUL Shift, °C | Weight Gain, Percent | Weight After Redry, b Percent | Dried Sample Condition | DTUL, °C | DTUL Shift, °C               | Weight Gain, Percent | Weight After Redry, b Percent | Dried Sample Condition |
| Epocryl 12                | 01   | 175                 | 155      | 48               | 131                           | 24             | 3.2                  | 100.80                        | OK                     | 133      | 22                           | 4.4                  | 101.52                        | c                      |
| Isophorone urethane       | 02   | 175                 | 165      | 50               | 125                           | 40             | 3.2                  | 100.97                        | ↑                      | 135      | 30                           | 4.3                  | 101.89                        | OK                     |
| Diacryl 101               | 03   | 175                 | 150      | 46               | 150                           | 0              | 0.85                 | 99.88                         | ↑                      | 150      | 0                            | 2.2                  | 98.76                         | c                      |

<sup>a</sup>Systems cured with 0.5 phr t-butylperbenzoate and 9.75 phr cumene hydroperoxide through 175°C  
<sup>b</sup>Two hours at 121°C redry  
<sup>c</sup>Casting OK except for air inhibited top surface which degraded slightly

## 2.2 SELECTION OF CANDIDATES FOR TOUGHENING INVESTIGATIONS

The untoughened resin candidates which, after 14-day water boil, provided a  $T_g$  in excess of  $121^\circ\text{C}$  ( $250^\circ\text{F}$ ) are listed below. Approaches exist to cure both the epoxy and methacrylate systems at  $121^\circ\text{C}$  ( $250^\circ\text{F}$ ) or lower temperatures. Low-temperature cure of cyanate resins is not well documented, and for this reason toughening efforts for this system were held in reserve.

| Resins                           | DTUL, $^\circ\text{C}$ | Moisture Weight Gain (percent) |
|----------------------------------|------------------------|--------------------------------|
| Epoxy:                           |                        |                                |
| EPON 828/1PDA                    | 131                    | 2.49                           |
| DEN 438/1PDA                     | 141                    | 2.92                           |
| Cyanate:                         |                        |                                |
| 2,2' DCTMDM                      | 145                    | 1.23                           |
| Acrylate:                        |                        |                                |
| Epocryl 12                       | 133                    | 4.4                            |
| Isophorone urethane methacrylate | 135                    | 4.3                            |
| Diacryl 101                      | 150                    | 2.2 (0.8)*                     |

\*Retest after scraping away soft top surface prior to water boil

For maximum opportunity to achieve program success due principally to unknowns in rubber toughening art, it was difficult to a priori select methacrylate over epoxy systems or vice versa. Both are rubber toughenable. The  $T_g$ 's of the linear components typically used to achieve crazing, polymethylmethacrylate for acrylates and poly(oxy-2-hydroxytrimethyleneoxy-1, 4-phenyleneisopropylidene-1, 4-phenylene) for epoxies, are  $105^\circ\text{C}$  ( $221^\circ\text{F}$ ) and  $100^\circ\text{C}$  ( $212^\circ\text{F}$ ), respectively (Reference 6). Use of these linear polymers in

the previously cited resin systems would lower both their initial and 14-day water-boiled Tg's. If the added rubber has some solubility in the matrix resin, further Tg lowering of the matrix occurs.

The outstanding moisture resistance of the Diacryl 101 monomer suggested that this monomer receive the major attention. Even after toughening, a ductile adhesive based on this monomer would be expected to have excellent moisture resistance. Further, its high Tg after 14-day water boil suggested a larger degree of formulating latitude than other untoughened systems.

Consequently, the resin candidate matrices were ordered for toughening investigations as follows:

- Diacryl 101
- Isophorone urethane methacrylate (IPUM)
- Epocryl 12
- EPON 828
- DEN 438
- 2,2' DCTMDM (cyanate)

The isophorone urethane methacrylate and Epocryl 12 which follow the Diacryl 101 preceded investigations with epoxy matrices. The simultaneous investigation of the three acrylate systems (all methacrylate end capped) would allow correlations between the systems to be made and help to accelerate results. Further, since crazing is expected for rubber-toughened linear matrices, use of methylmethacrylate and t-butylstyrene ( $T_g = 130^{\circ}\text{C}$ ) in combination with the difunctional monomers would show the influence of crosslink density on crazing. For instance, Diacryl 101 with an ABA block may not have sufficient linearity for craze formation, but with some portion of

methacrylate the properties of impact acrylics should become manifested.

Efforts required on epoxy systems would depend on the degree of success obtained with acrylate systems.

#### 2.2.1 Compatibility Testing of Available ABA Block Copolymers with the Selected Acrylate Monomers

Commercially available ABA block copolymers listed in Table 5 were screened for compatibility with the three candidate "rigid" divinyl monomers discussed above. Results of the compatibility testing of the ABA blocks with the selected monomers, two liquid (solvent) monomers, and blends of the systems are given in Table 6.

Readily apparent from Table 6 are the following items:

- Diacryl 101 dissolves the Acryloid tougheners, two of the Blendex tougheners, and the BTA 111F. Partial solubility for both the Kratons and Solprenes is exhibited. The superior solvating power of the Diacryl 101 over the isophorone bisurethane methacrylate (IPUM) and Epocryl 12 (Epon 828 reacted with methacrylic acid) is principally attributed to the lack of hydrogen bonding in the Diacryl 101 system, even though some difference in solubility parameters among the three systems exists.
- The VTRN's are compatible with all three candidates
- Methyl methacrylate (MMA) and t-butylstyrene (TBS) are, in general, good solvents for the commercially available ABA block copolymers and the VTRN's. That the Acryloids and Durastrength products used for PVC toughening are incompatible or only swell in the two solvents is probably due to mismatched solubility parameters. TBS dissolves butyl rubber.

TABLE 5. IMPACT MODIFIERS

| Number | Products         | Chemical Name  | Form   | Plastic(s)<br>Suggested<br>to Modify    | Vendor            |
|--------|------------------|--|--|---|-------------------|
| 1      | Acryloid KM 611  | Acrylic polymer<br>100 percent acrylic polymer   | Powder<br>Powder                                   | PVC                                     | Rohm and Hass     |
| 2      | Acryloid KM 323B |  |  |   |                   |
| 3      | Blendix 131a     | Acrylonitrile/butadiene/styrene (ABS)<br>Acrylonitrile/butadiene/styrene/methacrylate (MABS)<br>Methacrylate/butadiene/styrene (MBS)   | Powder<br>Powder<br>Powder<br>Powder               | PVC, ABS                                | Borg Warner       |
| 4      | Blendix 310a     |  |  |   |                   |
| 5      | Blendix 436a     |  |  |   |                   |
| 6      | Blendix 435a     |  |  |   |                   |
| 7      | 8TA 111Fa        |  |  |   |                   |
| 8      | Durastrength 200 | Acrylic impact modifier  | Powder   | PVC                                     | M and T Chemicals |
| 9      | Kraton 1101      | Styrene/butadiene/styrene (SBS)<br>Styrene/butadiene/styrene (SBS)<br>Styrene/isoprene/styrene (SIS)<br>Styrene/isoprene/styrene (SIS)<br>Styrene/ethylene/butylene/styrene (SEBS)<br>Styrene/ethylene/butylene/styrene (SEBS) | Crumb<br>Crumb<br>Crumb<br>Crumb<br>Crumb<br>Crumb | Styrenes,<br>polyolefins,<br>polyesters | Phillips          |
| 10     | Kraton 1102      |  |  |   |                   |
| 11     | Kraton 1107      |  |  |   |                   |
| 12     | Kraton 1111      |  |  |   |                   |
| 13     | Kraton G 1650    |  |  |   |                   |
| 14     | Kraton G 1652    |  |  |   |                   |
| 15     | Solprene 411     | Radial butadiene/styrene ABA blocks<br>Radial butadiene/styrene ABA blocks<br>Radial isoprene/styrene ABA blocks<br>Linear butadiene/styrene AB block  | Powder<br>Powder<br>Pellet<br>Crumb                | Styrene<br>Compatible<br>Resins         | Shell             |
| 16     | Solprene 414     |  |  |   |                   |
| 17     | Solprene 416     |  |  |   |                   |
| 18     | Solprene 312     |  |  |   |                   |
| 19     | Solprene 1205    |  |  |   |                   |
| 20     | VTBN 1300 x 22   | Vinyl terminated butadiene/acrylonitrile<br>Vinyl terminated butadiene/acrylonitrile<br>Vinyl terminated butadiene/acrylonitrile   | Liquid<br>Liquid<br>Liquid                         | Vinyl cured<br>resins                   | B. F. Goodrich    |
| 21     | VTBN 1300 x 23   |  |  |   |                   |
| 22     | VTBN 1300 x 24   |  |  |   |                   |
| 23     | Butyl 111        | Butyl rubber   | Gum  | Polyolefins                             | Polysar           |

a products not identified by composition



TABLE 6. SOLUBILITY OF COMMERCIALY AVAILABLE TOUGHENERS IN VINYL SYSTEMS

| Resin Type<br>Concentration of Toughener in<br>Resin (phr)a |              | IPUMb     | Diacyl 101 | Epocryl 12 | Methyl Methacrylate | TBSC | IPUM(50)/TBS(50) | Diacyl(50)/TBS(50) | Epocryl(50)/TBS(50) |
|---|--------------|-----------|------------|------------|---------------------|------|------------------|--------------------|---------------------|
| Code  | Toughener    | Type      | 20         | 20         | 40                  | 40   | 10               | 10                 | 20                  |
| 1   | Acryloid     | KM 611    |            |            |                     |      |                  |                    |                     |
| 2   | Acryloid     | KM 323    |            |            |                     |      |                  |                    |                     |
| 3   | Blendex      | 131       |            |            |                     |      |                  |                    |                     |
| 4   | Blendex      | 310       |            |            |                     |      |                  |                    |                     |
| 5   | Blendex      | 436       |            |            |                     |      |                  |                    |                     |
| 6   | Blendex      | 435       |            |            |                     |      |                  |                    |                     |
| 7   | ETA          | 111F      |            |            |                     |      |                  |                    |                     |
| 8   | Durastrength | 20G       |            |            |                     |      |                  |                    |                     |
| 9   | Kraton       | 1101      |            |            |                     |      |                  |                    |                     |
| 10  | Kraton       | 1102      |            |            |                     |      |                  |                    |                     |
| 11  | Kraton       | 1107      |            |            |                     |      |                  |                    |                     |
| 12  | Kraton       | 1111      |            |            |                     |      |                  |                    |                     |
| 13  | Kraton       | 61650     |            |            |                     |      |                  |                    |                     |
| 14  | Kraton       | 61652     |            |            |                     |      |                  |                    |                     |
| 15  | Solprene     | 411       |            |            |                     |      |                  |                    |                     |
| 16  | Solprene     | 414       |            |            |                     |      |                  |                    |                     |
| 17  | Solprene     | 416       |            |            |                     |      |                  |                    |                     |
| 18  | Solprene     | 312       |            |            |                     |      |                  |                    |                     |
| 19  | Solprene     | 1295      |            |            |                     |      |                  |                    |                     |
| 20  | VTBN         | 1300 x 22 |            |            |                     |      |                  |                    |                     |
| 21  | VTBN         | 1300 x 23 |            |            |                     |      |                  |                    |                     |
| 22  | VTBN         | 1300 x 24 |            |            |                     |      |                  |                    |                     |
| 23  | Butyl rubber |           |            |            |                     |      |                  |                    |                     |

a parts per hundred  
b Bisphenone bis urethane methacrylate  
c St-Butyl styrene

I = insoluble  
P = partially soluble  
S = soluble

1 = clear or opaque liquid  
2 = clear gel or some clear gel balls  
3 = opaque paste or gum

- The solubility of the ABA block copolymers in the 50/50 blends of the three candidates with TBS show the Diacryl 101 with TBS to have remarkable solubility characteristics. The IPUM/TBS (50/50) mixture showed reduced solubility characteristics over the individual components, and the insolubility of the VTBN's in the mixture was unexpected. Block ABA copolymers containing a urethane structure should provide compatible ABA systems. The Epocryl/TBS (50/50) mixture showed a propensity to give two-phase systems. "Vinyl ester" monomers such as those obtained from methacrylic acid with phenylglycidyl ether or butylglycidyl ether would probably be required in place of the TBS to obtain single-phase systems.

Owing to the surprisingly large number of commercially available ABA block copolymers found to be compatible, particularly with the Diacryl/TBS blend, we were able to proceed directly to adhesive testing for toughening optimization efforts. We had expected that much of the original program effort would be devoted to preparation of ABA blocks of varying composition and molecular weights (particularly the B block) for toughening optimization. This expectation, however, was derived principally from consideration of methods to achieve a bimodal rubber particle distribution which is known to benefit epoxy adhesives.

## 2.3 ADHESIVE DEVELOPMENT EFFORTS

### 2.3.1 Initial Selections of ABA Block Copolymers for Toughening Diacryl 101 Summary

Unless specified otherwise, all of the adhesive development efforts were carried out with 10 volt phosphoric acid anodized 2024 T-3 bare aluminum adherends. As previously mentioned, it is this surface treatment for aluminum as compared to other surface treatments such as FPL etch which provides good,

long term resistance to moisture and for which the development of more moisture resistant adhesives makes the most sense.

FPL etched aluminum foil peel bonds were prepared for testing the adhesive properties of the compatible blends shown in Table 6 and selecting some of the more promising ABA block copolymers. Untoughened resin matrices which required Cab-O-Sil addition to prevent starved gluelines all provided less than one PIW 180° peel strength. Four block copolymers which gave significantly higher peel strengths were selected (from the 15 compatible tougheners) for further investigation. A latin square technique was used to decipher trends in monomer ratios, combinations of the four ABA blocks, and similar items. Adhesive compositions selected from the latin square effort were then investigated for lap shear strength at room temperature, elevated temperature, and strength retention after 14-day water boil at 93°C (200°F).

Even though the tougheners provided increased lap shear strength at room temperature and several showed no strength reduction at 93°C (200°F) after 14-day water boil, bell peel strength improvements due to the ABA blocks were only up to three times better than the untoughened Diacryl/TBS matrix. This, in combination with the translucent nature of the Diacryl/TBS castings (instead of opaque, suggesting large rubber particle formulation), prompted investigation of other comonomers with the Diacryl 101, namely, methyl methacrylate, styrene, and acrylonitrile. Styrene with Diacryl 101 and Acryloid KM611 provided lap shear strengths of 21 MPa (3,000 psi) at room temperature and 93°C (200°F). The casting was opaque, suggesting that rubber particle phase-out provided larger rubber particles than those being obtained with the TBS comonomer. Styrene may be the preferred monomer to use with the Diacryl 101, since many commercially available ABA block copolymers have been tailored for use in styrene systems.

Bell peel strengths confirmed use of styrene with the Diacryl 101 to be more susceptible to toughening than blends of other monomers with the Diacryl. Further, increases in bell peel strengths were found to be related to increases in lap shear strengths. The following result is expected for homogeneous adhesive systems: as the adhesive's Tg approaches room temperature, its room temperature shear strength increases, usually with severe losses in elevated temperature shear strengths. Elevated temperature lap shear strengths of Acryloid-611-toughened Diacryl 101 blends with all four monomers, however, were not reduced significantly with good improvements in bell peel strengths.

Based on the good elevated temperature lap shear strengths, efforts then centered on optimization of the adhesive properties attainable with Acryloid tougheners. These efforts are described in the Section 2.3.2.

#### Detailed Investigations

Initial toughening of t-butylstyrene (TBS), Diacryl 101, and the 50/50 blend of the two monomers by commercially available ABA block copolymers (impact modifiers) was demonstrated by 180° aluminum foil peel tests. Bonds were prepared from the homogeneous blends indicated in Table 6. Results of these screening tests are given in Table 7. Homogeneous blends were not obtained in several instances and peel bonds could not be prepared.

All of the bonds prepared from the untoughened resin matrices provided less than one PIW peel strength. Thus, peel strength of the 50/50 resin blend with Acryloid KM611 which gave 4.8 PIW could be considered to be 4.8 times tougher than the untoughened 50/50 resin blend. The untoughened resins, however, required up to 10 phr Cab-O-Sil to prevent starved glue lines.

It was noted that the companion castings (cured with the bonds) showed very little haze with visible light. Thus, the formed rubber particles were either smaller than the wavelength of visible light or had indices of refraction close to the matrix. Light scattering occurs with particles whose

TABLE 7. INITIAL SCREENING OF COMMERCIALY AVAILABLE IMPACT MODIFIERS FOR TOUGHENING DIACRYL 101a,c

| Code | Toughener        | 20 phr Toughener in t-Butylstyrene (TBS) |                     | 20 phr Toughener in 50/50 Blend of TBS and Diacryl 101 |                     | 20 phr Toughener in Diacryl 101 |                     |
|------|------------------|--|---------------------|--|---------------------|---------------------------------|---------------------|
|      |                  | 180° Peel, PIW                           | Adhesive Failure, % | 180° Peel, PIW   | Adhesive Failure, % | 180° Peel, PIW                  | Adhesive Failure, % |
|      |                  | Rm. Temp.                                |                     | Rm. Temp.  |                     | Rm. Temp.                       |                     |
| 1    | Acryloid KM611   | 0  | 100                 | 4.8  | 90                  | 2.3                             | 80                  |
| 6    | Blendex 435      | 0  | 95                  | 2.0  | 75                  | 1.5                             | 95                  |
| 7    | 8TA 111F         | 0  | 50                  | <1   | 95                  | <1                              | 95                  |
| 8    | Durastrength 200 | -  | ---                 | <1   | 100                 | ---                             | ---                 |
| 9    | Kraton 1101      | <1                                       | 5                   | 5.2  | 95                  | ---                             | ---                 |
| 10   | Kraton 1102      | <1                                       | 40                  | 2.8 <sup>b</sup>                                       | 95                  | ---                             | ---                 |
| 11   | Kraton 1107      | <1                                       | 20                  | 2.3 <sup>b</sup>                                       | 100                 | ---                             | ---                 |
| 12   | Kraton 1111      | <1                                       | 10                  | 8.6 <sup>b</sup>                                       | 85                  | ---                             | ---                 |
| 13   | Kraton GI650     | <1                                       | 10                  | 4.5 <sup>b</sup>                                       | 90                  | ---                             | ---                 |
| 14   | Kraton GI652     | <1                                       | 40                  | 5.2  | 20                  | ---                             | ---                 |
| 16   | Solprene 414     | <1                                       | 60                  | 3.0  | 75                  | 4.0                             | 75                  |
| 17   | Solprene 416     | 1.5                                      | 60                  | 4.8 <sup>b</sup>                                       | 70                  | 3.5                             | 75                  |
| 20   | VTBN 1300x22     | 5.6                                      | 25                  | 7.0  | 10                  | 2.0                             | 75                  |
| 21   | VTBN 1300x23     | 7.0                                      | 70                  | 7.0  | 85                  | 3.0                             | 75                  |
| 22   | VTBN 1300x24     | <1                                       | 50                  | 7.8  | 0                   | 2.0                             | 75                  |

<sup>a</sup>Adhesives cured with 0.5 phr Cumene hydroperoxide and 0.75 phr t-butylperbenzoate through 150°C

<sup>b</sup>Crazing induced in resin by bending adherend. Crazing disappeared when bending force was removed

CFPL etched hardened 3 mil aluminum foil

diameter is larger than  $\sim 1,000\text{\AA}$  ( $1\text{ }\mu\text{m}$ ). In epoxy resins, small particles ( $0.2$  to  $1\text{ }\mu\text{m}$ ) are reported to lead to shear banding and larger particles ( $1$  to  $5\text{ }\mu\text{m}$ ) to crazing. The combined bimodal particle size leads to optimum toughening in these resins. In high impact styrene particles with diameters between  $10\text{ }\mu\text{m}$  and  $20\text{ }\mu\text{m}$  are optimum, whereas with ABS  $1\text{-}\mu\text{m}$  particles have been found to be optimum (Reference 3). As a consequence, particle size requirements for optimum toughening for the three matrices given in Table 7 are probably different. Furthermore, the most highly crosslinked system (100 percent Diacryl 101) should be more difficult to rubber-toughen since some matrix linearity is thought to be required for crazing.

The commercially available ABA block copolymers did not provide toughened TBS adhesives. Causes for this could be only low molecular weight TBS formed and/or poor definition of a second phase. TBS is known to be brittle. Two of the VTBN's showed increased peel strength. As discussed below, none of the TBS systems crazed under stress.

The 50/50 blend of TBS and Diacryl 101 showed significant increases in peel strength with the commercially available ABA tougheners and also the VTBN's. Even though none of the fracture surfaces were white (opaque), suggesting that crazing had occurred, in several instances flexing the fractured adherends induced crazing which disappeared when the flexing force was removed. It was concluded that some crazing had occurred during fracture; however, it healed after fracture. Craze healing in polymer glasses has been studied (Reference 7).

Even though the Kraytons were insoluble in the Diacryl 101, testing of the compatible systems suggests that the Diacryl 101 is not as susceptible to toughening as the 50/50 blend. As seen in Table 7, this is the case with the VTBN systems where a threefold decrease in peel strength was observed with

the Diacryl 101 system. These results are consistent with the expected result: crosslinking reduces a system's ability to be toughened.

Efforts then turned toward defining those ABA block copolymers which best toughen the t-butylstyrene (TBS)/Diacryl 101 resin system. As previously discussed, a large number of commercially available ABA block copolymers showed promise for toughening a 50/50 blend of the two monomers. Variables with this resin system include:

- Ratio of TBS to Diacryl 101 (matrix linearity)
- Quantity of ABA copolymers in the resin
- Rubber particle phase-out (sufficient solubility parameter mismatch between rubber and matrix and cure schedule variations)
- Toughening synergism which is obtained through use of more than one toughener

The latin square technique was employed to define trends for variables cited above and reduce the number of compositions requiring investigation. Tougheners used in the experiments were those which provided the best peel strength with the 50/50 blend of TBS and Diacryl 101 reported: Kraton 1111, Kraton G1650, Solprene 416S, and VTBN. Experimental design is provided in Figure 6.

Average results from the lap shear specimens and 180° aluminum foil peel bonds prepared from the 48 compositions are given in table 8. Average Barcol hardnesses obtained in companion castings are also given in the table. Individual lap shear specimens varied from 4.1 to 15.5 MPa (600 psi to 2,255 psi) and peel specimens from 0 to 1.8 kN/m (0 to 10.3 PIW). The average results suggested the following areas for more detailed investigation:

1. Between 1-to-1 and 1-to-2 vinyl equivalent weight ratios of t-butylstyrene to Diacryl 101
2. VTBN weight concentrations of about 4 percent

26.2% t-butylstyrene (TBS), 1 mole  
73.8% Diacryl 101 (DA), 1 mole

41.5% TBS, 2 moles  
58.5% DA101, 1 mole

| Toughener Concentration |     |     |     |
|-------------------------|-----|-----|-----|
| 12%                     | 17% | 22% | 27% |
| A                       | D   | C   | B   |
| B                       | A   | D   | C   |
| C                       | B   | A   | D   |
| D                       | C   | B   | A   |

| Toughener Concentration |     |     |     |
|-------------------------|-----|-----|-----|
| 12%                     | 17% | 22% | 27% |
| D                       | C   | B   | A   |
| A                       | D   | C   | B   |
| B                       | A   | D   | C   |
| C                       | B   | A   | D   |

VTBN  
(1300 x 23)  
Concentration  
0%  
4%  
8%  
12%

55% TBS  
45% DA101

70% TBS  
30% DA101

| Toughener Concentration |     |     |     |
|-------------------------|-----|-----|-----|
| 12%                     | 17% | 22% | 27% |
| C                       | B   | A   | D   |
| D                       | C   | B   | A   |
| A                       | D   | C   | B   |
| B                       | A   | D   | C   |

| Toughener Concentration |     |     |     |
|-------------------------|-----|-----|-----|
| 12%                     | 17% | 22% | 27% |
| B                       | A   | D   | C   |
| C                       | B   | A   | D   |
| D                       | C   | B   | A   |
| A                       | D   | C   | B   |

VTBN  
(1300 x 23)  
Concentration  
0%  
4%  
8%  
12%

Adhesives cured with 0.5 phr cumene hydroperoxide and 0.75 phr t-butylperbenzoate thru 150°C.

A = Solprene 416S radial isoprene/styrene ABA blocks  
B = Kraton G1650 styrene/ethylene/butylene/styrene blocks  
C = Kraton 1111 styrene/isoprene/styrene blocks  
D = Acryloid KM611 acrylic polymer - not included in this study because of solubility difficulties over the entire range of resin concentrations

Figure 6. Latin Square Experiment Structure for Toughening the TBS/Diacryl Resin System



TABLE 8. SUMMATION RESULTS ON DATA OBTAINED WITH THE LATIN SQUARE  
TECHNIQUE

| Variable Studied                | Average Barcol Hardness of 7g Castings | Percent of Samples with Stress whitening | Average 180° Peel Strength on Surface Treated Aluminum foil kN/m (PIW) | Average RT Tensile Strength MPa (psi) | Average -54°C (-65°F) 180° Peel Strength kN/m (PIW) | Compositions Selected for Further Study |
|---------------------------------|--|--|--|---------------------------------------|---|---|
| t-Butylstyrene/ Diacryl         | 27.2/72.8 <sup>a</sup>                 | 50                                       | 0.9 (5.3)  | 7.6 (1100)                            | 0.7 (4.2)   | X                                       |
|                                 | 42.7/57.3 <sup>b</sup>                 | 73                                       | 0.8 (4.6)  | 7.6 (1100)                            | 0.9 (5.0)   | X                                       |
| Wgt. ratio                      | 55/45                                  | 67                                       | 0.9 (5.2)  | 7.2 (1050)                            | 0.7 (3.9)   |   |
|                                 | 70/30                                  | 83                                       | 0.8 (4.8)  | 6.5 (940)                             | 0.9 (5.0)   |   |
| VTBN Concentration <sup>c</sup> | 0                                      | 82                                       | 0.5 (3.2)  | 6.8 (990)                             | 0.6 (3.2)   |   |
|                                 | 4                                      | 90                                       | 1.0 (6.1)  | 7.8 (1130)                            | 0.8 (4.7)   | X                                       |
| Wgt. percent                    | 8                                      | 58                                       | 9.3 (5.3)  | 7.4 (1070)                            | 0.8 (4.7)   |   |
|                                 | 12                                     | 42                                       | 9.3 (5.3)  | 7.0 (1020)                            | 1.0 (5.9)   |   |
| Toughener Concentration         | 12                                     | 50                                       | 0.8 (4.6)  | 6.5 (940)                             | 0.8 (4.8)   |   |
|                                 | 17                                     | 50                                       | 0.9 (5.2)  | 6.1 (890)                             | 0.9 (5.0)   |   |
| (VTBN + block copolymer)        | 22                                     | 75                                       | 0.8 (4.7)  | 6.3 (1200)                            | 0.7 (3.9)   | X                                       |
|                                 | 27                                     | 91                                       | 0.9 (5.2)  | 8.1 (1180)                            | 0.9 (5.0)   |   |
| Rubber type                     | 4145                                   | 60                                       | 0.9 (5.3)  | 7.1 (1030)                            | 0.8 (4.8)   |   |
|                                 | G1650                                  | 75                                       | 0.8 (4.4)  | 7.9 (1140)                            | 0.7 (4.0)   |   |
|                                 | 1111                                   | 63                                       | 0.9 (5.2)  | 6.8 (990)                             | 0.9 (4.9)   |   |
|                                 | KM6111                                 | --                                       | --   | --                                    | --  |   |

<sup>a</sup>This ratio is equivalent to a 1-to-1 mole ratio or a 1-to-2 vinyl equivalent weight ratio.

<sup>b</sup>This ratio is equivalent to a 2-to-1 mole ratio or a 1-to-1 vinyl equivalent weight ratio.

<sup>c</sup>Note that since total toughener concentrations are held constant, as the VTBN concentration increases, the average block copolymer rubber concentration decreases an equivalent amount.

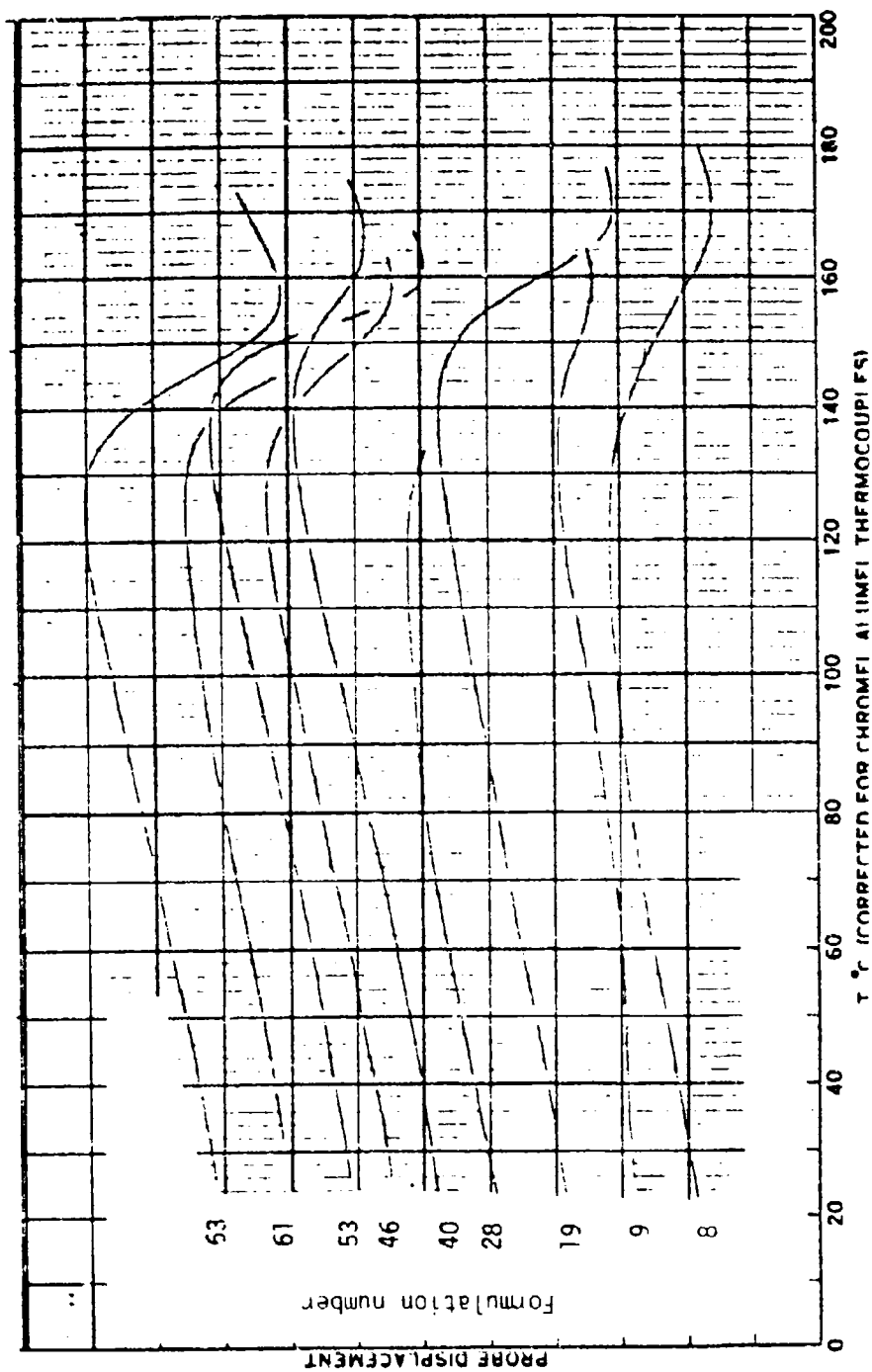
<sup>d</sup>See Figure 6.

3. Toughener concentrations (VTBN plus block copolymer) between 22 to 27 percent by weight
4. Kraton G1650 (SEBS block copolymer used commercially for high-temperature performance) gave the highest average tensile strengths and highest percentage of samples showing stress whitening of the three tougheners studied

The DTUL curves of selected individual formulations which gave the highest combined room temperature and -54°C (-65°F) peel strengths are given in Figure 7. The DTUL's which are well above 121°C (250°F) suggest that a large latitude for formulation of the basic resin matrix exists, while retaining the target performance temperature of (121°C) 250°F.

Lap shear and bell peel specimens were prepared from the compositions selected for further study in Table 8. These results are given in Table 9. Key features of the data presented in Table 9 are as follows:

- The untoughened control (Number 65) provided 10 PMA (1,500 psi) lap shear strength at room temperature, 93°C (200°F) and 149°C (300°F). Room temperature bell peel strength of the unmodified control was 0.1 kN/m (5.7 PIW).
- Up to a threefold increase in toughness was obtained as indicated by increases in bell peel strength. This is short of the tenfold increases expected from optimum systems. Furthermore, increases in peel strength appear in several instances to be related to reductions in lap shear strength. This is expected to occur with soluble rubbers.



- a. Distortion temperature under load at 3.1 MPa (449 psi) and 15°C/minute heating rate.
- b. Adhesives cured with 0.5 phr cumene hydroperoxide and 0.75 phr t-butylperbenzoate through 150°C.

Figure 7. Selected DTUL's of Individual Formulations

TABLE 9. ADHESIVE STRENGTHS OF DIACRYL 101/TRS COMPOSITIONS WITH SELECTED  
COMMERCIALLY AVAILABLE TOUGHENERS<sup>a</sup>

| Composition<br>Number | Toughener Type <sup>b</sup> | t-Butylstyrene<br>in Diacryl 101, % | VTBN, phr | Toughener, phr | Hardness of 7g Castings |         | DTUL,<br>MPa (449 psi)<br>15°C @ 1 min<br>heating | Lap Shear Strength MPa (psi) |                 |   | Room<br>Temperature<br>Bell Peel,<br>kW/m<br>(P/W) |
|-----------------------|-----------------------------|-------------------------------------|-----------|----------------|-------------------------|---------|---|------------------------------|-----------------|---|--|
|                       |                             |                                     |           |                | Barcol                  | Shore D |   | Room<br>Temperature          | 93°C<br>(200°F) | After 14 day<br>Water Boil<br>93°C(200°F) |  |
| 65                    | Control <sup>c</sup>        | 26.2 <sup>d</sup>                   | 0         | 0              | 30                      | --      | 130   | 10(1450)                     | 10(1474)        | 9.1(1313)                                 | 1.0(5.7)   |
| 66                    | A                           | 26.2                                | 4         | 18             | 0                       | 68      | 149   | 17(2418)                     | 14(2000)        | 8.0(1208)                                 | 0.8(4.8)   |
| 70                    | A                           | 26.2                                | 4         | 23             | 0                       | 65      | 82, 145   | 18(2608)                     | 9.3(1347)       | 6.5(938)                                  | 1.8(10.4)  |
| 67                    | B                           | 26.2                                | 4         | 18             | 0                       | 55      | 75, 150   | 16(2267)                     | 6.8(980)        | 3.4(564)                                  | 2.5(14.0)  |
| 71                    | B                           | 26.2                                | 4         | 23             | 0                       | 68      | 80, 154   | 14(2099)                     | 7.1(1029)       | 3.7(534)                                  | 2.8(15.8)  |
| 73                    | B                           | 41.5 <sup>e</sup>                   | 0         | 22             | 0                       | 70      | 155   | 17(2411)                     | 14(2052)        | 6.6(959)                                  | 1.6(9.3)   |
| 74 <sup>f</sup>       | B                           | 41.5                                | 0         | 22             | 0                       | --      |   | 15(2156)                     | 13(1814)        | 5.2(758)                                  | 1.9(11.0)  |
| 68                    | C                           | 26.2                                | 4         | 18             | 0                       | 66      | 78, 150   | 16(2280)                     | 10(1465)        | 7.2(1051)                                 | 1.3(7.4)   |
| 72                    | C                           | 26.2                                | 4         | 23             | 0                       | 55      | 68, 150   | 16(2360)                     | 11(1583)        | 4.7(683)                                  | 2.8(16.0)  |
| 69                    | D                           | 26.2                                | 4         | 18             | 21                      | 12      | 157   | 14(2020)                     | 12(1719)        | 9.1(1327)                                 | 1.9(10.7)  |

<sup>a</sup>Adhesives cured with 0.5 phr cumene hydroperoxide and 0.75 phr t-butylperbenzoate through 150°C. Bare 2024 T3 phos anodized adherends.

<sup>b</sup>A = Solprene 4165, B = Kraton G1650, C = Kraton 1111, D = Acryloid KM611

<sup>c</sup>Five percent Cab-O-Sil MS added for bonding; no Cab-O-Sil in the 7g casting

<sup>d</sup>This percentage is equivalent to a 1-to-1 mole ratio or a 1-to-2 vinyl equivalent weight ratio

<sup>e</sup>This percentage is equivalent to a 2-to-1 mole ratio or a 1-to-1 vinyl equivalent weight ratio

<sup>f</sup>Same as 73 except that metal and scrim primed with Z6082 (vinyltris[*n*-methoxyethoxy]silane)

- DTUL testing on the companion castings showed in several instances an early break in the DTUL curve, even though complete penetration did not occur. Although the premature slight indentation is not understood, two of the three toughened systems (Compositions 66, 74, and 69) which did not give this break had the highest strengths at 149°C (300°F).
- With the exception of the D toughener (Acryloid KM611), all of the tougheners gave castings with a zero Barcol hardness.
- Increasing the concentration of toughener A (Solprene 4165) from 18 to 23 percent lowered the percent strength retention of room temperature lap shear strength at elevated temperatures while increasing the peel strengths (Compositions 66 and 70).
- Increasing the concentration of toughener B (Kraton G1650) from 18 to 23 percent, essentially produced no change in peel strength or lap shear strength retention at elevated temperature (Compositions 67 and 71).
- Using toughener B (Kraton G1650) without VTBN (Compositions 73 and 74) provided increased elevated temperature strength retentions with some sacrifice in peel strength.
- Increasing the concentration of toughener C (Kraton 1111) from 18 to 23 percent (Compositions 68 and 72) essentially produced no change in lap shear strength retention at 193°C (200°F), while the peel strength was increased dramatically.
- Toughener D (Acryloid KM611) (Composition 69) appears to give the best balance of lap shear strength retention at elevated temperature with some benefit to peel strength. It essentially

lost none of its 93°C (200°F) lap shear strength after 14-day water boil exposure.

Figure 8 provides the DTUL curves of the Table 9 compositions. All of the curves suggest mechanical performance to temperatures above 121°C (250°F). Softening occurred in the systems at 149°C (300°F) and reduced lap shear strengths obtained were expected.

Questions about the ultimate toughenability of the Diacryl 101 (TBS system) with commercially available tougheners arise naturally from two directions.

- First, commercially available tougheners have not been tailored for use with TBS (ABA blocks should contain TBS for the A portions of the ABA blocks).
- Second, all of the resin castings are at best only translucent, suggesting absence of large rubber particle formation. Degree of toughening\* from optimum toughened systems (bimodal) should be far more than the three times observed in Table 9).

We then undertook testing the adhesive strengths of the toughened Diacryl 101 copolymerized with monomers other than TBS. Used in this study were methyl methacrylate, styrene, and acrylonitrile, with TBS as the control. As expected, a number of tougheners which were compatible with the Diacryl 101/TBS system were incompatible with Diacryl 101 blends with other monomers. Lap shear and bell peel data for these systems are given in Table 10. Composition 81 provided an opaque casting, suggesting large

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\*Peel strength of rubber-toughened blend divided by peel strength of unmodified resin.

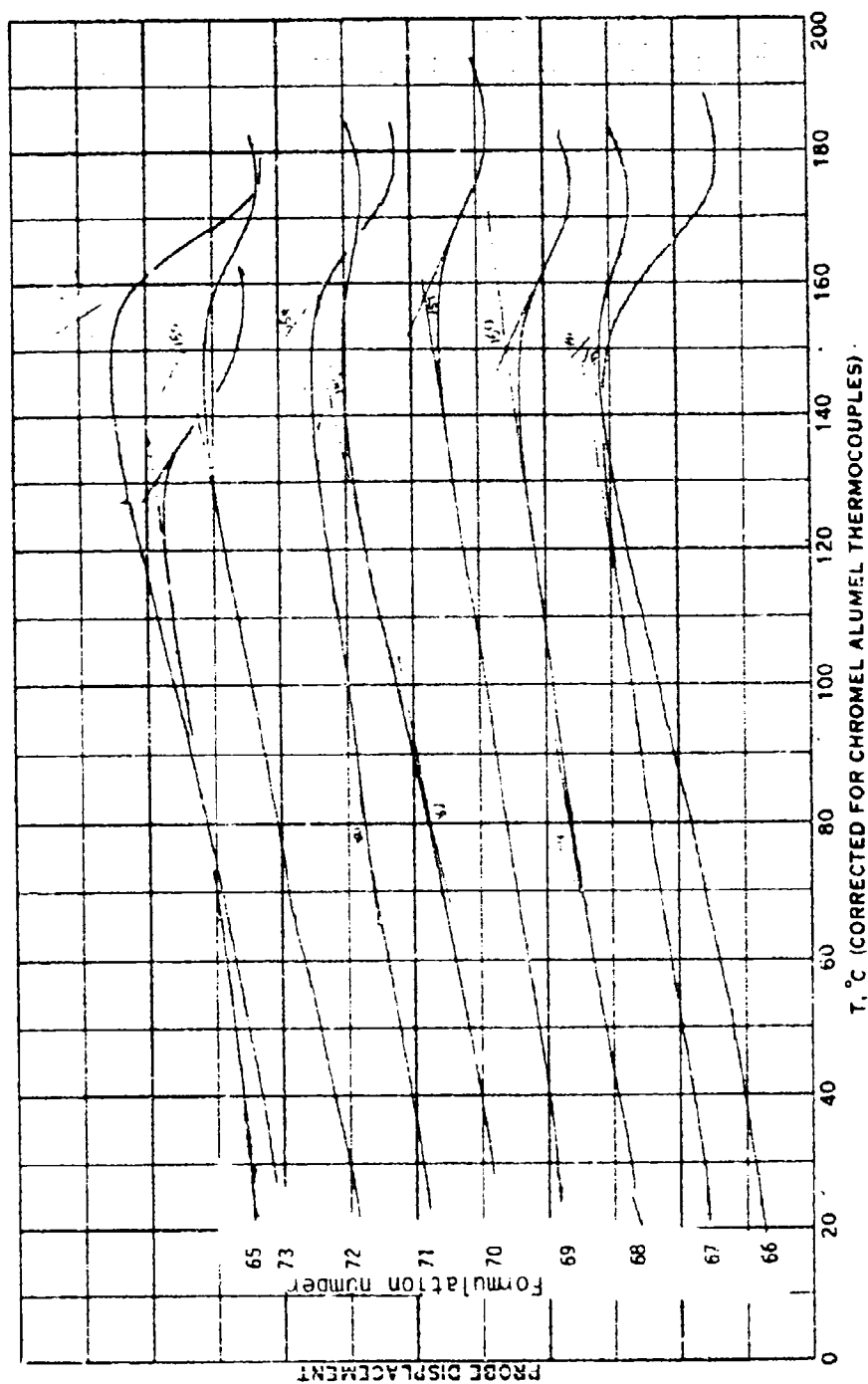


Figure 8. DTUL's of Table 9 Resin Systems

TABLE 10. ADHESIVE STRENGTHS OF DIACRYL 101 WITH ALTERNATE COMONOMERS AND SELECTED TOUGHENERS<sup>a</sup>

| Composition Number | Resin Composition, <sup>b</sup><br>Percent by Weight |                     |         |               | Additives, phr |              | Hardnesses of 7g Castings |                |        | Casting Appearance | Lap Shear Strength, MPa (psi) |                      |              |                       | Room Temperature Bell Peel Strength, kN/m (psi) |           |          |           |
|--------------------|--|---------------------|---------|---------------|----------------|--------------|---------------------------|----------------|--------|--------------------|-------------------------------|----------------------|--------------|-----------------------|---|-----------|----------|-----------|
|                    | Diacryl 101  | Methyl Methacrylate | Styrene | Acrylonitrile | t-Butylstyrene | Kraton S1550 | Acryloid K6611            | V501-1000 x 33 | L-2001 |                    | Test Temperature              |                      |              |                       |   |           |          |           |
|                    |  |                     |         |               |                |              |                           |                |        |                    | Room Temperature g/d          | Room Temperature #2d | 93°C (200°F) |                       |   |           |          |           |
| 75                 | 81.9   | 18.1                | --      | --            | --             | --           | --                        | --             | --     | 46                 | 47                            | --                   | --           | White, translucent    | 9.8(1418)                                       | 9.0(1302) | 14(1969) | 0.6(3.6)  |
| 76                 | 81.9   | 18.1                | --      | --            | --             | --           | 18                        | 4              | --     | 38                 | 57 <sup>c</sup>               | --                   | --           | Brown, foamy surface  | 12(1802)  | 10(1479)  | 14(2010) | 1.6(9.1)  |
| 77                 | 69.3   | 30.7                | --      | --            | --             | --           | --                        | --             | --     | 44                 | 44                            | --                   | --           | White, translucent    | 9.0(1324)                                       | 9.2(1340) | 12(1695) | 0.6(3.4)  |
| 78                 | 69.3   | 30.7                | --      | --            | --             | 22           | --                        | --             | --     | -----              | Incompatible Blend            | --                   | --           | White, translucent    | 9.0(1324)                                       | 9.2(1340) | 12(1695) | 0.6(3.4)  |
| 79                 | 69.3   | 30.7                | --      | --            | --             | 11           | --                        | --             | 11     | -----              | Incompatible Blend            | --                   | --           | White, translucent    | 9.0(1324)                                       | 9.2(1340) | 12(1695) | 0.6(3.4)  |
| 80                 | 81.3   | 18.7                | --      | --            | --             | --           | --                        | --             | --     | 45                 | 45                            | --                   | --           | White, translucent    | 9.6(1398)                                       | 9.1(1313) | 14(2031) | 1.0(5.5)  |
| 81                 | 81.3   | 18.7                | --      | --            | --             | --           | 18                        | 4              | --     | 25                 | 34                            | --                   | --           | Tan, opaque           | 21(3112)  | 19(2789)  | 20(2959) | 2.7(15.2) |
| 82                 | 68.5   | 31.5                | --      | --            | --             | --           | --                        | --             | --     | 46                 | 44                            | --                   | --           | White, translucent    | 9.9(1433)                                       | 8.3(1206) | 15(2143) | 0.6(3.7)  |
| 83                 | 68.5   | 31.5                | --      | --            | --             | 22           | --                        | --             | --     | -----              | Incompatible Blend            | --                   | --           | Blend                 | 9.9(1433)                                       | 8.3(1206) | 15(2143) | 0.6(3.7)  |
| 84                 | 68.5   | 31.5                | --      | --            | --             | 11           | --                        | --             | 11     | --                 | --                            | 78                   | 57           | Very white, opaque    | 16(2368)  | 14(2042)  | 12(1763) | 1.8(10.4) |
| 85                 | 89.5   | --                  | --      | 10.5          | --             | --           | --                        | --             | --     | 46                 | 46                            | --                   | --           | Lf. brown, translu.   | 13(1959)  | 9.9(1443) | 13(1949) | 0.6(3.2)  |
| 86                 | 89.5   | --                  | --      | 10.5          | --             | --           | 18                        | 4              | --     | --                 | 39                            | 20 <sup>c</sup>      | --           | Brown, foamy surface  | 11(1542)  | 11(1614)  | 13(1847) | 0.8(4.5)  |
| 87                 | 81.0   | --                  | --      | 19.0          | --             | --           | --                        | --             | --     | 49                 | 45                            | --                   | --           | Ok. Brown, translu.   | 11(1663)  | 9.9(1429) | 14(2061) | 0.4(2.5)  |
| 88                 | 81.0   | --                  | --      | 19.0          | --             | 22           | --                        | --             | --     | -----              | Incompatible Blend            | --                   | --           | White, translucent    | 16(2278)  | 15(2183)  | 18(2634) | 1.2(6.7)  |
| 89                 | 81.0   | --                  | --      | 19.0          | --             | 11           | --                        | --             | 11     | -----              | Incompatible Blend            | --                   | --           | White, translucent    | 8.0(1156)                                       | 3.6(536)  | 12(1732) | 0.4(2.2)  |
| 90                 | 73.8   | --                  | --      | --            | 26.2           | --           | 18                        | 4              | --     | 26                 | 27                            | --                   | --           | White, translucent    | 18(2594)  | 17(2485)  | 12(1742) | 1.8(11.0) |
| 91                 | 58.5   | --                  | --      | --            | 41.5           | --           | --                        | --             | --     | 34                 | 16                            | --                   | --           | White, translucent    | 16(2263)  | 13(1947)  | 15(2240) | 1.5(8.3)  |
| 92                 | 58.5   | --                  | --      | --            | 41.5           | 22           | --                        | --             | --     | --                 | 75                            | 66                   | --           | Very white, opaque    | 12(1729)  | 12(1684)  | 16(2309) | 0.9(5.3)  |
| 93                 | 58.5   | --                  | --      | --            | 41.5           | 11           | --                        | --             | 11     | --                 | --                            | 70                   | 64           | Solid, very light tan | 16(2263)  | 13(1947)  | 15(2240) | 1.5(8.3)  |
| 94                 | 73.8   | --                  | --      | --            | 26.2           | --           | 9                         | 4              | 9      | --                 | --                            | 35                   | 74           | Solid, very light tan | 16(2263)  | 13(1947)  | 15(2240) | 1.5(8.3)  |

<sup>a</sup>Adhesives cured with 0.5 phr t-butylperbenzoate and 0.75 phr cumene hydroperoxide through 150°C. Cure 2024 T3 phos anodized adherends.  
<sup>b</sup>Comprimed, 1619 scrim  
<sup>c</sup>Comonomer percentages are equivalent to 1-to-1 and 1-to-2 vinyl equivalent ratios  
<sup>d</sup>Coated top surface  
<sup>e</sup>Single specimen data, two tests



rubber particle formation, and gave the highest lap shear strengths of all the compositions tested.

The untoughened Diacryl 101 comonomer compositions (75, 77, 80, 82, 85, 87, and 91) provided nominal lap shear strengths at room temperatures of ~10 MPa (~1,500 psi) and appear to give higher strengths at 93°C (200°F).

Compositions 76, 81, 86, and 90 contain 18 percent of the Acryloid KM611 and 4 percent of the 1,300 x 23 VTBN. When methyl methacrylate was used as the comonomer with the Diacryl 101, no significant toughening benefit was observed with these tougheners (Composition 76 compared to Compositions 75 and 77). It is possible that rubber phase-out did not occur in this composition, since the KM611 is an acrylic and would be expected to be compatible. Significant toughening, however, occurred with Composition 81 when styrene was used as the comonomer. Slight improvement in toughness was observed with acrylonitrile as the comonomer (Composition 86) and good improvement occurred with TBS as the comonomer (Composition 90). Of note with this toughener combination (Acryloid KM611 and VTBN) is the retention of Barcol hardnesses compared to the loss of hardness obtained with other tougheners.

Bell peel strengths ranged from 0.4 kN/m (2.2 PIW) to 2.7 kN/m (15.2 PIW), as shown in Table 10. Composition 81 provided the highest value and the highest lap shear strengths of the Table 10 compositions: 21 MPa (3,110 psi) at RT and 20 MPa (2,960 psi) at 93°C (200°F).

Further observations for the bell peel data are as follows:

- The untoughened blends (Compositions 75, 77, 80, 82, 85, 87, and 91) all produced low levels of peel strength (less than 0.8 kN/m (5.0 PIW))

- The compositions containing 18-phr Acryloid KM611 and 4-phr VTBN produced threefold increases in peel strength over other respective control compositions with methyl methacrylate, styrene, and TBS as comonomers with the Diacryl 101 (Compositions 76, 81, and 90). Composition 86 with acrylonitrile as the comonomer did not show benefit to peel strength over its control composition.
- The compositions containing 11-phr Kraton G1650 and 11-phr powdered polyurethane (LPU 2001) produced threefold increases in peel strength with styrene and TBS as comonomers with the Diacryl 101 (Compositions 84 and 93). With methyl methacrylate and acrylonitrile as comonomers, incompatible blends were obtained and no peel data possible.
- The Kraton G1650 (Composition 92) produced a fivefold increase in peel strength in the TBS/Diacryl blend.

The results of bell peel testing suggested the following:

- Investigation of Diacryl blends using other available Acryloids for peel strength benefit.
- Use of Kraton G1650 for peel strength benefit if compatible adhesive compositions can be developed for its use. It should be compatible with styrene, for instance, with which it was found to be incompatible at 22 phr (Composition 83).

A relationship between the previously reported room temperature lap shear strengths and the bell peel strengths exists. This relationship is given in Figure 9. Of further note are the Barcol hardness measurements on the companion castings. Compositions 84, 92, and 93 had zero Barcol hardness (and would be expected to be tougher). Compositions 76, 81, and 90 all have

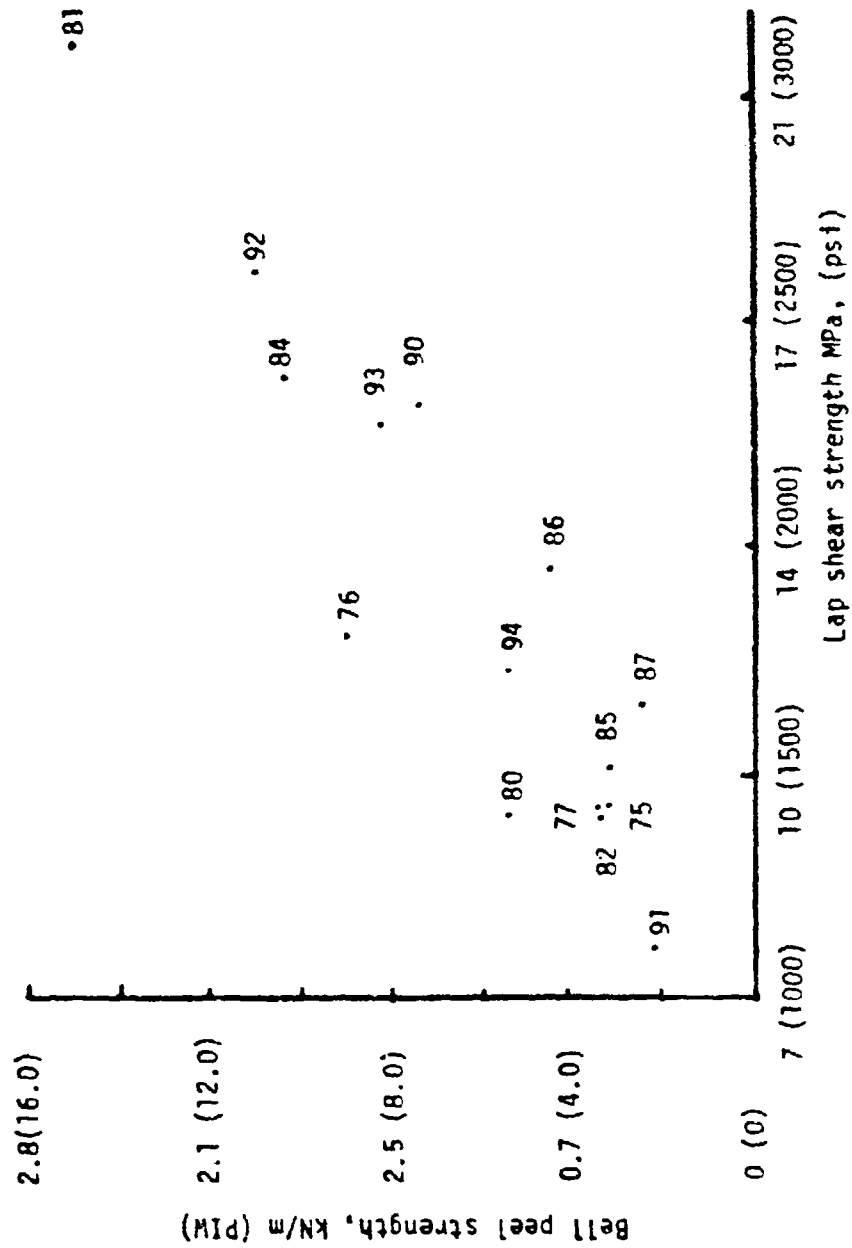


Figure 9. Relationship Between Room Temperature Lap Shear and Bell Peel Strengths of Table 10 Compositions

Barcol hardnesses above 20. The first three compositions contained the Kraton G1650 and the latter three, the Acryloid KM611 with VTRN.

### 2.3.2 Optimization of Acryloid Tougheners for Diacryl 101

#### Summary

Three additional Acryloid tougheners were investigated in Diacryl/styrene blends. Acryloid KM653 phases out upon cure, much like CTBN-toughened amine-cured epoxy resins, to give white, opaque castings. Like the Acryloid KM611, Barcol hardness values were obtained on the cured castings containing the KM653.

Formulating efforts to demonstrate the effect of the Diacryl/styrene system's linearity on crazing, however, resulted in obtaining reduced lap shear strengths. This prompted investigation of adhesive strength versus adhesive preparation method, e.g., milled versus unmilled.

Due to its good adhesive properties, Composition 81 (Table 10), containing Diacryl, styrene, KM611, and VTRN, was selected for investigating process parameters. The study showed Composition 81 was not stable to aging, probably because of dissolution of the KM611 Acryloid (with time), and is therefore not suitable for use in aerospace adhesives.

This disappointing result led to investigation of Kratons and Solprenees for toughening the Diacryl 101 adhesive. These results are described in Section 2.3.3.

#### Detailed Investigations

Further formulation efforts around the Table 10 Composition 81 were carried out with three additional Acryloid block copolymers, KM653, KM330, and KM323R. Results of this lap shear study are given in Table 11. All failures were cohesive. Formulary items investigated for the styrene/Diacryl blends with the KM611 toughener included use of high molecular-weight

TABLE 11. ADHESIVE STRENGTHS OF DIACRYL 101 WITH STYRENE AND ACRYLOIN TOUGHENERS<sup>a</sup>

| Composition No. | Resin Composition, parts by weight |         |             |        |        |        |         |                |                     |                       | Barcol Hardness<br>of 7g Casting | Lap Shear Strength, MPa (psi) |                            |
|-----------------|------------------------------------|---------|-------------|--------|--------|--------|---------|----------------|---------------------|-----------------------|----------------------------------|-------------------------------|----------------------------|
|                 |                                    |         |             |        |        |        |         |                |                     |                       |                                  | Test Temperature              |                            |
|                 |                                    |         |             |        |        |        |         |                |                     |                       |                                  | Room Temp. #1 <sup>e</sup>    | Room Temp. #2 <sup>e</sup> |
|                 | Diacryl                            | Styrene | Polystyrene | KM 611 | KM 653 | KM 330 | KM 323B | VTBN 1300 x 23 | t-Butylper-berzoate | Cumene hy-droperoxide |                                  |                               |                            |
| 95              | 81.3                               | 18.7    | 2           | 18     |        |        |         | 4              | 0.5                 | 0.75                  | 26                               | 16(2390)                      | 16(2290) 13(1860)          |
| 96              | 81.3                               | 18.7    | 2           |        | 18     |        |         | 4              | 0.5                 | 0.75                  | 22                               | 19(2710)                      | 12(1750) 13(1890)          |
| 97              | 81.3                               | 18.7    | 2           |        |        | 18     |         | 4              | 0.5                 | 0.75                  | 10                               | 20(2960)                      | 19(2800) 15(2130)          |
| 98              | 81.3                               | 18.7    | 2           |        |        |        | 18      | 4              | 0.5                 | 0.75                  | 0                                | 21(3000)                      | 16(2250) 16(2270)          |
| 99              | 81.3                               | 12.5    | 7.6         | 18     |        |        |         | 4              | 0.5                 | 0.75                  | b                                | 16(2360) <sup>c</sup>         | 16(2250) 14(1970)          |
| 100             | 81.3                               | 6.2     | 13.1        | 18     |        |        |         | 4              | 0.5                 | 0.75                  | b                                | 13(1930) <sup>c</sup>         | 12(1700) 11(1530)          |
| 101             | 81.3                               | 0       | 18.7        | 18     |        |        |         | 4              | 0.5                 | 0.75                  | b                                | 9(1350) <sup>d</sup>          | 9(1330) 8(1220)            |
| 102             | 81.3                               | 18.7    | 2           | 18     |        |        |         | 2              | 0.5                 | 0.75                  | 28                               | 18(2550)                      | 17(2500) 13(1890)          |
| 103             | 81.3                               | 18.7    | 2           | 18     |        |        |         | 3              | 0.5                 | 0.75                  | 32                               | 16(2360)                      | 14(2100) 13(1920)          |
| 104             | 81.3                               | 18.7    | 2           | 18     |        |        |         | 5              | 0.5                 | 0.75                  | 25                               | 18(2660)                      | 8(1220) 14(2010)           |
| 105             | 81.3                               | 18.7    | 2           | 14     |        |        |         | 4              | 0.5                 | 0.75                  | 25                               | 18(2680)                      | 14(2020) 15(2150)          |
| 106             | 81.3                               | 18.7    | 2           | 22     |        |        |         | 4              | 0.5                 | 0.75                  | 26                               | 21(3110)                      | 19(2700) 13(1940)          |
| 107             | 75                                 | 25      | 2           | 18     |        |        |         | 4              | 0.5                 | 0.75                  | 29                               | 21(2990)                      | 20(2960) 14(1990)          |
| 108             | 70                                 | 30      | 2           | 18     |        |        |         | 4              | 0.5                 | 0.75                  | 22                               | 21(3060)                      | 18(2650) 13(1820)          |

<sup>a</sup>Bara 2024-T3 phos anodized adherends unprimed, 1659 scr/m, cured through 150°C

<sup>b</sup>Casting foamed upon cure

<sup>c</sup>10 percent void in bondline

<sup>d</sup>30 percent void in bondline

<sup>e</sup>Single specimen data, two tests

polystyrene for possible benefit to crazing, varying amounts of VTBN, higher total rubber content, and increased quantities of styrene monomer. Polystyrene was used to thicken all compositions instead of the previously employed Cab-O-Sil.

Appearance of Compositions 95 through 98, containing the four Acryloids before and after cure, were as follows:

- KM611                      Initially translucent and very little change with cure
- KM653                      Initially nearly clear and turned opaque (white) with cure
- KM330 and 323B           Both compositions were opaque (white) upon makeup and very little change occurred with cure

Composition 95 was the control formulation and was intended to be identical to the previously discussed Composition 81. As seen in Table 11, lap shear strengths of Composition 95 were less than Composition 81, which provided 21 MPa (3,110 psi) at room temperature and 20 MPa (2,960 psi) at 93°C (200°F). We suspected the strength differences in the two compositions were principally due to preparation method. Table 10 compositions, including Number 81, were three-roll-milled, whereas Table 11 compositions were stirred together. Three-roll-milling provides milling benefit but at some expense to compositional accuracy since a small percentage of rubber is lost. Other correlations of the Table 11 data are given below.

- Compositions 96 through 98 showed lap shear strength increases over the strength obtained with the Composition 95 control

- Use of large quantities of polystyrene with the Diacryl appears counterproductive, as shown with Compositions 99 through 101. A firm assessment cannot be made due to the foamed nature of the bondlines. Compatibility was achieved by dissolution of the blend ingredients in Freon 11 (bp 23.7°C) and subsequent removal of the Freon under vacuum at room temperature. Foaming was due to incomplete removal of the Freon prior to cure.
- Varying the amounts of the VTBN used may provide strength benefit. Composition 102 with 2-phr VTBN showed strength benefit over the control composition strength.
- Increasing the total rubber content of the system appears to benefit lap shear strength, as shown with Composition 106.
- Use of a higher quantity of styrene is indicated with Compositions 107 and 108, compared to Composition 95.

Percent lap shear strength retention of the compositions at 93°C (200°F), although good, is not as high as those previously obtained with the Table 10 compositions. This may be related to the cited differences in preparation: three-roll-milling versus stirring.

The next formulation effort attempted to demonstrate the effect of linearity (reduced crosslink density) on the Diacryl 101 adhesive system strength. Several percentages of styrene and methyl methacrylate were blended with the Diacryl 101 monomer, the two Acryloids added, and casting and adhesive properties of these blends measured. All blends were then three-roll-milled, as occurred with Composition 81.

The results of this study (Compositions 121 through 157) are given in Table 12. Lap shear strength and peel strengths are lower than the Table 10 compositions. The KM653-toughened Diacryl blends did not show improved

TABLE 12. CASTING HARDNESS AND ADHESIVE PROPERTIES OF ACRYLOID-TOUGHENED DIACRYL 101/COMONOMER BLENDS<sup>a,b</sup>

| Weight Percent Diacryl in Resin Portion | With KM 611 (24 phr) |                         |                         |  | With KM 653 (24 phr)                   |                                  |                                  |                                  |
|---|----------------------|-------------------------|-------------------------|--|--|----------------------------------|----------------------------------|----------------------------------|
|   | Monomer System       |                         |                         |  | Monomer System                         |                                  |                                  |                                  |
|   | Styrene              | 83.3% Styrene 16.7% MMA | 66.7% Styrene 33.3% MMA | Styrene                                | 83.3% Styrene 16.7% MMA                | 66.7% Styrene 33.3% MMA          | Styrene                          | 83.3% Styrene 16.7% MMA          |
| 0                                       | Crumb                | Crumb                   | Crumb                   | 0(630)/1.5(220)/1.9(11.0) <sup>e</sup> | 0(670)/2.3(340)/2.0(11.5) <sup>e</sup> | --                               | --                               | --                               |
| 33                                      | 4/0.5(70)/0.4(2)     | --                      | --                      | 4/9.2(1340)/0(0)                       | --                                     | --                               | --                               | --                               |
| 50                                      | 18/7.5(310)/0.4(2)   | 24/4.2(610)/0(0)        | 27/11.2(1620)/0(0)      | 19/7.0(1010)/0(0)                      | d/7.4(1080)/0.2(1)                     | 10/9.7(1400)/0.4(2) <sup>e</sup> | 10/9.7(1400)/0.4(2) <sup>e</sup> | 10/9.7(1400)/0.4(2) <sup>e</sup> |
| 67                                      | d/9.7(1400)/0.4(2)   | 27/4.3(620)/0.2(1)      | 28/10.3(1490)/0.4(2)    | 22/7.9(1150)/0(0)                      | d/5.0(720)/0.5(3)                      | 20/8.0(1160)/0(0) <sup>e</sup>   | 20/8.0(1160)/0(0) <sup>e</sup>   | 20/8.0(1160)/0(0) <sup>e</sup>   |
| 80                                      | 31/10.9(1580)/0.4(2) | 29/1.1(160)/0.4(2)      | 32/8.3(1200)/0.4(2)     | 24/8.8(1280)/0(0)                      | 10/8.8(1276)/0(0)                      | 30/6.6(960)/0(0)                 | 30/6.6(960)/0(0)                 | 30/6.6(960)/0(0)                 |
| 89                                      | 34/15.6(2260)/0.4(2) | --                      | --                      | 29/8.1(1180)/0.2(1)                    | --                                     | --                               | --                               | --                               |
| 100                                     | 28/7.8(1130)/0.2(1)  | 28/7.8(1130)/0.2(1)     | 28/7.8(1130)/0.2(1)     | 32/3.4(490)/0(0)                       | 32/3.4(490)/0(0)                       | 32/3.4(490)/0(0)                 | 32/3.4(490)/0(0)                 | 32/3.4(490)/0(0)                 |
| With Varying Rubber Contents            |                      |                         |                         |  |  |                                  |                                  |                                  |
| AS Above                                | KM 611 (24 phr)      | KM 611 (28 phr)         | KM 611 (32 phr)         | KM 653 (24 phr)                        | KM 653 (28 phr)                        | KM 653 (32 phr)                  |                                  |                                  |
| 80                                      | 31/7.5(1580)/0.4(2)  | 27                      | 27                      | 24/6.8(1280)/0(0)                      | 22/11.1(1620)/0(0)                     | 18/11.5(1670)/0(0)               |                                  |                                  |

<sup>a</sup>Barcol hardness (Shore D)/Lap shear strength, MPa (psi)/aluminum foil 1HCO peel KH/m (P/M) by formulation: 100 parts indicated blend with 24 to 32 phr Acryloid, 2 phr V16N (1300 x 23), 0.5 phr t-butyl perbenzoate, 0.75 phr cumene hydroperoxide and 3.0 phr cab-o-sil MS  
<sup>b</sup>Acryloid dissolved in the resin and produced an intractable system  
<sup>c</sup>Sample foamed  
<sup>d</sup>Peel adherend crazed under stressing



strengths over the KM611 system, even though the systems turned white upon cure, indicating larger rubber particle formation.

Compared to previously obtained good adhesive strengths, the reduced strengths obtained from the study indicate that resin blend preparation was the key to how the good adhesive properties of Composition 81 were obtained. Milling time, mill settings, temperature, order of ingredient addition, and similar process variables appear to be controlling the rubber particle size(s) obtained in the blends and subsequent susceptibility to crazing. Formulation efforts to address these items with Composition 81 are discussed below.

Even though the adhesive strengths shown in Table 12 are not optimum, some correlations appear to exist.

- The Acryloid KM611 provides better peel strength than the KM653
- The addition of linear comonomers to the Diacryl 101 does not appear to significantly influence adhesive strengths between 50 and 90 weight percent

Results of varying the preparation methods of Composition 81 are given in Table 13. The principal focus of this study was to demonstrate that the variation in lap shear of Composition 81 was due to its processing. This in fact proved to be the case, as the results in Table 13 indicate.

Unfortunately, the study indicates that aging or heating Composition 81 prior to bonding reduces lap shear strengths. Composition 179 (bonded immediately) had a lap shear strength of 18.7 MPa (2,715 psi), whereas Composition 178 (bonded 24 hours after preparation) had a lap shear strength of 14.6 MPa (2,115 psi).<sup>\*</sup> This behavior is unacceptable in aerospace

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<sup>\*</sup>Any attempt to increase the solubility of the KM611 (mill, heat, time) generally resulted in reduced adhesive strengths.

TABLE 13. THE INFLUENCE OF PROCESSING VARIABLES ON THE CASTING AND ADHESIVE PROPERTIES OF COMPOSITION 81

(Composition 81 - 81.3% Diacryl 101, 18.7% Styrene; 18 phr KM611, 4 phr VTBN 1300X23)

| Composition Number | Process Variable <sup>a</sup> Studied                | Casting Appearance         | Barcol Hardness (Bottom) | Average 180° Peel Strength on 3 Mil Aluminum Foil kN/m (lbf/in) | % Adhesive Failure in Peel Bonds | Average Room Temperature Lap Shear Strength MPa (psi) |
|--------------------|--|----------------------------|--------------------------|---|----------------------------------|---|
| 158                | Stir, let stand, stir, add styrene                   | Brown, translucent         | 29                       | 0.8 (4.6)   | 90                               | 15.2 (2203)   |
| 159                | Stir, heat 7 hr @ 60°C, add styrene                  | ↓                          | 28                       | 0.9 (5.2)   | 95                               | 15.3 (2225)   |
| 160                | Stir, let stand, stir, add Diacryl 101               | ↓                          | 25                       | 0.8 (4.6)   | 90                               | 17.4 (2528)   |
| 161                | Stir, heat 7 hr @ 60°C, add Diacryl 101 <sup>b</sup> | ↓                          |                          |   |                                  |   |
| 162                | Control, mix all ingredients @ room temperature      |                            | 25                       | 0.6 (3.3)   | 90                               | 17.0 (2468)   |
| 163                | Heat 7 hr @ 60°C                                     | Brown, clear — translucent | 27                       | 0.7 (4.0)   | 95                               | 14.4 (2093)   |
| 164                | Not milled   | Brown, translucent opaque  | 31                       | 1.0 (6.0)   | 85                               | 20.7 (3005)   |
| 165                | One pass on 3 roll mill                              | ↓                          | 28                       | 1.0 (5.6)   | 90                               | 17.6 (2555)   |
| 166                | 10 Passes on 3 roll mill                             | ↓                          |                          |   |                                  |   |
| 167                | Mill @ 60°C  | Brown, clear — translucent | 27                       | 0.7 (4.2)   | 90                               | 18.5 (2683)   |
| 168                | 8% of #158 plus 1% of #160                           | ↓                          | 31                       | 0.4 (2.5)   | 95                               | 15.2 (2203)   |
| 169                | #162 + 3 phr Cab-O-Sil before milling                | Tan, opaque                | Foam                     | 0.7 (3.9)   | 95                               | 19.1 (2776)   |
| 170                | #162 + 6 phr Cab-O-Sil before milling                | Brown, translucent opaque  | 27                       | 0.5 (3.1)   | 100                              | 18.3 (2650)   |
| 171                | #162 + 3 phr Cab-O-Sil after milling                 | Tan, cheesy, opaque        | 28                       | 0.2 (1.2)   | 100                              | 3.0 (436)   |
| 172                | #162 + 6 phr Cab-O-Sil after milling                 | Brown, translucent opaque  | 25                       | 0.2 (1.0)   | 100                              | 15.8 (2299)   |
| 173                | #162 Peel metal phosandized                          | Tan, cheesy, opaque        | 22                       | 0.2 (0.9)   | 100                              | 2.4 (350)   |
| 174                | #162 Vacuum degas                                    | Tan, translucent           | 24                       | 1.6 (9.3)   | 0                                | 18.1 (2630)   |
| 175                | #162 Add one percent H <sub>2</sub> O                | Brown, clear — translucent | 25                       | 0.7 (4.1)   | 95                               | 20.2 (2928)   |
| 176                | #162 Beat in air                                     | ↓                          | 28                       | 0.7 (4.1)   | 90                               | 16.0 (2328)   |
| 177                | #162 Metal not giving final water rinse              | Brown, translucent         | 27                       | 0.8 (5.0)   | 85                               | 15.9 (2303)   |
| 178                | #162 Let stand for 24 hours                          | ↓                          | 27                       | 0.0 (0.0)   | 100                              | 0.0 (0000)  |
| 179                | #162 Bond immediately                                | ↓                          | 25                       | 0.8 (5.0)   | 95                               | 14.6 (2115)   |
| 180                | #162 Heat @ 52°C overnight                           | ↓                          | 27                       | 0.7 (4.2)   | 90                               | 18.7 (2715)   |
|                    |  |                            | 28                       | 0.5 (2.8)   | 100                              | 15.8 (2288)   |

<sup>a</sup> All compositions cured with 0.5 phr t-butylperbenzoate and 0.75 phr cumene hydroperoxide through 150°C and subjected to three passes on a 3 roll mill unless stated otherwise

<sup>b</sup> Lost 10 percent of weight, which is most of the styrene, bonds not made

<sup>c</sup> Lost 6 percent weight

<sup>d</sup> No stress whitening induced in casting flash

<sup>e</sup> IFT etched, unprimed, 1659 glass scrim

<sup>f</sup> Bare 20/4 IJ phosandized adherends, unprimed, 1659 glass scrim, N<sub>2</sub> bagged, four specimens

adhesives and use of other block copolymers to toughen the Diacryl 101 system is clearly indicated. Other lap shear data presented in Table 13 support this conclusion. For instance, Composition 164, with a lap shear strength of 20.7 MPa (3,005 psi), was unmilled and had a significantly higher lap shear strength than milled compositions (162, 165, and 166).

Other conclusions from the study include:

- The two controls did not give the same lap shear strength, indicating that not all of the variables were included in the study (Composition 162 versus 173)
- Degassing benefits the composition (Composition 174)
- The adhesive gives only cohesive failures to phos anodized aluminum (all lap shear bonds) but gives adhesive failure to FPL etch (peel bonds). The single phos anodized peel bond gave cohesive failure and the highest peel strength (Composition 173).

Prior to obtaining the test results in the processing study, another study was conducted to show what effects the use of two ABA block copolymers has on the crazability of the system. Fifty percent of the Acryloid KM611 was removed from Composition 81 and replaced with an equivalent weight of a series of ABA block copolymers. The results of this study are given in Table 14 and the ABA block copolymers added are indicated in the table. The specific effect sought was permanent crazing upon failure of the neat resin, as occurs with FM-73 and Versilok 201. Lap shear data were also obtained on the compositions.

Flash from all of the resin castings crazed with stressing but upon removal of the stress, the whitening disappeared.

TABLE 14. CASTING AND ADHESIVE PROPERTIES OF COMPOSITION 81 WITH ALTERNATE TOUGHENERS

| Composition Number   | Toughener indicated was used to replace 9 phr of KM611 in Composition 81 <sup>a</sup> | Note  | Cap-O-Sil (phr) | Milling | Roll Mill Passes | Casting Appearance <sup>f</sup> | Barcol Hardness (Bottom) | Average Room Temperature Lap Shear Strength MPa (psi) <sup>j</sup> |
|--|---|-------|-----------------|---------|------------------|---------------------------------|--------------------------|--|
| 181 Control - 18 phr KM611                                 |   | e     | No              | No      | No               | Translucent                     | 29                       | 19.3 (2805)  |
| 182 Acryloid KM653 - MBS block                             |   | b     | 1.8             | Yes     | Yes              | opaque                          | 26                       | 17.8 (2575)  |
| 183 Acryloid KM330   |   | b,c   | No              | Yes     | Yes              | Opaque                          | 19                       | 18.6 (2693)  |
| 184 Solprene 414 - radial butadiene/styrene                |   | e,f   | 0.4             | Yes     | Yes              | clear, translucent              | 22                       | 18.3 (2650)  |
| 185 Solprene 416S - radial isoprene/styrene                |   | e     | 0.4             | Yes     | Yes              | Translucent                     | 17                       | 16.8 (2440)  |
| 186 Kraton 1650G - styrene/ethylene/butylene/e,f,g styrene |   | e,f,g | 0.4             | Yes     | Yes              | Translucent,                    | 14                       | 14.6 (2113)  |
| 187 Kraton 1111 - styrene/isoprene/styrene                 |   | e,f,h | 0.2             | Yes     | Yes              | Translucent                     | 19                       | 16.9 (2445)  |
| 188 Blendex 435  |   | b,c,d | No              | Yes     | Yes              | clear, translucent              | 21                       | 20.0 (2905)  |

<sup>a</sup>Composition 81 - 81.3 percent Diacryl 101, 18.7 percent styrene, 18 phr KM611 4 phr VTBN 1300x23. All compositions cured with 0.5 phr t-butylperbenzoate and 0.75 phr cumene hydroperoxide through 150°C

<sup>b</sup>Particles did not phase out, suspension at room temperature

<sup>c</sup>Particles did not phase out, suspension at room temperature - after 1/2 hour at 60°C before milling

<sup>d</sup>Almost completely soluble before milling

<sup>e</sup>Phase out of the added toughener to the KM611 system before milling at room temperature and 60°C

<sup>f</sup>Not homogeneous after milling

<sup>g</sup>Lost approximately 20 percent of rubber during milling

<sup>h</sup>Lost approximately 4 percent of rubber during milling

<sup>i</sup>Stress whitening induced in the casting flash of every composition, all compositions were brittle

<sup>j</sup>Bare Al 2024 T3 phos-anodized adherends, unprimed, 1659 glass scrim, N<sub>2</sub> atmosphere, four specimens

### 2.3.3 Investigation of Kraton and Solprene Tougheners for Diacryl 101

#### Summary

Initial focus of the efforts was identification of commercially available ABA block copolymers which would give a stable, clear, homogeneous blend with styrene and Diacryl 101. Further high matrix linearity through use of only small quantities of Diacryl 101 was investigated for increasing the bell peel strength of the adhesive.

Excellent bell peel strengths were obtained using this approach and bell peel strength retention at -54°C (-65°F) was remarkable. Lap shear strengths, however, were not as high as those obtained with the Acryloid KM611 and a good balance between lap shear strength, bell peel strength, and DTUL was needed. Use of t-butylstyrene, higher concentrations of Diacryl 101, and lower concentrations of block copolymers all produce increases in the DTUL and lap shear strength, with reduction in the bell peel strength.

The final adhesive compositions investigated included use of higher Diacryl 101 and reduced styrene concentrations. These compositions all had DTUL's in excess of 100°C (212°F), and some were as high as 150°C (302°F). Room temperature lap shear as high as 23 MPa (3,300 psi) were obtained with Solprene ABA radial block copolymers. Elevated temperature adhesive strength tests provided 93°C (200°F) strengths up to 17 MPa (2,500 psi).

The variation in fracture modes of the numerous resin castings when penetrated by a nail was striking. Fracture modes varied from shattering into several pieces, penetration without fracture (usually with stress whitening), to nonpenetration (even after several attempts). No correlation to adhesive properties could be made from fracture of the resin castings.

Final adhesive formulation efforts are described in Section 2.3.4.

### Detailed Investigations

The ABA block copolymers described in Table 5 were tested for compatibility with styrene monomer. These results are presented in Table 15. (Compatibility tests were reported for these copolymers with Diacryl, Epocryl, methyl methacrylate, t-butylstyrene, and t-butylstyrene resin blends in Table 6). Most of the Kratons (Phillips) and Solprenes (Shell) which are suggested for toughening polystyrene were found to be soluble in the styrene monomer. This result parallels the previously reported results for the t-butylstyrene monomer. The results of tests with styrene are given in Column 5 of Table 15.

A portion of the ABA block copolymer/styrene compositions were diluted with Diacryl 101 to give 50/50 styrene/Diacryl 101 blends. Both the styrene and styrene/Diacryl 101 blends were cured into castings and qualitative assessment of the cured castings carried out. The obvious toughness of the Kraton and Solprene/100-percent polystyrene castings and permanence of crazing upon failure (failed surfaces remained white) was in marked contrast to brittleness of the castings reported on in previous sections. The styrene/Diacryl 101 castings indicated in Table 15 had only one-half of the rubber content of the 100-percent styrene castings.

Several Kraton and Solprene/styrene blends were selected for further investigation. The compositions investigated and properties of the cured castings are indicated in Table 16. Diacryl 101 was used in these compositions at relatively low levels (up to 10 percent). All of the castings had approximately the same hardness (Shore D 56 to 59). DTUL measurements showed that softening occurred in most of the compositions at about 80°C (176°F). A few measurements showed that anomalies and lower DTUL's were observed. Due to the high rubber content of the samples, reduced DTUL's were expected.

TABLE 15. COMPATIBILITY OF COMMERCIALY AVAILABLE BLOCK COPOLYMERS WITH STYRENE AND STYRENE/DIACRYL 101a

| Composition Number | Rubber Type  | Copolymer Content in Resin Percent | Handleability of Copolymer in Styrene Monomer | Properties of Cured Resin Blend |                         |                       |                               | Properties of Cured 50/50 Mix of Diacryl and Resin |                         |                       |                               |
|--------------------|--------------|------------------------------------|---|---------------------------------|-------------------------|-----------------------|-------------------------------|--|-------------------------|-----------------------|-------------------------------|
|                    |              |                                    |   | Homo- geneity <sup>b</sup>      | Appearance <sup>c</sup> | Qualita- tively Tough | Stress Whitening <sup>d</sup> | Homo- geneity <sup>b</sup>                         | Appearance <sup>c</sup> | Qualita- tively Tough | Stress Whitening <sup>d</sup> |
| 190                | Acrylnid     | 11                                 | Paste   | 2                               | --                      | No                    | --                            | 1  | 3                       | No                    | --                            |
| 191                | KM23         | 12                                 | Partially sol.                                | Two phases                      | --                      |                       | --                            | 3  | --                      |                       | --                            |
| 192                | KM30         | 29                                 | Waxy  | 2                               | 9                       |                       | T                             | Two phases   | --                      |                       | T                             |
| 193                | KM51         | 12                                 | Clear liquid                                  | 1                               | 6                       |                       | --                            | 2  | --                      |                       | --                            |
| 194                | Blendex      | 29                                 | Paste   | 1                               | 6                       |                       | P                             | Two phases   | --                      |                       | --                            |
| 195                |              | 25                                 | Waxy  | 2                               | 8                       |                       | --                            | 3  | --                      |                       | --                            |
| 196                |              | 27                                 | Crumb   | 2                               | 8                       |                       | --                            | 2  | --                      |                       | --                            |
| 197                |              | 12                                 | Clear paste                                   | 1                               | 4                       |                       | --                            | 1  | 3                       |                       | --                            |
| 198                | BTa          | 31                                 | Clear paste                                   | 2                               | 7                       |                       | T                             | 2  | --                      |                       | --                            |
| 199                | Durastrength | 17                                 | Paste   | Two phases                      | --                      |                       | --                            | Two phases   | --                      |                       | --                            |
| 200                | Kraton       | 27                                 | Hazy liquid                                   | 1                               | 3                       | Yes                   | P                             | 2  | 4                       |                       | T                             |
| 201                |              | 24                                 | Clear liquid                                  | 1                               | 3                       | No                    | P                             | 2  | --                      |                       | T                             |
| 202                |              | 27                                 | Clear liquid                                  | 1                               | 3                       | Yes                   | P                             | 1  | 3                       |                       | --                            |
| 203                |              | 24                                 | Clear liquid                                  | 1                               | 3                       | Yes                   | P                             | 1  | 3                       |                       | --                            |
| 204                |              | 27                                 | Clear liquid                                  | 1                               | 9                       | Yes                   | P                             | 2  | --                      |                       | --                            |
| 205                |              | 29                                 | Clear liquid                                  | 1                               | 6                       | Yes                   | P                             | 2  | --                      |                       | --                            |
| 206                | Solprene     | 4115                               | Hazy liquid                                   | 1                               | 5                       | Yes                   | P                             | 2  | --                      |                       | --                            |
| 207                |              | 27                                 | Clear liquid                                  | 1                               | 4                       | Yes                   | P                             | 1  | 4                       |                       | T + P                         |
| 208                |              | 24                                 | Clear liquid                                  | 1                               | 6                       | No                    | P                             | 1  | 4                       |                       | T + P                         |
| 210                |              | 25                                 | Clear liquid                                  | 1                               | 3                       | Yes                   | P                             | 2  | --                      |                       | T + P                         |
| 211                | Butyl Rubber | 111                                | Partially sol.                                | 1                               | 8                       | (Elastic)             | --                            | Two phases   | --                      |                       | --                            |
| 212                | FEF          | 2101                               | Hazy paste                                    | 3                               | --                      | No                    | --                            | 2  | --                      |                       | --                            |
| 213                | Polyflon     | 190                                | Hazy paste                                    | 3                               | 11                      | No                    | --                            | 2  | --                      |                       | --                            |

<sup>a</sup>Compositions cured using 0.5 phr t-butylperoxide and 0.75 phr cumene hydroperoxide overnight at 90°C (1940F).

<sup>b</sup>1 = homogeneous; 2 = homogeneous with small quantity of lumps; 3 = homogeneous with some lumps.

<sup>c</sup>On a scale of 1 to 10, castings were rated for clarity: 1 = clear; 10 = nearly opaque and white.

<sup>d</sup>On flexing the flash from the castings temporary stress whitening could be induced, T, and in some instances permanent stress whitening occurred, P. Several castings had insufficient flash for testing in this manner.

TABLE 16. PROPERTIES FOR KRATON AND SOLPRENE ARA BLOCK COPOLYMERS IN STYRENE<sup>a,b</sup>

| Rubber Type | Composition Number | 1 Percent Diacryl and 72 Percent Styrene |           |                               |                        | 3 Percent Diacryl and 70 Percent Styrene |                  |           |                               | 10 Percent Diacryl and 63 Percent Styrene |                    |                  |           |                               |                        |       |
|-------------|--------------------|--|-----------|-------------------------------|------------------------|--|------------------|-----------|-------------------------------|---|--------------------|------------------|-----------|-------------------------------|------------------------|-------|
|             |                    | Shore D Hardness                         | DTUL (°C) | Stress Whitening <sup>c</sup> | Nail Test <sup>d</sup> | Composition Number                       | Shore D Hardness | DTUL (°C) | Stress Whitening <sup>c</sup> | Nail Test <sup>d</sup>                    | Composition Number | Shore D Hardness | DTUL (°C) | Stress Whitening <sup>c</sup> | Nail Test <sup>d</sup> |       |
| Kraton      | 1107               | 215                                      | 60        | 77                            | P                      | 5  | 224              | 63        | 63                            | T   | 5                  | 233              | 62        | 53                            | T                      | 4     |
|             | 1111               | 216                                      | 65        | 79                            | P                      | 6  | 225              | 64        | 77                            | P   | 6                  | 234              | 66        | 86                            | T                      | 1     |
| Solprene    | 4115               | 217                                      | 63        | 29                            | T                      | 1  | 226              | 62        | 75                            | T   | 4                  | 235              | 63        | 69                            | T                      | 1     |
|             | 4145               | 218                                      | 68        | 85                            | T                      | 7  | 227              | 68        | 79                            | T   | 6                  | 236              | 69        | 73                            | P                      | Mixed |
|             | 4165               | 219                                      | 64        | 65                            | T                      | 4  | 228              | 64        | 85                            | P   | 6                  | 237              | 60        | 28                            | P                      | 2     |
|             | 3125               | 228                                      | 56        |                               | T                      | —  | 229              | 57        |                               | T   | —                  | 238              | 56        | 77                            | T                      | 1     |
|             | 1205C              | 221                                      | 60        | 81                            | P                      | 5  | 230              | 61        | 47                            | T   | 3                  | 239              | 56        | 53                            | T                      | 1     |

<sup>a</sup>Compositions cured with 0.5 phr t-butylperbenzate + 0.75 phr cumene hydroperoxide.

<sup>b</sup>Copolymer content in all compositions.

<sup>a</sup>Compositions cured with 0.5 phr t-butylperbenzate + 0.75 phr cumene hydroperoxide overnight at 90°C (194°F).  
<sup>b</sup>Copolymer content in all compositions was 27 percent.  
<sup>c</sup>P = failed surfaces remained whitened, permanent stress whitening.  
<sup>d</sup>1 = stress whitening only under stress, temporary stress whitening.

2 = 1/4 in. crack on each side of nail occurred without stress whitening.  
3 = 1/8 in. crack on each side of nail occurred with a small amount of stress whitening.  
4 = through hole - minimum cracking and increasing area of stress whitening.  
5 = no cracking and -1/4 in. stress whitened area around nail.



It is not possible to drive a nail through castings from the majority of available structural thermoset resins without shattering the casting (or at least breaking the casting into two pieces). In distinct contrast to this behavior, all of the Table 16 compositions, when punctured by the -0.10-in. diameter nail, did not shatter or break into two pieces. Several showed permanent stress whitening. Some castings cracked with nail penetration, but the cracks did not propagate far in any of the castings (-1/4 in. from the nail). Crack propagation in Composition 236 was arrested by crazing (stress whitening) to give a mixed failure mode, as indicated in Table 16. The very ductile behavior of these systems is consistent with the ductile failures observed with FM-73-type adhesives.

The behavior described above was precisely that sought by the program, and compositions described below were tested for their adhesive properties. Even though the moisture resistance of all of the compositions was expected to be excellent, the DTUL's observed in Table 16 suggest little improvement over FM-73 and Versilok 201 at elevated temperatures.

Increasing the DTUL's of the Table 16 compositions could occur by several methods, e.g.:

- Using t-butylstyrene in the blends (or other high T<sub>g</sub> monomer)
- Reducing ABA block copolymer concentrations in the blends
- Increasing crosslink density through use of higher concentrations of Diacryl 101

New formulations were prepared with the objective of increasing the DTUL by the three formulation changes cited above. Properties of castings from these systems is presented in Table 17. The compositions represent combinations of two monomers (styrene and t-butylstyrene), two rubbers (Kraton 1107 and Solprene 414S), two rubber concentrations (16 and 24 percent), and three

TABLE 17. PROPERTIES OF KRATON AND SOLPRENE BLOCK COPOLYMERS IN STYRENE AND t-BUTYLSTYRENE

| Composition Number | Composition, Percent by Weight <sup>a</sup> |              |                            | Appearance                 | Shore D Hardness | DTUL, OC           |                          | Stress Whitening <sup>c</sup> | Nail Test                     |                               |
|--------------------|---|--------------|----------------------------|----------------------------|------------------|--------------------|--------------------------|-------------------------------|-------------------------------|-------------------------------|
|                    | KL107                                       | 4145 Styrene | t-Butylstyrene Diacryl 101 |                            |                  | Cured <sup>b</sup> | Post Cured Hour at 175°C |                               | Initial Response <sup>d</sup> | Stress Whitening <sup>e</sup> |
| 241                | 24  | 56           | 20                         | Translucent to opaque      | 68               | 95                 | 103                      | T                             | P                             | 4                             |
| 242                | 24  | 66           | 10                         |                            | 66               | 87                 |                          | T P                           | P                             | 4                             |
| 243                | 24  | 71           | 5                          |                            | 66               | 86                 | 95                       | T P                           | P                             | 4                             |
| 244                | 16  | 64           | 20                         |                            | 74               | 120b               |                          | S                             | C                             | 7                             |
| 245                | 16  | 74           | 10                         |                            | 73               | 98                 | 97                       | P                             | C                             | 4                             |
| 246                | 16  | 79           | 5                          |                            | 72               | 87                 |                          | P                             | C                             | 5                             |
| 247                |   | 56           | 20                         |                            | 67               | 105b               |                          | P                             | C                             | 5                             |
| 248                | 24  | 66           | 10                         |                            | 67               | 99                 | 108                      | T P                           | P                             | 1                             |
| 249                | 24  | 71           | 5                          |                            | 71               | 89                 |                          | P                             | CT                            | 2                             |
| 250                | 16  | 64           | 20                         |                            | 77               | 28/115b            | 117                      | T                             | C                             | 6                             |
| 251                | 16  | 74           | 10                         | Transparent to translucent | 75               | 78                 |                          | S                             | H                             | 3                             |
| 252                | 16  | 79           | 5                          |                            | 75               | 80                 | 106                      | S                             | H                             | 3                             |
| 253                | 24  | 56           | 20                         |                            | 64               | 123                |                          | S                             | P                             | 7                             |
| 254                | 24  | 66           | 10                         |                            | 62               | 58/110             | 111                      | S                             | P                             | 7                             |
| 255                | 24  | 71           | 5                          |                            | 60               | 56/86b             |                          | S                             | P                             | 7                             |
| 256                | 16  | 64           | 20                         |                            | 72               | 122b               | 137b                     | S                             | C                             | 7                             |
| 257                | 16  | 74           | 10                         |                            | 70               | 113                |                          | S                             | C                             | 7                             |
| 258                | 16  | 79           | 5                          |                            | 71               | 100                | 113                      | S                             | C                             | 7                             |
| 259                |   | 56           | 20                         |                            | 67               | 104                | 68/137b                  | P                             | C                             | 5                             |
| 260                | 24  | 66           | 10                         |                            | 69               | 54/115             |                          | P                             | P                             | 1                             |
| 261                | 24  | 71           | 5                          |                            | 66               | 0/105              | 121                      | P                             | S                             | 7                             |
| 262                | 16  | 64           | 20                         |                            | 75               | 120b               |                          | P                             | H                             | 3                             |
| 263                | 16  | 74           | 10                         |                            | 74               | 111b               |                          | S                             | C                             | 5                             |
| 264                | 16  | 79           | 5                          |                            | 110              |                    |                          | S                             | S                             | 5                             |

<sup>a</sup> Composition all cured with 0.5 phr t-butylperbenzoate and 0.75 phr cumene hydroperoxide cured overnight at 90°C (into cold oven)

<sup>b</sup> Strength recovery after initial penetration

<sup>c</sup> P = permanent stress whitening

<sup>d</sup> T = stress whitening only under stress, temporary stress whitening

<sup>e</sup> C = cracked; P = nail penetrated sample; H = nail did not penetrate sample

<sup>f</sup> S = sample shattered; CT = cracked terminated in stress whitened area

<sup>g</sup> 1 through 7 represent an arbitrary scale for degree of whitening 1 is highest and 7 is very little if any

Diacryl 101 concentrations (5, 10, and 20 percent). These castings demonstrated a wide range of resin properties ranging from brittle to extremely tough, and several of the formulations showed the sought whitening under stress.

The castings with styrene were translucent to opaque (like medium-to-high-density polyethylene), contrasted to the TBS systems, which were nearly clear (very slight haze). This suggests that the copolymer was either more soluble in the TBS or phases out in much smaller particles.

The results presented in Table 17 show that substitution of TBS for styrene increases the DTUL's of the systems an average of 15°C to 20°C over the corresponding styrene systems. The TBS systems appear to be not as hard as the styrene systems, even though their DTUL's are higher. Increasing the Diacryl concentrations from 5 to 20 percent also increases the DTUL's without significantly affecting the hardness. Decreasing the rubber content from 24 to 16 percent leads to an increase in the DTUL's of about 5°C; however, this increases the hardness of the castings an average of 7 points.

Qualitative tests on the neat resin castings show wide variations in fracture modes and toughness. Tests on flash from the resin castings show that stress whitening occurred in the Solprene 414S castings more readily than in the Kraton K1107 castings. Styrene appears to be more susceptible to crazing than TBS. This latter finding is consistent with the relative clarity of the TBS systems over the styrene systems.

Nail penetration tests were conducted on the castings and fracture modes noted. In the tests, a 0.25-cm by 6-cm (0.1-in. by 2.5-in.) diameter steel nail was driven through the 0.5-cm (0.2-in.) casting with a hammer. All of the formulations with 5 percent Diacryl and TBS (Compositions 255, 258, 261, and 264) shattered into several pieces. Three castings could not be

penetrated, even after several attempts (Compositions 251, 252, and 262). These formulations contained 16 percent of the Solprene 414S.

The greatest extent of stress whitening with the nail tests occurred in the 24 percent Solprene 414S systems with 10 percent Diacryl (Compositions 258 and 260). Minimum stress whitening occurred in the formulations which contained both Kraton 1107 and TBS.

Tensile lap shear and bell peel bonds were also prepared from these systems on 10V phosphoric acid anodized 2024-T3 aluminum. Test results are presented in Table 18. Unfortunately, many of the bondlines were resin-starved due to the relatively low viscosity of the systems. As discussed below, lap shear and bell peel bonds were remade from the more promising compositions. Even with the starved glue lines, tensile shear strength as high as 2,600 psi and bell peel strength as high as 43 PIW were obtained. Trends in the adhesive property data suggest that tensile strength is best with high (20 percent) Diacryl concentrations and with the Solprene 414S copolymer. From data presented in Table 17, high DTUL compositions do not appear readily attainable from styrene, and some use of t-butylstyrene appears to be required.

Examination of the failed bonds shows 100 percent cohesive failure; however, many of the failures appear visually to be adhesive failures. Examination under a microscope, however, reveals that a thin layer of adhesive is left on the adherend. This failure mode seems to occur most frequently in the higher strength bonds.

New compositions were prepared using the same formulation scheme, but modified slightly to incorporate the above observations, e.g., use of higher concentrations of Diacryl 101. Lap shear and peel bonds were prepared and Cab-O-Sil was employed to increase the viscosity of the systems to prevent

TABLE 18. TENSILE SHEAR AND PEEL DATA FOR TABLE 17 COMPOSITIONS

| Composition Number | Composition, Percent by Weight <sup>a</sup> |                  |         |                | RT Tensile Strength<br>MPa (psi); % Bond Area <sup>b</sup> |   | RT Ball Peel Strength<br>(adjusted) b.c |
|--------------------|---|------------------|---------|----------------|--|---|---|
|                    | Kraton<br>K1107                             | Solorene<br>4145 | Styrene | t-Butylstyrene | Diacryl 101  | Cured <sup>d</sup><br>Post Cured<br>1 Hour at 175°C |   |
| 241                | 24  | 56               | 20      | 20             | 8.0 (1260); 70   | 11.2 (1620); 50                                     | 6.5 (38)                                |
| 242                | 24  | 66               | 10      | 10             | 13.2 (1920); 100   | 13.2 (1910); 48                                     | 7.1 (41)                                |
| 243                | 24  | 71               | 5       | 5              | 13.0 (1880); 100   | 13.6 (1970); 100                                    | 2.7 (51)                                |
| 244                | 16  | 64               | 20      | 20             | 17.5 (2550); 100   | 17.4 (2530); 100                                    | 4.6 (27)                                |
| 245                | 16  | 74               | 10      | 10             | 14.6 (2110); 100   | 15.9 (2300); 100                                    | 5.9 (34)                                |
| 246                | 16  | 79               | 5       | 5              | 7.7 (1110); 80   | 8.3 (1200); 90                                      | 7.2 (42)                                |
| 247                | 24  | 56               | 20      | 20             | 14.3 (2080); 100   | 14.0 (2030); 60                                     | 5.9 (34)                                |
| 248                | 24  | 66               | 10      | 10             | 8.5 (1230); 100  | 10.7 (1550); 60                                     | 6.4 (37)                                |
| 249                | 24  | 71               | 5       | 5              | 5.0 (730); 25  | 5.2 (750); 20                                       | 7.7 (45)                                |
| 250                | 16  | 64               | 20      | 20             | 11.4 (1650); 50  | 17.0 (2470); 90                                     | 2.8 (16)                                |
| 251                | 16  | 74               | 10      | 10             | 9.2 (1400); 70   | 7.9 (1150); 20                                      | 4.1 (24)                                |
| 252                | 16  | 79               | 5       | 5              | 3.9 (560); 20  | 4.2 (610); 20                                       | 4.0 (23)                                |
| 253                | 24  | 56               | 20      | 20             | 9.4 (1370); 100  | 12.6 (1820); 100                                    | 7.2 (42)                                |
| 254                | 24  | 66               | 10      | 10             | 3.4 (500); 90  | 8.7 (1260); 85                                      | 7.9 (46)                                |
| 255                | 24  | 71               | 5       | 5              | 8.1 (1180); 80   | 9.4 (1370); 75                                      | 6.2 (36)                                |
| 256                | 16  | 64               | 20      | 20             | 15.6 (2260); 100   | 16.6 (2400); 100                                    | 4.1 (24)                                |
| 257                | 16  | 74               | 10      | 10             | 6.8 (990); 35  | 6.6 (960); 50                                       | 3.6 (21)                                |
| 258                | 16  | 79               | 5       | 5              | 4.8 (700); 35  | ...   | 1.9 (11)                                |
| 259                | 24  | 56               | 20      | 20             | 14.6 (2120); 90  | 17.9 (2590); 90                                     | 4.8 (28)                                |
| 260                | 24  | 66               | 10      | 10             | 7.7 (1120); 80   | 11.2 (1620); 50                                     | 5.0 (29)                                |
| 261                | 24  | 71               | 5       | 5              | 9.0 (1300); 95   | 6.8 (990); 40                                       | 3.4 (20)                                |
| 262                | 16  | 64               | 20      | 20             | 12.3 (1790); 85  | 15.5 (2250); 70                                     | 2.5 (17)                                |
| 263                | 16  | 74               | 10      | 10             | 4.9 (710); 50  | 5.5 (800); 40                                       | 2.9 (17)                                |
| 264                | 16  | 79               | 5       | 5              | 3.3 (480); 25  | 7.3 (1060); 25                                      | 2.4 (14)                                |

<sup>a</sup>Compositions all cured with 0.5 phr t-butylperbenzoate and 0.75 phr cumene hydroperoxide; cured overnight at 90°C (into cold oven)  
<sup>b</sup>Ball failures were cohesive; however, many tensile failures were cohesive failures near the interface  
<sup>c</sup>Certain peel values have been adjusted upward to correct for resin starved bond lines. This adjustment was accomplished by reading the peel strength curve only in areas with high resin content

starved bond lines. Diacryl concentrations were shifted from 5, 10, and 20 percent to 10, 20, and 30 percent. The styrene content was limited to 46 percent (Compositions 265 through 276). Data obtained on Cab-O-Sil free castings of these formulations is given in Table 19.

Hardness readings (Table 19) average about 4 points lower than comparable formulations from the previous study (Table 17). Hardness increase from lowering the rubber content of the formulations is quite evident in both studies. Comparable formulations from the two studies give equivalent DTUL results after cure; however, postcured samples result in an average increase of about 10°C in the Table 19 data. The Table 19 DTUL data show values consistently above 100°C, contrasted to the previous formulating study which had several values below 100°C. The best DTUL values are obtained using t-butylstyrene with K1107 rubber in a cured condition and using 414S rubber in a postcured condition.

Nail tests on the castings showed a wide response similar to the previous study; however, the amount of stress whitening was slightly less than previously observed. It is expected that the degree of stress whitening should correlate with peel strength; however, Tables 17 and 18 data indicate only a very slight trend between the two properties. A correlation does exist, however, between puncture or sample breaking in the nail test. Samples which broke or shattered have about 10 PIW less peel than samples that are penetrated by the nail.

Lap shear and bell peel strengths of Compositions 265 through 288 are provided in Tables 20 and 21, respectively. Room-temperature lap shear strengths up to 23 MPa (3,330 psi) and 17.4 MPa (2,520 psi) at 93°C (200°F) were obtained. Bell peel strengths as high as 8.4 kN/m (48 PIW) and as high as 7.2 kN/m (41 PIW) at -54°C (-65°F) were obtained at room temperature.

TABLE 19. PROPERTIES OF KRATON AND SOLPRENE ABA BLOCK COPOLYMERS IN STYRENE AND t-BUTYLSTYRENE

| Composition Number | Composition, Percent by Weight <sup>a</sup> |               |         |                            | Shore D Hardness | DTG, °C            |                            | Nail Test          |                             |
|--------------------|---|---------------|---------|----------------------------|------------------|--------------------|----------------------------|--------------------|-----------------------------|
|                    | Kraton K1107                                | Solprene 4145 | Styrene | t-Butylstyrene Diacryl 101 |                  | Cured <sup>d</sup> | Post Cured 1 Hour at 175°C | Initial b Response | Relative Stress c Whitening |
| 265                | 24  |               | 46      | 30                         | 61               | 117                | 135                        | C                  | 8                           |
| 266                | 24  |               | 46      | 20                         | 66               |                    |                            | P                  | 5                           |
| 267                | 24  |               | 46      | 20                         | 67               | 115                |                            | P                  | 5                           |
| 268                | 16  |               | 46      | 30                         | 72               | 114                | 137                        | C                  | 8                           |
| 269                | 16  |               | 46      | 20                         | 73               |                    |                            | C                  | 8                           |
| 270                | 16  |               | 46      | 28                         | 72               | 110                | 125                        | S                  | 8                           |
| 271                | 24  | 24            | 46      | 0                          | 65               | 125                | 122                        | C                  | 8                           |
| 272                | 24  | 24            | 46      | 10                         | 65               |                    |                            | C                  | 8                           |
| 273                | 24  | 24            | 46      | 20                         | 62               | 103                | 129                        | P                  | 5                           |
| 274                | 16  | 16            | 46      | 8                          | 73               | 117                | 145                        | C                  | 7                           |
| 275                | 16  | 16            | 46      | 20                         | 72               |                    |                            | H                  | 3                           |
| 276                | 16  | 16            | 46      | 28                         | 72               | 113                |                            | P                  | 2                           |
| 277                | 24  |               | 46      | 30                         | 61               | 125                | 142                        | C                  | 8                           |
| 278                | 24  |               | 56      | 20                         | 60               | 121                |                            | P                  | 7                           |
| 279                | 24  |               | 66      | 10                         | 56               | 124                |                            | P                  | 7                           |
| 280                | 16  |               | 54      | 30                         | 73               | 120                | 139                        | C                  | 4                           |
| 281                | 16  |               | 64      | 20                         | 71               | 130                |                            | C                  | 6                           |
| 282                | 16  |               | 74      | 10                         | 71               | 120                | 135                        | C                  | 8                           |
| 283                | 24  | 24            | 46      | 30                         | 68               | 110                | 148                        | C                  | 8                           |
| 284                | 24  | 24            | 56      | 20                         | 60               | 110                | 152                        | C                  | 7                           |
| 285                | 24  | 24            | 66      | 10                         | 63               | 110                | 158                        | P                  | 3                           |
| 286                | 16  | 16            | 54      | 30                         | 66               | 118                | 153                        | C                  | 7                           |
| 287                | 16  | 16            | 64      | 20                         | 66               | 118                | 156                        | C                  | 5                           |
| 288                | 16  | 16            | 74      | 10                         | 72               | 130                | 152                        | C                  | 7                           |

<sup>a</sup>Composition all cured with 0.5 phr t-butylperbenzoate and 0.75 phr cumene hydroperoxide cured overnight at 90°C (into cold oven)

bc = cracked; P = nail penetrated sample; H = nail did not penetrate sample

S = sample shattered

c) through 8 represent an arbitrary scale for degree of whitening; 1 is highest; and 8 is very little if any

TABLE 20. LAP SHEAR PROPERTIES OF KRATON AND SOLPRENE ABA BLOCK COPOLYMERS  
IN STYRENE AND t-BUTYLSTYRENE<sup>a</sup>

| Composition No. | Composition <sup>b</sup><br>Percent by Weight |               |         |                |             | Tensile Lap Shear Strength, MPa (psi) |   |                               |   |
|-----------------|---|---------------|---------|----------------|-------------|---------------------------------------|---|-------------------------------|---|
|                 | Kraton K1107                                  | Solprene 4145 | Styrene | t-Butylstyrene | Diacryl 101 | Room Temperature Test                 |   | 90°C (200°F) Test Temperature |   |
|                 |   |               |         |                |             | Cured<br>~18 hr at 90°C               | Cured<br>~18 hr at 90°C<br>+1 hr at 175°C | Cured<br>~18 hr at 90°C       | Cured<br>~18 hr at 90°C<br>+1 hr at 175°C |
| 265             | 24  |               | 46      | 0              | 30          | 10.1 (1460)                           | 10.3 (1500)                               | 4.3 (630)                     | 3.7 (540)                                 |
| 266             | 24  |               | 46      | 10             | 20          | 5.6 (810)                             | 12.3 (1790)                               | 4.1 (600)                     | 6.1 (880)                                 |
| 267             | 24  |               | 46      | 20             | 10          | 3.1 (450)                             | 3.7 (530)                                 | 0.7 (100)                     | —   |
| 268             | 16  |               | 46      | 8              | 30          | 16.4 (2380)                           | 15.2 (2210)                               | 7.5 (1090)                    | 11.1 (1610)                               |
| 269             | 16  |               | 46      | 18             | 20          | 11.7 (1700)                           | 12.8 (1860)                               | 1.7 (240)                     | 1.9 (280)                                 |
| 270             | 16  |               | 46      | 28             | 10          | 3.2 (470)                             | —   | 2.4 (350)                     | 0.3 (40)                                  |
| 271             |   | 24            | 46      | 0              | 30          | 14.2 (2060)                           | 16.4 (2380)                               | 7.0 (1010)                    | 8.9 (1290)                                |
| 272             |   | 24            | 46      | 10             | 20          | 7.1 (1030)                            | 5.2 (760)                                 | 2.3 (330)                     | 2.0 (290)                                 |
| 273             |   | 24            | 46      | 20             | 10          | 5.1 (740)                             | 12.8 (1860)                               | 2.3 (330)                     | 5.9 (850)                                 |
| 274             |   | 16            | 46      | 8              | 30          | 16.3 (2360)                           | 18.5 (2680)                               | 3.8 (550)                     | 9.1 (1320)                                |
| 275             |   | 16            | 46      | 18             | 20          | 12.3 (1790)                           | 17.4 (2520)                               | 4.8 (690)                     | 0.4 (60)                                  |
| 276             |   | 15            | 46      | 28             | 10          | 5.2 (750)                             | 2.0 (290)                                 | 0.8 (120)                     | 0.6 (90)                                  |
| 277             | 24  |               |         | 46             | 30          | 12.3 (1780)                           | 13.5 (1960)                               | 5.1 (740)                     | 7.9 (1150)                                |
| 278             | 24  |               |         | 56             | 20          | 13.6 (1970)                           | 13.7 (1990)                               | 5.5 (800)                     | 6.8 (980)                                 |
| 279             | 24  |               |         | 66             | 10          | 7.0 (1010)                            | 9.9 (1430)                                | 2.4 (350)                     | 2.4 (350)                                 |
| 280             | 16  |               |         | 54             | 30          | 14.0 (2030)                           | 15.7 (2270)                               | 6.8 (980)                     | 6.0 (870)                                 |
| 281             | 16  |               |         | 64             | 20          | 15.7 (2270)                           | 17.0 (2470)                               | 5.6 (810)                     | 9.7 (1410)                                |
| 282             | 16  |               |         | 74             | 10          | 16.4 (2380)                           | 11.0 (1600)                               | 5.3 (770)                     | 8.1 (1170)                                |
| 283             |   | 24            |         | 46             | 30          | 21.2 (3080)                           | 21.8 (3160)                               | 9.9 (1440)                    | 16.6 (2400)                               |
| 284             |   | 24            |         | 56             | 20          | 20.5 (2970)                           | 23.0 (3330)                               | 9.6 (1390)                    | 12.4 (1800)                               |
| 285             |   | 24            |         | 66             | 10          | 12.2 (1770)                           | 21.4 (2960)                               | 6.1 (890)                     | 14.1 (2050)                               |
| 286             |   | 16            |         | 54             | 30          | 19.2 (2780)                           | 19.2 (2780)                               | 11.7 (1700)                   | 17.4 (2520)                               |
| 287             |   | 16            |         | 64             | 20          | 16.8 (2430)                           | 15.9 (2300)                               | 9.8 (1420)                    | 14.1 (2040)                               |
| 288             |   | 16            |         | 74             | 10          | 11.2 (1620)                           | 16.5 (2390)                               | 9.4 (1370)                    | 13.9 (2020)                               |

<sup>a</sup> 2024 T3 bare aluminum, 10 V phos anodized, no primer, all failures cohesive

<sup>b</sup> Compositions all cured with 0.5 phr t-butylperbenzoate and 0.75 phr cumene hydroperoxide, and contain Cab-O-Sil to control viscosity



TABLE 21. BELL PEEL PROPERTIES OF KRATON AND SOLPRENE ABA BLOCK COPOLYMERS  
IN STYRENE AND t-BUTYLSTYRENE<sup>a</sup>

| Composition No. | Composition <sup>b</sup><br>Percent by Weight |               |         |                | Bell Peel Strength, kN/m (PIV) |                          |                                |                          |
|-----------------|---|---------------|---------|----------------|--------------------------------|--------------------------|--------------------------------|--------------------------|
|                 | Kraton K1107                                  | Solprene 4145 | Styrene | t-Butylstyrene | Room Temperature Test          |                          | -54°C (-65°F) Test Temperature |                          |
|                 |   |               |         |                | Cured<br>~18 hr at 90°C        | Cured<br>~18 hr at 175°C | Cured<br>~18 hr at 90°C        | Cured<br>~18 hr at 175°C |
| 265             | 24  |               | 46      | 0              | 4.6 (26)                       | 3.7 (21)                 | 5.6 (32)                       | --                       |
| 266             | 24  |               | 46      | 10             | 7.0 (40)                       | 4.9 (28)                 | 7.9 (45)                       | --                       |
| 267             | 24  |               | 46      | 20             | 8.1 (46)                       | 0.7 (4)                  | 6.7 (38)                       | --                       |
| 268             | 16  |               | 46      | 8              | 5.4 (31)                       | 2.8 (16)                 | 5.3 (30)                       | --                       |
| 269             | 16  |               | 46      | 18             | 5.6 (32)                       | 2.8 (16)                 | 5.3 (30)                       | --                       |
| 270             | 16  |               | 46      | 28             | 7.5 (43)                       | 1.4 (8)                  | 7.2 (41)                       | --                       |
| 271             |   | 24            | 46      | 0              | 5.8 (33)                       | 3.9 (22)                 | 5.8 (33)                       | 3.3 (19)                 |
| 272             |   | 24            | 46      | 10             | 7.0 (40)                       | 5.6 (32)                 | 6.5 (37)                       | 3.9 (22)                 |
| 273             |   | 24            | 46      | 20             | 8.4 (48)                       | 7.4 (42)                 | 4.9 (28)                       | 3.3 (19)                 |
| 274             |   | 16            | 46      | 8              | 4.6 (26)                       | 3.5 (20)                 | 3.5 (20)                       | 2.8 (16)                 |
| 275             |   | 16            | 46      | 18             | 5.6 (32)                       | 4.0 (23)                 | 3.7 (21)                       | 2.6 (15)                 |
| 276             |   | 16            | 46      | 28             | 7.4 (42)                       | 5.4 (31)                 | 4.9 (28)                       | 2.6 (15)                 |
| 277             | 24  |               |         | 46             | 6.3 (36)                       | 4.4 (25)                 | 5.6 (32)                       | 2.4 (14)                 |
| 278             | 24  |               |         | 56             | 6.1 (35)                       | 3.3 (19)                 | 5.9 (34)                       | 1.9 (11)                 |
| 279             | 24  |               |         | 66             | 6.5 (37)                       | 3.2 (18)                 | 2.9 (17)                       | 1.8 (10)                 |
| 280             | 16  |               |         | 54             | 3.7 (21)                       | 2.5 (14)                 | 3.7 (21)                       | 1.6 (9)                  |
| 281             | 16  |               |         | 64             | 4.0 (23)                       | 2.5 (14)                 | 3.3 (19)                       | 1.9 (11)                 |
| 282             | 16  |               |         | 74             | 3.2 (18)                       | 2.1 (12)                 | 2.6 (15)                       | 2.1 (12)                 |
| 283             |   | 24            |         | 46             | 4.9 (28)                       | 3.7 (21)                 | 4.1 (23)                       | 1.6 (9)                  |
| 284             |   | 24            |         | 56             | 4.9 (28)                       | 4.0 (23)                 | 2.9 (17)                       | 1.4 (8)                  |
| 285             |   | 24            |         | 66             | 5.4 (31)                       | 3.9 (22)                 | 3.7 (21)                       | 1.8 (10)                 |
| 286             |   | 16            |         | 54             | 3.2 (18)                       | 2.5 (14)                 | 2.6 (15) <sup>c</sup>          | 1.4 (8)                  |
| 287             |   | 16            |         | 64             | 2.6 (15) <sup>c</sup>          | 2.1 (12) <sup>c</sup>    | 2.4 (14) <sup>c</sup>          | 1.1 (6) <sup>c</sup>     |
| 288             |   | 16            |         | 74             | 3.5 (20)                       | 2.6 (15)                 | 2.6 (15)                       | 1.8 (10)                 |

<sup>a</sup> 2024 T3 bare aluminum, 10 V phos anodized, no primer, all failures cohesive

<sup>b</sup> Compositions all cured with 0.5 phr t-butylperbenzoate and 0.75 phr cumene hydroperoxide, and contain Cab-O-Sil to control viscosity

<sup>c</sup> Sample has 50% voids in bond line

Variation in the strength data is consistent in most instances, with the following expectation:

- Increased lap shear strength leads to lower bell peel strength within a given compositional set, e.g., 265 through 270 or 271 through 276, etc.

Examination of the data in Tables 20 and 21 for selection of the superior monomer(s), monomer concentration(s), and/or ABA block copolymers shows the following:

- Solprene 414S has a clear strength advantage over the Kraton K1107 with three test conditions (room temperature, 93°C shear, and room-temperature peel). It also demonstrates a slight strength advantage with the three test conditions for the 24-percent loading level versus the 16-percent loading level in the adhesive compositions. The -54°C bell peel strengths show a slight advantage for use of Kraton K1107 over the Solprene 414S.
- Use of styrene in the compositions shows benefit to room- and low-temperature peel strengths, whereas t-butylstyrene greatly improves the lap shear results at room temperature and 93°C.
- As the Diacryl concentrations are increased from 10 to 30 percent, the lap shear strengths increase significantly with all of the systems based on styrene (Compositions 265 through 276), with an expected loss in peel strength. Even though the t-butylstyrene systems show a similar trend with lap shear strength (Compositions 277 through 288), very little loss in peel strength occurs with increased Diacryl concentration.

The compositions with the best overall properties are Numbers 283 and 284, which contain t-butylstyrene, 24 percent Solprene, and 20 or 30 percent

Diacryl. Slightly improved 93°C tensile shear strength is obtained in Composition 286, which has only 16 percent Solprene; however, a significant loss in peel strength results. The best system containing styrene is Composition 271, which also contains 24 percent Solprene and 30 percent Diacryl. This has only a slight improvement in peel strength, with a significant loss in tensile shear properties.

It was concluded that t-butylstyrene with Solprene 414S is superior to styrene with Solprene 414S, and Kraton K1107 gives inferior results with both monomers. Diacryl 101 is useful for improving lap shear strengths.

Attempts to correlate the results presented in Tables 20 and 21 with the stress whitening/nail test data in Table 19 did not succeed. The best peeling compositions were punctured by the nail with cracking and without regard to stress-whitening rating, whereas high lap shear strength was obtained from compositions which cracked and showed little stress whitening.

The effect of continued cure and/or heat aging on the bond strengths is also shown in Tables 20 and 21. The 90°C cured specimens were treated for an additional 1 hr at 175°C (347°F). A universal loss in peel strength occurred with this treatment. Stronger lap shear bonds improved in strength, whereas lap shear strengths which were low originally tended to get worse after this treatment. This indicates that additional crosslinking is occurring when the samples are heated and that an optimum cure was probably not achieved with the 90°C cure.

#### 2.3.4 Adhesive Optimization Efforts With Solprene-Toughened Diacryl Summary

Effort continued toward optimization of the vinyl-cured system containing t-butylstyrene, Diacryl 101, and Solprene 414S, ABA radial block copolymer. Some compositions demonstrated initial adhesive properties which

are superior to the vinyl-cured Versilok 201 for aerospace applications. Table 22 provides comparative data on the program-developed Compositions 283 and 284 and Versilok 201.

Even though room-temperature lap shear strengths of the program compositions are slightly less than the Versilok 201, the elevated-temperature lap shear strength is superior, and the  $-54^{\circ}\text{C}$  ( $-65^{\circ}\text{F}$ ) bell peel strength is much improved over the Versilok system. Of key significance is the marked difference between the odor of the program compositions and Versilok 201. A longstanding handicap of all acrylate adhesives, such as the Versilok 201, has been their obnoxious odor. The program adhesives, on the other hand, have low odor, which is due to either styrene or t-butylstyrene, depending on the specific composition. The odor of styrene is very familiar to the polyester resin industry. Ten parts of MD 105 aluminum powder in Composition 283 provided 2,530 psi lap shear strength at  $93^{\circ}\text{C}$  ( $200^{\circ}\text{F}$ ), and after 14-day water boil, 2,660 psi at  $93^{\circ}\text{C}$  ( $200^{\circ}\text{F}$ ). The poor peel strength of the Versilok 201 at  $-65^{\circ}\text{F}$  virtually excludes serious consideration of its use in military aircraft.

Low loading levels of powdered aluminum and Wollastonite (10 phr) fillers to the adhesive appear to provide benefit to the shear strength, whereas talc and cure schedule variations offered no improvement. Low-temperature ( $-65^{\circ}\text{F}$ ) bell peel strengths showed an increase over room-temperature bell peel results. This result is not consistent with previous program findings; the test results appear valid at first glance. Bond age prior to test is the most obvious difference between the room-temperature and  $-65^{\circ}\text{F}$  bell peel tests. The room temperature bell peel testing occurred several weeks before the  $-65^{\circ}\text{F}$  bell peel testing which required delivery of liquid nitrogen from the vendor.

TABLE 22. COMPARISON OF PROGRAM ADHESIVE COMPOSITIONS TO VERSILOK 201<sup>a</sup>

| Tensile Lap Shear Strength Test, MPa (psi)         |   |  |                                 |                                   |
|--|---|--|---------------------------------|-----------------------------------|
| Composition 283<br>Composition 284<br>Versilok 201 | -54°C (-65°F)   | Room Temperature,<br>°C (°F)   | +82°C (180°F)                   | +90°C (200°F)                     |
|  | No Data<br>No Data<br>13 (1940)   | 22 (3160)<br>23 (3330)<br>25 (3590)  | No Data<br>No Data<br>10 (1440) | 17 (2400)<br>12 (1800)<br>No Data |
| Bell Peel Strength Test, kN/m (PIH)                |   |  |                                 |                                   |
| Composition 283<br>Composition 284<br>Versilok 201 | -54°C (-65°F)   | Room Temperature,<br>°C (°F)   | +82°C (180°F)                   | +90°C (200°F)                     |
|  | 4.1 (23), 1.6 (9) <sup>b</sup> ,<br>2.9 (17), 1.4 (8) <sup>a</sup> ,<br>0.7 (4) | 4.9 (28), 3.7 (21) <sup>b</sup> ,<br>4.9 (28), 4.0 (23) <sup>b</sup> ,<br>7 (42) | No Data<br>No Data<br>7 (38)    | No Data<br>No Data<br>No Data     |

<sup>a</sup>Versilok data from Reference 5

<sup>b</sup>Second set of strengths after 175°C postcure

### Detailed Investigations

Additional adhesive studies (Compositions 291 through 314) were conducted to further define the proper ratio of monomer(s), Diacryl, and ABA block copolymers and to further determine the effects of fillers, silane coupling agents, and cure conditions on the system. This study used Composition 283 from Table 20 as control formulation, which was repeated twice in the current study with Compositions 292 and 309\* (two separate mixes of the same fomulation). Variations in formulation around the control point, along with test data obtained from the resin castings, is shown in Table 23.

Compositions 291 through 296 further study the effects of resin composition by varying the ratios of t-butylstyrene monomer, Diacryl 101, and the rubber toughener Solprene 414S through a fairly narrow range around the control formulation. Compositions 297 through 305 study the effects of adding talc, Wollastonite, and aluminum powder to the adhesives in the ratio of 10, 30, and 100 parts per 100 parts of resin mixture. The talc and aluminum fillers dispersed in the formulations easily, while the formulations with Wollastonite were more difficult to disperse and required mixing on a three-roll mill. All of the formulations with 100 phr of filler had sufficient body\* not to require the addition of Cab-O-Sil.

Compositions 306 through 308\* study the effect of a vinyl-silane coupling agent (Z-6082) when used as an integral blend with the adhesive and when used as a primer on the aluminum adherends.

Compositions 309 through 314 study the effect of curing agent concentration and cure cycle (time and temperature) on the adhesive

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\*Adhesive 308 is also a separate identical formulation; however, bonds made with composition 308 were primed, while the others were unprimed.

TABLE 23. PROPERTIES OF NEAT RESIN CASTINGS, COMPOSITIONS 291 THROUGH 314

| Composition No. | Composition, Percent by Weight |                |        |      |              |          |               |                    |                      |           | Hardness (Bottom Surface) |                    |                    | DTUL, 15°C/min; 3.1 MPa (450 psi) |          |                          | Weight Change (Initial Weight = 100) |                             |                          |                                    |        |        |
|-----------------|--------------------------------|----------------|--------|------|--------------|----------|---------------|--------------------|----------------------|-----------|---------------------------|--------------------|--------------------|-----------------------------------|----------|--------------------------|--------------------------------------|-----------------------------|--------------------------|------------------------------------|--------|--------|
|                 | Solprene 4145                  | t-Butylstyrene | Diaryl | Talc | Mollastonite | Aluminum | Z-6082 Silane | t-Butylperbenzoate | Cumene Hydroperoxide | Cab-O-Sil | Z-6082 Primer Adherent    | Cure 16 hr at 95°C | Cure 4 hr at 120°C | Cure 2 hr at 130°C                | Barcol   |                          |                                      | As Cured + 24 hr Water Boil | As Cured + 1 hr at 175°C | After Redry 24 hr After Water Boil |        |        |
|                 |                                |                |        |      |              |          |               |                    |                      |           |                           |                    |                    |                                   | As Cured | As Cured + 1 hr at 175°C | Shore D                              |                             |                          |                                    |        |        |
| 291             | 24                             | 41             | 35     |      |              |          |               | 0.5                | .75                  | ↓         | ↓                         | ↓                  | ↓                  | ↓                                 | 0        | 3                        | 71                                   | 77                          | 137                      | 172                                | 157    | 100.42 |
| 292             | 24                             | 46             | 30     |      |              |          |               | 0.5                | ↓                    | ↓         | ↓                         | ↓                  | ↓                  | ↓                                 | 0        | 3                        | 69                                   | 74                          | 144                      | 162                                | 155    | 103.22 |
| 293             | 24                             | 51             | 25     |      |              |          |               | 0.5                | ↓                    | ↓         | ↓                         | ↓                  | ↓                  | ↓                                 | 0        | 0                        | 68                                   | 73                          | 153                      | 159                                | 155    | 99.75  |
| 294             | 20                             | 45             | 35     |      |              |          |               | 0.5                | ↓                    | ↓         | ↓                         | ↓                  | ↓                  | ↓                                 | 0        | 8                        | 71                                   | 77                          | 150                      | 157                                | 170    | 97.16  |
| 295             | 20                             | 50             | 30     |      |              |          |               | 0.5                | ↓                    | ↓         | ↓                         | ↓                  | ↓                  | ↓                                 | 0        | 6                        | 72                                   | 77                          | 138                      | 170                                | 170    | 100.50 |
| 296             | 20                             | 55             | 25     |      |              |          |               | 0.5                | ↓                    | ↓         | ↓                         | ↓                  | ↓                  | ↓                                 | 0        | 8                        | 70                                   | 76                          | 146                      | 184                                | 184    | 98.12  |
| 297             | 24                             | 46             | 30     | 10   |              |          | 0.5           | 0.5                | .75                  | ↓         | ↓                         | ↓                  | ↓                  | ↓                                 | 0        | 2                        | 71                                   | 74                          |                          |                                    |        | 101.85 |
| 298             | 24                             | 46             | 30     | 30   |              |          | 0.5           | 0.5                | ↓                    | ↓         | ↓                         | ↓                  | ↓                  | ↓                                 | 0        | 0                        | 68                                   | 74                          |                          |                                    |        | 99.58  |
| 299             | 24                             | 46             | 30     | 100  |              |          | 0.5           | 0.5                | ↓                    | ↓         | ↓                         | ↓                  | ↓                  | ↓                                 | 0        | 0                        | 72                                   | 73                          |                          |                                    |        | 100.55 |
| 300             | 24                             | 46             | 30     | 100  |              |          | 0.5           | 0.5                | ↓                    | ↓         | ↓                         | ↓                  | ↓                  | ↓                                 | 0        | 6                        | 70                                   | 77                          |                          |                                    |        | 99.07  |
| 301             | 24                             | 46             | 30     | 100  |              |          | 0.5           | 0.5                | ↓                    | ↓         | ↓                         | ↓                  | ↓                  | ↓                                 | 0        | 12                       | 73                                   | 76                          |                          |                                    |        | 100.56 |
| 302             | 24                             | 46             | 30     | 100  |              |          | 0.5           | 0.5                | ↓                    | ↓         | ↓                         | ↓                  | ↓                  | ↓                                 | 0        | 30                       | 77                                   | 82                          |                          |                                    |        | 99.40  |
| 303             | 24                             | 46             | 30     | 100  |              |          | 0.5           | 0.5                | ↓                    | ↓         | ↓                         | ↓                  | ↓                  | ↓                                 | 0        | 5                        | 72                                   | 75                          |                          |                                    |        | 98.63  |
| 304             | 24                             | 46             | 30     | 100  |              |          | 0.5           | 0.5                | ↓                    | ↓         | ↓                         | ↓                  | ↓                  | ↓                                 | 0        | 9                        | 74                                   | 73                          |                          |                                    |        | 100.56 |
| 305             | 24                             | 46             | 30     | 100  |              |          | 0.5           | 0.5                | ↓                    | ↓         | ↓                         | ↓                  | ↓                  | ↓                                 | 0        | 22                       | 76                                   | 78                          |                          |                                    |        | 98.09  |
| 306             | 24                             | 46             | 30     | 100  |              |          | 0.5           | 0.5                | .75                  | ↓         | ↓                         | ↓                  | ↓                  | ↓                                 | 0        | 4                        | 70                                   | 73                          |                          |                                    |        | 99.58  |
| 307             | 24                             | 46             | 30     | 100  |              |          | 0.5           | 0.5                | ↓                    | ↓         | ↓                         | ↓                  | ↓                  | ↓                                 | 0        | 3                        | 68                                   | 74                          |                          |                                    |        | 97.76  |
| 308             | 24                             | 46             | 30     | 100  |              |          | 0.5           | 0.5                | ↓                    | ↓         | ↓                         | ↓                  | ↓                  | ↓                                 | 0        | 3                        | 69                                   | 75                          |                          |                                    |        | 103.28 |
| 309             | 24                             | 46             | 30     | 100  |              |          | 0.5           | .75                | ↓                    | ↓         | ↓                         | ↓                  | ↓                  | ↓                                 | 0        | 3                        | 69                                   | 73                          | 122                      | 152                                | 143    | 102.23 |
| 310             | 24                             | 46             | 30     | 100  |              |          | 0.5           | ↓                  | ↓                    | ↓         | ↓                         | ↓                  | ↓                  | ↓                                 | 0        | 3                        | 69                                   | 73                          | 141                      | 164                                | 147    | 99.62  |
| 311             | 24                             | 46             | 30     | 100  |              |          | 0.5           | ↓                  | ↓                    | ↓         | ↓                         | ↓                  | ↓                  | ↓                                 | 0        | 4                        | 69                                   | 74                          | 151                      | 156                                | 148    | 104.72 |
| 312             | 24                             | 46             | 30     | 100  |              |          | 0.32          | .48                | ↓                    | ↓         | ↓                         | ↓                  | ↓                  | ↓                                 | 0        | 2                        | 68                                   | 75                          | 132                      | 166                                | 157    | 100.83 |
| 313             | 24                             | 46             | 30     | 100  |              |          | 0.5           | ↓                  | ↓                    | ↓         | ↓                         | ↓                  | ↓                  | ↓                                 | 0        | 72                       | 74                                   | 152                         | 162                      | 152                                | 103.62 |        |
| 314             | 24                             | 46             | 30     | 100  |              |          | 0.5           | ↓                  | ↓                    | ↓         | ↓                         | ↓                  | ↓                  | ↓                                 | 0        | 2                        | 69                                   | 73                          | 155                      | 156                                | 155    | 100.42 |

properties. The standard curing agent mixture (0.5 phr of t-butylperbenzoate and 0.75 phr cumene hydroperoxide) was selected for its smooth cure characteristics, but this level is higher than is probably necessary to ensure a complete cure. Optimum cures for vinyl systems are usually achieved with a slow gelation followed by gradual heating to cure in all of the unreacted monomers. However, slow cures are not usually desirable in production situations. These compositions look at the effect of speeding up the cure time. In this study, the bonds were placed in a cold oven and heated rapidly to the cure temperature, thereby giving the adhesive a chance to gel at a lower temperature and a slower rate.

Examination of the data in Table 23 shows relatively little change in hardness between unfilled systems; however, slight increases are noted with decreasing ABA block copolymer content and increasing Diacryl content. As expected, large increases in hardness are observed when high levels of hard fillers are added to the formulations.

Examinations of the DTUL data shows that distortion temperatures are all significantly above the 121°C (250°F) target temperature, that the major effect of a 24-hr water boil on the samples is to continue the cure rather than to cause softening of the adhesive matrix, and that postcuring 1 hr at 175°C causes additional cure.

Weight changes on 0.6 cm (0.25 in.) cubes of adhesives after 24-hr water boil and after redry (2 hr at 120°C) show relatively little water pickup; however, about 2 weight percent of material is removed from the samples during water boil and redry. It is likely that the material removed is unreacted monomer and peroxide-initiator decomposition products. Several of the formulations have fairly large water pickup during water boil (e.g., 2 to 5 percent). Two of these (Compositions 311 and 313) are due to voids in



the sample, which resulted from blowing during the more rapid cure which they received. The other high moisture pickups are Compositions 292, 308, and 309, which are the three control formulations. No explanation for this is immediately apparent.

Water-boil/redry data on some of the better commercial epoxy adhesives systems under identical conditions (Reference 5) show weights after water boil at 104 and 123 and weights after redry at 91 to 100 (initial weight = 100). Likewise, weights on commercial acrylic adhesives were between 95 and 127 after water boil and between 86 and 95 after redry. In comparison with these commercial adhesives, Compositions 291 through 314 appear excellent. Moisture weight gain of postcured samples would be expected to be lower than the values shown in Table 23.

Tensile shear and bell peel bonds prepared from Compositions 291 through 314 were prepared and tested. The tensile shear bonds in this study are on 6061-T6 aluminum, while the peel bonds are on 2024-T3 aluminum. All previous tensile shear and bell peel bonds were on 2024-T3 aluminum. All adherends are 10V-phosphoric acid anodized, and 11 bonds utilized the 1659 open-weave glass cloth scrim for bondline thickness control.

Adhesive tests were conducted on Compositions 291 through 314. Tensile lap shear data are presented in Table 24 and bell peel data are in Table 25. The data led to three significant observations: peel strength is not lost at -54°C (-65°F), only a minor loss in tensile lap shear strength occurs at 93°C (200°F), and almost no loss in tensile lap shear strength occurs after a 2-week water boil when tested at 93°C (200°F). Very little information regarding the formulation can be concluded, due to the scatter in the data. Some trends are evident and are discussed below.

TABLE 24. TENSILE SHEAR STRENGTHS OF COMPOSITIONS 291 THROUGH 314

| Composition No. | Composition, Percent by Weight |         |      |              |          |           |                          |               |           |                         | Tensile Lap Shear Strength, <sup>a</sup> MPa (psi) |                                |                                |  |
|-----------------|--------------------------------|---------|------|--------------|----------|-----------|--------------------------|---------------|-----------|-------------------------|--|--------------------------------|--------------------------------|--|
|                 | Isoprene 414                   | Diacryl | Talc | Wollastonite | Aluminum | CHP (phr) | 1-Butylperbenzoate (phr) | 2-6062 Stiane | Cab-O-Sil | Z-6082 Prized Adherends | As Cured   | Post Cured<br>1 hr at<br>175°C | Post Cured<br>1 hr at<br>175°C | Post Cured<br>1 hr at<br>175°C and<br>2 week<br>water boil |
|                 | 24                             | 46      | 30   |              |          | .75       | .50                      |               | Y         | X                       | Room Temp.   | Room Temp.                     | 93°C (200°F)                   | 93°C (200°F)   |
| 291             | 24                             | 41      | 35   |              |          | .75       | .50                      |               | Y         | X                       | 19.2 (2790)  | 14.7 (2130)                    | 13.9 (2020)                    | 13.2 (1910)  |
| 292             | 24                             | 46      | 30   |              |          | .75       | .50                      |               | Y         | X                       | 18.4 (2663)  | 17.9 (2600)                    | 13.7 (1990)                    | 12.8 (1860)  |
| 293             | 24                             | 51      | 25   |              |          | .75       | .50                      |               | Y         | X                       | 19.5 (2830)  | 15.2 (2200)                    | 14.1 (2050)                    | 10.5 (1520)  |
| 294             | 20                             | 45      | 35   |              |          | .75       | .50                      |               | Y         | X                       | 20.7 (3000)  | 14.7 (2130)                    | 16.7 (2420)                    | 15.1 (2190)  |
| 295             | 20                             | 50      | 30   |              |          | .75       | .50                      |               | Y         | X                       | 17.8 (2580)  | 11.4 (1660)                    | 14.9 (2160)                    | 12.8 (1860)  |
| 296             | 20                             | 55      | 25   |              |          | .75       | .50                      |               | Y         | X                       | 2.9 (420)  | 18.1 (2630)                    | 16.2 (2350)                    | 13.9 (2020)  |
| 297             | 24                             | 46      | 30   | 10           |          | .75       | .50                      | 0.5           | Y         | X                       | 15.0 (2170)  | 17.1 (2490)                    | 13.5 (1960)                    | 9.2 (1330)   |
| 298             | 24                             | 46      | 30   | 30           |          | .75       | .50                      | 0.5           | Y         | X                       | 11.9 (1720)  | 15.2 (2200)                    | 12.3 (1780)                    | 8.3 (1200)   |
| 299             | 24                             | 46      | 30   | 100          |          | .75       | .50                      | 0.5           | Y         | X                       | 12.2 (1770)  | 12.5 (1810)                    | 10.6 (1530)                    | 9.5 (1380)   |
| 300             | 24                             | 46      | 30   |              | 10       | .75       | .50                      | 0.5           | Y         | X                       | 22.5 (3270)  | 24.0 (3480)                    | 15.5 (2250)                    | 15.1 (2190)  |
| 301             | 24                             | 46      | 30   |              | 30       | .75       | .50                      | 0.5           | Y         | X                       | 18.2 (2640)  | 13.0 (1890)                    | 16.6 (2400)                    | 12.1 (1760)  |
| 302             | 24                             | 46      | 30   |              | 100      | .75       | .50                      | 0.5           | Y         | X                       | 17.7 (2570)  | 20.5 (2970)                    | 15.4 (2240)                    | 13.2 (1910)  |
| 303             | 24                             | 46      | 30   |              |          | .75       | .50                      | 0.5           | Y         | X                       | 20.6 (2990)  | 15.4 (2230)                    | 17.4 (2530)                    | 18.3 (2660)  |
| 304             | 24                             | 46      | 30   |              | 10       | .75       | .50                      | 0.5           | Y         | X                       | 19.1 (2770)  | 19.9 (2890)                    | 14.8 (2140)                    | 14.6 (2130)  |
| 305             | 24                             | 46      | 30   |              | 100      | .75       | .50                      | 0.5           | Y         | X                       | 15.1 (2190)  | 15.9 (2310)                    | 15.6 (2260)                    | 13.2 (1920)  |
| 306             | 24                             | 46      | 30   |              |          | .75       | .50                      | 0.5           | Y         | X                       | 19.0 (2760)  | 17.9 (2600)                    | 14.2 (2060)                    | 12.9 (1870)  |
| 307             | 24                             | 46      | 30   |              |          | .75       | .50                      | 0.5           | Y         | X                       | 18.7 (2710)  | 20.6 (2980)                    | 13.4 (1950)                    | 12.1 (1760)  |
| 308             | 24                             | 46      | 30   |              |          | .75       | .50                      | 0.5           | Y         | X                       | 15.1 (2190)  | 16.1 (2630)                    | 12.0 (1740)                    | 11.3 (1640)  |
| 309             | 24                             | 46      | 30   |              |          | .75       | .50                      | 0.5           | Y         | X                       | 18.8 (2730)  | 19.0 (2760)                    | 15.2 (2200)                    | 14.6 (2130)  |
| 310             | 24                             | 46      | 30   |              |          | .75       | .50                      | 0.5           | Y         | X                       | 20.0 (2900)  | 20.2 (2930)                    | 14.6 (2120)                    | 13.7 (1940)  |
| 311             | 24                             | 46      | 30   |              |          | .75       | .50                      | 0.5           | Y         | X                       | 17.9 (2580)  | 20.1 (2920)                    | 14.6 (2110)                    | 13.0 (1880)  |
| 312             | 24                             | 46      | 30   |              |          | .75       | .50                      | 0.5           | Y         | X                       | 20.1 (2920)  | 19.0 (2760)                    | 13.2 (1920)                    | 13.9 (2010)  |
| 313             | 24                             | 46      | 30   |              |          | .75       | .50                      | 0.5           | Y         | X                       | 16.3 (2370)  | 17.7 (2560)                    | 13.0 (1890)                    | 12.0 (1740)  |
| 314             | 24                             | 46      | 30   |              |          | .75       | .50                      | 0.5           | Y         | X                       | 17.2 (2500)  | 17.4 (2530)                    | 12.8 (1860)                    | 11.2 (1620)  |

<sup>a</sup> 6051-15 aluminum adherends; 10-volt phosphoric acid anodized

TABLE 25. BELL PEEL STRENGTHS OF COMPOSITIONS 291 THROUGH 314

| Composition No. | Composition, Percent by Weight |         |      |              |          |     |                    |                  |                  |                  | Bell Peel Strength, <sup>a</sup> kN/m (PII) |                                |                       |                                |
|-----------------|--------------------------------|---------|------|--------------|----------|-----|--------------------|------------------|------------------|------------------|---|--------------------------------|-----------------------|--------------------------------|
|                 | Solvent 214                    | Diethyl | Talc | Wollastonite | Aluminum | TBP | t-Butylperbenzoate | 2-Ethylhexanoate | 2-Ethylhexanoate | 2-Ethylhexanoate | As Cured                                    | Post Cured<br>1 hr at<br>175°C | As Cured              | Post Cured<br>1 hr at<br>175°C |
|                 |                                |         |      |              |          |     |                    |                  |                  |                  |   |                                |                       |                                |
| 291             | 24                             | 41      | 35   |              |          | 75  | 50                 |                  |                  |                  | -54°C (-65°F)                               | -54°C (-65°F)                  | Room Temp.            | Room Temp.                     |
| 292             | 24                             | 46      | 30   |              |          | 75  | 50                 |                  |                  |                  | 4.4 (25)                                    | 3.0 (17)                       | 3.3 (19)              | 2.6 (15)                       |
| 293             | 24                             | 51      | 25   |              |          | 75  | 50                 |                  |                  |                  | 4.2 (24)                                    | 3.7 (21)                       | 3.3 (19)              | 2.1 (12)                       |
| 294             | 20                             | 45      | 35   |              |          | 75  | 50                 |                  |                  |                  | 5.1 (29)                                    | 1.9 (11)                       | 3.5 (20)              | 2.6 (15)                       |
| 295             | 20                             | 52      | 30   |              |          | 75  | 50                 |                  |                  |                  | 4.7 (27)                                    | 2.1 (12)                       | 2.8 (16)              | 1.9 (11)                       |
| 296             | 20                             | 55      | 25   |              |          | 75  | 50                 |                  |                  |                  | 3.8 (22)                                    | 1.4 (8)                        | 3.0 (17)              | 1.9 (11)                       |
|                 |                                |         |      |              |          | 75  | 50                 |                  |                  |                  | 3.1 (18)                                    | 3.3 (19)                       | 3.5 (20)              | 2.3 (13)                       |
| 297             | 24                             | 46      | 30   | 10           |          | 75  | 50                 | 0.5              | Y                | X                | 3.8 (22)                                    | 2.6 (15)                       | 3.0 (17)              | 2.3 (13)                       |
| 298             | 24                             | 46      | 30   | 30           |          | 75  | 50                 | 0.5              | Y                | Y                | 3.5 (20)                                    | 2.3 (13)                       | 2.1 (12)              | 1.2 (7)                        |
| 299             | 24                             | 46      | 30   | 100          |          | 75  | 50                 | 0.5              | N                |                  | 3.3 (19)                                    | 4.4 (25)                       | 1.2 (7)               | 0.5 (3)                        |
| 300             | 24                             | 46      | 30   |              | 10       | 75  | 50                 | 0.5              | Y                | Y                | 4.0 (23)                                    | 3.7 (21)                       | 3.7 (21)              | 2.6 (15)                       |
| 301             | 24                             | 46      | 30   | 30           |          | 75  | 50                 | 0.5              | Y                | Y                | 3.9 (22)                                    | 3.5 (20)                       | 3.0 (17)              | 2.1 (12)                       |
| 302             | 24                             | 46      | 30   | 100          |          | 75  | 50                 | 0.5              | N                |                  | 3.7 (21)                                    | 3.0 (17)                       | 2.5 (14)              | 1.6 (9)                        |
| 303             | 24                             | 46      | 30   |              | 10       | 75  | 50                 | 0.5              | Y                | Y                | 4.4 (25)                                    | 3.3 (19)                       | 2.8 (16)              | 2.8 (16)                       |
| 304             | 24                             | 46      | 30   |              | 30       | 75  | 50                 | 0.5              | Y                | Y                | 3.8 (22)                                    | 3.5 (20)                       | 3.1 (18)              | 2.1 (12)                       |
| 305             | 24                             | 46      | 30   |              | 100      | 75  | 50                 | 0.5              | Y                | Y                | 3.6 (22)                                    | 2.8 (16)                       | 1.9 (11)              | 2.6 (15)                       |
| 306             | 24                             | 46      | 30   |              |          | 75  | 50                 | 0.5              | Y                | X                | 4.0 (21)                                    | 3.1 (18)                       | 3.3 (19)              | 3.0 (17)                       |
| 307             | 24                             | 46      | 30   |              |          | 75  | 50                 | 0.5              | Y                | Y                | 3.7 (21)                                    | 2.3 (13)                       | 3.0 (17)              | 1.9 (11)                       |
| 308             | 24                             | 46      | 30   |              |          | 75  | 50                 | 0.5              | Y                | X                | 3.5 (20)                                    | 2.8 (16)                       | 2.6 (16)              | 2.5 (14)                       |
| 309             | 24                             | 46      | 30   |              |          | 75  | 50                 | 0.5              | Y                | X                | 4.9 (28)                                    | 4.5 (26)                       | 2.0 (16)              | 1.9 (11)                       |
| 310             | 24                             | 46      | 30   |              |          | 75  | 50                 | 0.5              | Y                | X                | 2.8 (16) <sup>b</sup>                       | 4.0 (23) <sup>b</sup>          | 2.1 (12) <sup>b</sup> | 1.4 (8) <sup>b</sup>           |
| 311             | 24                             | 46      | 30   |              |          | 75  | 50                 | 0.5              | Y                | X                | 3.5 (20)                                    | 3.7 (21)                       | 4.7 (27)              | 3.1 (18)                       |
| 312             | 24                             | 46      | 30   |              |          | 75  | 50                 | 0.5              | Y                | X                | 3.1 (18)                                    | 3.5 (20)                       | 3.5 (19)              | 2.5 (14)                       |
| 313             | 24                             | 46      | 30   |              |          | 75  | 50                 | 0.5              | Y                | X                | 4.0 (23)                                    | 4.2 (24)                       | 3.7 (21)              | 3.1 (13)                       |
| 314             | 24                             | 46      | 30   |              |          | 75  | 50                 | 0.5              | Y                | X                | 4.0 (23)                                    | 4.7 (24)                       | 4.2 (24)              | 2.6 (15)                       |

<sup>a</sup> 0.25-13 aluminum acetate, 10-vol% phosphoric acid anhydride  
<sup>b</sup> Resin starved bondline

Formulations 291 through 296 study the effects of resin composition by varying the ratios of t-butylstyrene monomer, Diacryl 101, and the rubber toughener Solprene 414S, through a fairly narrow range around the control formulation (Compositions 292 and 309). The data show a slight improvement in peel strength with 24-percent Solprene 414S, but loss in lap shear strength compared to 20 percent Solprene 414S.

Compositions 297 through 305 study the effects of adding talc, Wollastonite, and aluminum powder to the adhesives in the ratio of 10, 30, and 100 parts of resin mixture. The data show that talc (Numbers 297 to 299) offers no advantages as a filler. However, low concentrations of Wollastonite and aluminum powder fillers do offer some advantages over the unfilled compositions. Formulation 300, with 10 phr of Wollastonite, has the most consistently good results of the bonding set. However, 10 phr of aluminum filler (Composition 303) gives significantly improved tensile shear strength at 93°C.

Compositions 306 through 308 study the effect of a vinyl-silane coupling agent (Z-6082) when used as an integral blend with the adhesive and when used as a primer on the aluminum adherends. The data show no benefit in bond strength with the silane; however, little benefit would be expected since failure modes are cohesive in nature.

Compositions 309 through 314 study the effect of curing agent concentration and cure cycle (time and temperature) on the adhesive properties. No clear trends are evident from the data, indicating that a fast cure cycle may be possible with the adhesive system.

Basically, the adhesive data indicate that two key properties (-65°F peel and 200°F shear) were achieved with measurable success. That is, urethanes which have good -54°C (-65°F) properties (shear and peel) have poor

93°C (200°F) properties, and unmodified epoxies which have good 93°C (200°F) strengths usually have poor -54°C (-65°F) peel strengths. The good moisture resistance of the system, of course, was expected.

It should be noted that the 1659 E glass scrim used for glueline control is not appreciably "wet out" by these hydrophobic compositions, and scrim contribution to peel strength is absent.

#### 2.3.5 Film Adhesive Development Efforts

##### Summary

Prognosis for development of a film version of the candidate paste adhesive within the remaining program resources was reviewed after preliminary investigations had been conducted. Based on several unknowns associated with the new adhesive chemistry, it appears that film development efforts could not be brought to their optimum conclusion within the remaining program resources. As described in this section, sufficient resin thickening does not occur with low levels of additives, and higher additive levels are expected to alter the adhesive properties of the composition. Further, wetting of several scrims produced only marginal results, and the supported film version of the adhesive will probably require that the scrims be surface treated. Precedent does not appear to exist for the developed program adhesive composition, and even though acrylate adhesives are related, the hydrophobicity of the program adhesive suggests that use of hydrophillic acrylate adhesion promoters such as 2-hydroxyethyl acrylate should be avoided, if possible.

##### Detailed Investigations

The items required to obtain a film product from the developed composition were:

1. Add a suitable thickener so that the adhesive can be made into film form

2. Find a carrier cloth that will have minimum moisture wicking problems
3. Study the peroxide curing agents to find a suitable system that has good storage stability

Some efforts on the first two of these changes were investigated. The first study examined 18 carrier cloths for their potential to reinforce and provide bondline control for the adhesive. None of the cloths studied had the hoped-for good adhesion with the program adhesive; however, five of the 18 did show some adhesion. Of these five, all but one was rejected because they were too polar and therefore subject to water degradation.

The data obtained in this study on the 18 one-ply laminates is shown in Table 26. Of these laminates, only the first five fabrics listed in the table showed any residual adhesive on the exposed fibers after the laminate was failed. These fabrics contain three acrylonitrile polymers, a nomex (polyamide) polymer and a polyester polymer. Of these, the polyester fiber is much less polar than the others and is expected to have better moisture resistance. A number of other fabrics were also evaluated without success, including cloth made from polypropylene, glass, and Kevlar. A number of fabrics were also eliminated from consideration because they tend to trap air during lay-up, or they are springy and cause air to suck back into the bondline area when bonding pressure is reduced.

The best of these fabrics was Pellon's 9315, which is a nonwoven (mat) polyester fabric that weighs 50 gm/m<sup>2</sup> and which resulted in a 7-mil laminate (glueline). Pellon supplied a large number of fabrics, most of which were not evaluated in the first screening study. Several additional polyester fabrics should be evaluated in future studies, along with possible

TABLE 26. EVALUATION OF CARRIER FABRICS<sup>a</sup>

| Vendor                      | Fabric       |                            |               |                   | 1 Ply<br>Laminate<br>Thickness<br>Mils | Flex-<br>Crease<br>Cycles<br>To<br>Failure | Clean<br>Crack<br>In<br>Flex-<br>Crease <sup>b</sup> | Adhesion<br>To Fiber<br>By<br>Cured<br>Resin | Notes                               |
|-----------------------------|--------------|----------------------------|---------------|-------------------|--|--|--|--|-------------------------------------|
|                             | Vendor<br>ID | Weight<br>g/m <sup>2</sup> | Weave<br>Type | Fiber<br>Type     |  |  |  |  |                                     |
| Pellon                      | T1772        | 21                         | Non woven     | Polyacrylonitrile | 5                                      | 9  | No   | Some   | Sucks in air: yellows during cure   |
| Pellon                      | T1774        | 35                         | Non woven     | Polyacrylonitrile | 11                                     | 2  | Yes  | Some   | Trapped air: yellows during cure    |
| Pellon                      | T1744        | 40                         | Non woven     | Polyacrylonitrile | 4                                      | 20+  | No   | Some   | Sucks in air: yellows during cure   |
| Pellon                      | H1103        | 20                         | Non woven     | Nomex             | 11                                     | 19   | Yes  | Some   | Trapped air                         |
| Pellon                      | 9315         | 50                         | Non woven     | Polyester         | 5                                      | 20+  | No   | Some   |                                     |
| Pellon                      | T1781 BK     | 27                         | Non woven     | Polyester         | 7                                      | 20+  | No   | None   |                                     |
| 3M                          | AF3306       | 8                          | Non woven     | Polyester         | 7                                      | 20+  | Yes  | None   | Trapped air                         |
| Oakhurst                    | Unknown      | 150                        | Double knit   | Polyester         | 13                                     | 20+  | No   | None   | Sucks in air                        |
| Unknown                     | Unknown      | 110                        | Double knit   | Polyester         | 11                                     | 20+  | No   | None   | Sucks in air                        |
| Unknown                     | Unknown      | 70                         | Single knit   | Polyester         | 10                                     | 20+  | No   | None   |                                     |
| Kimberly<br>Clark           | S813960      | 68                         | Non woven     | Polypropylene     | 9                                      | 20+  | No   | None   |                                     |
| Pellon                      | 2106         | 40                         | Non woven     | Polypropylene     | 7                                      | 4  | Yes  | None   |                                     |
| Pellon                      | FS2125       | 80                         | Non woven     | Polypropylene     | 6                                      | 20+  | No   | None   |                                     |
| Pellon                      | T1785E62     | 15                         | Non woven     | E glass           | 10:2                                   | 1  | —  | None   | Very poor wet strength: trapped air |
| Pellon                      | T1776G53     | 27                         | Non woven     | C glass           | 10                                     | 1  | —  | None   | Trapped air                         |
| Thalco                      | Unknown      | 30                         | Woven         | Nylon Tricot      | 12                                     | 20+  | Yes  | None   | Trapped air                         |
| Fiberglass<br>Reinforcement | 740          | 71                         | Woven         | Kevlar 29         | 13                                     | 20+  | No   | None   | Trapped air                         |
| Fiberglass<br>Reinforcement | 354          | 160                        | Woven         | Kevlar 49         | 15                                     | 20+  | No   | None   |                                     |

<sup>a</sup>Cured through 1 hr at 350°F (into cold press); 24% 414s; 30% diacryl; 46% TBS, 0.5 phr TBPB, 0.75 phr CMB  
<sup>b</sup>Crack vs no crack -- on first Flex Crease cycle: crack = clean cleavage with only fiber holding it together;  
 no crack = stress-whitened area and irregular bend line on first cycle of flex crease test.

surface modification studies such as flame-treating the fabric for an instant.

The other study to develop a film adhesive from the current liquid system looked at 10 potential thickeners that would hopefully convert the liquid adhesive into a viscous film-forming material. Of these 10 thickeners, none showed an adequate change in adhesive viscosity when used at up to 25 percent of the weight of the system.

The ten thickeners studied are shown in Table 27 and include Cab-O-Sil (fumed silica), seven rubbers that were selected from those evaluated earlier for rubber toughening studies, Cosden 550 high molecular weight polystyrene, and a sample of a nonproduct, t-butyl styrene-acrylonitrile polymer, provided by Dow Chemical.

The first four materials in Table 27 show the greatest effect on viscosity for 60/40 t-butylstyrene/Diacryl blend; however, none of these mixtures approaches a film-forming viscosity. While the addition of the 4145 rubber toughener and aluminum or Wollastonite filler would improve the viscosity characteristics, this is not adequate to breach the gap in viscosities.

#### 2.3.6 Adhesive Characterization Efforts

Several items were scheduled for more complete evaluation of the adhesive. They included, in addition to the familiar low- and high-temperature testing of the adhesive for shear, peel, cleavage, and creep testing, aging of the adhesive at room temperature prior to bond assembly. As discussed below, the results of these tests indicate an aging effort which needs to be clarified prior to proceeding with adhesive evaluation efforts.

The composition selected for characterization efforts was Composition 303 indicated in Table 23.



TABLE 27. EVALUATION OF POTENTIAL THICKENERS FOR ADHESIVES

|    | Thickener        | IN t-Butylstyrene            |                   | IN 60% TBS + 40% Diacryl         |                   |
|----|------------------|------------------------------|-------------------|----------------------------------|-------------------|
|    |                  |                              | Percent Thickener |                                  | Percent Thickener |
| 1  | Cab-O-Sil MS     | Semiopaque paste-thixotropic | 9                 | Very cloudy paste -- Thixotropic | 5.66              |
| 2  | G1650            | Clear liquid                 | 25                | Cloudy viscous liquid            | 17                |
| 3  | 312              | Cloudy liquid                | 25                | Cloudy viscous liquid            | 17                |
| 4  | KM323B           | Crumb likea                  | 25                | Semiopaque viscous liquid        | 17                |
| 5  | KM330            | Crumb likea                  | 25                | Semiopaque liquid                | 17                |
| 6  | 1205C            | Clear liquid                 | 25                | Clear viscous liquid             | 17                |
| 7  | 435              | Clear pastea                 | 25                | Clear liquid                     | 17                |
| 8  | 436              | Clear pastea                 | 25                | Clear liquid                     | 17                |
| 9  | 550              | Clear liquidb                | 25                | Clear liquid                     | 17                |
| 10 | TBS/AN copolymer | Clear liquid                 | 25                | Clear liquid                     | 17                |

aMixed on 3 roll mill  
bVery slow to dissolve

Compatibility of the composition with primers was screened. Two primers were evaluated in this study, along with an unprimed counterpart. The primers that were evaluated were BR-127 (American Cyanamide), a primer made from the adhesive matrix (without aluminum filler), and strontium chromate in toluene. Test data obtained from the study is shown in Table 28. The table contains data from both as-cured and 1-day-steamed bonds. It can be seen from the data that unprimed adherends give the best results when tested at room temperature; however, the matrix primer is slightly better when tested at 121°C (250°F). Based on these data, it was decided to evaluate the 303 adhesive without a primer in the characterization study. The data in Table 28 show an unexpected loss in strength at elevated temperature when compared to the data obtained previously with this adhesive formulation at 93°C (200°F). The previous data showed bond strengths averaging about 18 MPa (2,600 psi) at both room temperature and 93°C (200°F).

It was established that the liquid adhesive system containing 46 weight percent t-butylstyrene, 30 percent Diacryl 101, and 24 percent Solprene 414S rubber toughener, when catalyzed with 0.5 phr t-butylperbenzoate and 0.75 phr cumene hydroperoxide, had an apparent usable shelf life of at least 1 month at room temperature. A sample of the catalyzed resin did not gel over a period of 1 month at room temperatures, and the resin cures normally when heated to 350°F for 1 hr. When bonds were prepared after 1- and 3-week storage, however, the lap shear strengths shown in Table 29 were obtained. The strength loss observed with storage time is unacceptable and suggests that catalyst addition must occur to the resin immediately prior to bond assembly (two-part system).

An alternate interpretation of the data is that bond strength increases with aging time (after cure) at room temperature. Since the initial, 1-week, and 3-week bonds were tested on the same day, the initial and 1-week bonds were aged at room temperature for a longer period of time. Another set of bonds

TABLE 28. TENSILE LAP SHEAR STRENGTH AT ROOM TEMPERATURE AND +250°F WITH DIFFERENT PRIMERS<sup>a</sup>

| Surface Preparation-b-c | RT Test<br>MPa (PSI); % AF |  | +250°F Test Temperature<br>MPa (PSI); % AF |  |
|-------------------------|----------------------------|--|--|--|
|                         | As cured                   | Conditioned 1 day at<br>212°F and 100% RHE | As Cured                                   | Conditioned 1 day at<br>212°F and 100% RHE |
|                         |                            |  |  |  |
| Phosphoric Anodize      | 19.8 (2,870); 5            | 17.7 (2,570); 5                            | 10.1 (1,460); 0                            | 9.6 (1,390); 5                             |
| B2-127 Primer           | 16.4 (2,380); 100          | 15.0 (2,170); 95                           | 7.9 (1,140); 100                           | 7.3 (1,060); 100                           |
| Mat. 1x Primer-d        | 17.5 (2,540); 95           | 15.1 (2,190); 95                           | 11.0 (1,590); 15                           | 11.0 (1,590); 0                            |

<sup>a</sup>Data represents average of 3 specimens per data point.

Adhesive cure cycle: 1°C/min heat rise to 250°F + 2 hrs at 250°F.

Average bondline thickness = 2 mils.

<sup>b</sup>Adherends are 2024-T3 aluminum, 10V phosphoric acid anodized

-Primers cured 1 hour at 250°F

<sup>c</sup>Matrix primer: 90 toluene, 1.5 SrCrO<sub>4</sub>, 8.5 Matrix Resin (24 solprene, 46 t-Butylstyrene, 30 diacryl 101, 0.5 t-Butylperbenzoate, 0.75 cumene hydroperoxide)

<sup>d</sup>Bonds were over rapidly boiling water in a closed flask equipped with a condenser

TABLE 29. EFFECT OF STORAGE IN THE ROOM-TEMPERATURE LAP SHEAR STRENGTH OF COMPOSITION 303<sup>a</sup>

| Adhesive Stored at RT |            |                    |                 | Adhesive Stored at 5°C (40°F) |                    |                 |
|-----------------------|------------|--------------------|-----------------|-------------------------------|--------------------|-----------------|
|                       | Average    | Standard Deviation | Number of Bonds | Average                       | Standard Deviation | Number of Bonds |
| Initial               | 10 (2,740) | 2 (250)            | 4               | 19 (2,740)                    | 2 (250)            | 4               |
| 1 week                | 15 (2,210) | 2 (296)            | 4               | 18 (2,580)                    | 2 (243)            | 4               |
| 3 weeks               | 14 (2,040) | 1 (72)             | 4               | 14 (2,060)                    | 1 (135)            | 4               |

<sup>a</sup>Average GLT, 3 mils; strengths given in MPa (psi)

prepared on the same day as the 1-week bonds from fresh adhesive had room temperature lap shear strengths of 20 MPa (2,800 psi) after aging at room temperature for 6 weeks. This apparent strength increase with aging time at room temperature was also suggested by the observed increase in bell peel strengths seen in Table 25 and discussed on page 68.

### SECTION 3

#### CONCLUSIONS AND RECOMMENDATIONS

1. The major program objective -- the development of a low moisture-absorbing structural adhesive was achieved. The good adhesion of the very low polarity adhesive compositions to the phosphoric acid anodized aluminum is not understood. Adhesion promoters may be required with the program's adhesive composition on other surfaces.
2. The objective of developing a paste adhesive for bonding portable shelters appears also to have been met. However, a two-part kit may be required since the shelf life of the one-part kit may not be adequate.
3. The objective of developing a film adhesive will require further development efforts to be carried out. The technology developed by this program is expected eventually to lead to such a product or family of products.
4. It is evident from the initial adhesive properties contained in this report that, in fact, two types of adhesives can be pursued. One would be of the structural type addressed on this program, and the second would be a high peel strength, intermediate shear strength adhesive as used for sealbonding integral fuel tanks.

5. Since the program adhesive(s) do not turn white upon failure (peel mode) it is concluded that good potential exists for improving the adhesive strengths of the program compositions.
6. Although a more comprehensive evaluation of the program adhesives is needed, from the reported adhesive data, two major shortcomings of acrylate adhesives appear to have been overcome. Familiar acrylate adhesives are brittle at -54°C and have a distinctive (unpleasant) odor.
7. The use of ABA block copolymers not containing unsaturation (butadiene) would be preferred in future development efforts with program compositions.

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