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Chemical Bonding Technology for Terrestrial Photovoltaic Modules

Status to February, 1983

D. R. Coulter
E. F. Cuddihy
E. P. Plueddemann



November 15, 1983

Prepared for
U.S. Department of Energy
Through an Agreement with
National Aeronautics and Space Administration
by
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California Institute of Technology
Pasadena, California

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ABSTRACT

Encapsulated photovoltaic modules must hold together for 20 years, reliably resisting delamination and separation of any of the component materials. Delamination of encapsulation materials from each other, or from solar cells and interconnects, can create voids for accumulation of water, promoting corrosive failure. Delamination of silicone elastomers from unprimed surfaces was a common occurrence with early modules, but the incidences of silicone delamination with later modules decreased when adhesion promoters recommended by silicone manufacturers were used. An investigation of silicone delamination from unprimed surfaces successfully identified the mechanism, which was related to atmospheric oxygen and moisture. This early finding indicated that reliance on physical bonding of encapsulation interfaces for long life in an outdoor environment would be risky.

For long outdoor life, the material components of a module must therefore be held together by weather-stable adhesion promoters that desirably form strong, interfacial chemical bonds. The Environmental Isolation Task of the Flat-Plate Solar Array Project (FSA), managed by the Jet Propulsion Laboratory (JPL) for the U.S. Department of Energy (DOE), conducts a program to identify, develop, and validate weather-stable chemical bonding adhesion promoters for terrestrial photovoltaic modules. This program is a joint effort currently involving Dow Corning Corp., Case Western Reserve University, Rockwell International, Springborn Laboratories, Inc., and JPL.

This report, the Task's second on chemical bonding technology, is intended to accomplish three purposes:

- (1) Provide a status report on chemically bonding adhesion promoters, with data on bond strength performance.
- (2) Describe and discuss the theories of the chemically bonded interface.
- (3) Identify processing considerations relevant to achieving long-term interfacial chemical bonding.

FOREWORD

This report on chemical bonding technology for terrestrial photovoltaic modules includes information on the current status of chemical bonding technology, a description of the theories of the chemically bonded interface, and an introduction to processing considerations relevant to achieving long-term interfacial chemical bonding. It has been prepared at the Jet Propulsion Laboratory, California Institute of Technology, by Daniel R. Coulter and Edward F. Cuddihy, members of the Materials Science Group of the Applied Mechanics Technology Section, and Edwin P. Plueddemann of the Dow Corning Corporation.

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INTRODUCTION

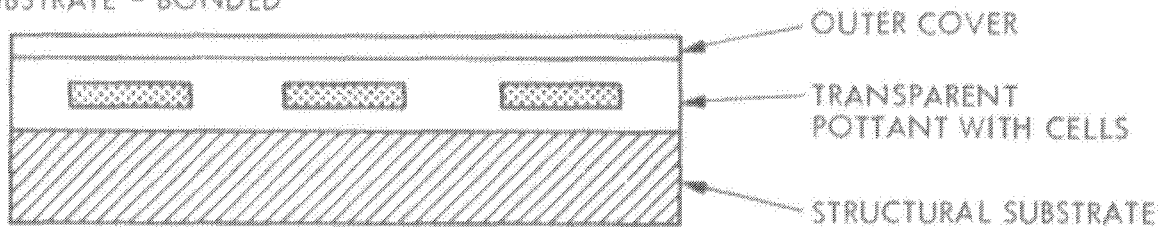
A. BACKGROUND

Photovoltaic (PV) modules contain strings of electrically interconnected solar cells capable of producing practical quantities of electricity when illuminated by sunlight. Silicon solar cells are fragile and are especially sensitive to brittle failure in tension and bending. The electrically conductive metallization materials (functioning as grids, interconnects, bus bars, and terminals) are sensitive also to excessive flexing, corrosion and other interactions with the terrestrial environment. To ensure the durability of PV modules, their silicon solar cells must be mechanically supported, and the electrically conductive metallization materials must be isolated from environmental exposure.

Encapsulation materials are defined as all construction materials (excluding cells and electrical conductors) required in a PV module to provide mechanical support and environmental isolation. Early efforts to identify a single material that could satisfy all of the encapsulation requirements and needs were unsuccessful (References 1 and 2). The understanding evolved that more than one material would have to be assembled in a composite package to fabricate an encapsulated module satisfying the requirements.

After an examination of all commercial and experimental flat-plate module designs, it was observed that they could be separated into two basic classes (Figure 1). These are designated as substrate-bonded and superstrate-bonded designs, referring to the method by which the solar cells are supported

SUBSTRATE - BONDED



SUPERSTRATE - BONDED

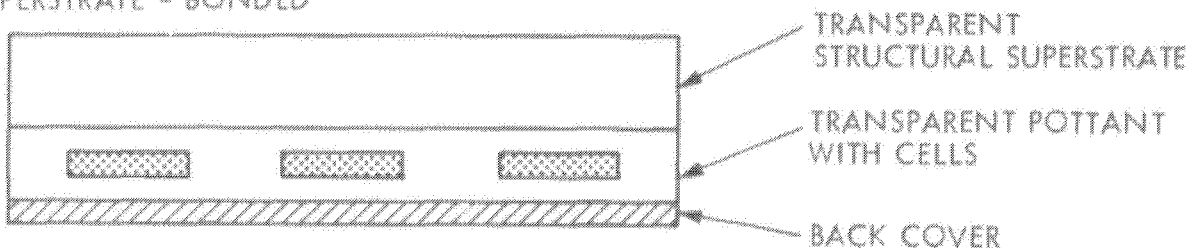


Figure 1. Flat-Plate Solar Module Design Classification

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mechanically. In the substrate design, the cells are supported mechanically by a structural substrate, and in the superstrate design, the cells are supported by a transparent structural superstrate. From these two design options, eight basic encapsulation construction elements can be identified. These are illustrated in Figure 2, with their designations and encapsulation functions. Fabricated modules do not need to use all eight of these construction elements, but combinations of these basic elements are incorporated in most module designs. Materials identified for each of these construction elements are listed below:

(1) Low-Soiling Surface Materials:

- Fluorinated silane, L-1668 (3M Co.)
- Perfluorodecanoic acid with Dow Corning Corp. Z-6020 primer, E-3820

(2) UV-Screening Front Covers:

- Low-iron, tempered float glass (e.g., Sunadex glass, ASG)
- UV-screening PMMA acrylic films (3M):
 - Acrylar X-22416, 2 mils thick
 - Acrylar X-22417, 3 mils thick
- UV-screening PVF fluorocarbon film (Du Pont Co.)
 - Tedlar 100BG30UT, 1 mil thick



PLUS NECESSARY PRIMER-ADHESIVES

Figure 2. Material Construction Elements and Interfaces in Photovoltaic Encapsulation Systems

(3) Pottants:

Ethylene vinyl acetate (EVA) (A-9918, Springborn, Du Pont, and Rowland, Inc., Berlin, Connecticut)

Ethylene methyl acrylate (EMA) (A-11877, Springborn)

Poly-n-butyl acrylate (PnBA) (BA-13870, Springborn)

Polyurethane (PU) (Z-2591, Development Associates, Inc., North Kingston, R.I.)

(4) Porous Spacer:

Craneglas non-woven E-glass mat, type 230, 5 mils thick (Electrolock, Inc., Chagrin Falls, Ohio)

(5) Dielectric Films:

Candidates are the front-cover and back-cover plastic films

(6) Substrates:

Mild steel

Hardboards

Super-Dorlux, 1/8-in thick (Masonite)

Duron, 1/8-in thick (U.S. Gypsum)

(7) Back Covers (White-Pigmented Plastic Films):

Tedlar 150BL 30 WH, 1.5 mils thick (Du Pont)

Scotchpar 20CF WH, 2.0 mils thick (3M Co.)

Korad 63000 White, 3.0 mils thick (Xcel Corp.)

(8) Edge Seal and Gasket:

Butyl edge sealing tape (5354, 3M)

EPDM gasket material (E-633, Pawling Rubber Co., Pawling, N.Y.)

Figure 2 also illustrates the interfaces between adjacent construction elements that will be generated in assembled modules. All of these interfaces in encapsulated modules must hold together for 20 years, reliably resisting partial delamination or total separation. If, for example, delamination of the pottant from solar cells or interconnects occurs, then voids will be formed where liquid water can accumulate, leading to corrosive failure. As another illustration, if back covers are adhesively attached to wood substrate panels to provide humidity protection, and if an adhesion failure were to occur at this joint resulting in a separation of the back cover, then humidity protection for the wood would be lost.

Modules manufactured in the early 1970s generally used silicone elastomers as the pottant material, and delamination from unprimed substrate surfaces was a common occurrence. However, the incidences of silicone delamination virtually ended when adhesion promoters recommended by the silicone manufacturers were used. In the absence of primers or other adhesion promoters, adhesion of the silicone elastomers to the substrate surfaces

involves physical bonding only. A study (References 3 and 4) of silicone delamination from unprimed substrate surfaces identified the mechanism, which was related to atmospheric oxygen and moisture. These results indicated that reliance on purely physical bonding of encapsulated interfaces for long life in an outdoor environment would be risky.

An alternative to physical bonding for interfacial adhesion is chemical bonding (References 5 and 6), where primary chemical bonds bridge the interface between two adjacent materials and hold them together. The adhesion promoters referred to above were formulated to generate such interfacial chemical bonds, resulting in dramatic improvement in resistance against weather-induced delamination.

It therefore became a major FSA activity to identify, develop, and validate durable and weather-stable interfacial chemical bonding techniques for encapsulated photovoltaic modules. The first FSA report on chemical bonding technology (Reference 7) was published in September, 1979, and this, the second report, is a status update. It is divided into four sections: Section I briefly presents definitions and essential descriptions of chemical bonding for readers not familiar with the subject; Section II is an updated listing of chemical bonding agents and an account of performance testing to date; Section III describes modern theories of physical and chemical adhesion, and Section IV presents briefly some of the processing considerations relevant to the formation of strong durable interfacial bonds in PV modules.

B. BASIC DEFINITIONS

Chemical bonding materials can be divided into three classifications: adhesives, coupling agents, and primers, defined as follows:

Adhesive: A gap-filling material between two rigid (solid) adherends (Figure 3) such as steel and wood, glass and plastic films, etc. The adhesive, when applied, is fluid or viscous to facilitate filling of the gap under some pressure, and to achieve uniform spread over the surfaces of the solid adherends. The adhesive will later lose its fluid flow properties and develop mechanical toughness, either by cooling, if a hot melt, or by being cured to become a thermosetting elastomer or resin. Interfacial adhesion at the adhesive-adherend interface can be established by attracting forces that are physical in nature (physical bonding), by molecular penetration, and/or by primary chemical bonds bridging the adhesive-adherend interfaces.

Coupling Agent: A material that is positioned at the adhesive-adherend interface, and that is chemically reactive with both the adhesive and adherend to generate primary chemical bonds bridging the adhesive-adherend interface (see Figure 4). For two different solid adherends with a common gap-filling adhesive between them, two different coupling agents matched to each adhesive-adherend interface may be needed. In theory, a coupling agent need only be a monomolecular-thick layer between the adhesive and adherend, as its function is chemical bridging.

Primer: A coupling agent dissolved in a volatile solvent, usually at a very low concentration (e.g., 1 to 5 wt %), to achieve a very thin

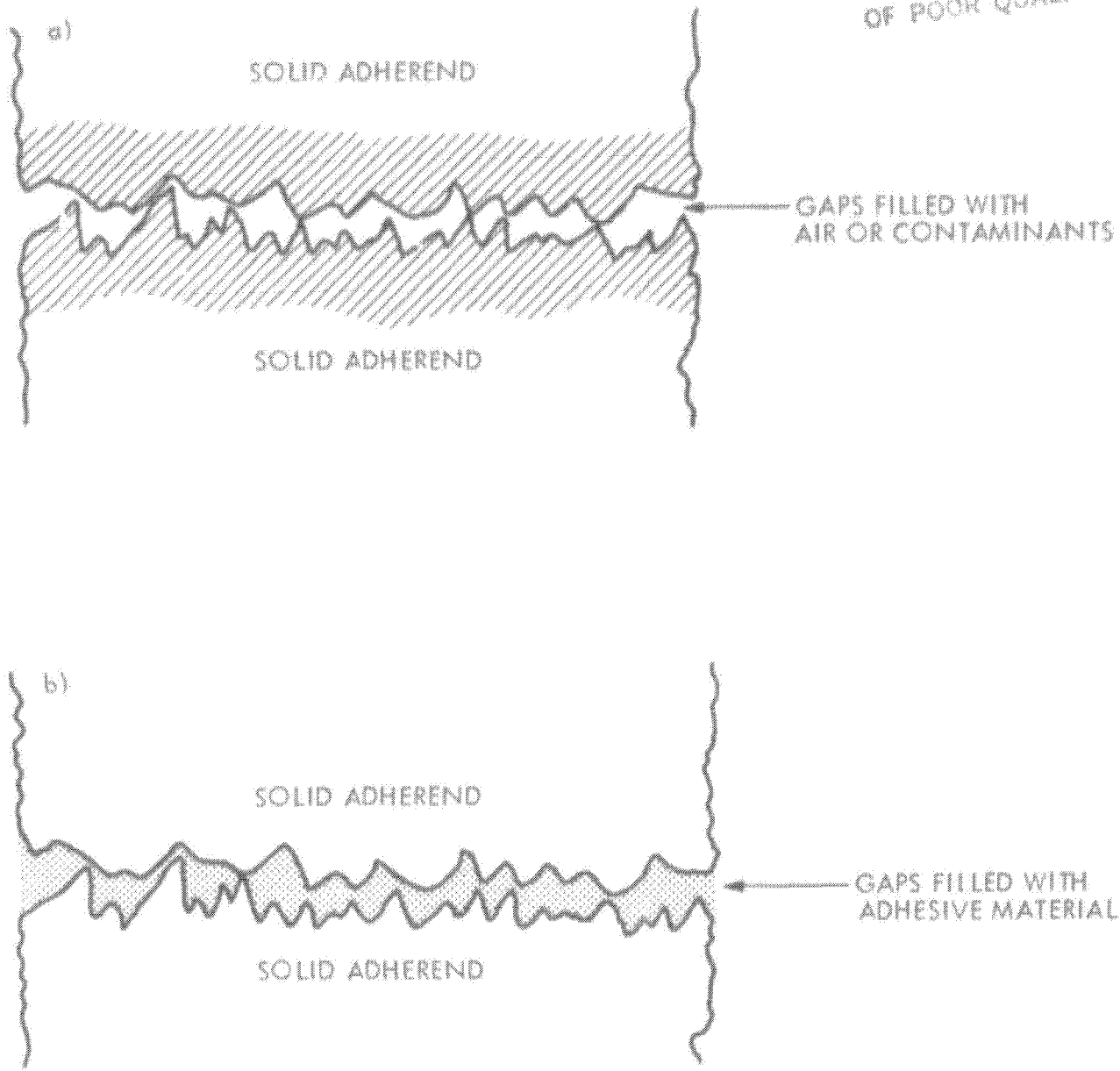
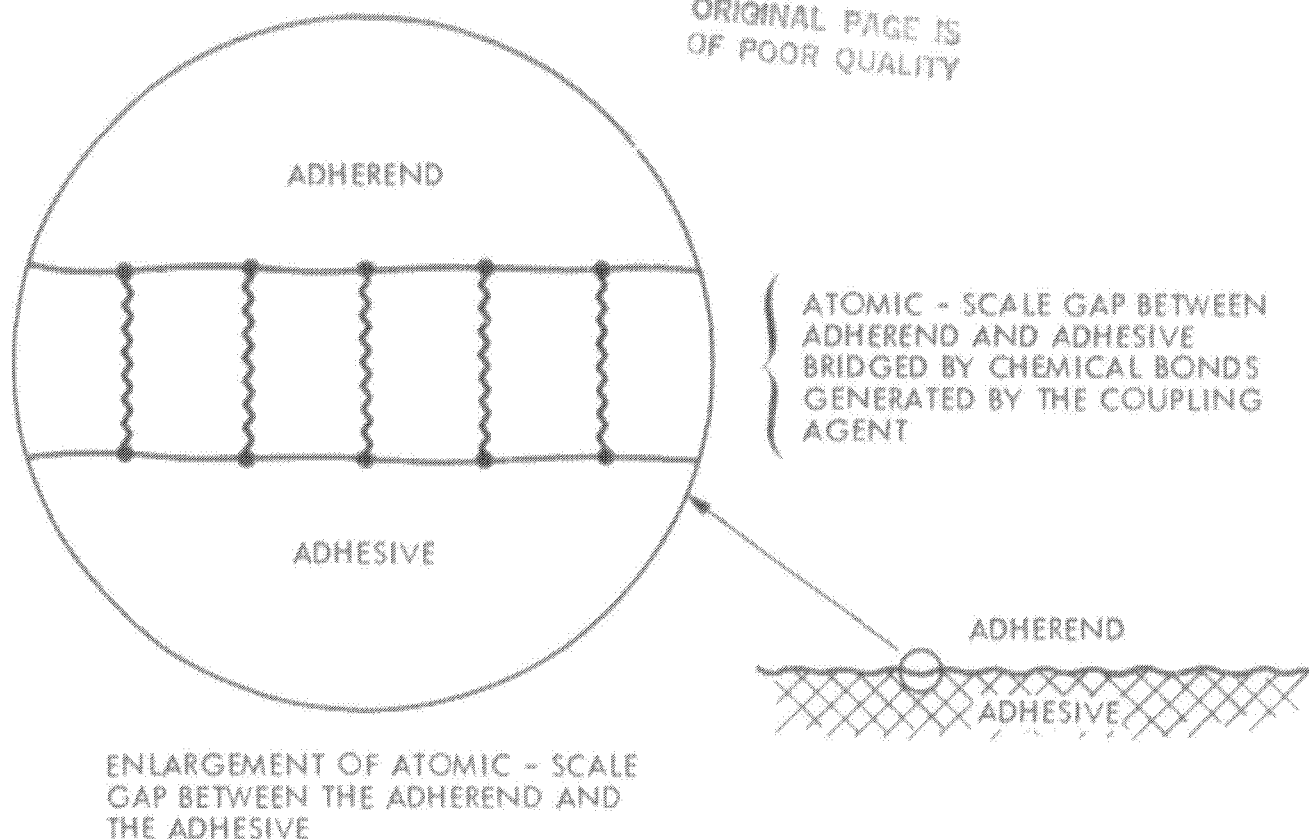


Figure 3. Representation of Two Non-Conforming Solid Surfaces in Contact With Each Other: (a) in the Absence of Adhesive Material, Leaving Gaps That Can Fill With Air or Contaminants, and (b) with Gap-Filling Adhesive Present

deposited layer of the coupling agent on a surface. Sometimes coupling agents need catalysts, reaction promoters, or other chemical compounds to facilitate interfacial chemical bonding. These necessary ingredients are also dissolved in the primer solvent at a concentration chemically related to the coupling agent. (As shown in Section III, coupling agents based on silane chemistry are being investigated for FSA encapsulation interfaces. In many cases water is needed as a reaction promoter and consequently will be used as a primer ingredient in many systems.)

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ENLARGEMENT OF ATOMIC - SCALE
GAP BETWEEN THE ADHEREND AND
THE ADHESIVE

Figure 4. Schematic Illustration of Chemically Bonded Interface

In practice, it could be a property of an adhesive and an adherend to form chemical bonds across their interface naturally, but if it is not, then a properly selected primer solution must be used. If such a solution is used, it is a usual practice to deposit it on the solid adherend surface(s). Alternatively, the coupling agent (and its necessary ingredients) could be dispersed into the adhesive material, to generate a self-priming adhesive. When such an adhesive is applied to an adherend, the coupling agent migrates to the interface to establish the interfacial chemical bonding.

Based on the foregoing definition of an adhesive, a pottant in a PV module can be considered to be such a material, in the sense that the pottant fills the gap between solid front and back encapsulation materials and that it develops mechanical toughness during the heating stages of module fabrication. If a pottant and an adherend such as glass do not naturally form interfacial chemical bonds, then an appropriate primer needs to be identified or developed. As shown in Figures 1 and 2, the pottant in a module achieves mutual contact with the majority of all other encapsulation materials as well as the solar cells and associated electrical circuitry. FSA emphasis in identification and development of primers is directed therefore to the pottant. Since the pottant material, in its current use, with all of its associated primers, has been found to be an effective adhesive, it is logical to examine the potential of this material for adhesive application in other areas of the module. For example, an adhesive is needed to bond white-pigmented plastic-film back covers

to a mild-steel panel. If primers have been identified or developed for chemically bonding a pottant to plastic-film front covers, and to solar-cell metallization, then the pottant and these primers can be investigated as an adhesive and primer system for the back covers and mild steel. As noted in Section III, this approach has worked for several back-cover and panel interfaces.

Sometimes the surface of a solid adherend does not have the proper chemistry to form chemical bonds with a chemically reactive adhesive, primer, or other coating. This occurs in PV applications with the low-soiling surface coatings L-1668 and E-3820 (p. 2). These two coatings contain chemical groups that will react readily with the surface of glass to form chemical bonds for strong, durable attachment. These same coatings, however, behave differently with Acrylar and Tedlar plastic films. It was found that the chemical attachment of E-3820 to Acrylar, and that of L-1668 to Tedlar, was weak (Reference 8). Therefore, for these specific coatings, the surfaces of the plastic films were treated with ozone to generate polar groups for enhanced chemical reactivity and therefore enhanced chemical attachment. This technique worked well. This adhesion-promoting technique, called surface activation, has only been needed so far for low-soiling coatings on plastic films.

Mechanically, the strength of an adhesive bond is measured under dry conditions, but in outdoor applications, the real assessment of an adhesive bond results from measurements of its bond strength under wet conditions. When wet, the simple criteria of bond quality are that the bonded parts do not readily separate, and that there be a measurable bond strength, greater than zero. Generally, wet bond strength will be lower than dry bond strength, which is not a concern as long as the wet bond strength is sufficient to hold the parts together against the stress encountered in service. Of course, the best condition would be that both wet and dry failure are cohesive.

For evaluating the durability of a chemically bonded interface, replicas of the bonded system can be immersed in water at room temperature, and the peel strength of a wet sample measured periodically. A clear failure is ready separation of the bonded parts (zero peel strength); success is considered to be cohesive failure, even after seven days. The gray area for assessing durability and service-life expectation relates to adhesive failure in which the level of peel strength is intermediate between zero and the cohesive value. There is strength to the bond, but it is difficult to use the data in predicting outdoor life because among other things, it is not known how the bond strength values will change over a 20 year life.

Experience with bond durability indicates that under wet conditions, or exposure to moist atmospheres at high temperatures and humidities, the strength of the bonded interface generally decays logarithmically, with the rate influenced by stress, temperature and relative humidity. The strength of the bonded interface, however, recovers reversibly as environmental conditions become drier, and begins to decay again as moist conditions return. The bond strength does not appear to undergo cumulative damage with such cycling as would be encountered outdoors where weather patterns cycle between wet, moist, and dry conditions.

SECTION II

ADHESIVES, PRIMERS, AND ADHESION-PROMOTING TECHNIQUES

A. INTRODUCTION

This section tabulates all of the adhesives, primers, and adhesion-promoting techniques being evaluated for FSA encapsulation interfaces. In this chapter adhesives, primers, and adhesion promoting techniques are referred to collectively as bonding agents.

The sequence that has been adopted for initially qualifying a bonding agent consists of measuring the dry bond strength (peel strength) of control specimens, then measuring the bond strength of identical specimens that have been immersed in room-temperature water and/or boiling water for various periods. A bonding agent is rejected if its control or its wet value is zero. For some bonding agents, it will be noted that the dry control values are reported, but not the wet strengths; these values were yet to be determined at the time of this publication, and hence an accept-or-reject decision has yet to be made. They are to be considered as promising candidates.

A bonding agent that passes this initial qualification test is considered an experimental candidate that will then be subjected, in bonded test specimens, to accelerated and/or abbreviated aging tests involving ultraviolet light (UV), atmospheric oxygen, humidity, elevated temperatures, and cyclical mechanical and thermal stressing. Aging tests have not yet begun; hence, the bonding agents listed herein are to be considered experimental.

It should also be remarked that the magnitudes of the dry (control) and wet bond-strength values have not been a factor in the initial qualification rating. One reason is that in some cases more than one bonding agent has been identified for a considerable variety of interfaces, which yields a range of bond strengths and therefore creates a temptation to favor the bonding agent with the highest overall dry and wet values. But as none of the bonding agents has yet been aged over long times, under field exposure conditions, there is concern that the initial best performer may age the worst. A second reason is that some of the interfaces are very difficult to bond chemically; therefore, achievement of any measurable dry and wet bond strengths is an accomplishment. For these, it is hoped that the bond strengths will be found adequate for the engineering loads, as well as resistant to change from weathering. The third reason is that, in some cases, the cohesive strength of an adhesive or adherend is low, and therefore this value becomes the maximum bond strength value that can be measured in a mechanical peel test. An example is the poly-n-butyl acrylate (PnBA) pottant, which exhibits cohesive failures within the range of 3 to 8 lb/in. of width (peel test). Such low cohesive strength prevents mechanical measurement of the actual interfacial bond strength, which may be higher, but cannot be measured mechanically because the strength limitation resides in the PnBA. A novel chemical approach (Reference 9) to investigating interfacial bond strengths without this mechanical limitation is discussed in Section III.

Table 1 lists vertically and horizontally all of the encapsulation materials listed on pp. 2 and 3 and includes metals associated with solar cells and interconnects. All combinations of materials and metals are generated by this matrix format; therefore, combinations that are not seen as practical or possible are identified by an X in the common box generated by the crossing of the row and column of the respective materials or metals. Furthermore, the boxes containing X's are shaded for contrast. The common locations of all other interfacial combinations seen as practical or possible are unshaded, and identified with a letter, or left blank.

The letter S indicates that the interfacial combination requires no primers or adhesives; that is, they bond chemically during module fabrication. This has occurred with only certain combinations of the low-soiling coatings and other cover plastic films, as indicated in Table 1.

The letter B indicates that a bonding agent, primer, adhesive, or adhesion-promoting technique has been either developed or commercially recommended. There are 22 such bonding agents under evaluation; these are listed and described in Table 2, which also includes, where known, their chemical formulations. In this report the bonding agents will be referred to by their assigned numbers in Table 2, 1 to 22, prefixed with the relevant bonding-agent description (primer or adhesive, whichever applies). For example, primer No. 2 is the primer for bonding EVA to glass, and adhesive No. 18 is an adhesive system for bonding Scotchpar plastic film to mild steel. A word of caution about Table 2: The initial development or commercial recommendation of a primer or adhesive arises from the identified need for a specific interfacial combination (e.g., EVA and glass). Once available, however, such a system can be evaluated for use with many other interfacial combinations, often with success. The description of the primer or adhesive system given in Table 2 is a statement of the initial need for the system, but should not be construed as being its only use. Lastly, primers No. 4, 10, 11, and 19 (Table 2) were very recent commercial recommendations, and therefore have not yet been evaluated by FSA.

A blank in Table 1 indicates that the natural bonding behavior and/or needs and requirements for bonding agents for those interfacial combinations has not yet been experimentally determined.

Of all of the interfacial combinations noted in Table 1, only those established by the low-soiling coatings on the outer covers cannot be monitored by mechanical peel testing. A different procedure is therefore followed for these coatings. Water poured onto surfaces coated with these materials will quickly bead up into small, discrete droplets, and on tilted surfaces, will readily drain off, in contrast with uncoated outer cover surfaces on which water will spread into a film and will resist run-off when the surfaces are tilted. In addition, the low-soiling property reduces natural soil accumulation as compared with uncoated outer cover surfaces.

Outer-cover materials, coated with all three low-soiling coatings, and uncoated controls were mounted outdoors for natural exposure to weather and soil (References 10 and 11). The FC-721 and FC-723 coatings were, within a few weeks, totally lost from the surfaces as evidenced by both water-spread

Table 2. Primers, Adhesives, and Adhesion-Promoting Techniques

System		Remarks
1.	Adhesion-Promoting Technique for Low-Soiling Coatings Surface activation with ozone	1. Exposure of Acrylar and Tedlar surfaces to ozone results in sufficient development of surface polar groups to react chemically with the low-soiling coatings L-1668 and E-3820; see text for experimental description
2.	Primer for Bonding EVA to Glass <u>Component</u> <u>Composition</u> Z-6030 silane 9.0 parts by wt (Dow Corning) Benzyl dimethyl 1.0 parts by wt amine Lupersol 101 0.1 parts by wt (Pennwalt Corp.) Methanol 90.0 parts by wt	2. Primer developed by Dow Corning for bonding A-9918 EVA to glass; primer found suitable for bonding EMA to glass, and also both EVA and EMA to mild steel
3.	Primer for Bonding PnBA to Glass <u>Component</u> <u>Composition</u> Z-6020 silane 10 parts by wt (Dow Corning) Ethyl ortho- 10 parts by wt silicate Isopropanol 180 parts by wt	3. Primer developed by Dow Corning for bonding PnBA to glass; primer found to give fair performance with Tedlar 100BG30UT plastic film, and found to be ineffective with metals tested (aluminum, copper, mild steel, and solder)
4.	Primer for Bonding Z-2591 Polyurethane to Glass and Metals Z-3012	4. Commercial primer recommended by and available from Development Associates; primer is one-component system ready for use as received
5.	Primer for Bonding Z-2591 Polyurethane to Glass <u>Component</u> <u>Composition</u> Z-6020 silane 5 parts by wt (Dow Corning) Methanol 95 parts by wt	5. Primer developed by Dow Corning for bonding Z-2591 polyurethane to glass; primer found suitable for bonding Z-2591 polyurethane to Tedlar 100BG30UT and Korad 63000 plastic films

Table 2. Primers, Adhesives, and Adhesion-Promoting Techniques (Cont'd)

System		Remarks										
6.	Primer for Bonding EVA to Acrylar X-22417	6. Primer developed by Dow Corning for bonding EVA to Acrylar X-22417 plastic film; as Acrylar is an acrylic film, this primer is evaluated for all material combinations involving acrylic materials; primer has been found suitable for bonding EMA to Acrylar, EVA to Korad 63000 (an acrylic film), and PnBA to Korad 63000; this primer did not work for bonding PnBA to Acrylar X-22417										
	<table border="1"> <thead> <tr> <th><u>Component</u></th> <th><u>Composition</u></th> </tr> </thead> <tbody> <tr> <td>Z-6020 (Dow Corning)</td> <td>3 parts by wt</td> </tr> <tr> <td>Z-6030 (Dow Corning)</td> <td>1 part by wt</td> </tr> <tr> <td>Acroloid AT-51 (Rohm and Haas)</td> <td>100 parts by wt</td> </tr> <tr> <td>Toluene</td> <td>174 parts by wt</td> </tr> </tbody> </table>	<u>Component</u>	<u>Composition</u>	Z-6020 (Dow Corning)	3 parts by wt	Z-6030 (Dow Corning)	1 part by wt	Acroloid AT-51 (Rohm and Haas)	100 parts by wt	Toluene	174 parts by wt	
<u>Component</u>	<u>Composition</u>											
Z-6020 (Dow Corning)	3 parts by wt											
Z-6030 (Dow Corning)	1 part by wt											
Acroloid AT-51 (Rohm and Haas)	100 parts by wt											
Toluene	174 parts by wt											
7.	Adhesive for Bonding EVA to Tedlar	7. Commercial, one-component, adhesive system available from Du Pont; adhesive also found to work for bonding EVA to Acrylar X-22417 and Korad 63000, for bonding PnBA to Tedlar and Korad 63000, and for bonding a modified EMA (see text) to Tedlar										
	68040 acrylic contact adhesive											
8.	First Primer for Bonding EVA to Tedlar	8. First primer developed by Dow Corning for bonding EVA to Tedlar that gave satisfactory performance (subsequently an improved version, primer No. 21; was developed); this primer, No. 8, is still included in this table because it was experimentally found to work satisfactorily with ICI Melinex white-pigmented polyester films. Note that primer No. 15 was developed for bonding EVA to polyester films, but did not work with the Melinex polyester film										
	<table border="1"> <thead> <tr> <th><u>Component</u></th> <th><u>Composition</u></th> </tr> </thead> <tbody> <tr> <td>Z-6030 (Dow Corning)</td> <td>0.25 parts by wt</td> </tr> <tr> <td>Z-6040 (Dow Corning)</td> <td>0.25 parts by wt</td> </tr> <tr> <td>Resimene 740* (Monsanto)</td> <td>10.0 parts by wt</td> </tr> <tr> <td>Methanol</td> <td>90.0 parts by wt</td> </tr> </tbody> </table>	<u>Component</u>	<u>Composition</u>	Z-6030 (Dow Corning)	0.25 parts by wt	Z-6040 (Dow Corning)	0.25 parts by wt	Resimene 740* (Monsanto)	10.0 parts by wt	Methanol	90.0 parts by wt	
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Z-6040 (Dow Corning)	0.25 parts by wt											
Resimene 740* (Monsanto)	10.0 parts by wt											
Methanol	90.0 parts by wt											
	*Resimene 714 may be used as a substitute for Resimene 740											

Table 2. Primers, Adhesives, and Adhesion-Promoting Techniques (Cont'd)

System		Remarks																					
9.	Primers for Bonding Z-2591 Polyurethane to Tedlar	9. Two experimental primer systems recently developed by Dow Corning; of several exploratory systems investigated by Dow Corning, these two yielded equally the highest bond strength on freshly made test specimens; however, neither system has yet been immersed in water maintained at room temperature, or in boiling water; therefore, they are still to be considered experimental.																					
	<table border="0"> <tr> <td></td> <td><u>Component</u></td> <td><u>Composition</u></td> </tr> <tr> <td>a.</td> <td>{ Z-6020 silane (Dow Corning)</td> <td>9.5 parts by wt</td> </tr> <tr> <td></td> <td>{ Water</td> <td>0.5 parts by wt</td> </tr> <tr> <td></td> <td>{ Methanol</td> <td>90 parts by wt</td> </tr> <tr> <td>b.</td> <td>{ Z-6020 silane (Dow Corning)</td> <td>5 parts by wt</td> </tr> <tr> <td></td> <td>{ Z-6082 silane (Dow Corning)</td> <td>5 parts by wt</td> </tr> <tr> <td></td> <td>{ Methanol</td> <td>180 parts by wt</td> </tr> </table>			<u>Component</u>	<u>Composition</u>	a.	{ Z-6020 silane (Dow Corning)	9.5 parts by wt		{ Water	0.5 parts by wt		{ Methanol	90 parts by wt	b.	{ Z-6020 silane (Dow Corning)	5 parts by wt		{ Z-6082 silane (Dow Corning)	5 parts by wt		{ Methanol	180 parts by wt
	<u>Component</u>		<u>Composition</u>																				
a.	{ Z-6020 silane (Dow Corning)		9.5 parts by wt																				
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10.	Primer for Bonding Z-2591 Polyurethane to Acrylar and Korad 63000																						
	Z-2881																						
10.		10. Commercial primer recommended by and available from Development Associates; primer is one-component system ready for use as received																					
11.	Adhesive for Bonding Z-2591 Polyurethane to Hardboard	11. Z-2891 is a white-pigmented polyurethane paint available from Development Associates, formulated to achieve good adhesion to wood and to Z-2591 polyurethane																					
	Z-2891 urethane paint																						
12.	Adhesive-Primer System for Bonding Acrylar and Korad 63000 to Hardboard.	12. The Z-2591 polyurethane potant functions in this application as an adhesive between Acrylar (or Korad) and the hardboard; chemical bonding of the adhesive to each of the adherents is accomplished respectively with the Z-2881 primer, and the Z-2891 urethane paint. All are Development Associates products. Testing by FSA indicates good initial adhesion, but aging tests not yet done																					
	Acrylar																						
	Z-2881 Primer (No. 10)																						
	Z-2591 Polyurethane																						
	Z-2891 Urethane Paint																						
	Hardboard																						
		3-Component adhesive and primer System																					

Table 2. Primers, Adhesives, and Adhesion-Promoting Techniques (Cont'd)

System		Remarks										
13.	Adhesive for Bonding Scotchpar, Acrylar, and Karad 63000 to Hardboard 4910 acrylic pressure-sensitive adhesive	13. Commercial adhesive marketed by the Adhesives, Coatings, and Sealants Division of the 3M Co., St. Paul, Minn.; the adhesive is dissolved in a solvent, and the adhesive solution can be brushed onto a surface as paint. After solvent drying, the resultant adhesive layer is an instant contact adhesive, and therefore requires care in film alignment. Initial film adhesion is good, but aging tests have not yet been carried out										
14.	Primer for Bonding EVA to Mild Steel, Copper, and Aluminum <table border="1"> <thead> <tr> <th>Component</th> <th>Composition</th> </tr> </thead> <tbody> <tr> <td>Z-6030 silane (Dow Corning)</td> <td>99 parts by wt</td> </tr> <tr> <td>Zinc chromate powder</td> <td>100 parts by wt</td> </tr> <tr> <td>Benzyl dimethyl amine</td> <td>1 part by wt</td> </tr> <tr> <td>Methanol</td> <td>300 parts by wt</td> </tr> </tbody> </table>	Component	Composition	Z-6030 silane (Dow Corning)	99 parts by wt	Zinc chromate powder	100 parts by wt	Benzyl dimethyl amine	1 part by wt	Methanol	300 parts by wt	14. Primer developed by Dow Corning for bonding EVA to mild steel, copper, and aluminum; also found to work in bonding EVA to chrome steel, stainless steel, titanium, and brass. Attempts by different investigators to use this primer for bonding EVA to solder have led to mixed results; some achieve strong bonds, others observe zero bond strength, dry or wet. This necessitated a new primer development for bonding EVA to solder, described in No. 16 below
Component	Composition											
Z-6030 silane (Dow Corning)	99 parts by wt											
Zinc chromate powder	100 parts by wt											
Benzyl dimethyl amine	1 part by wt											
Methanol	300 parts by wt											
15.	Primer for Bonding EVA to Scotchpar <table border="1"> <thead> <tr> <th>Component</th> <th>Composition</th> </tr> </thead> <tbody> <tr> <td>Z-6040 silane (Dow Corning)</td> <td>5 parts by wt</td> </tr> <tr> <td>Resimene 740 (Monsanto)</td> <td>95 parts by wt</td> </tr> <tr> <td>Isopropanol</td> <td>300 parts by wt</td> </tr> </tbody> </table>	Component	Composition	Z-6040 silane (Dow Corning)	5 parts by wt	Resimene 740 (Monsanto)	95 parts by wt	Isopropanol	300 parts by wt	15. Primer developed by Dow Corning for bonding EVA to Scotchpar polyester film; has been found to work in general with all polyester films except Melinex white-pigmented polyester film, as described in No. 8 above. Also found to work in bonding EVA to Tedlar		
Component	Composition											
Z-6040 silane (Dow Corning)	5 parts by wt											
Resimene 740 (Monsanto)	95 parts by wt											
Isopropanol	300 parts by wt											

Table 2. Primers, Adhesives, and Adhesion-Promoting Techniques (Cont'd)

System		Remarks	
16.	Primer for Bonding EVA to Solder	16. Primer developed by Dow Corning for bonding EVA to solder. Similar to primer No. 14 without zinc chromate, and with substitution of isopropanol for methanol. Presumably the key to successful use is proper and thorough cleaning of the solder surface, and for this, isopropanol is more satisfactory than methanol. Additionally, it is recommended that the solder surface be cleaned before priming with acetone and/or ordinary household kitchen cleanser	
	<u>Component</u> <u>Composition</u>		
	Z-6030 (Dow Corning) 99 parts by wt		
	Benzyl Dimethyl Amine 1 parts by wt		
	Isopropanol 300 parts by wt		
17.	Adhesive and Primer System for Bonding Tedlar to Mild Steel (requires 20 min at 150°C)	17. The EVA A-9918 pottant functions in this application as an adhesive between Tedlar and mild steel; chemical bonding of the EVA adhesive to Tedlar and mild steel is accomplished, respectively, by use of the 68040 adhesive, and one or another of the EVA/metal primers (No. 2 or 14)	
	Tedlar		
	68040 adhesive		
	EVA (A-9918 formulation)		
	Metal primer (No. 2 or 14)	3-component adhesive and primer system	
	Mild Steel		
18.	Adhesive and Primer System for Bonding Scotchpar to Mild Steel (requires 20 minutes at 150°C)		18. The EVA A-9918 pottant functions in this application as an adhesive between Scotchpar and mild steel; chemical bonding of the EVA adhesive to Scotchpar and mild steel is accomplished, respectively, by use of the EVA/polyester primer (No. 15), and one or other of the EVA/metal primers (No. 2 or 14)
	Scotchpar		
	Polyester		
	Film primer (No. 15 above)		
	EVA (A-9918 formulation)	3-component adhesive and primer system	
	Metal primer (No. 2 or 14)		
	Mild Steel		
19.	Primer for Bonding Z-2591 Polyurethane to Mild Steel		19. Commercial primer recommended by and available from Development Associates, Inc.; primer is one-component system ready for use as received
	I-1022		

Table 2. Primers, Adhesives, and Adhesion-Promoting Techniques (Cont'd)

System		Remarks										
20.	<p>Adhesive-Primer System for Bonding Korad 63000 to Mild Steel</p> <table border="0"> <tr> <td style="vertical-align: middle;"> <p>Korad 63000 68040 adhesive (No. 7) EVA A-9918 Metal primer (No. 2 or 14) Mild Steel</p> </td> <td style="vertical-align: middle; font-size: 3em;">}</td> <td style="vertical-align: middle;"> <p>3-component adhesive and primer system</p> </td> </tr> </table>	<p>Korad 63000 68040 adhesive (No. 7) EVA A-9918 Metal primer (No. 2 or 14) Mild Steel</p>	}	<p>3-component adhesive and primer system</p>	20. The EVA A-9918 potent functions in this application as an adhesive between Korad 63000 and mild steel; chemical bonding of the EVA adhesive to Korad 63000 and mild steel; chemical bonding of the EVA adhesive to Korad 63000 and mild steel is accomplished, respectively, by use of the DuPont adhesive 68040 (No. 7) and one or the other of the EVA-metal primers (No. 2 or 14)							
<p>Korad 63000 68040 adhesive (No. 7) EVA A-9918 Metal primer (No. 2 or 14) Mild Steel</p>	}	<p>3-component adhesive and primer system</p>										
21.	<p>Second Primer for Bonding EVA to Tedlar</p> <table border="0"> <thead> <tr> <th style="text-align: left;"><u>Component</u></th> <th style="text-align: left;"><u>Composition</u></th> </tr> </thead> <tbody> <tr> <td>2-6040 silane Dow Corning</td> <td>1.0 part by wt</td> </tr> <tr> <td>Cymel 303 (American Cyanamid)</td> <td>9.0 parts by wt</td> </tr> <tr> <td>Methanol</td> <td>30.0 parts by wt</td> </tr> </tbody> </table>	<u>Component</u>	<u>Composition</u>	2-6040 silane Dow Corning	1.0 part by wt	Cymel 303 (American Cyanamid)	9.0 parts by wt	Methanol	30.0 parts by wt	21. Second, and better, primer developed by Dow Corning for bonding EVA to Tedlar; also found to work fairly well in bonding EVA to Scotchpar polyester films. Trial testing with bonding EVA to Tedlar and Scotchpar films resulted in very poor performance, but may be explainable by differences in flow properties of EVA versus EMA during processing; see text for expanded discussion		
<u>Component</u>	<u>Composition</u>											
2-6040 silane Dow Corning	1.0 part by wt											
Cymel 303 (American Cyanamid)	9.0 parts by wt											
Methanol	30.0 parts by wt											
22.	<p>Primer for Bonding PnBA to Tedlar</p> <table border="0"> <thead> <tr> <th style="text-align: left;"><u>Component</u></th> <th style="text-align: left;"><u>Composition</u></th> </tr> </thead> <tbody> <tr> <td>2-6032 silane (Dow Corning)</td> <td>25.0 parts by wt</td> </tr> <tr> <td>Water</td> <td>5.0 parts by wt</td> </tr> <tr> <td>Acetic acid</td> <td>0.2 parts by wt</td> </tr> <tr> <td>Methanol</td> <td>20.0 parts by wt</td> </tr> </tbody> </table>	<u>Component</u>	<u>Composition</u>	2-6032 silane (Dow Corning)	25.0 parts by wt	Water	5.0 parts by wt	Acetic acid	0.2 parts by wt	Methanol	20.0 parts by wt	22. Primer developed by Dow Corning for bonding PnBA to Tedlar; also found, in trial testing, to give marginal performance with Scotchpar and Korad plastic films
<u>Component</u>	<u>Composition</u>											
2-6032 silane (Dow Corning)	25.0 parts by wt											
Water	5.0 parts by wt											
Acetic acid	0.2 parts by wt											
Methanol	20.0 parts by wt											

behavior and no differences in soiling behavior as compared with uncoated controls. This was expected, as FC-721 and FC-722 are not chemically formulated to bond to the surfaces. On the other hand, I-1668 and E-3620 are formulated for chemical bonding to surfaces. Outer covers coated with these two materials have been outdoors for more than 20 months, and some or all of the initially deposited coatings are still on the outer cover surfaces, as evidenced by water bead behavior; soil accumulation remains lower as compared with the uncoated controls. This real-time outdoor behavior indicates at least 20 months of weathering durability for both of the coating materials, and for the interfacial chemical bonds.

All of the outer interfaces can be evaluated by mechanical peel test; the bond-strength values will be found in Tables 3 through 8. These tables are organized by potant; therefore, Tables 3, 4, and 5 contain bond strengths for EVA bonded systems, Table 6 EMA bonded systems, Table 7 PnBA bonded systems, and Table 8 polyurethane bonded systems.

B. EVA PRIMERS AND ADHESIVES

The first EVA primer system developed was for bonding cured A-9918 EVA to glass (Reference 7). This is primer No. 2 in Table 2, which is also referred to as the glass-EVA primer. Experimental quantities of this primer are available from Springborn, under the designation A-11861 primer. As described in more detail below, this glass-EVA primer resulted in very strong bonding to glass, under both dry and wet exposure conditions. This favorable experience with glass prompted a follow-on evaluation of this primer system for bonding EVA to many other materials (Reference 8). Immediate difficulties, however, were then encountered with copper, aluminum, Tedlar fluorocarbon film and Scotchpar polyester film.

As copper and aluminum represent potential low-cost metals for solar-cell metallization, emphasis was next given to developing a primer system for bonding cured A-9918 EVA to these two metals. The composition of this metal-EVA primer, primer No. 14, is given in Table 3. Another primer system had to be developed separately for bonding cured A-9918 EVA to polyester films such as Scotchpar (3M) and Mylar (Du Pont). The composition of this primer, commonly referred to as the polyester-EVA primer, is also given in Table 2 (No. 15).

For bonding cured A-9918 EVA to Tedlar film products, Du Pont identified an acrylic contact adhesive designated 68040 (No. 7, Table 2). As supplied by Du Pont, the acrylic adhesive system is a solution in toluene, which is spread on the Tedlar surface and allowed to dry. The resultant adhesive coating is dry and nontacky, and the coated Tedlar film can be wound and unwound. Experimental work with this adhesive system has used a coating thickness of 0.3 to 0.4 mil, which has yielded acceptable performance. The contact adhesive develops its bonding qualities at the high temperature of the EVA lamination cycle. A PV manufacturer may coat Tedlar optionally with the adhesive as part of its manufacturing operation, or arrange to have the coating put on by an independent coating vendor.

Table 3. Adhesive Bond Strengths for EVA (A-9914) Bonded to Various Materials

Materials	Primer Number	Bond Strengths, lb/in. of width			
		Control	6 days Immersion	2 wk Immersion	2 hours Boiling Water
Sunalex glass	2	34.8	-	30.0	32.3
Window glass	2	39.6	-	37.9	27.1
Window glass (self-priming EVA)	2	35.4	-	41.9	Cohesive
Galvanized steel	2	2.5	-	-	-
Mild steel	2	56.0	-	42.6	50.7
Mild steel	14	-	17.6	-	-
Mild steel	21	2.3	-	2.3	3.9
Aluminum	2	41.0	-	2.3	2.6
Aluminum	14	-	Cohesive	-	-
Tedlar 100BG30UT	2	4.5	-	0	0
Tedlar 100BG30UT	7	6.2	-	6.5	7.8
Tedlar 100BG30UT	8	13.0	-	6.3	6.5
Tedlar 100BG30UT	21	30.0	-	12.6	13.0
Scotchpar 20CP WH	15	35.3	-	31.3	21.3
Scotchpar 20CP WH	21	11.5	-	26.8	1.1
Acrylar X-22417	2	1.0	-	0	0
Acrylar X-22417	6	15.4	-	-	-
Acrylar X-22417	7	Cohesive	-	Cohesive	Cohesive

Table 3. Adhesive Bond Strengths for EVA (A-9918) Bonded to Various Materials (Cont'd)

Materials	Primer Number	Bond Strengths, lb/in. of width			
		Control	6 days Immersion	2 wk Immersion	2 hours Boiling Water
*Plexiglas V-811	6	5.6	-	7.8	5.5
Plexiglas V-811	7	40.2	-	-	44.1
Copper	14	32.5	Cohesive	Cohesive	37.6
Copper	16	5.1	-	40.7	3.9
Korad 63000	6	Cohesive	-	Cohesive	Weak
Korad 63000	7	Cohesive	-	5.4	Cohesive
Korad 63000	21	1.6	-	-	-
Korad 212	2	1.1	-	-	-
Tedlar 150BL30WH	7	Cohesive	-	Cohesive	Cohesive
Titanium	14	-	Cohesive	-	-
Brass	14	-	Cohesive	-	-
Stainless steel	14	-	19.8	-	-
Chrome steel	14	-	Cohesive	-	-
Nickel	2	In Test			

*Similar chemistry as Acrylar films, but available in thicker versions in order to prepare mechanical peel-test specimens. Testing Acrylar peel specimens is experimentally difficult due to film's low fold resistance.

Table 4: Adhesion of EVA (A-9918) to Solder Using Primer No. 16,
Showing Importance of Surface Cleanliness for Solder Bonding

Solder Surface Condition	Method of Cleaning	Primer Used	Bond Strengths, lb/in. of width	
			Dry	After 1 Day in Water
Dull	None	No	8.8	0
Dull	None	Yes	15.4	11.0
Dull	Acetone	Yes	Cohesive	Cohesive
Dull	Cleanser	Yes	Cohesive	Cohesive
Shiny	None	No	6.6	0
Shiny	None	Yes	8.8	0
Shiny	Acetone	Yes	Cohesive	Cohesive
Shiny	Cleanser	Yes	Cohesive	Cohesive

Table 5. Adhesion of New*, Experimental A-15295 EVA to Sunadex Glass and Mild Steel

Materials	Primer Number	Bond Strengths, lb/in. of width		
		Control	2 wk Water Immersion	2 hours Boiling Water
Sunadex glass	2	51.3	32.9	33.3
Mild steel	2	15.6	-	-

*This EVA incorporates an experimental peroxide curing agent, designated TBEC, in substitution for Lupersol 101 (used in A-9918 EVA). Other than this substitution, A-15295 EVA is the same as A-9918 EVA.

Table 6. Adhesive Bond Strengths for EMA Bonded to Various Materials

Materials	Primer or Adhesive Number	EMA Peroxide Curing Agent	Bond Strengths, lb/in. of width		
			Control	2 wk Water Immersion	2 hours Boiling Water
Sunadex glass	2	L-101	60.2	40.0	27.7
Sunadex glass	2	L-TBEC	Glass broke	64.2	45.5
Mild steel	2	L-101	5.6	14.6	13.9
Mild steel	2	L-TBEC	35.1	Low	2.8
Tedlar 100BG30UT	7	L-101	0.5	NT	NT
Tedlar 100BG30UT	21	L-101	0.8	NT	NT
Tedlar 100BG30UT	7	L-TBEC	Cohesive	NT	Cohesive
Scotchpar 20CP WH	21	L-101	0.8	0.4	1.2
Tedlar 150BL30WH	7	L-101	1.9	NT	NT
Acrylar X-22417	6	L-TBEC	Cohesive	Cohesive	Cohesive
Plexiglas V-811	6	L-TBEC	3.6	Low	6.4

Table 7. Adhesive Bond Strengths for PnBA (BA-13870) Bonded to Various Materials

Materials	Primer or Adhesive Number	Bond Strengths, lb/in. of width		
		Control	2 wk Water Immersion	2 hours Boiling Water
Sunadex glass	None	0	-	-
Sunadex glass	3	3.0	1.2	1.4
Sunadex glass	22	0.9	0.4	0.6
Tedlar 100BG30UT	None	0	-	-
Tedlar 100BG30UT	3	1.3	PnBA failure	0.8
Tedlar 100BG30UT	7	PnBA failure	PnBA failure	PnBA failure
Tedlar 100BG30UT	22	2.4	2.4	2.3
Scotchpar 20CP WH	None	0	-	-
Scotchpar 20CP WH	22	1.5	-	-
Korad 63000	None	0	-	-
Korad 63000	6	8.3	PnBA failure	3.4
Korad 63000	7	PnBA failure	PnBA failure	PnBA failure
Korad 63000	22	0.7	-	-
Acrylar X-22417	None	0	-	-
Acrylar X-22417	6	Low	-	-
Acrylar X-22417	7	Very low	Very low	-
Aluminum	3	0	-	-
Copper	3	0	-	-
Mild steel	3	0	-	-
Solder	3	0	-	-

Table B. Adhesive Bond Strengths of Z-2591 Polyurethane to Various Materials

Materials	Primer or Adhesive Number	Bond Strengths, lb/in. of width		
		Control	2 wk Water Immersion	2 hours Boiling Water
Sunadex glass	None	0	-	-
Sunadex glass	5	31.4	37.2	45.2
Tedlar 100BG30UT	None	0	-	-
Tedlar 100BG30UT	5	4.8	1.6	1.3
Tedlar 100BG30UT	9A; 9B	7.0	-	-
Scotchpar 20CP WH	None	0	-	-
Scotchpar 20CP WH	5	0.2	-	-
Scotchpar 20CP WH	8	Low	Low	Low
Korad 63000	None	0	-	-
Korad 63000	5	3.6	2.6	2.7

Note: The commercial primers available from Development Associates, No. 4, 10, 11 and 19, have not yet been evaluated by PSA.

Table 3 is a master table of adhesive bond-strength measurement accumulated for cured EVA bonded to a variety of materials, with various combinations of primers and the 68040 adhesive. These data, generated at different experimental laboratories, result from a similar experimental pattern: measurement of control values at ambient conditions, followed by measurement (again at ambient conditions) of specimens that have been immersed in water maintained at room temperature, and of specimens immersed in boiling water. The exception is work carried out with the metal-EVA primer system, No. 14, for all metals but copper. Bond-strength measurements for these test specimens were made after 6 days' immersion in water maintained at room temperature, and no control values were measured.

The glass-EVA primer (No. 2) can be used optionally as either a wipe-on primer or as a compounding additive to generate a self-priming EVA. If used as a compounding additive, the methanol solvent is not used, and the three-component mixture is blended into the EVA at a concentration of 1.0 wt %. A concept used in the formulation of this primer is that the addition of a small amount of the Lupersol 101 peroxide causes a localized generation of active free radicals during the heating and curing of the A-9918 EVA, resulting in a substantially higher crosslinking at the polymer-substrate interface.

The glass-EVA primer was tested by priming clean soda-lime glass slides with a thin layer of the primer (wiped on with a moistened pad) and air drying for 15 min. The fully formulated EVA compound (A-9918) was then compression-molded and cured against the surface. The resulting specimen was tested for peel strength by ASTM D-903. The results (Table 3) were excellent, yielding an average peel strength of 39.6 lb/in. of width. Duplicate specimens placed in boiling water for 2 hours and evaluated by the same process yielded an average peel strength of 27 lb/in. of width, still excellent adhesion. A quantity of the primer formulation was prepared without the alcohol diluent and blended into the standard A-9918 EVA formulation at 1 wt % to test the self-priming effect. The resulting resin was then compression-molded and cured against a clean glass slide, as before, and tested for peel strength by the same method. The average strength was 35.4 lb/in. of width (Table 4). The bond strength of the self-priming EVA after room-temperature water immersion for 2 weeks increased from the initial value of 35.4 to 41.9 lb/in. of width, and resulted in cohesive failure after 2 hours in boiling water.

As shown in Table 3, the glass-EVA primer (No. 2) not only gives excellent and durable bonds to regular soda-lime (microscope slides) and low-iron (Sunadex) glass, but also is marginally effective with aluminum, and very effective with mild steel. Aluminum, primed with A-11861 (primer No. 2) gave an average dry-bond peel strength of 41.0 lb/in. of width and the adhesion to mild steel was even higher, with an average dry strength of 56.0 lb/in. of width. This is the highest strength found between EVA and any other material. The wet-bond strength is excellent to mild steel and poor to aluminum. Dry-bond strengths to Tedlar were very low, and virtually zero when wet. The A-11861 primer was essentially ineffective for copper and for Scotchpar polyester film, for both dry and wet exposure conditions. On the other hand, the polyester-EVA primer No. 15 worked excellently, yielding a dry control value of 35.3 lb/in., dropping slightly to 31.3 lb/in. after 2 weeks of room-temperature water immersion, and still retained a high value of 21.3 lb/in. after 2 hours of immersion in boiling water.

Metal-EVA primer No. 14 achieved outstanding bonding of cured A-9918 EVA to aluminum and copper (Table 3), with peel testing resulting in cohesive failure of the EVA after 6 days of water immersion. Cohesive failure of the cured EVA also occurred for bonding to chrome steel, titanium, and brass. The metal-EVA primer is apparently not as effective with mild steel as the glass-EVA primer, A-11861, but the bond strength values of 17.6 lb/in. is still acceptably high.

The two Tedlar films listed in Table 3, Tedlar 100BG30UT and Tedlar 200PT, are clear and transparent UV-screening films. The former is 1 mil thick and the latter is 2 mils thick. The third Tedlar film listed in Table 3, Tedlar 105BL30WH, is a 1.5 mil-thick white-pigmented film. The bond strength data given in Table 3 reveal that the 68040 adhesive yielded comparable wet and dry performance for the two UV screening films, and yielded outstanding performance with the white-pigmented Tedlar film. Involvement of the white-pigment material in enhancing the bond strength can only be conjectured.

With all three Tedlar films, the adhesive 68040 retained wet-bond strength, as compared with the zero bond strength of the glass-EVA primer No. 2. Recently Dow Corning Corp. developed two additional, still experimental, primer systems for bonding Tedlar films to EVA. These primers are designated as primers No. 8 and No. 21. With primer No. 21, control bond strengths were near 30 lb/in. After 2 weeks of water immersion the bond strength dropped to 12.6 lb/in, and 2 hours of exposure in boiling water reduced the bond strength to near 13 lb/in.

One of the low-cost structural panel materials being investigated for module application is mild steel (p. 3), specifically cold-rolled mild steel. However, the concern with this material in an outdoor application is corrosion. There is literature evidence (References 12 through 15) that indicates that use of chemical bonding agents can prevent metallic corrosion. This approach to corrosion prevention in mild steel is being evaluated experimentally by using a chemical bonding adhesive system for bonding white-pigmented plastic films to both surfaces of mild-steel panel. A trial film-adhesive-primer system has evolved (No. 18), which consists of the following layers of materials on mild steel:

Outer film	Scotchpar 20CP WH
Primer	Polyester primer No. 15
Adhesive	Cured A-9918 EVA
Primer	Metal primer No. 14
Panel	Mild steel

Panels of mild steel coated with this film-adhesive-primer system have survived more than 4,500 hours of continuous exposure to salt spray (ASTM B-117) without any evidence of corrosion (Reference 10). Unprotected mild steel, on the other hand, begins to corrode within hours after exposure to salt spray. This use of EVA as an adhesive offers an another possible application area for these low-cost materials in terrestrial photovoltaic modules.

Very recently, laboratory attempts to bond EVA to solder with metal primer No. 14 were unsuccessful, usually with little to zero dry bond strength; this prompted a directed effort focused on EVA-solder bonding, which resulted in primer No. 16. It should be noted that this is essentially primer No. 14 without the zinc chromate, and that isopropanol solvent has been substituted for methanol. The substitution of isopropanol, which is a better surface-cleaning agent than methanol, emphasized the important requirement of surface cleanliness for EVA-solder bonding. This is shown in the bond-strength data in Table 4, where precleaning of the solder surface either with acetone or with a common household kitchen cleanser resulted in cohesive bonding of EVA to solder. This work was performed with a variety of solder specimens whose surfaces could be qualitatively characterized as shiny or dull. No effort was made to find an explanation for the differences, even though it was noticed that a primed, dull surface without pre-cleaning gave better dry and wet performance than did a primed, shiny surface that also was not precleaned. In each case, however, precleaning appeared to eliminate any bonding effects related to initial surface quality.

Since it is desired to have a single metal primer for EVA rather than two, a study is now under way that will attempt to identify a single primer combining the features of primers No. 14 and No. 16, and the cleaning procedures described above.

Recently (Reference 8), Springborn identified a new peroxide curing agent for EVA, which results in a faster cure at lower temperatures. The new peroxide is marketed by the Lucidol Division of Pennwalt under the designation Lupersol-TBEC, or L-TBEC for short. The standard peroxide currently employed in A-9918 EVA is marketed by Lucidol under the designation L-101. The potential substitution of L-TBEC for L-101 in advanced EVA formulations prompted concern for its possible effects on EVA adhesion. Two preliminary adhesion test results for Sunadex glass and mild steel with TBEC-cured EVA are shown in Table 5. The results suggest no problems with adhesion to Sunadex glass, although interestingly there is an unexplained increase in the dry (control) strength as compared to L-101-cured EVA. The wet strengths are essentially the same. The dry (control) strength with mild steel is considerably reduced (from 56.0 to 15.6) for the TBEC-cured-EVA, as compared with the L-101-cured EVA, but any conclusions or judgments at this time would be premature. The wet strengths were not available at the time of this publication.

C. EMA PRIMERS AND ADHESIVES

In terms of peroxide curing and chemical bonding, EMA is chemically very similar to EVA. Therefore the first curing formulation for EMA was based on L-101 chemistry, and worked well for EMA (Reference 11). Subsequently, with the identification of L-TBEC, this was evaluated for EMA and found to result in a faster cure at lower temperatures (Reference 8), as observed with EVA. Two versions of EMA are now under evaluation, one with L-101 and another with L-TBEC. Adhesion results accumulated for both versions are reported herein.

Because of chemical similarity, primers and adhesives that have been found to work for EVA become trial candidates for EMA. Table 6 summarizes the results. The first primer effort was with the primer developed for EVA-glass

(No. 2), which yielded for glass and L-101-cured EMA a very high control value of 60.2 lbs/in., very respectable wet-bond strength values of 40.0 lb/in. after 2 weeks of water immersion, and 27.7 lb/in. after 2 hours in boiling water. Actually, the wet-bond strength values for L-101-cured EMA-glass are almost the same as those for L-101-cured EVA-glass (Table 3), with the major difference being the dry control values. The adhesion to glass with TBEC-cured EMA is remarkable. The glass breaks during efforts to measure the dry bond strength mechanically, and wet strengths are extremely high.

With the two exceptions of TBEC-cured EMA bonded to Acrylar and Tedlar, using EVA primer and adhesive systems, the general trend is toward lower control and wet-bond-strength values, as compared with bonding of these same materials to EVA. There are, however, indications from the mild steel and Scotchpar test results that wet-bond strengths with L-101-cured EMA tend to be higher than the initial control values, indicating that time, water, and/or heat may be promoting additional bonding reactions, suggesting strongly a possibility that full bond-strength potential was for some reason not initially developed.

One explanation may be related to differences in the high-temperature processing characteristics of EVA and EMA. Above 70°C, EVA becomes a viscous fluid that will facilitate spread and wetting over a mating surface, and therefore will tend to increase the intimacy of contact and interpenetration with a coupling agent deposited from a primer solution. On the other hand, EMA does not become fluid upon heating; it becomes a softer solid that requires some pressure for flow and spread over a mating surface. Thus intimacy of contact and interpenetration with a deposited coupling agent may be reduced, as compared with EVA. Since the data trends in Table 6 indicate that primers and adhesives found for EVA appear to work with EMA, perhaps physical effects such as the one just described, rather than chemical effects, are initially limiting achievements of full bond-strength potential. This area of EMA bonding will be investigated. There is also a hint in the data of Table 6 that L-TBEC peroxide seems to enhance the development of higher interfacial bond strengths; this also will be investigated.

EMA, like EVA, is a dry laminaton film at room temperature, and is formulated to undergo peroxide curing to a thermosetting elastomer at processing temperatures in the order of 150°C. For EVA, peroxide crosslinking is an absolute necessity, in order to generate an encapsulation pottant having thermal stability against fluid flow at service temperatures above 70°C. Accordingly (and this is very important), all of the primers developed at Dow Corning for EVA are formulated to generate their interfacial chemical bonding as an integral part of the high-temperature EVA crosslinking reaction. Since the same crosslinking formulation is compounded into EMA, the Dow Corning primers developed for EVA will require that EMA undergo the peroxide crosslinking reaction.

However, the need for EMA to undergo peroxide crosslinking is not clear, as it is for EVA, and some preliminary module testing using uncured EMA as a pottant suggests that it has adequate thermal stability against flow and creep at temperatures up to 90°C. The elimination of a potentially unnecessary processing step for EMA is attractive, but the chemical requirements for EMA bonding agents would then be changed. Indeed, efforts to use primer No. 2 for

non-curing EMA against glass were unsuccessful, with no wet strength, and little to zero dry strength.

New work to develop bonding agents specifically for non-curing EMA is under way. The first candidate for non-curing EMA on glass is as follows:

<u>Component</u>	<u>Composition</u>
Z-6020 silane (Dow Corning)	2 parts by weight
Parlon-5CS (Hercules Inc.)	100 parts by weight
Toluene	100 parts by weight

The control bond strength for non-curing EMA-glass using this primer was near 22 lb/in. and after 1 day in room temperature water was 11.7 lb/in. These initial results are encouraging.

D. PnBA PRIMERS AND ADHESIVES

Poly-n-butyl acrylate (PnBA) is a liquid casting acrylic that cures to a temperature-stable, clear white elastomer (Reference 11). Specifically, the PnBA in liquid form is a polymer-monomer syrup, which is a solution of poly-n-butyl acrylate in n-butyl acrylate monomer. Included in the syrup mixture are additives that activate, at elevated temperatures, the polymerization of the n-butyl acrylate monomer, and then subsequent crosslinking of the total polymer system.

Early attempts to develop bonding agents for PnBA quickly revealed that the n-butyl acrylate monomer was functioning as a solvent for the deposited coupling agents on a mating surface. The n-butyl acrylate would apparently dissolve away most of the coupling agent, leaving the interface with significantly reduced capacity for any substantial interfacial chemical bonding.

Chemical efforts to counter the dissolution problem have resulted in the development of two primer systems intended specifically for PnBA, primers No. 3 and 22; the performance results of these primers are given in Table 7, along with some results using primer No. 6 and adhesive No. 7. It should also be pointed out that PnBA apparently has a very low cohesive strength, somewhere in the range of 3 to 8 lb/in. This naturally low cohesive strength, plus the solvent action for coupling agents, creates a difficult task in assessing the true level of interfacial bond strength by mechanical peel testing. PnBA systems are prime candidates for study of their chemically bonded interfaces by the chemical technique (Reference 9) discussed in Section III. The development of bonding agents for PnBA is a major program effort.

E. POLYURETHANE (Z-2591) PRIMERS AND ADHESIVES

Z-2591 is a liquid-casting, clear white polyurethane (PU) system available from Development Associates. Development Associates markets a variety of proprietary primers for this polyurethane, each appropriate to the

material that is to be bonded to the polyurethane. Primers No. 4, 10, 11, and 19, available from Development Associates, were recently recommended by them for glass and metals, Acrylar and Korad 63000, hardboard, and mild steel respectively. These primers have not yet been evaluated by FSA.

Dow Corning had developed primer systems for many industrial polyurethane materials, and was able to suggest primer systems for evaluation from their industrial experience. These are primers No. 3, 9(a), and 9(b); results of performance testing with these primers are given in Table 8. Primer No. 8 was also tested with Scotchpar. It should be noted that primer No. 5, the PU-glass primer, performs very well and almost identically with primer No. 2 for both EVA and EMA with glass. Primer No. 5 worked acceptably with Korad and Tedlar. The other primer systems, 9(a) and 9(b), yielded a higher control value with Tedlar than did primer No. 5, but wet values have yet to be taken. Further FSA work on PU bonding agents will include the testing of the primers recommended by Development Associates.

F. ADDITIONAL NOTES

In the introduction to this section it was remarked that long-term aging tests of the bonding agents has yet to begin. This is only partially true, as one coupling agent (Z-6020, Dow Corning), and one adhesive system (No. 18) have been aged as a consequence of testing for other purposes.

Z-6020 is the coupling agent used to bond perfluorodecanoic acid chemically to outer-cover surfaces, to generate a low-soiling surface coating (designated E-3820 on p. 2 and in Table 1). The E-3820 coating has been outdoors for more than 20 months, being directly exposed on surfaces to the natural weathering elements consisting of UV, oxygen, moisture, dirt, and other atmospheric chemicals and pollutants. The low-soiling property is still functional at 20 months, suggesting the continuing presence of the surface coating, and thereby implying the continuing presence of the Z-6020 coupling agent on the surface. If so, weathering stability of the Z-6020 is also implied; this holds some promise of weather stability for all of the primers containing Z-6020 listed in Table 2.

Adhesive system No. 18 is used to bond Scotchpar polyester film to mild steel adhesively, for evaluation as a corrosion protection coating. Panels of mild steel coated with Scotchpar and No. 18 adhesive system have survived more than 4500 hours of exposure to ASTM B-117 salt spray (which also exposes the test specimens to 100% relative humidity at 100°C), and to a continuing condensation of hot water. This harsh environment caused no corrosion of the protected mild steel, and also did not affect the protection system, which included two coupling agents, Z-6030 and Z-6040. The stability of these two coupling agents in atmospheric oxygen and humidity at high temperatures holds promise of stability for all of the primers containing Z-6030 and/or Z-6040 listed in Table 2.

SECTION III

THEORIES OF THE CHEMICALLY BONDED INTERFACE

A. INTRODUCTION TO INTERFACIAL BONDING THEORY

To achieve 20- to 30-year life, the various components of solar-cell modules should be held together by strong adhesive bonds, with the interfacial bonding materials being durable and resistant to delamination, corrosion or other failures resulting from the weathering environment. The scope of potential adhesion problems associated with current and future module designs is very broad because of the widely diverse nature of the component materials (glasses, metals, organic polymers, wood, etc.). While a unifying theory of adhesion and performance is not yet achieved, fundamental principles governing interfacial bond formation and durability common to many material combinations are emerging. A large portion of the adhesion research activities associated with solar modules has involved bonding of organic polymers to inorganic substrates (glasses, metals). Consequently, the discussion of interfacial bonding theory that follows draws heavily on results from many sources active in this aspect of bonding technology for demonstration of fundamental concepts.

The work of adhesion, W_A , which is the measure of the strength of a bond between two surfaces, is proportional to their area of contact. Many solid adherends do not have surfaces that will conform to each other on contact (Figure 3a). The gaps between two such solids are filled with air or contaminants, which usually lower W_A . An adhesive is simply a gap-filling material placed between the two solid adherends to establish the intimate molecular contact at the interface that is necessary for developing strong joints (Figure 3b). Interfacial adhesion may be achieved by any of several means, including:

- (1) The action of attractive forces that are physical in nature.
- (2) The formation of primary (covalent or ionic) chemical bonds bridging the adhesive-adherend interface.
- (3) Molecular penetration (interdiffusion) of the adhesive-adherend molecules.

In most instances, bonding results from a combination of these mechanisms.

The importance of establishing strong, durable interfacial bonds to the integrity of solar modules can be inferred from composites technology, where it is known that degradation of the material as a whole is dominated by degradation of the interfacial bonds between the matrix and the reinforcing fibers. If any of the interfacial bonds in solar modules fails, the performance of the entire module may be jeopardized. There are three principal modes of interfacial bond failure:

- (1) Physical displacement of the interface.
- (2) Debonding at the interface due to chemical reactions.
- (3) Cohesive failure of adhesives or adherends.

The failure mode of a particular bond (if indeed it fails) will be determined by the environmental stresses, including moisture, temperature, UV light, and mechanical loading to which it is subjected.

Studies of bonding in solar modules have emphasized water as the primary environmental agent of concern with regard to bond durability. It is found that the kinetics of failure for unprotected adhesive joints often are governed by diffusion of water into the joint. To increase the moisture durability of solar-module interfacial bonds, coupling agents or adhesion promoters have been widely used. Organofunctional silanes have received the most attention in this connection because of their proven moisture resistance and ability to bond to a wide variety of materials, including metals, metal oxides, glasses and organic polymers.

As has been pointed out in preceding sections of this report, very little data are available on the aging of bonded interfaces. More work is required to assess the potential for failure due to long-term exposure to water and other environmental stresses.

B. PRINCIPLES OF PHYSICAL ADHESION

When any materials are brought into close contact with each other, forces act between the atoms on their surfaces that are totally independent of any chemical interactions. The nature and strength of these forces control all non-chemical surface phenomena, including wettability and physical adhesion.

Material situated on the surface of a body is at a higher energy than that in the bulk. Atoms situated below the surface experience attractive and repulsive interactions with their nearest neighbors in all directions. These interactions are responsible for the cohesive strength of the material. Atoms on the surface however, can interact with only half as many nearest neighbors, which are in or below the plane of the surface. This situation gives rise to physical adhesion. When the surfaces of an adherend and an adhesive are brought into intimate contact, the atoms on one surface interact with those on the other in a manner similar to that of the nearest-neighbor interactions in the bulk of a homogeneous body. Physical adhesion occurs if there is a net attractive force acting across the interface between the atoms on the two surfaces.

Regardless of bonding ability, a strong interfacial bond will not result unless the adhesive spreads spontaneously over the adherend surface, leaving no air gaps when the joint is formed. Consequently, before considering the potential strength of a bond, it is necessary to ensure wettability of the adherend surface by the adhesive. A criterion for wettability is that the adhesive solution exhibit zero (or near zero) contact angle on the adherend surface at some time during the bonding process. The contact angle θ , an experimentally measured parameter of a liquid-solid interface, is defined as the angle between the plane of the solid surface and a line drawn tangential to the surface of a small liquid droplet at the point where it contacts the surface (Figure 5). It is easy to see that θ going to zero corresponds to the collapse of the droplet as it spreads across the surface.

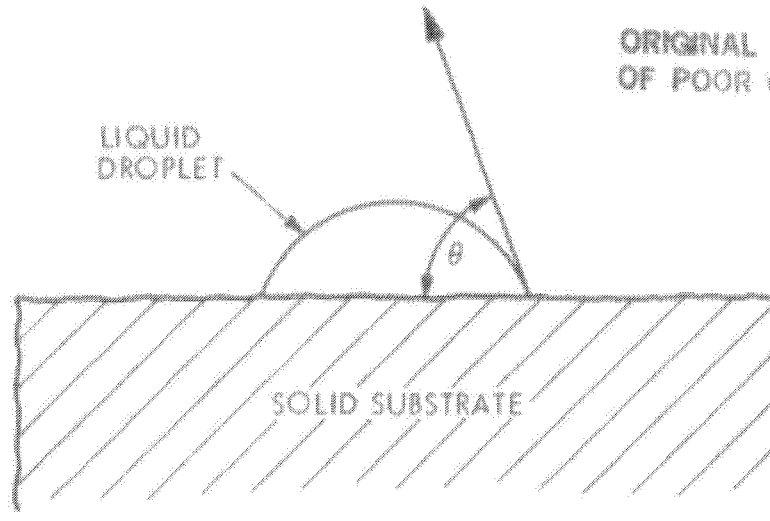


Figure 5. Diagram of a Liquid Droplet on a Solid Surface, Showing the Contact Angle (the Angle Between the Solid Surface and a Line Drawn Tangential to the Droplet's Surface at the Point Where it Touches the Solid Surface)

The contact angle, although a fundamental measure of wettability, is not a practical criterion in module design because it is a property of the combination of adhesive and adherend. For material selection purposes it is desirable that wettability be predictable from inherent properties of the individual materials rather than their combination. Fortunately, that is possible. Figure 6 shows a plot of $\cos\theta$ vs γ_{LV} , the surface tension, for a number of liquids on two polymer surfaces (Reference 16). That value of γ_{LV} where $\cos\theta$ reaches unity is called the critical value of the surface tension and represents the point where θ goes to zero. From a design point of view, a more suitable criterion for ensuring spreading of an adhesive on an adherend's surface is then that the surface tension of the adhesive solution must be less than the critical surface tension of the adherend surface, or

$$\begin{array}{c} \text{adhesive} \quad \text{adherend} \\ \gamma_{LV} \leq \gamma_{crit} \end{array} \quad (1)$$

Values of these parameters are available in the literature or from manufacturers for a variety of materials.

If the surface of an adherend is suitably wettable by an adhesive, then it is possible for a bond to be formed. The bond strength is typically described in terms of the work of adhesion, which is the energy required per unit bonded area to separate the adhesive bond. The greater the value of W_A as measured by, for example, a peel test, the stronger the bond.

The interatomic forces responsible for physical adhesion are usually divided into two classes, polar and dispersion. The contributions of each type of force can be determined from surface free-energy measurements. An expression for the work of adhesion can then be written in terms of the

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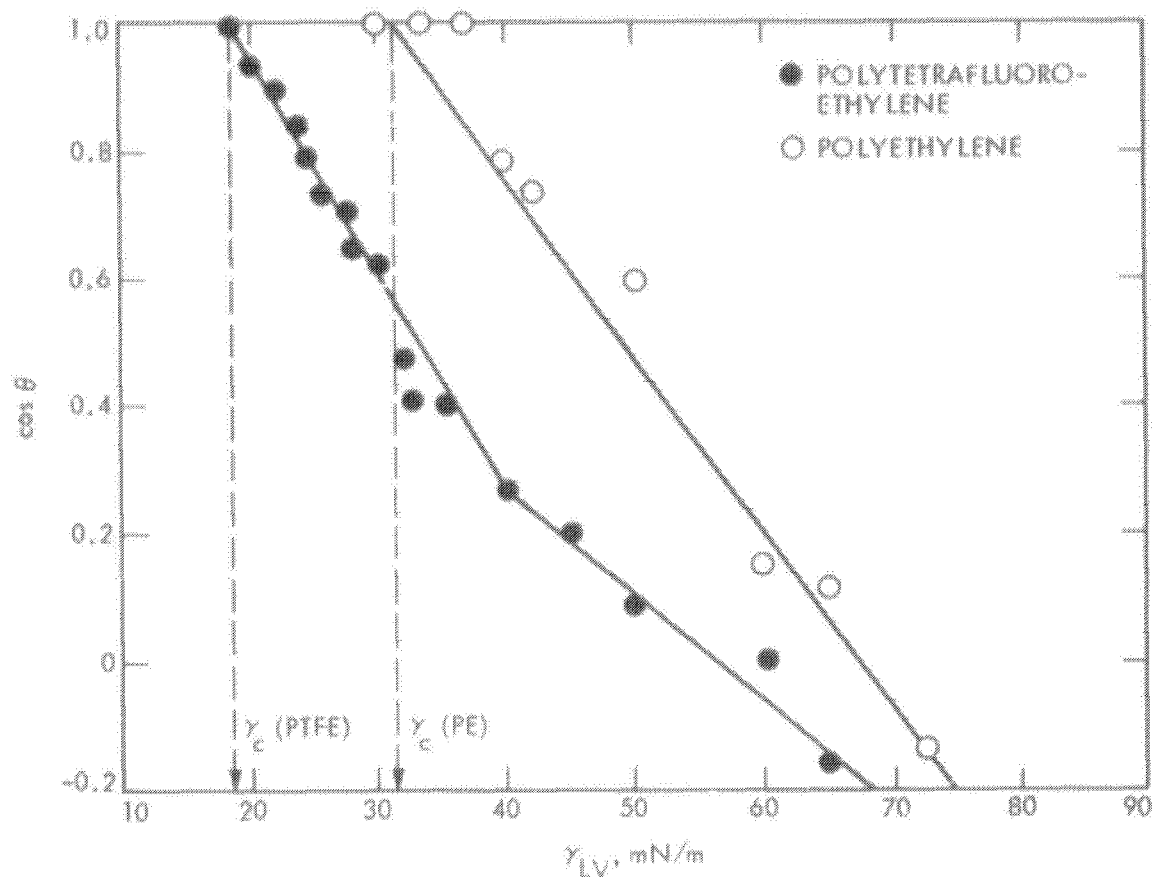


Figure 6. Plot of $\cos \theta$ vs γ_{LV} (Surface Tension) for a Number of Liquids on the Surfaces of Polytetrafluoroethylene and Polyethylene

polar-force and dispersion-force components of the surface free energies, γ_P and γ_D respectively, of the adhesive and the adherend. The work required to separate a joint formed between materials designated A and B (Reference 16) is:

$$W_A^{AB} = W_P^{AB} + W_D^{AB} = 2 \left[\left(\gamma_P^A \gamma_P^B \right)^{1/2} + \left(\gamma_D^A \gamma_D^B \right)^{1/2} \right] \quad (2)$$

Basically, Equation 2 says that polar materials tend to bond well to other polar materials, and materials with large dispersion forces tend to bond well to other materials with large dispersion forces; in other words, like bonds to like.

Silane primers are used extensively in the production of solar modules to bond to organic and inorganic substrates. While the chemical bonding ability of these primers is usually emphasized, they also exhibit physical adhesion properties. Table 9 lists experimentally measured values of γ_P and γ_D for a series of commercial silanes. It is seen that through chemical substitution, the properties of these materials can be altered so as to bond physically to

Table 9. Surface Energy Dispersion and Polar Force Components of Polymerized Silane Coupling Agents With Structure R-Si(OCH₃)₃

R-Structure	Commercial Designation	γ_D dyn/cm	γ_P dyn/cm
H ₂ N(CH ₂) ₂ NH(CH ₂) ₃ -	DC Z-6020	30.0	4.6
$\begin{array}{c} \text{CH}_3\text{O} \\ \\ \text{CH}_2=\text{C}-\text{C}-\text{O}-(\text{CH}_2)_3- \\ \\ \text{H} \end{array}$	DC Z-6030	8.4	41.7
$\begin{array}{c} \text{O} \\ \\ \text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-(\text{CH}_2)_3- \\ \text{(catalyzed)} \end{array}$	DC Z-6040	10.2	43.6
$\begin{array}{c} \text{O} \\ \\ \text{CH}_2-\text{CH}-\text{CH}_2-\text{O}-(\text{CH}_2)_3- \\ \text{(noncatalyzed)} \end{array}$	DC Z-6040	17.6	25.4
Cl-(CH ₂) ₃ -	DC XZ-8-0999	36.5	3.8
NH ₂ -(CH ₂) ₃ -	UC A-1100	17.9	19.8
HS-(CH ₂) ₃ -	DC XZ-8-0951	67.4	0.0
CH ₂ =CH-		28.5	2.1

almost any desired substrate. Dow-Corning's Z-6030, for example, would be expected to bond well to highly polar surfaces while Z-6020 should bond well to materials with a large dispersion-force component.

Equation 2 works well for predicting bonding ability of organic polymers, inorganic glasses and similar materials. However, in many cases, bonding to metal surfaces is described in terms of a different formalism. This results from the fact that many adhesion properties of metals are dominated by the acid-base interactions of the oxides that cover metals, under ambient atmospheric exposure (Reference 17). As pointed out by Parks (Reference 18) and Bolger and Michaels (Reference 19), experience shows that different metals and their oxides display widely different types of interactions with adhesives and corrosion agents based upon the isoelectric point of their surface (IEPS).

The IEPs is defined as the pH where the immersed metal oxide surface has zero net surface charge or where the concentration of hydrogen and hydroxide ions on the surface are equal. The IEPs of common metal oxide surfaces in water are given in Table 10 in order of increasing basicity.

The principles of bonding polymers to metal surfaces are, however, still not well known. The adhesion of polystyrene and functionalized styrene copolymers to various metal surfaces has been studied (Reference 7) and no consistent pattern of performance is discernible. For example, acid-modified copolymers do not necessarily form the strongest, most durable bonds with alkaline (heavy metal) surfaces, nor are amine-functionalized materials necessarily best on acid surfaces. Clearly, this is an area that requires further study.

C. CHEMICALLY BONDED INTERFACES

In the laboratory, η_A is always measured under dry, inert conditions. In the field, however, solar modules are subjected to environmental attack. Experience indicates that under wet conditions or exposure to moist atmospheres at high temperatures, the strength of bonded interfaces decays with a rate influenced by stress, temperature and relative humidity.

In general, an adhesive bond should not be pictured as a static sandwich of an interface region between adhesive and adherend, but as a dynamic equilibrium of an adhesive competing with various potential-weak boundary layers of the adherend surface. In polymer-to-organic adhesion, the weak boundary layers will most likely be oils, low polymers or other additives of

Table 10. Isoelectric Points of Metal (Oxide) Surfaces in Water

Oxide Surface	IEPS	Oxide Surface	IEPS
Silicon	2.2	Aluminum	9.1
Manganese	4.2	Zinc	9.0
Tin	4.5	Copper	9.1
Titanium	6.0	Nickel	11.0
Zirconium	6.5	Iron (reduced)	12.0
Chromium	7.0	Magnesium	12.2
Iron (oxidized)	8.5	Silver	>12
		Gold	>12

low cohesive strength. In polymer-to-mineral adhesion, the weak boundary layer is usually water or a loose corrosion product, resulting from the environment, on the mineral surface. In either case, the adhesive (polymer) must be capable of competing effectively with the potential-weak boundary layers for the substrate surface.

If the surface energy components γ_p and γ_D are known for a substrate and an adhesive, then the thermodynamic stability of the interface between them in the presence of water (an environmental agent of major concern) can be determined. If water diffuses into a joint between two materials A and B, then the work of adhesion can be written (Reference 20) as

$$W_A^{AB, H_2O} = 2 \left[\gamma_{H_2O}^{H_2O} - \left(\gamma_D^A \gamma_D^{H_2O} \right)^{1/2} - \left(\gamma_P^A \gamma_P^{H_2O} \right)^{1/2} - \left(\gamma_D^B \gamma_D^{H_2O} \right)^{1/2} - \left(\gamma_P^B \gamma_P^{H_2O} \right)^{1/2} + \left(\gamma_D^A \gamma_D^B \right)^{1/2} + \left(\gamma_P^A \gamma_P^B \right)^{1/2} \right] \quad (3)$$

The parameter $\gamma_{H_2O}^{H_2O}$ is the surface free energy of water and is equal to the sum of $\gamma_D^{H_2O}$ and $\gamma_P^{H_2O}$, which are 22.0 mJ/m² and 50.2 mJ/m², respectively. If

$W_A^{AB, H_2O} < W_A^{AB}$, as calculated from Equation 2, then the bond has been weakened by the water. If $W_A^{AB, H_2O} \leq 0$, debonding occurs and the joint fails.

Using Equation 3, interfacial stability in a moist environment can be predicted graphically for a given substrate as a function of γ_p and γ_D of the adhesive. For example, Figure 7 indicates the regions of stability and instability for bonding to an iron oxide substrate in a wet environment (Reference 20). The line represents those values of γ_p and γ_D for the adhesive that result in a bond strength of exactly zero. It must be kept in mind that this approach to bond durability prediction is thermodynamic in nature and does not include any kinetic considerations. If the time required for water to penetrate the interface is long compared to the life of the module, then even a thermodynamically unstable bond may perform excellently.

To stabilize a joint, then, either water must be prevented from reaching the interface during the module's useful life or the resistance of the interface to water must be increased. One approach to this problem is to seal the joints with materials that have low water-diffusion rates, such as epoxies or phenolic resins. Unfortunately, many of these materials fail to meet one or more requirements for use in solar modules, such as transparency, processibility, etc. The other alternative of stabilizing the interface against attack by water can be achieved by controlled chemical bonding between the

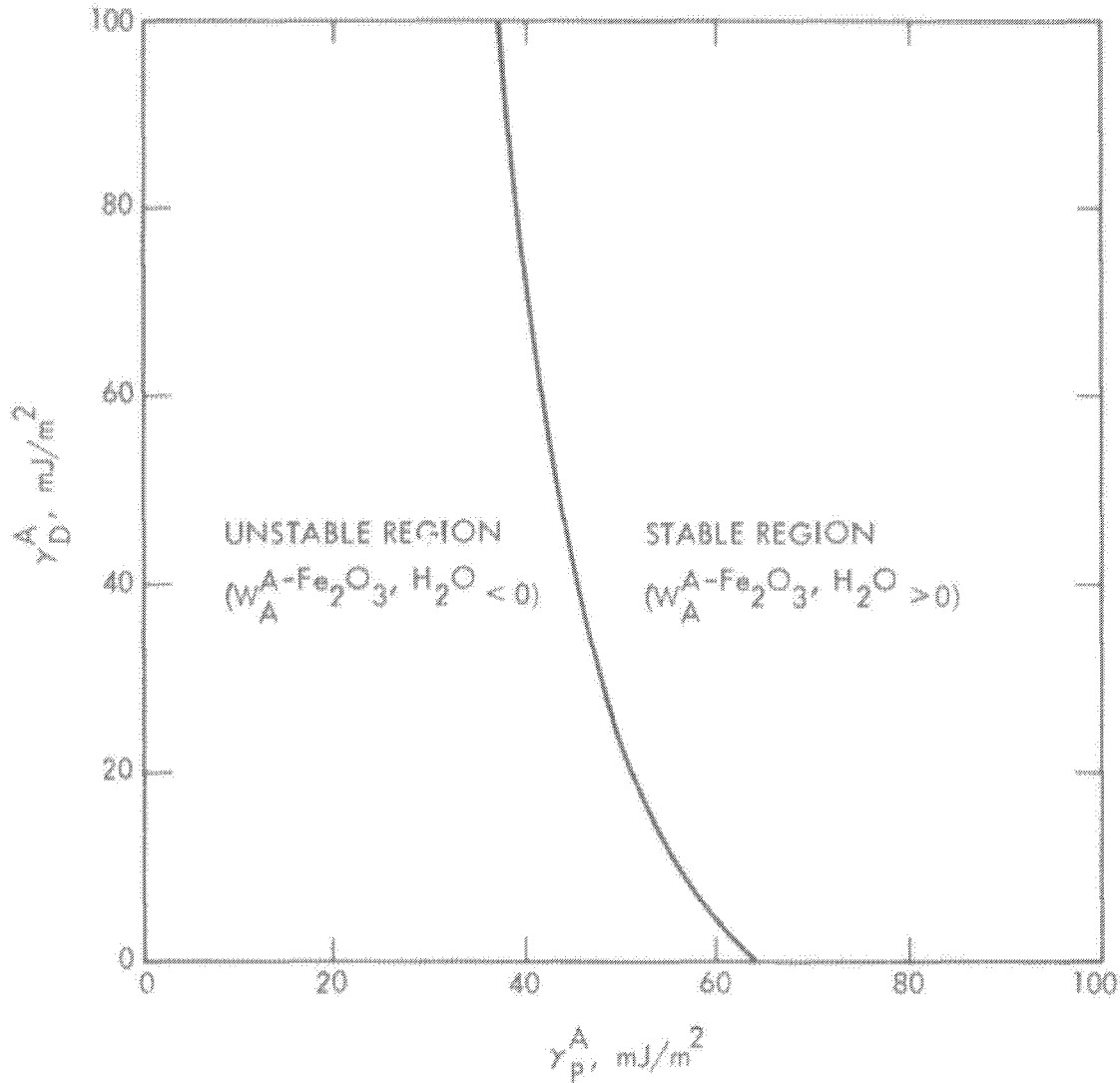


Figure 7. Prediction of Interface Stability for Fe_2O_3 Substrate in a Wet Environment as a Function of γ_p and γ_D of Potential Adhesives; Calculation Was Made Using Equation 3 and the Values of 107 mJ/m^2 and 1250 mJ/m^2 for γ_D and γ_p of Fe_2O_3

adhesive and the substrate through the use of a coupling agent. An excellent example of this approach is seen in fiberglass-reinforced boats, wherein the fiberglass is chemically coupled with silane to the laminating resin. The successful experience of many thousands of such boats in water inspires confidence.

A number of chemically bonding coupling agents have been identified, including modified silanes, titanates, phosphates and chromium complexes. The FSA program has emphasized the use of silane primers because of their water resistance, transparency and ability to bond to a wide variety of materials (organic polymers, metals, metal oxides, glasses, etc.). Furthermore,

organofunctional silane compounds have been used for many years as coupling agents on glass fibers to improve the performance of glass-reinforced polymer composites, and to allow retention of properties upon exposure to moisture. Commercial silane coupling agents are available (Table 11) for bonding to virtually any organic polymer.

The coupling mechanism of adhesion through silanes is complex and only partially understood. The general idea has been to use an ambifunctional silane that will undergo two reactions, one with a mineral substrate and one with an organic adhesive, thus forming a continuous, covalent chemically bonded bridge between the two.

Although the concept that the observed durability of silane-primed interfaces was due to chemical bonding (rather than improved physical adhesion) has existed for many years, only recently has direct evidence of it been available. Ishida and König (Reference 21) have used Raman and FTIR spectroscopic techniques to observe coupling-agent-to-substrate interfacial bonds in various glass-silane systems. Largely as a result of their work, the details of bonding to the inorganic substrates are far better understood than those of the bonding to the organic adhesives. The chemistry of a typical silane coupling agent on a silicate glass is outlined in Figure 8 (Reference 22).

Commercial coupling agents are usually available as functionalized trialkoxy compounds. The functional group X is chosen for maximum bonding ability to the organic adhesive. The alkyl groups R (typically methyls) are removed by hydrolysis in hot water and the resulting silanols dissolved in a suitable solvent. The primer is then applied to the clean glass surface and the solvent evaporated, leaving a hydrogen-bonded network. The final step is to cure the system by heating and drying, resulting in the formation of a polysiloxane material bound to the glass by means of Si-O-Si bonds. The cured coupling agent shown in Figure 8 is a linear polysiloxane; however, by changing the functionality or mixing multiple silanols, a three-dimensional polysiloxane network can be formed. A major contribution of König and coworkers to the study of silane-glass bonding has been the development of a computer-aided FTIR technique with which they can distinguish silicon-oxygen bonds across the interface from those in the polymer. Using this technique, they are able to quantify interfacial bond strengths in systems where mechanical (peel) testing is difficult or impossible, and to identify optimum bonding conditions (Reference 9).

D. INTERPHASE STRUCTURE

It was pointed out in the preceding section that the nature of the coupling agent bonding to an inorganic substrate is fairly well understood. What is still uncertain (and quite controversial) is the nature of the region between the coupling-agent--substrate interface and the bulk organic adhesive, called the interphase. There are at least two models for this region that have attained some acceptance in the adhesion community. However, before examining the details of these different pictures, it is necessary to understand the importance of the interface-interphase region to the integrity of the bond.

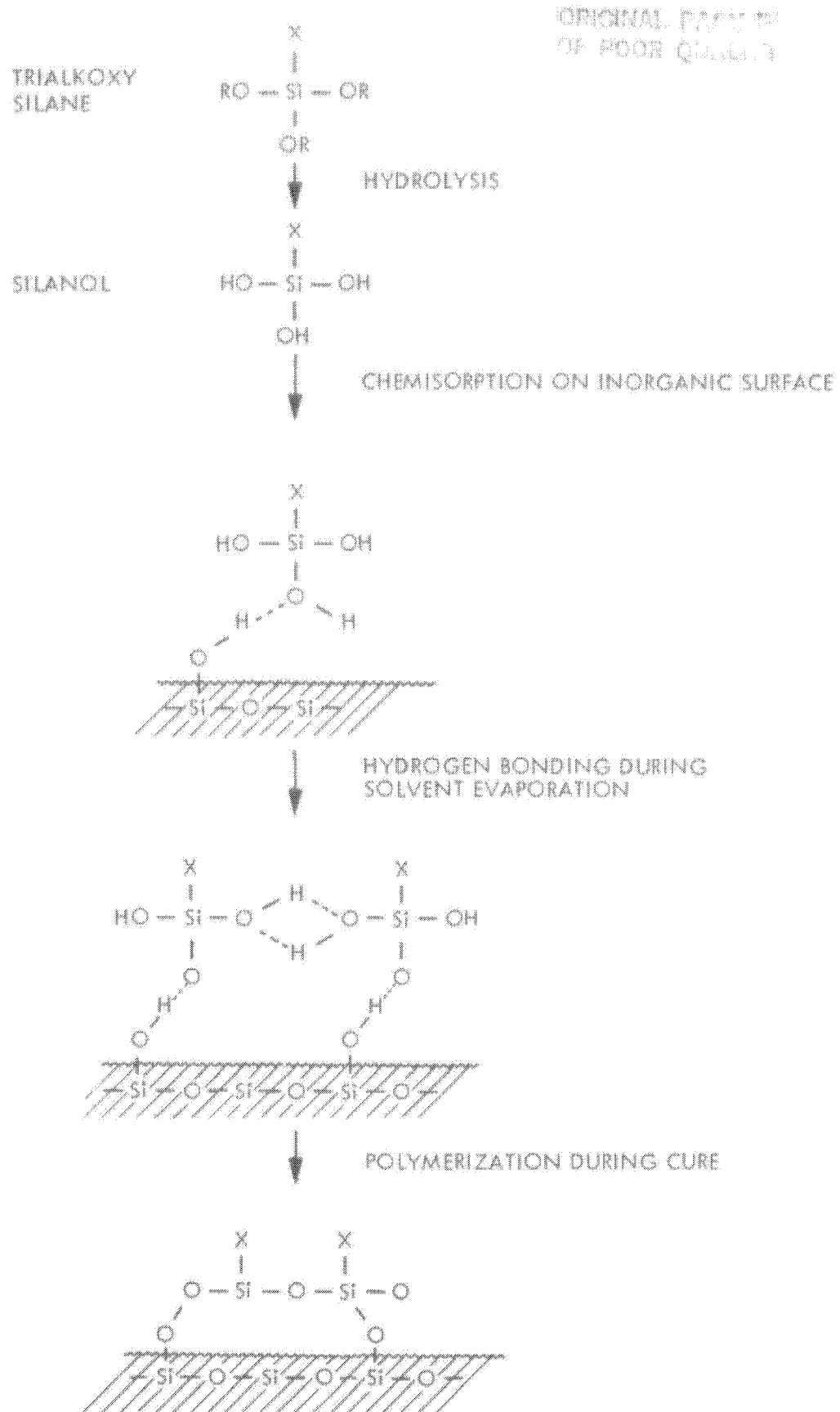


Figure 8. Formation of Polysiloxane on Glass Surface

Table 11. Typical Commercial Coupling Agents and Recommended Applications

Organofunctional Silane	Dow Corning Designation	Recommended Applications
Vinylbenzyl (cationic)	Z-6032	All resins and rubbers
Vinyl	Z-6075	Unsaturated polymers
Methacrylate (nonionic)	Z-6030	Unsaturated polymers
Methacrylate (cationic)	Z-6031	Unsaturated polymers (ketone peroxide)
Amine	Z-6020	Epoxy, phenolic, Nylon
Epoxy	Z-6040	Thermosets
Mercaptan	Z-6062	Thermosets, rubber

Adhesive joints usually debond as a result of cohesive failure in one of the adherends or in the interphase region itself. Presumably, mechanical strength requirements of materials used in solar modules have been assessed and considered in selection of the structural components (Reference 23). However, even with optimum chemical modification of an interface, a durable, water-resistant bond will not be formed unless the interphase region also has adequate cohesive strength and mechanical properties such as rigidity, tensile strength and toughness to carry the mechanical load when the bonded system is stressed. Furthermore, these properties of the interphase must be relatively insensitive to hydrolysis.

On the basis of many observations, a master curve has been developed (Figure 9) relating total performance (including moisture resistance) of composites under stress to the degree of structure in the interphase region of organic-inorganic composites (Reference 7). In all cases, the performance curve of Figure 9 assumes optimum chemical bonding at the interface.

Many of the polymeric materials used in fabricating solar modules have mechanical properties in the range of minimum performance in Figure 9. To develop water-resistant bonds to such polymers, the interfacial region must be modified in such a way as to develop either a tacky (viscoelastic) interphase or a crosslinked resinous interphase. In all cases it is necessary to modify only a very thin region for optimum bonding. This makes it possible to obtain water-resistant bonds of flexible or rubbery coatings to metals and glasses by means of crosslinking without sacrificing total flexibility.

The traditional view of chemically bonded interfaces, coming principally as an extension of physical adhesion ideas, is the sandwich structure shown in Figure 10. This model describes the primed interface (glass-EVA, for example)

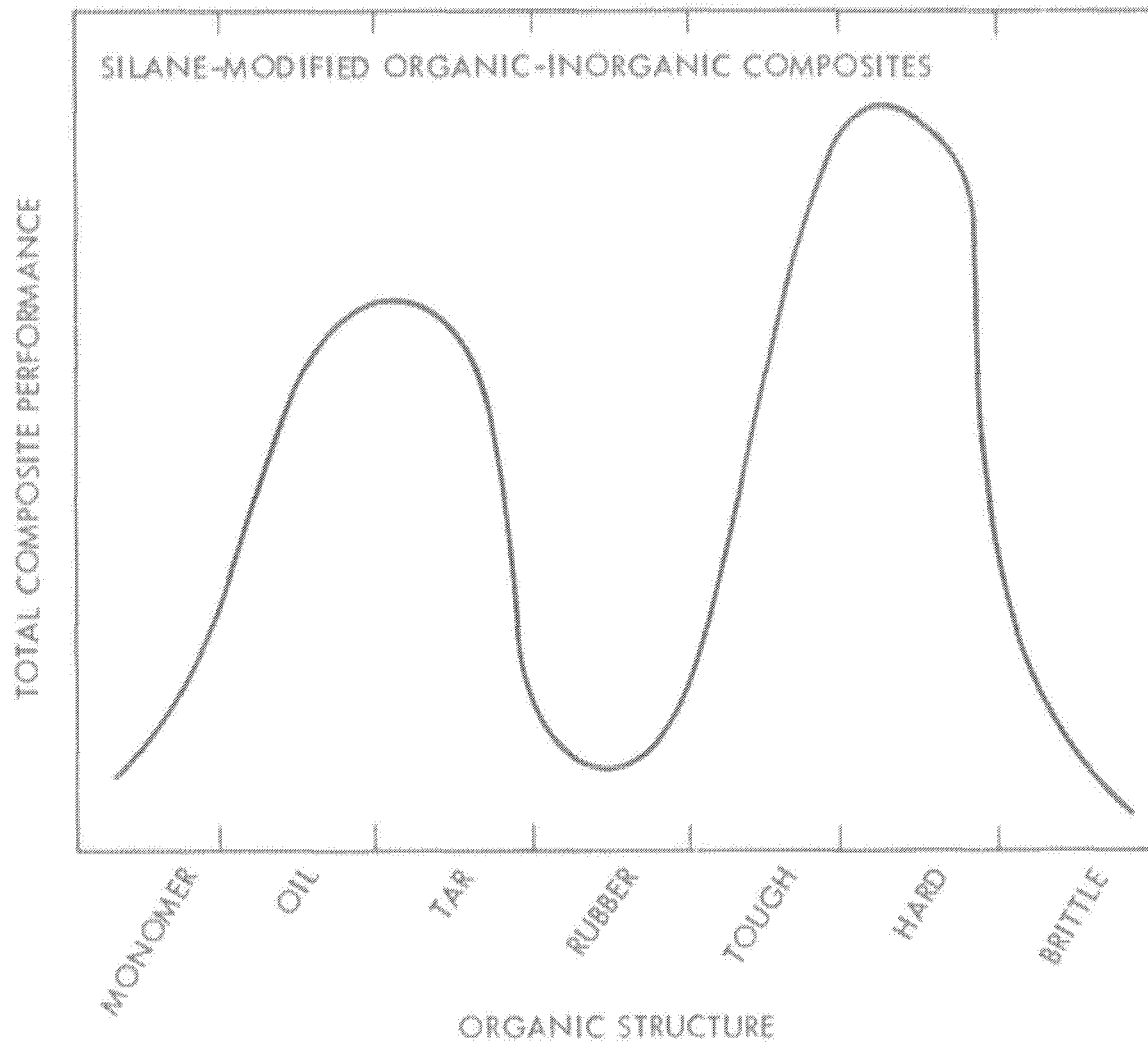


Figure 9. Variation in Total Performance of Organic-Inorganic Composites With Change in Polymer Morphology Near the Interface

as a series of discrete layers of clearly identifiable composition and structure. These layers include:

- (1) The bulk glass substrate.
- (2) A region including the surface monolayer of glass molecules and the contacting monolayer of polysiloxane molecules between which there are chemical bonds (interface 1).
- (3) A region of bulk polysiloxane (interphase).
- (4) A region including the surface monolayer of EVA molecules and the contacting monolayer of functionalized polysiloxane molecules between which there are chemical bonds (interface 2).
- (5) The bulk EVA region.

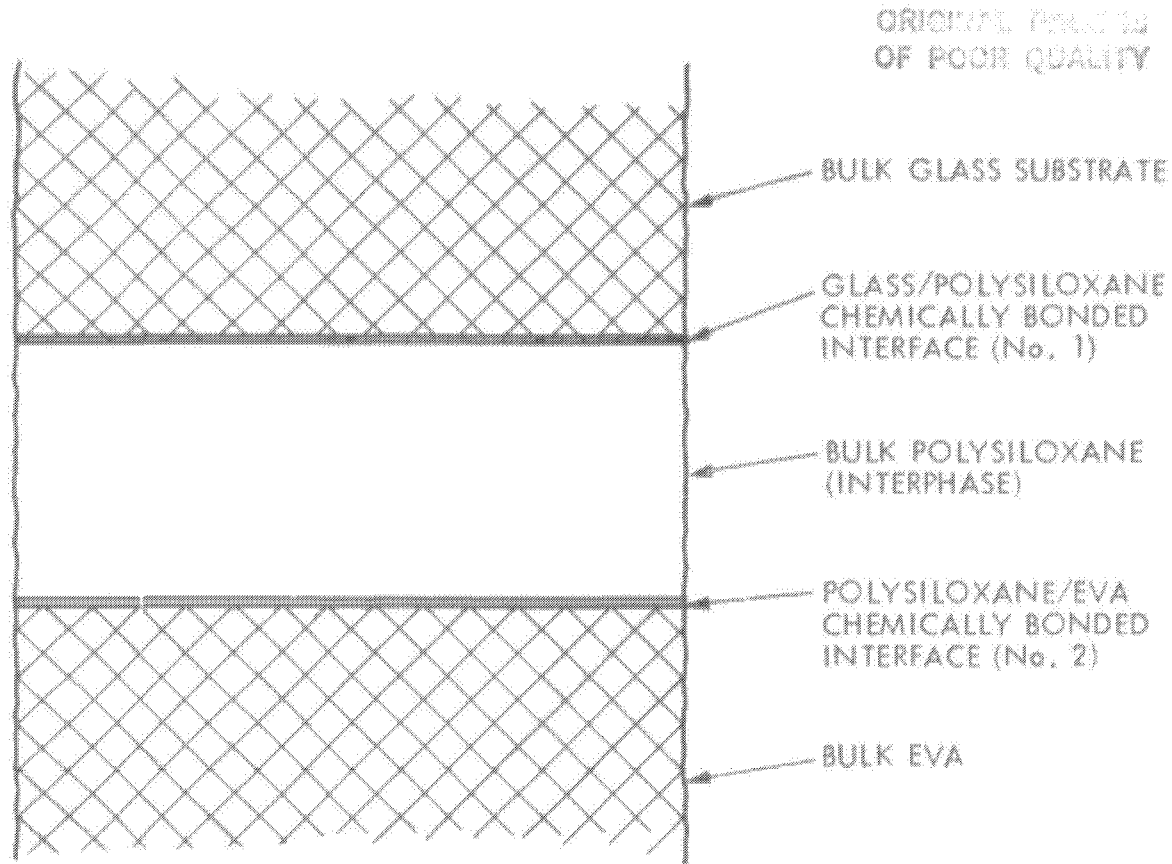


Figure 10. Sandwich Model of Silane-Primed Glass-EVA Joint

Within the framework of the sandwich model, two clearly defined interfaces and an interphase region consisting of bulk polymerized coupling agent can be identified. If this is an accurate picture of the bond, then, assuming adequate chemical bonding strength at the interface, the performance of bonds in solar modules using silane primers will depend on the performance of the bulk polysiloxane interphase.

The properties of the polysiloxane layer are primarily dependent on the nature and extent of the curing (polymerization) process. The initially deposited silanols must be crosslinked in order to form a water-resistant bond (Reference 24). Before or during the early stages of cure, the bulk primer region consists of a multilayered structure of oligomeric siloxanols that are soluble and fusible. As heating continues, this condenses into a crosslinked silicone structure that is insoluble and infusible.

The ability of such a network to absorb and dissipate energy when stressed is a function of a number of material properties. Two of these, the glass transition temperature (T_g) and the fracture energy, are of primary importance.

It has been suggested that a good criterion for the T_g of the interphase is that it be in the middle of the service temperature range of the modules. This is based on the fact that a material's ability to dissipate low-frequency

stresses, which are presumably the most important in solar modules, is maximum near T_g . The T_g of the polysiloxane will be a function of the processing conditions. Kasible (Reference 25) and coworkers at Rockwell International have carried out some preliminary studies on the T_g of several cured silane primers (DC-Z6020, DC-Z6030 and DC-Z6031) by thermal mechanical analysis. Silanes were mixed with acidified water (pH 4) in a weight ratio of 50:50 and allowed to polymerize and evaporate, simultaneously, by heating at 130°C overnight. Small sample pieces were then removed and T_g was measured (at a scan rate of 10°C/min). After scanning to about 400°C, samples were cooled and rescanned to determine the effect of the first scan (postcuring) on the T_g of the silanes.

Figure 11 shows the glass transition temperatures of the silanes after polymerization at 130°C and after thermal scanning to about 400°C. The data show that silanes polymerized at 130°C (as recommended in customary processing conditions) have rather low T_g (i.e., 37°C, -33°C, and 25°C for Z-6020, Z-6030, and Z-6031, respectively). However, postcuring raised the T_g substantially, especially for silanes Z-6020 and Z-6030. This increase in T_g is conceivably due to additional network formation or network rearrangement as a result of postcuring.

The criterion of high fracture energy is more difficult to meet in the case of the silane coupling agents than that of T_g ; bulk polymerized silanes are known generally to possess little mechanical strength. They are, in fact, widely used as mold release agents for high-temperature curing processes.

Critics of the sandwich model argue that if there is a layer of bulk polysiloxane present at an interface, then the bond will be inherently weak because of the low cohesive strength of this material. Recently, experimental evidence that appears to support this argument has come to light. Studies by Koenig (Reference 9) of bond strengths of epoxy-glass interfaces coated with silane primers show that as the amount of primer on the surface of the glass before bonding is increased, the bond strength initially rises, reaches a maximum and then declines. The interpretation of these results is that the initial increase in bond strength is due to increasing density of interfacial chemical bonds. Once a chemically bound monolayer and a few (probably <10) strongly chemisorbed layers of coupling agent have been deposited on the glass surface, addition of further primer only results in the formation of a bulk silanol layer which, due to its poor mechanical properties after cure, is subject to cohesive failure, resulting in a lowered bond strength (Figure 12) (Reference 26). If excess primer is deposited on the surface, it can be removed by washing with hot water or alcohol before bonding, with a resulting increase in bond strength being realized. It is apparent that this phenomenon is not limited to silane primers. Matsuoka (Reference 27) has reported a similar bond strength dependence on adhesive thickness in studies of Al/Nylon 12 laminates.

Recently, an alternative picture of the chemically bonded interface and the interphase region in particular has begun to emerge. The interdiffusion model, as we shall call it, is depicted in Figure 13 for a silane-primed glass-EVA interface. This model differs from the sandwich model in that there is no bulk coupling agent layer present, nor is there a clearly defined coupling-agent-organic interface. Rather there is an interphase region where

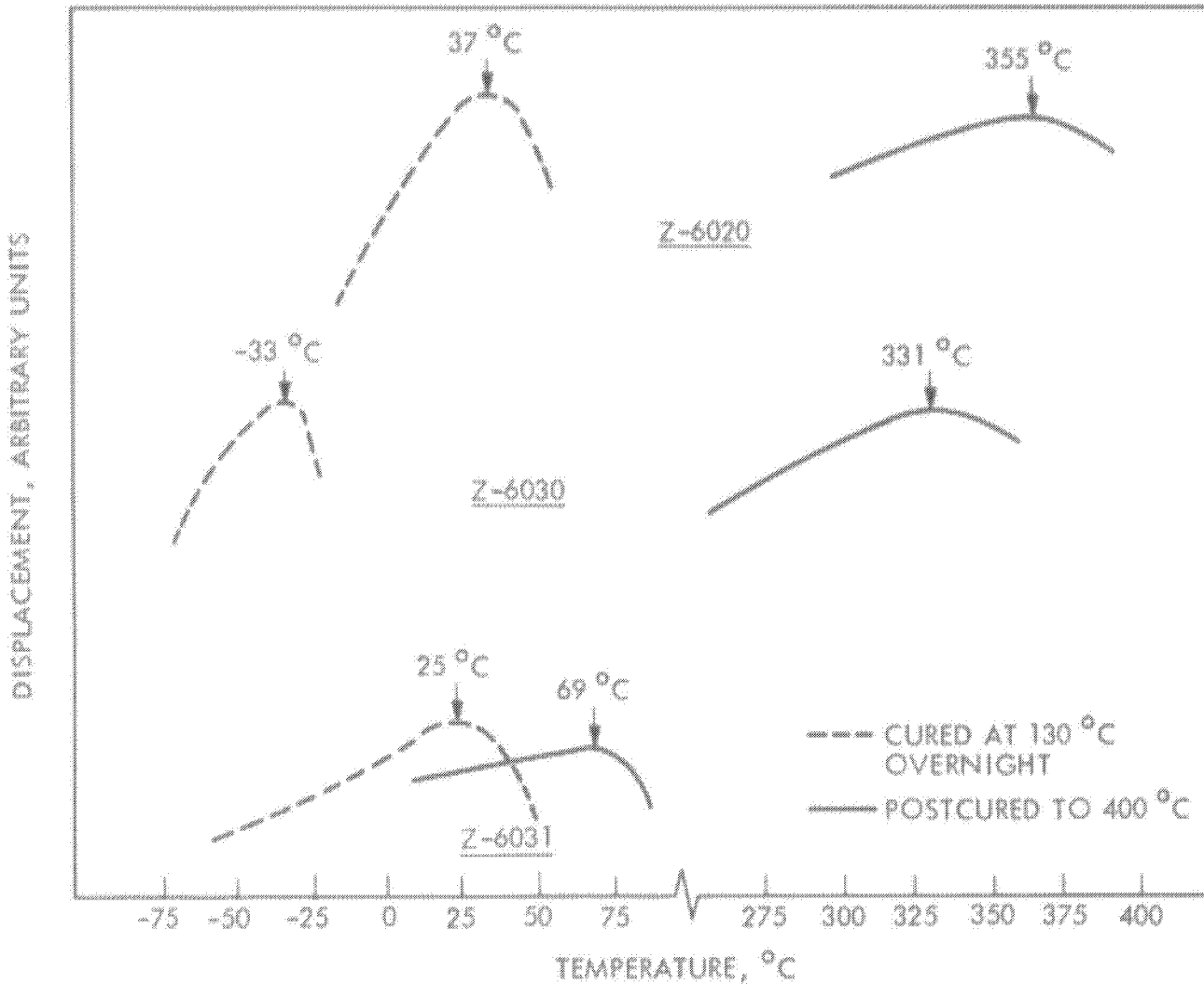


Figure 11. Glass Transition Temperatures of Silane Coupling Agents

interdiffusion has occurred between the coupling agent and the organic adhesive before cure. The composition of this region as a function of distance from the silane-glass interface is shown schematically in Figure 14.

To establish a density gradient of the organic adhesive in the interphase region, it is necessary that it be soluble in the coupling agent or primer solution and that at some time during the bonding process these two materials have low enough viscosity to allow mixing. Once the materials have mixed, the system can be cured, resulting in the formation of a heterogeneous network. Proponents of the interdiffusion model argue that such a network will be much stronger than a pure bulk polysiloxane layer and that it is this type of structure that is responsible for the high bond strengths observed in chemically bonded organic-inorganic interfaces.

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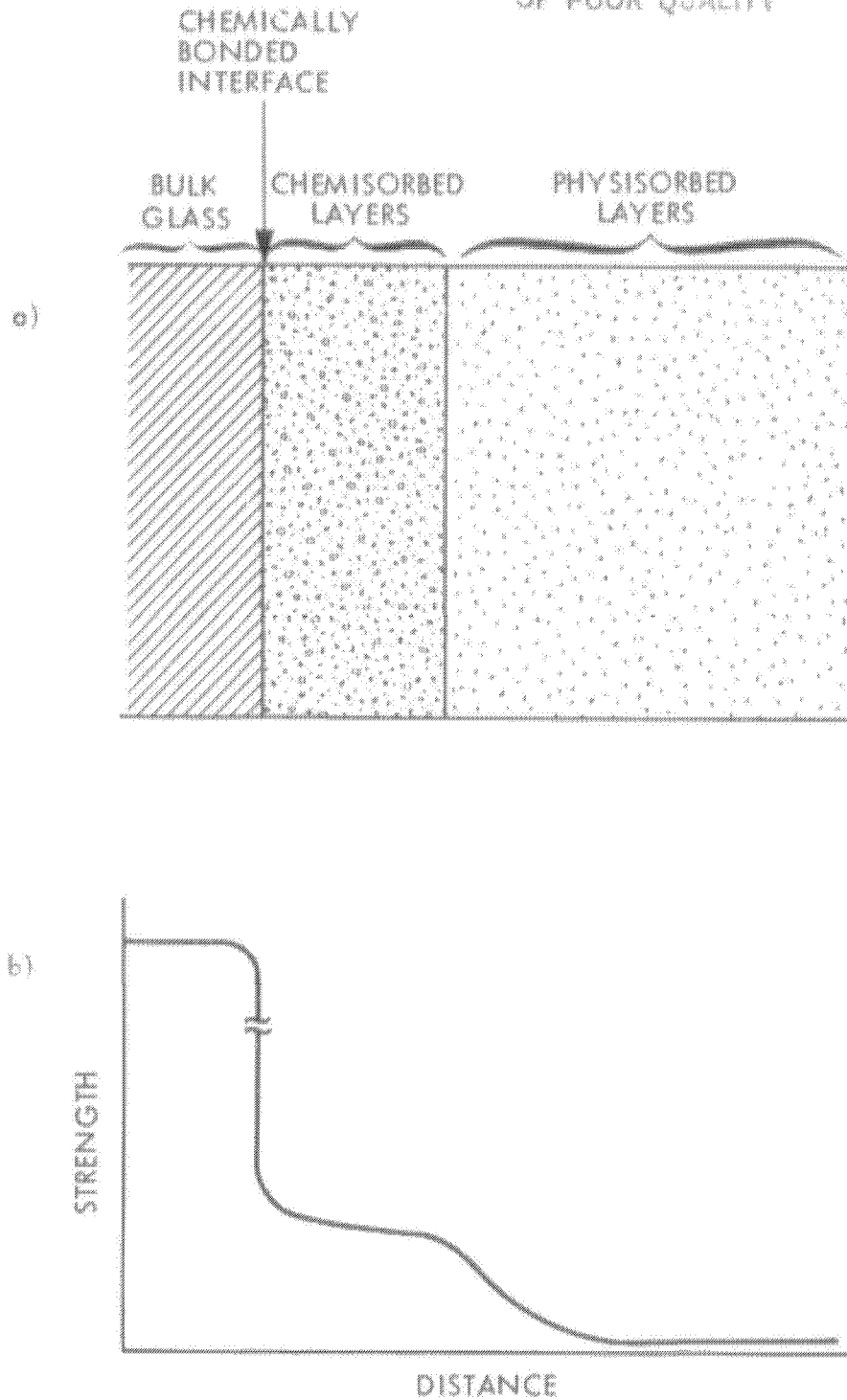


Figure 12. Silane Coupling Agent on Glass: (a) Schematic Representation Showing Chemically Bonded Interface, Strongly Chemisorbed Region and Weakly Physisorbed Region; (b) Plot of the Mechanical Strength of Various Regions Near the Interface, Showing Weakness in the Physisorbed Bulk Silane

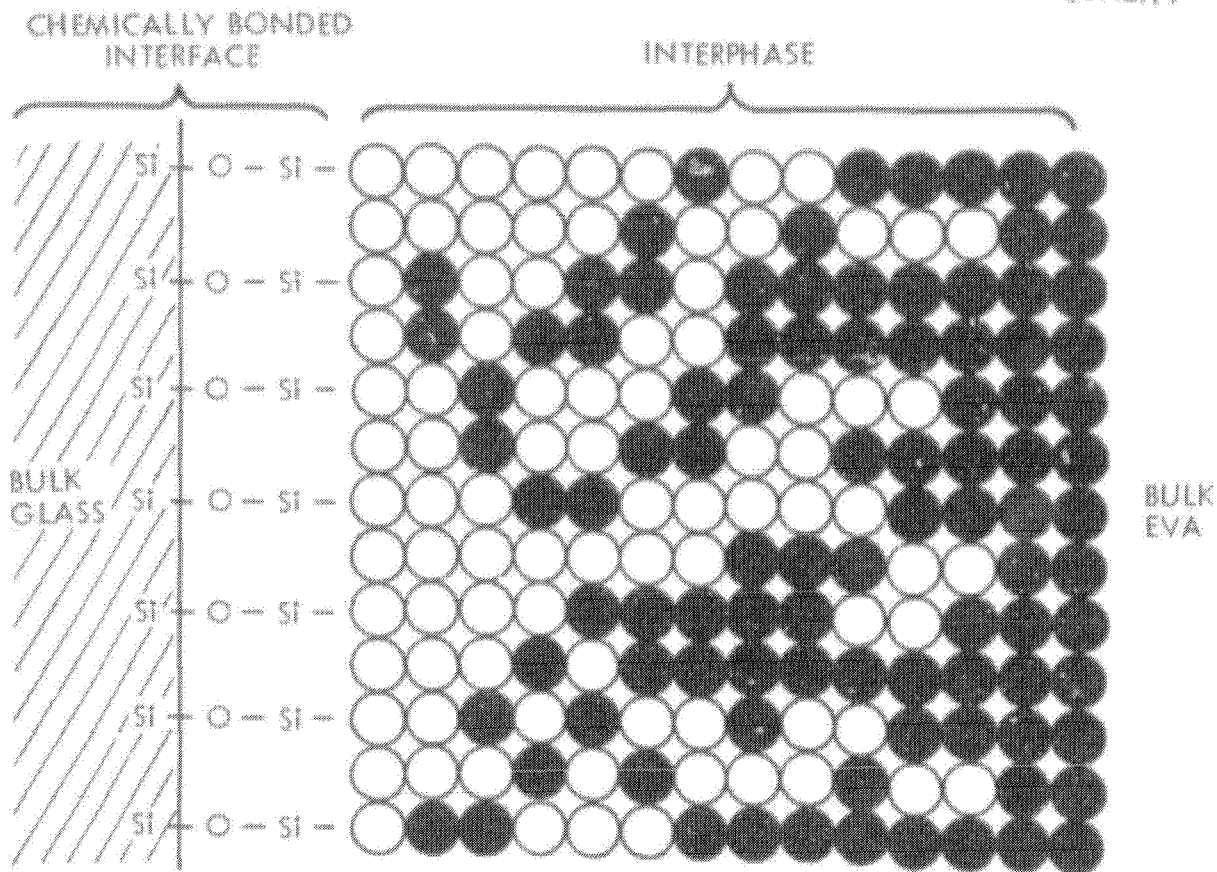


Figure 13. Schematic Representation of the Interdiffusion Model for a Silane-Primed Glass-EVA Joint; Open Circles Indicate Regions of Coupling Agent, Filled Circles Indicate Regions of EVA

The structural details of the interphase region are largely unknown. However, depending on the nature of the coupling agent and the organic adhesive, one of four basic structures is likely. In bonding to reactive thermoset resins, the coupling agent may diffuse into the resin and copolymerize during cure, forming a very strong chemically bonded network. In less reactive resins, partial diffusion may occur followed by separate polymerization of the coupling agent and the organic adhesive, resulting in the formation of an interpenetrating network. In the case of non-reactive thermoplastics such as polyethylene or polypropylene, after interdiffusion only the coupling agent will crosslink, leaving a pseudo-interpenetrating polymer network. Finally, in some cases long-chain linear coupling agents will be used, which will interdiffuse with the polymer matrix but will not crosslink, leaving either a pseudo-interpenetrating network or simply a heterogeneous mixture of long-chain polymers, depending on the nature of the organic adhesive.

Studies of bonding of silane-primed glass/EVA joints appear to support the interdiffusion model. If the silane coupling agents used cure before melting of the EVA, there is little chance for interdiffusion and the bonding

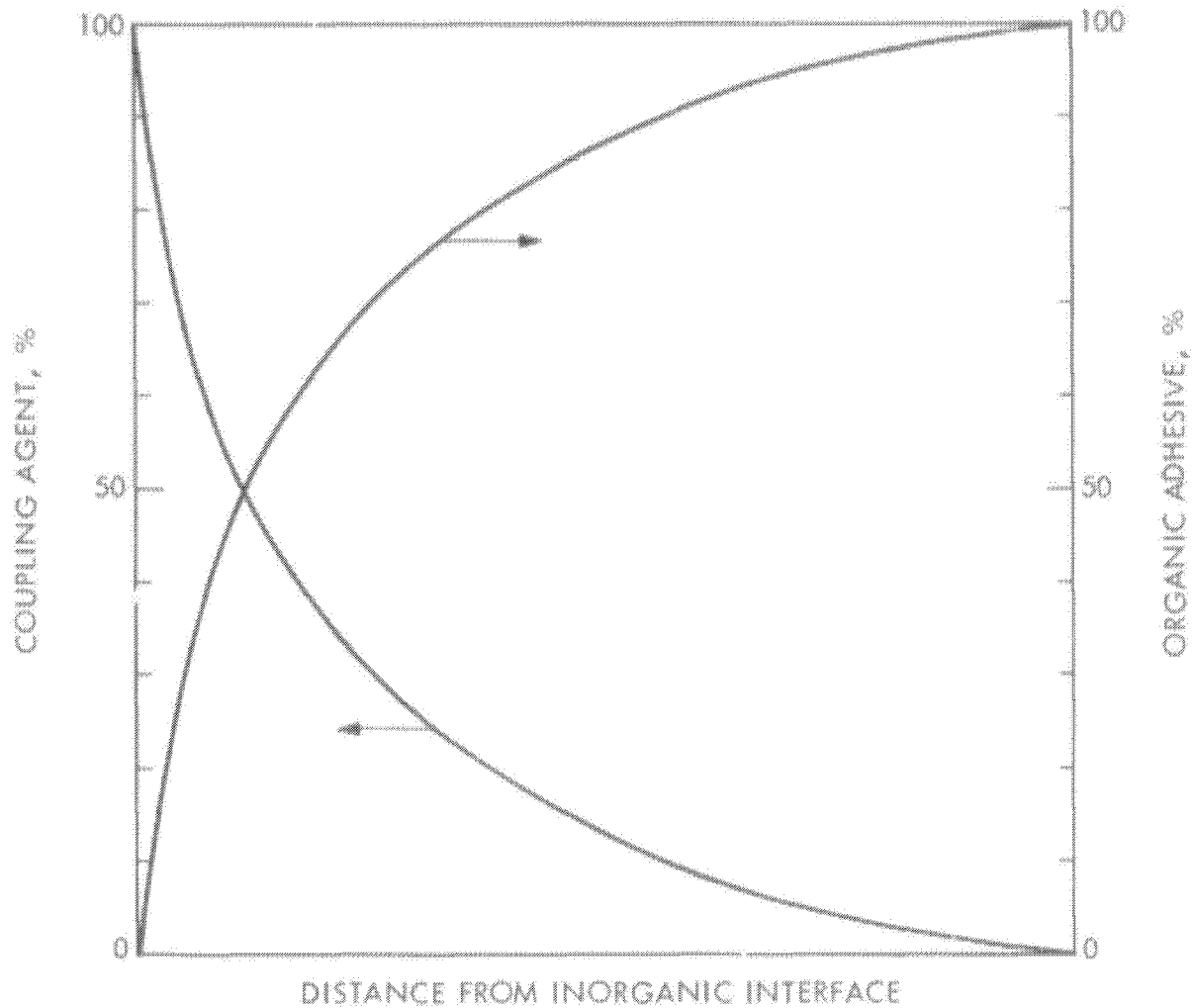


Figure 14. Plot of Silane-Adhesive Concentration Gradient as a Function of Distance From Inorganic Interface

is weak. It is observed, however, that bond strengths improve if silanols that cure at a temperature similar to that of EVA are used, allowing interdiffusion of the two polymers. Furthermore, if a crosslinking agent (Lupersol 101) is added to the EVA, an interpenetrating network can be formed with further significant increases in bond strength being realized.

At the time of this report, the theories of interfacial bonding are in a state of flux. Many of the new concepts being proposed and discussed are not yet proven experimentally. However, considerable work is being done in these areas and, it is hoped, in the near future the picture will become much clearer.

SECTION IV

PROCESSING CONSIDERATIONS RELEVANT TO INTERFACIAL BONDING

Even if optimum systems for bonding in solar modules are identified in the laboratory, strong durable interfacial bonds may not be obtained if careful consideration is not given to processing techniques. Development of production guidelines to insure adequate bond performance is not complete; however, a growing body of experience and research has identified some basic principles.

Processing considerations of importance to interfacial bonding fall into three broad categories:

- (1) Surface preparation.
- (2) Application.
- (3) Curing.

In this section, some (but certainly not all) of the processing issues of relevance to bonding will be discussed. In many instances the issues will be presented for information, without specific recommendations, due to a lack of sufficient data.

A. SURFACE PREPARATION

Preparation of adherend surfaces before application of a primer or adhesive is of fundamental importance. Unless weakly bound surface layers are removed, they will likely lead to failure of the joint. The surface layers may be water, oil, organics, oligomeric species, corrosion products or other contaminants. For a given surface, the nature of these layers must be determined and suitable cleaning procedures (abrasion, washing, etching, etc.) established. Furthermore, the time between cleaning and application of the bonding materials should be kept to a minimum to avoid recontamination.

Most inorganic materials also have oxide and/or hydroxide layers on their surfaces. In a humid environment, the durability of clean glass or silicon oxide surfaces of solar cells is controlled by the reaction



Landsford (Reference 28) has given an expression for the depth (D) of hydroxyl conversion of glass as follows:

$$D^2 = Kt \quad (5)$$

where t is time in years and $K = 3.3 \times 10^{-9} \text{ m}^2/\text{yr}$ is the diffusion rate constant for water in glass. Using Equation 5, a simple calculation shows that a 1-Å-thick hydroxide layer will build on a glass surface in approximately 11 days. In order to eliminate completely the surface hydroxide

layer on E-glass fibers used in glass-reinforced epoxy, they are coated with primer immediately (<1 sec) after being drawn.

It is important to understand the effects of the presence of oxidized or hydrolyzed surface layers on bonding to determine whether it is necessary or desirable to minimize them. Generally, it is found that bonding to a glass surface is more efficient if the hydroxide layer is removed. The presence of such a layer may adversely affect the bond strength by causing the coupling agent to orient itself in a less than optimum geometry on the surface (Reference 29). Removal of the hydroxide layer can be achieved by etching the glass in a strong acid solution. On the other hand, there is some suggestion (Reference 30) that treatment of metal surfaces should maximize surface hydroxylation to produce optimum bonding. Subsequent chemical reaction with low-pH groups of adhesives and coupling agents seems to provide durable, corrosion-resistant interfaces.

B. APPLICATION

Once the adherend surfaces have been properly cleaned, they are ready for application of the coupling agents and/or adhesives. These are usually applied as neat liquids or solutions. The physical methods of application may include dipping, spraying, wiping, painting, etc. The method of choice will be based on the nature (viscosity, temperature, reactivity, etc.) of the liquids being applied.

If a material is not applied as a neat liquid then care must be taken in choosing a solvent and preparing the solution. If we consider the preparation of a primer, the first and most obvious criteria for selection of a solvent are that it must dissolve the coupling agents and that it must be non-reactive with them. It must also be capable of wetting the surfaces of the adherends, as discussed in Section III.B above, and it should be sufficiently volatile to evaporate in a reasonable amount of time under relatively mild conditions. The pH of the solution may also need to be adjusted, since it may affect the stability of the coupling agents as well as their deposition on the adherend surfaces.

Boerio and coworkers (Reference 31) have defined specific pH effects on aminosilane orientation on oxidized iron with an isoelectric point of $\text{pH} \cong 8.5$. When the aminosilane is applied from basic solution, $\text{pH} \cong 10.5$, there is a strong tendency for the molecules to deposit upside down (with the amino groups next to the oxide). At lower pH there is a reported tendency to reverse this orientation with silanols bonding to the oxide. At high pH the tendency to form the ring structures of amine to silane is enhanced and lowering the pH tends to open the rings and enhance the amine reactivity with the organic resin phase.

In Section III it was emphasized that the thickness of the coupling agent layer is critically important to bonding. In practice, the amount of coupling agent deposited on the surface is most easily controlled by adjusting the concentration of the primer solution. However, the concentration must never be allowed to reach such a level that molecular association begins to occur. It has been found that under such conditions the strength and durability of

the interface degrades (Reference 32). After deposition and initial drying of the primer, it may be desirable to remove some excess coupling agent before application of the adhesive and cure. This can be achieved by washing the surface in an appropriate solvent (e.g., hot water, alcohol) followed by a second drying.

C. CURE

The final category of processing considerations relevant to bonding involves curing of the coupling agents and adhesives. The physical and mechanical properties of the bulk adhesive and the interphase region are of critical importance to maintaining a strong bond. Most of these properties, such as T_g , fracture energy, crosslink density, network topology, etc., are strongly dependent on the details of cure, and slight changes in the curing cycle can alter the materials significantly.

Cure chemistry of multifunctional, multicomponent systems is so complex that it is almost impossible to predict the relationship of cure cycle to final mechanical properties; consequently, studies of these relationships are virtually all empirical in nature. For this reason, it is almost impossible to give even rudimentary guidelines for cure of bonded interfaces. The guiding principle, however, must be that the cure produces an interphase region with mechanical properties that give maximum performance in terms of bond stability and durability (Section III.D.).

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