The present research has confirmed that it is possible to form durable bonded joints on aluminium-lithium alloys using a toughened acrylonitrile adhesive, Permabond 224. Although the bonded alloy showed excellent durability in the as-received condition, such a surface is unlikely to be encountered in practical engineering environments. However, it appears from the present work that abrading under polar monomer could be a basis for a viable pretreatment in areas where more complex pretreatments (etching and/or anodizing) are not feasible; such situations include field repair and industrial sites where control for chemical or electrolytic processing is inadequate. The monomer could be produced in paste form and applied to the adherend prior to abrasion; this would provide a simple pretreatment.

Conclusions

Aluminium-lithium alloys bonded in the as-received condition with a toughened acrylonitrile adhesive show excellent durability; this is attributed to the nature of the surface oxide film on the alloy adherend. Abrasion of the 8009 alloy in the presence of water results in joints with lower durability, but abrasion under a polar monomer gives rise to bonds of excellent strength and durability. These observations may provide the basis of a simple pretreatment for adhesive bonding of aluminium-lithium alloys.

References


Authors

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Effects of environmental exposure on adhesively bonded joints

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* (Martin Marietta Laboratories, Inc. / The Smithsonian Institution, USA)

The use of adhesive bonding for airframes and other engineering structures offers significant advantages over the commonly used mechanical fasteners. However, not all adhesives are able to withstand the environmental extremes encountered by a structure over its service lifetime. Therefore, the selection of an adhesive for bonding these structures must include an evaluation of its performance under adverse environments, primarily moisture. Studies of moisture absorption by several adhesives reveal that the adhesives gain the bulk of their water weight within 1-2 days. The effects of this moisture ingress on adhesively bonded joints were evaluated via stress relaxation and fracture analysis. Stress-relaxation results show that some adhesives can retain about half their 'dry' strengths at equilibrium moisture strain, whereas the fracture toughness analysis suggests that ductility decreases with increased duration of exposure.

Key words: adhesives; moisture absorption; stress relaxation; instantaneous stress; equilibrium stress; fracture toughness; elastic energy release rate; plastic energy dissipation rate

The process of selecting an adhesive for outdoor structures must include an evaluation of not only its material properties, such as strength and modulus, but also its performance and durability under real exposure conditions. Studies have shown that the long-term durability of an adhesively bonded joint can be limited by the response of the adhesive, as well as the interphase, to environmental factors, primarily moisture. Since there are treatments available today which inhibit the attack of moisture at the interphase (e.g., phosphoric acid anodization), the primary focus of this paper was limited to the response of the adhesive to moisture uptake.

The effects of moisture on an adhesively bonded joint may be related to the adhesive's ability to absorb moisture. In many cases, an adhesive will absorb moisture very readily since its backbone is made up of many hydrophilic units. Thus, in a wet or humid environment, moisture may easily penetrate into the backbone, causing swelling and deformation of the adhesive matrix, as well as breakdown of chemical bonds and consequent weakening of the polymer backbone. Furthermore, moisture may migrate to the adhesive/interfaced interface and displace bonding sites formed along the substrate. In any case, the overall strength and toughness of an adhesive joint may be severely compromised as a result of exposure to moisture.

In the following report, we describe the results of moisture studies on films of two commercial adhesives - Hysoyl EA994 (an aluminium- and silica-filled modified epoxy) and Industrial Formulators of Canada LP-31 (an amine-bonded epoxy) — and four adhesives modified at Martin Marietta Laboratories (designated MML). Properties investigated were:

1. (1) moisture pick-up in water and humidity; and
2. (2) changes in stress-relaxation and fracture behaviour as a function of humidity exposure.

Experimental

Formulations

The adhesives used in this investigation are listed in Table 1. The two commercial systems are both two-part modified epoxies: Hysoyl EA994 is an aluminium- and silica-filled resin with an amine hardener, and Industrial Formulators of Canada LP-31 is an amine-bonded epoxy with an amine hardener. Adhesives MML-14 and MML-96 were formulated by chain-advancing DER 331, a Dow bisphenol A-based epoxy resin of equivalent weight 189 with a diol containing two azomethine linkages (see Fig. 1a) and 10% carbon-terminated butadiene-styrene polymer (Gurit Hycar CRM from B.F. Goodrich) to an equivalent of 14.0%

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Table 1. Adhesives investigated in the programme

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resin</th>
<th>Additive</th>
<th>Toughener</th>
<th>Curing agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>EA 9394*</td>
<td>DER 331**</td>
<td>Bisazosmethidol</td>
<td>Epon V40 (40%)</td>
<td></td>
</tr>
<tr>
<td>MML-3H</td>
<td>ATBN 1300 x 16</td>
<td>CTBN 1300 x 13 (10%)</td>
<td>Dow TETA (9%)</td>
<td></td>
</tr>
<tr>
<td>MML-14</td>
<td>ATBN 1300 x 16</td>
<td>CTBN 1300 x 13 (10%)</td>
<td>Dow TETA (9%)</td>
<td></td>
</tr>
<tr>
<td>MML-16</td>
<td>ATBN 1300 x 16</td>
<td>6% F-isophend A</td>
<td>Dow TETA (9%)</td>
<td></td>
</tr>
<tr>
<td>MML-96</td>
<td>ATBN 1300 x 16</td>
<td>cf-azosmethidol</td>
<td>Dow TETA (9%)</td>
<td></td>
</tr>
</tbody>
</table>

*Commercial systems

See also patent (pat. 189)

.weight (EW) of 250, MML-14 contained CTBN 1300 x 13 (20% acrylic butadiene), and MML-96 contained CTBN 1300 x 8 rubber (18% acrylic butadiene). Both resins were cured with 9 phr triethylene diamine (TEDA) from Dow.

MML-3H was formulated via chain advancement of DER 331 to EW = 250 with the diazomethane dicyan (see above) and 3% Hycar 1872, a high-molecular-weight CTBN from B.F. Goodrich. Before curing, 10 phr ATR 1300 x 16 (amine-terminated butadiene acrylonitrile) was added. The resin was then cured with 40 phr Epon V40, a polynamide (from Shell) containing reactive primary and secondary amine groups.

Adhesive MML-16 was chain advanced to EW = 250 with 1,1,3,3,3-hexafluoro-2,2- bisphenol propane (Fig. 1)(a) and 10% CTBN 1300 x 13, and cured with 9 phr TETA. The development work on the MML formulations was supported by the US Army, Belov and Research and Engineering Center, Ft. Belvoir, VA.

Test methods

Moisture absorption

Test the film specimens for moisture absorption were cast by pouring the thoroughly mixed adhesive composition onto an aluminium block, 30.5 cm x 12.7 cm x 1.5 cm, covered with a silicone release sheet, placing another sheet on top, and rolling the adhesive pool with a glass rod to remove entrapped air. Another aluminium block of the same size, with four 1.5 cm shims attached to its corners, was then placed on top of the adhesive sandwich, the entire assembly was clamped, and the adhesive was allowed to cure. The cure schedule for each adhesive test was 16 h at ambient temperature. The test was conducted for 2.5 days at 323 K. Once fully cured, the resultant 2.54 mm thick strips were cut to 7.62 x 2.54 cm.

Moisture uptake in the adhesive strips was measured for two conditions: (1) direct water immersion; and (2) controlled humidity exposure. For immersion studies, the specimens were fully immersed in water-filled containers at ambient temperature (ASTM D707-81, Standard Test Method for Water Absorption of Plastic). For the controlled humidity experiment, the specimens were suspended from a rack within a Blue M model VP-10-AT 1 controlled humidity chamber maintained at 323K and >95% relative humidity (RH). Prior to exposure, the specimens were weighed on a Mettler H31A1 analytical balance to the nearest 0.0001 g, and their initial weight was recorded. The specimens were removed from their exposure environment after various exposure times, unwrapped, measured, and then returned to their test environment. Weight gain was calculated and recorded as a function of immersion time.

Stress relaxation

Specimens for stress-relaxation measurements were cast, cured and post-cured in the same manner and from the same adhesives as those for the moisture absorption experiments, except the strips were cut to 17.8 x 0.508 cm. The strips were placed in self-contained stress jigs (Fig. 3) positioned inside a humidity chamber controlled at 323K and >95% RH. After reaching equilibrium, the strips were placed under roughly 10% of their ultimate strain. The relaxation of the stress as the adhesive stretched caused a logarithmic decrease in the stress level until an equilibrium was reached after 8-16 h. At that point, another increment of strain was applied. This procedure was repeated until the strain level exceeded 6% or until failure. The result was a measure of sustainable stress as a function of strain for an adhesive in equilibrium with its environment.

Fracture toughness

The procedure used for fracture toughness testing was the energy separation technique developed by Mckerninger et al. for testing toughened ambient temperature curing adhesive systems. The specimens used for testing were 12.7 x 254 mm (C(T) plan, bonded aluminium samples with the dimensions shown in Fig. 3. The adherends were machined from 6061 T6 aluminium and were bonded with thoroughly mixed adhesive in alignment jigs to provide a bondline of 2.54 x 10^-4 m.

Adherent surfaces were prepared for bonding by: (1) degreasing at 33K in an aerated alkaline soap solution (Turco 421S) for 20 min; (2) thoroughly rinsing with distilled water; (3) etching at 321K in an aerated chromic acid solution for 15 min with Forest Products Laboratory aluminum etch: 12 vol% concentrated sulphuric acid and 69 g/l sodium dichromate; (4) thoroughly rinsing with distilled water; (5) anodization at 10 V in 10% aqueous phosphoric acid solution for 30 min; (6) thoroughly rinsing with distilled water; and (7) air drying.

Each bonded specimen was allowed to cure at ambient temperature for 16 h, followed by a post-cure at 323K for 2.5 days. After post-cure, the specimens were exposed to 323K and >95% RH in a Blue M model VP-10-AT 1 controlled humidity chamber. At intervals, specimens were removed from the chamber and tested for fracture toughness on an Instron model 1125 mechanical testing equipment equipped with an MTS model 632-02B2-20 clip-on displacement gauge. The tester was interfaced to a Zentron data system ZW-248-83 computer, which recorded the raw data and calculated fracture parameters for each test.

Results and discussion

Moisture absorption

Fig. 4 shows the plots of the moisture absorption data, weight gain vs. time, for the water immersion experiment for the two commercial adhesives and three of the in-house formulated adhesives. The plots for each are a result based on an average of three specimens for each adhesive.

The bulk of the water weight for each adhesive was gained fairly quickly — within a day or two; additional absorption proceeded at a moderate rate for the remainder of the exposure period. EA 9394 appeared to absorb moisture fairly quickly: about 4% by the first day (or 60% of its capacity), and 7% in 21 days. This may be due in part to the aluminium and silica fillers within its matrix. The other systems demonstrated some resistance to moisture ingress, with only moderate weight gain within the first day, and only a 2-2.5% gain overall. It might be expected that these more moisture-resistant systems will prove to be more durable over time.

Fickian diffusion plots of water uptake vs. (time) for the adhesives tested in the water immersion experiments are shown in Fig. 5. For the adhesives studied there is an initial linear region, then an intermediate region. The absence of a plateau in each plot indicates that equilibrium has not been established. From the slope of the initial linear regions the apparent diffusion coefficient $D$ was calculated using the equation:

$$D = \frac{\pi}{16} \left( \frac{M_s}{r} \right)$$

where $M_s$ is the water absorbed at time $t$, and $M_s$ is the water absorbed at equilibrium. The diffusion
Table 2. Diffusion coefficients of the adhesives studied for moisture absorption

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Diffusion coefficient ( [\text{m}^2 \text{s}^{-1}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>EA 9394 (immersion)</td>
<td>4.43</td>
</tr>
<tr>
<td>EA 9394 (humidity)</td>
<td>5.83</td>
</tr>
<tr>
<td>LP2-31</td>
<td>1.23</td>
</tr>
<tr>
<td>MML-14</td>
<td>2.91</td>
</tr>
<tr>
<td>MML-16</td>
<td>3.46</td>
</tr>
<tr>
<td>MML-96</td>
<td>4.52</td>
</tr>
</tbody>
</table>

Fig. 6 shows a plot of weight gain vs. log(t) for various adhesives in humid conditions. The data is scattered around a linear relationship with a slope of \( m = 3.05 \) and an intercept of \( b = 0.5 \), indicating a diffusion coefficient of \( D = \frac{b}{m} = 1.43 \times 10^{-2} \text{m}^2 \text{s}^{-1} \).

This relationship does not hold for EA 9394 exposed to humid conditions. For the initial portion of the curve, \( m = 2.6 \), which is similar to that obtained for immersed EA 9394, but the long-duration portion of the curve fits a much lower value slope, \( m = 0.7 \). This phenomenon could be due to different absorbing rates of the filler particles vs. the matrix. Most likely the filler materials will absorb the water molecules at a quick rate. Once the filler is fully saturated the matrix will absorb the rest, but at a much slower rate.

**Stress Relaxation**

In warm, moist environments, an adhesive with absorb moisture and swell until it is in equilibrium with its environment. Imposition of a load upon the adhesive produces additional stress, which causes the adhesive to deform until a new stress equilibrium is reached. The decrease in stress observed under constant deformation is known as stress relaxation, and the reduction in strength it induces is detrimental to most adhesive systems, especially in outdoor structure applications.

Figs 9(a) and 9(b) represent plots of stress-relaxation tests for adhesives LP3-31 and MML-96. The locus of the lowest points on all stress-relaxation segments for each plot represents the equilibrium tensile stress-strain curve. In most cases, equilibrium was reached within 16 h of the time of the initial stress. Also shown in both figures are the instantaneous stress-strain curves for the adhesive in a controlled humidity environment, which were generated to determine ultimate adhesive strength during exposure. The difference in the performance of the two systems is quite evident. The equilibrium stress curve appears considerably lower for the commercial system, indicating very little retention of strength after equilibrium. MML-96, on the other hand, exhibits much better resistance to moisture, retaining over 50% of the instantaneous stress applied at the 0% strain level.

Table 3 shows the effect of stress relaxation on adhesives under stress in a warm, moist environment. The data are listed for increments of 2%, 4%, and 6% strain, and are based on an average of three runs for each adhesive. The second (larger) number under each strain increment represents the average instantaneous stress applied to the adhesive, while the first (smaller)
number is the average equilibrium stress for each strain increment. Also shown is the ultimate tensile strength of each material under a rapid loading in the humid environment, and the dry ultimate tensile strength of the adhesive.

Adhesive LP-31 appeared to have the lowest strength retention. In essence, it lost most of its load-bearing capacity at equilibrium, a result that does not correlates well with its observed moisture retention (see Table 2). In fact, the data are quite contradictory, since the diffusion coefficient is lowest of all the adhesives yet it shows the weakest response to moisture ingress. The relaxation results obtained for EA 9394 show that it performed quite well despite its limited resistance to moisture uptake. Adhesive MML-3H showed some strength retention under the high-humidity conditions. Although MML-14 and MML-96 exhibited excellent strength retention compared with the others. In their case, the stress-relaxation results correlate quite well with their resistance to moisture ingress (Table 2). In addition, MML-96 was observed to retain more than half its dry strength at equilibrium moisture strain at 6% strain level.

Table 3. Stress-relaxation results for test adhesives

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>2% Strain (MPa)</th>
<th>4% Strain (MPa)</th>
<th>6% Strain (MPa)</th>
<th>Rapid load to failure (MPa)</th>
<th>Ultimate tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MML-96</td>
<td>8.96/20.69</td>
<td>17.93/28.96</td>
<td>24.13/37.92</td>
<td>48.95</td>
<td>73.85</td>
</tr>
<tr>
<td>MML-14</td>
<td>6.21/17.24</td>
<td>4.72/22.75</td>
<td>13.79/25.51</td>
<td>33.10</td>
<td>60.88</td>
</tr>
<tr>
<td>EA 9394</td>
<td>3.45/17.24</td>
<td>11.03/20.00</td>
<td>15.86/26.20</td>
<td>24.82</td>
<td>75.43</td>
</tr>
<tr>
<td>MML-3H</td>
<td>1.59/8.41</td>
<td>2.85/8.64</td>
<td>3.59/11.03</td>
<td>20.69</td>
<td>42.36</td>
</tr>
<tr>
<td>LP-31</td>
<td>0.138/1.38</td>
<td>0.276/1.38</td>
<td>0.414/3.46</td>
<td>22.06</td>
<td>57.50</td>
</tr>
</tbody>
</table>

Apparent, adhesive systems modified with additives such as high molecular weight rubbers and for fillers in LP-31 may have limited load-bearing capacity in humid environments, despite their resistance to moisture pick-up.

Fracture resistance

Previous studies by the authors have shown that the plastic component of fracture energy correlated well with differences in adhesive behaviour and can be used to monitor improvements in adhesive chemistry. Linear elastic fracture mechanics was not applicable to our systems due to their extensive ductile behaviour. The test method used in our analysis was the standard unload-compliance J integral test (ASTM E 1132). The J integral is a single-valued parameter that combines both elastic and plastic components of energy. Our

previous studies suggest that a clearer distinction of these energies was necessary, because modifications to an adhesive composition affected the elastic and plastic components independently. A brief description of the energy separation technique is given below.

Fig. 10 shows a typical plot of load vs. load-line displacement curve obtained for a bonded (ct) specimen. The area under the curve is equal to the sum of the elastic, plastic, and potential energies as explained below:

Area OAA'O = $\Delta U_e$ plastic energy dissipated during crack extension
Area O'AB = $\Delta U_p$ elastic energy released during crack extension
Area O'B'D = $\Delta U_s$ = stored elastic strain (potential) energy before crack extension
Area OAC = $\Delta U_{s+e}$ = stored elastic strain (potential) energy after crack extension

$k_1$ = stress intensity for the ith increment
$s_{i+1} = s_i + 1$ increment of crack extension

By partitioning the energies, one can separate the total area into elastic and plastic components according to the equation:

$\Delta U_e = G_e + \int \frac{dU}{da} = \frac{1}{B_w} \int \frac{dU}{da}$

where

$\Delta U_e = \text{the total energy release rate}$

$G_e = \text{the plastic energy release rate}$

$I = \text{the plastic energy dissipation rate}$

Using the technique, we were able to obtain the elastic energy release rate and the plastic energy dissipation rate, $G_e$ and $I$, respectively, for each specimen tested. Both of these parameters are related to the fracture toughness of the adhesive, i.e., the total energy required for crack initiation and propagation.

Table 4 shows the results of the load-unload compliance testing carried out on exposed bonded ct specimens for three different adhesives: EA 9394, LP-31 and MML-3H. The peak load is the load at which crack growth begins. Results are based on an average of three to five replicates for each adhesive and each exposure time. In all specimens tested, failure was within the adhesive. Figs 11(a), 11(b) and 11(c) are plots of the fracture parameters $G_e$, $I$ and $k_1$ vs. high-humidity exposure for each adhesive. In addition, each figure contains a plot of the peak load vs. exposure time. When the plastic energy dissipation rate, $I$, or the elastic energy release rate, $G_e$, is used as a ‘gauge’, the toughness of the adhesives appears to decrease with increasing exposure time. Peak load also decreased with increasing exposure time. This (reasonable) finding suggests that moisture has an adverse effect on the toughness of these adhesives which is contrary to previous reports that the fracture resistance increases with water absorption. Since the chemical nature of the adhesives studied in this paper is not identical to those studied by others, a mechanism other than plasticization must account for this behaviour. Apicella et al. have suggested that moisture absorption by a
The fracture data for Hyos E9394 are consistent with its stress-relaxation behaviour, which indicated a minimal effect of moisture on its performance. Although EA9394 fracture values were relatively low, they were still in a useful range (i.e., the adhesive is not brittle). In addition, stress-relaxation results showed that EA9394 is one of the best performers. LP2-31 exhibited more susceptibility to moisture than the other two systems, i.e., the value of f fell by a factor of 10 after 20 days of exposure. This trend in fracture toughness correlates very well with the adhesive’s stress-relaxation data, which suggest that this system would have limited use in humid environments. The results for MML-3H show minimal reduction in fracture toughness, and a moderate reduction in peak load with prolonged exposure. Correlation of its fracture results with the results for stress-relaxation indicates that it has a good balance of moisture-resistant properties.

Conclusion

Moisture absorption studies were conducted on two commercial systems, Hyosol EA9394 and Industrial Formulators of Canada LP2-31, and four in-house formulations, MML-3H, MML-14, MML-16 and MML-96. In direct immersion experiments (ASTM D789-81), the adhesives gained the bulk of their water weight within a day or two, with more moderate gains thereafter. EA9394 absorbed approximately three times more moisture than any of the other adhesives in the same time span. In addition, diffusion coefficients were reported for each system tested. In high-humidity exposure tests, EA9394 absorbed only one-half as much moisture as in the water-immersion experiment. The difference is most likely due to rates of absorption and in two environments, since the diffusion coefficient reported is greater in the humid environment.

Stress-relaxation measurements performed on EA9394, LP2-31, MML-3H, MML-14 and MML-96 showed that the in-house formulations (MML-14 and MML-96) could retain more than half their instantaneous stress at equilibrium at 6% strain. EA9394 also performed well, retaining about half its stress values at the same stress at the given moisture-strain equilibrium at 6% strain. The modified adhesive MML-3H showed some strength retention. However, LP2-31 lost most of its load-bearing capacity at equilibrium. Since several of the adhesives had good instantaneous strengths, joints weakened by moisture would still have satisfactory properties under transient stress conditions, such as those experienced by airframes and mobile bridges.

Fracture toughness studies on exposed samples of EA9394, LP2-31 and MML-3H indicated that fracture toughness decreases with increasing time of exposure to high humidity. This is contrary to previous reports on anhydride-toughened epoxies that indicate an increase in fracture resistance with moisture uptake. We believe that, due to differences in chemistries of the adhesives studied in this paper vs. adhesives studied in other reports, a mechanism other than plasticization of the matrix is responsible for this phenomenon. The adhesives studied in this report are inherently tough and it is expected that the values reported are a result of loss of cohesive strength of the bulk adhesive due to water absorption.

Overall, adhesive MML-3H showed a good balance of moisture resistance, load-bearing capacity and fracture toughness when exposed to high humidity. EA9394 showed exceptional stress-relaxation results and moderately good fracture behaviour, despite its rapid water weight gain. LP2-31 showed the lowest values of stress retention and fracture toughness, despite its low moisture pick-up. It may therefore be of only limited use in bonding outdoor structures.

Acknowledgement

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Table 4. Fracture toughness data for 1/2T compact tension specimens exposed to high humidity

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Exposure (days)</th>
<th>Peak load (kg)</th>
<th>G</th>
<th>J* (N m^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EA9394</td>
<td>0</td>
<td>69.4</td>
<td>73.2</td>
<td>107.1</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>73.9</td>
<td>75.0</td>
<td>67.8</td>
</tr>
<tr>
<td></td>
<td>43</td>
<td>70.3</td>
<td>55.4</td>
<td>37.5</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>65.8</td>
<td>48.2</td>
<td>89.3</td>
</tr>
<tr>
<td>LP2-31</td>
<td>0</td>
<td>97.1</td>
<td>146.4</td>
<td>714.2</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>98.8</td>
<td>116.1</td>
<td>392.8</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>81.6</td>
<td>94.3</td>
<td>160.7</td>
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<tr>
<td></td>
<td>20</td>
<td>52.2</td>
<td>39.3</td>
<td>69.6</td>
</tr>
<tr>
<td>MML-3H</td>
<td>0</td>
<td>74.8</td>
<td>103.6</td>
<td>212.5</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>62.1</td>
<td>78.6</td>
<td>173.2</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>54.4</td>
<td>60.7</td>
<td>169.6</td>
</tr>
</tbody>
</table>

Note: J* determined by the method in ASTM E1152