JOURNAL OF APPLIED POLYMER SCIENCE VOL. IV, ISSUE NO. 12, PAGES 343-348 (1960)

Defects Present within Adhesive Layers*

HAROLD TARKOW

Forest Products Laboratory, Forest Service, U. S. Department of Agriculture, Madison, Wisconsin†

INTRODUCTION

Recent work at the U. S. Forest Products Laboratory directed toward the development of nondestructive methods for evaluating glue bonds has led to close examination of the nature of defects that may be present in such bonds. This report describes some of the defects that were observed. It is not implied that all are serious, or that they have not been recognized before. The defects are described because of the novel procedures used in their detection.

The experimental specimen was the adhesive film obtained from a conventional adhesive-bonded aluminum panel. The 4 × 4 in. or 8 × 8 in. panels, bonded with different adhesives, were cut into 1-in. squares. These were immersed in 15% $CuCl_2$. In about 2 hr. with occasional agitation, the aluminum dissolved, liberating the adhesive film in an apparently intact condition. Visual inspection of the air-dried films showed a markedly nonhomogeneous structure. Markings present on the adherend were clearly replicated on the surface of the films. Different physical measurements and observations were made with these films.

WEIGHT OF LIBERATED FILM PER UNIT AREA

The simplest measurement that would still reveal a type of variability is weight per unit area. In order for such measurements to be meaningful, it is essential that the spread rate of the uncured adhesive over the aluminum be uniform. Sheets of an unsupported, uncured vinyl–phenolic resin film adhesive, precisely cut a little larger than the 8 × 8 in. panel, were conditioned at 30% R.H. and only those were selected that weighed within 0.1 g. of each other. Using these for the adhesive, three aluminum panels (from etched, $1/20$-in. sheets) were made under conditions shown in Table I. Because of the uniformity in weight of the large sheet of uncured resin and its mechanical preparation, the spread rate in the three panels was assumed to be the same.

TABLE I
Curing Conditions of Panels Prepared with a Vinyl–Phenolic Resin Film Adhesive

Curing conditions	Panel a	Panel b	Panel c
Temperature, °F.	335	335	300
Pressure, psi	100	300	100
Time, hr.	0.5	0.5	1

A $5/8$-in. margin was trimmed off each panel edge and a grid scribed on each panel as shown in Figure 1. The 1-in. squares were cut out, and the adhesive film from a few were liberated, washed, conditioned at 30% R.H., and weighed (Table II). Within a given panel, the unit film weight is always greatest at the center (Station 25). This fact

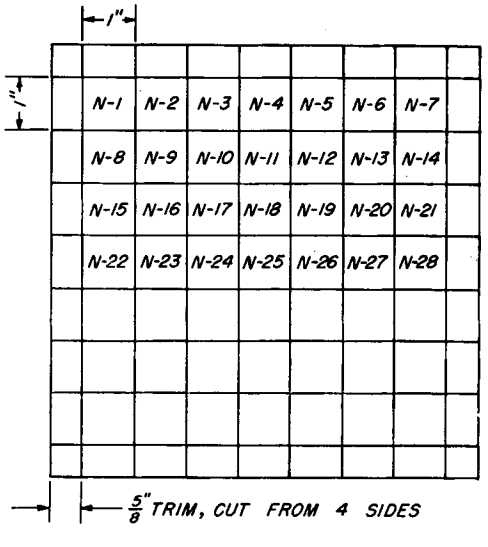

Fig. 1. Pattern of test specimens cut from 8 × 8 in. panel.

* This work was done in cooperation with Ordnance Corps, Picatinny Arsenal, Plastics and Packaging Laboratory, Dover, New Jersey.

† Maintained at Madison, Wisconsin, in cooperation with the University of Wisconsin.

TABLE II
Effect of Location of Test Square on Its Weight at 30% R.H.

Station[a]	Weight, g.		
	Panel a	Panel b	Panel c
4	0.2457	0.2601	0.2735
22	0.2653	0.2601	0.2722
25	0.2822	0.2829	0.2857

[a] See Figure 1.

suggests that during cure, the flow of adhesive at the center is mainly one of compaction. Elsewhere, and perhaps to an increasing degree, as an edge is approached, outward lateral flow also occurs, thereby causing a reduction in unit weight. Regardless of the cure condition, the weight at the center is approximately constant, whereas near the edge it is variable, again indicating the absence of flow away from the center. Elsewhere, and to varying degrees, both types of flow occur, as indicated by the lower and varying weights. This rheological behavior was shown to be unrelated to the slight nonparallelism of the platens. It must, therefore, be a consequence of the hydrodynamics of viscous or plastic flow between parallel plates approaching each other. Nadai[1] showed that under such conditions the normal pressure is not uniform, but ranges from a maximum at the center to zero at the edges. This is a consequence of the decreasing viscous resistance as an edge is approached.

FILM DENSITY

Film density was determined[2] by measuring the density of a solution of CCl_4 and hexane in which the film remained suspended. The film was placed in a thermostatted 2-in. glass tube containing about 100 ml. of a solution of CCl_4 and hexane (conditioned at 30% R.H.). Depending on the condition of the film, CCl_4 or hexane was added until, following agitation, the film remained essentially stationary. Supplementary work showed the films did not swell in the liquid mixture over a period of half an hour. The values in Table III are believed to be in error by no more than 0.0002 g./cc.

TABLE III
Effect of Location of Test Square on its Density at 30% R.H.

Station[a]	Density, g./cc.		
	Panel a	Panel b	Panel c
4	1.1093	1.2443	1.2056
22	1.1365	1.2445	1.2271
25	1.1163	1.2442	1.1971

[a] See Figure 1.

The highest density at a particular station is found in panel b. Thus, with increasing curing pressure, the amount of compaction increases over the entire panel. A longer cure time, even at a somewhat lower temperature, resulted in more compaction. Within a given panel, the density at the center is not higher than it is elsewhere, as was expected on the basis of the previous section. This may be due to a slight recovery of strain during liberation. Very likely, when the panel was withdrawn from the press (cold), a density gradient from the center and outwards did exist; however, on cutting up the squares and liberating the films, some compressive strain in the film was recovered. Thus, the measured film density may not reflect exactly the density immediately following cure. If this interpretation (partial strain recovery) is correct, then some systematic variation in thickness within a panel would be expected.

EFFECT OF LOCATION ON THICKNESS OF LIBERATED FILMS

Since the liberated films were 1 in. square, a knowledge of their weight and density (conditioned at 30% R.H.) permits calculation of the average film thickness. The error in the values given in Table IV is estimated to be a few hundredths of a mil.

TABLE IV
Effect of Location in Panel on Film Thickness at 30% R.H.

Station[a]	Film thickness, mils		
	Panel a	Panel b	Panel c
4	13.9	13.1	14.3
22	14.7	13.1	14.0
25	15.9	14.3	14.9

[a] See Figure 1.

As expected, the film thickness within a panel is greatest at the center station. This is due both to the increased mass at the center as well as to the increased strain recovery during liberation. For any station, the film thickness is least for the panel pressed at the highest pressure.

These data suggest a complex flow pattern during cure, resulting in a systematic variation in weight of adhesive per unit area and presumably in compressive strain. No attempt was made to relate these variations to bond performance. The fre-

quently observed variability in bond performance may be due to these "defects."

FRACTIONAL VOID VOLUME OF LIBERATED FILMS

In reference to Table III, it is noted that the density varies appreciably. The value of 1.2440 g./cc. must be an "ultimate" density, since the same value was found for films cured at pressures of 500 and 1000 psi. An indication of the fractional void volume, v_f is obtained as follows:

$$v_f = 1 - (d/1.244)$$

where d is the film density (Table V).

TABLE V
Fractional Void Volume of Liberated Films

Station[a]	Void volume, %		
	Panel a	Panel b	Panel c
4	11	0	3
22	9	0	2
25	10	0	4

[a] See Figure 1.

Owing to recovery of some compressive strain during liberation, the above values must not be taken too literally. They do indicate some variability in void volume depending on cure condition. Defects such as these may not be serious. Of greater importance is the shape of the voids.

EXAMINATION OF CROSS SECTIONS OF FILMS

Liberated films were soaked overnight in water and gripped in a microtome between blocks of balsa. Cross sections, 25 μ thick, were cut. The thin ribbons were carefully dried, mounted in a hydrocarbon medium between cover glasses, and examined with polarized light at 200-fold magnification. Figure 2 shows photographs of cross sections obtained from films cured at 100 psi. The plane of the figures is perpendicular to the plane of the liberated films, that is, to the adherend–adhesive interface. The physical reality of a void volume as suggested in Table V is clearly shown. The pronounced optical birefringence effects may be related to a stress created by the differential thermal coefficient of contraction between metal adherend and adhesive. The films show inhomogeneities other than voids and frozen-in stress concentrations, for example, the "swirly" character of the solid substance, suggesting nonuniform mixing. The significance of the lines radiating from some of the voids is not clear as yet. The physical effect of the microtome cutting is still to be established. Some of the films (not shown)

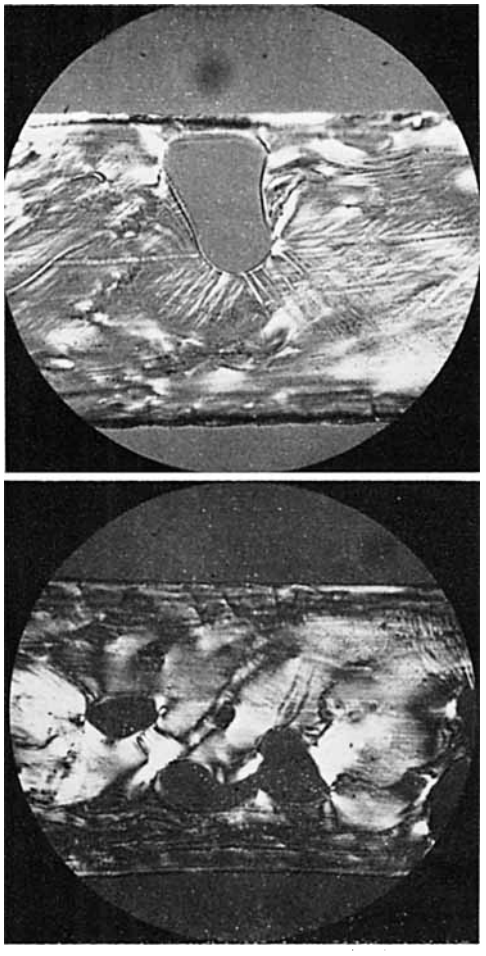

Fig. 2. Photomicrographs of cross sections of liberated films cured at 100 psi. Polarized light. 110× magnification.

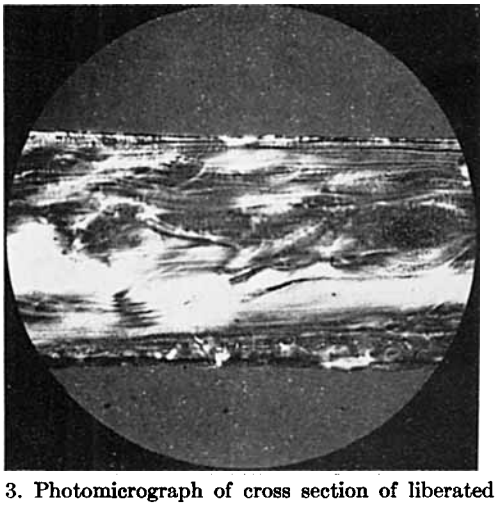

Fig. 3. Photomicrograph of cross section of liberated film cured at 300 psi. 110× magnification.

have highly elliptically shaped voids, suggesting that some of the voids may even be present as fine hairline cracks with trapped gas. These are extremely vulnerable to "unzippering" on loading normal to the long axis, as was first pointed out by Griffith.[3] Figure 3 shows a cross section of a film cured at 300 psi. The absence of visible voids explains the high density of these films (Table III).

ANISOTROPY OF LIBERATED FILMS

The existence of long-range anisotropy in the cured adhesive layer has never been established. Obviously, this would have a pronounced influence on the mechanical performance of the bond. Since, for materials that swell, mechanical anisotropy is related to swelling anisotropy, the existence of directional effects in these films was examined by determining the swelling in two directions within the plane and at right angles to the plane.

A system of lines was scratched on one of the sheets of aluminum, which was then bonded to a second sheet by means of vinyl–phenolic resin, unsupported film adhesive. Following liberation, the lines were found to be replicated on the 1-in. squares. They served as reference lines for measuring the swelling in the two mutually perpendicular directions in the plane of the film between 30 and 90% R.H. After conditioning the films in saturated-salt humidifiers, they were placed within a suitable cell and examined with a travelling microscope. These data, together with the weight and density of the films conditioned at 30 and 90% R.H., permitted the swelling in the thickness direction to be calculated (Table VI).

Statistical examination showed no significant difference in swelling in the two plane directions.

TABLE VI
Swelling of Vinyl–Phenolic Resin Films in Three Mutually Perpendicular Directions

Specimen[a]	Plane swelling, %		Thickness swelling, %
	Perpendicular	Parallel	
4a	1.04 ± 0.02	1.07 ± 0.02	1.24 ± 0.15
4b	1.05	1.11	1.19
4c	1.05	1.08	1.53
22a	1.10	1.08	1.51
22b	1.05	1.02	1.31
22c	1.06	1.01	1.30
25a	1.16	1.14	1.62
25b	1.11	1.10	1.35
25c	1.13	1.10	1.35

[a] Panel and station.

The error in measuring the thickness swelling is considerably higher; nevertheless, as a first approximation, the swelling is the same as that within the plane. The slightly higher swelling in the thickness direction would indicate a somewhat smaller elastic modulus; however, the effect is small. Thus, there is very little anisotropy within these films. Similar measurements with a liberated epoxy film (aluminum bonded with a liquid epoxy) again indicated an absence of anisotropy. Measurements with a liberated nitrile rubber–phenolic resin, unsupported adhesive were not complete, but they showed about 60% more dimensional change in one direction than at right angles to this direction within the same plane. The uncured adhesive comes in the form of an unsupported film. In an attempt to trace the plane anisotropy of the cured liberated film to an anisotropy in the uncured film, the initial elastic modulus of the uncured film was measured in the two mutually perpendicular directions within the plane of the uncured film (Instron testing machine). Almost a 3-fold variation in modulus was found in the two directions, in the sense that the direction in the uncured film with the higher modulus was the direction in the cured film with the lower degree of swelling. Thus, the plane anisotropy within the liberated nitrile rubber–phenolic resin film is derived from the anisotropy in the uncured film. Long-range anisotropy in the cured film does not derive from the curing process itself.

EFFECT OF SUBJECTING BONDED PANELS TO HIGH TEMPERATURES

Pairs of sheets of aluminum were acid etched, spread with epoxy resin, and bonded together; 1-in. squares were cut and heated (before liberation) at 350°C. for 1 hr. The adhesive layers that were then liberated were severely darkened and very brittle. Generally, both faces had scuffed regions, and the face that had been uppermost in the press during cure was usually scuffed to a greater degree (see Fig. 4). Although the significance is not clear, it does suggest a disymmetry between both bonded faces. It may be related to a tendency for some of the trapped bubbles to rise to the upper surface during cure.

Occasionally, following liberation of the film, evidence of delamination was found (Fig. 5). This suggests that a plane of weakness may exist where the two sheets of aluminum with their spread adhesive are brought together. In Figure 5, one

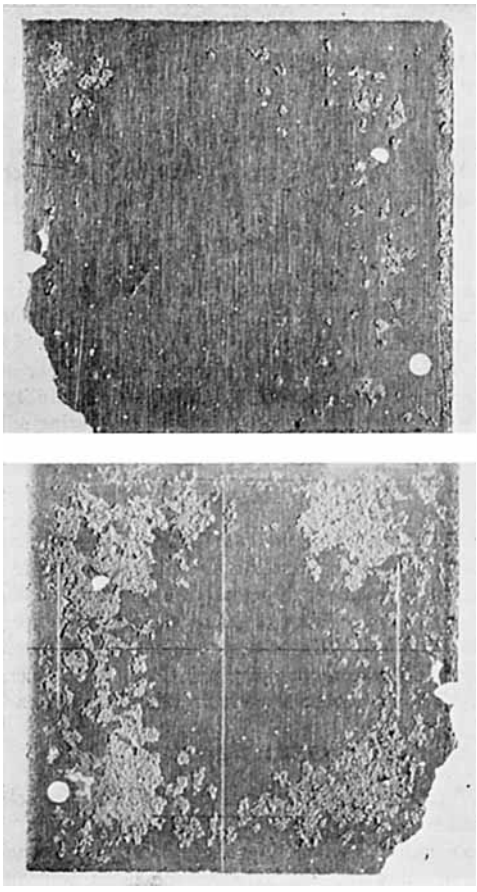

Fig. 4. Appearance of an adhesive film following liberation from an aluminum panel that had been heated at 350°C. for 1 hr. before liberation: (top) the face that was up in the press during cure; (bottom) the face that was down in the press.

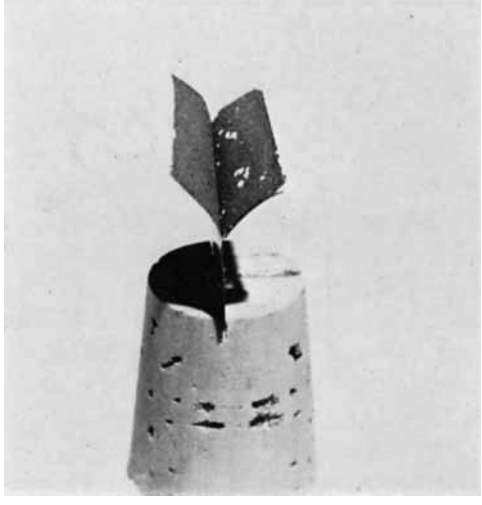

Fig. 5. Delamination of an adhesive film liberated from an aluminum panel that had been heated at 350°C. for 1 hr. before liberation.

of the two leaves contains holes. This leaf, too, was uppermost in the press during cure. Such planes of weakness are not observed within the liberated films if the panels are not given the high temperature treatment. The high temperature treatment is necessary to point out the planes of weakness, since their existence could constitute a serious defect.

PLANES OF WEAKNESS AT INTERFACES

Planes of weakness within the adhesive suggest that a similar plane may exist at the metal–adhesive interface. DeBruyne[4] has pointed out that the degree of contact between adhesive and adherend is not only a function of the cleanness of the surface, but also of the geometry of surface defects and the rate with which air can be displaced by the viscous resin. An attempt to examine this was made in the following manner. An 8-mil groove was milled on the surface of a sheet of aluminum. The sheet was placed on end and photographed at 150-fold magnification (Fig. 6). The sheet was then acid-etched and bonded to a second sheet with a vinyl–phenolic resin. The film was

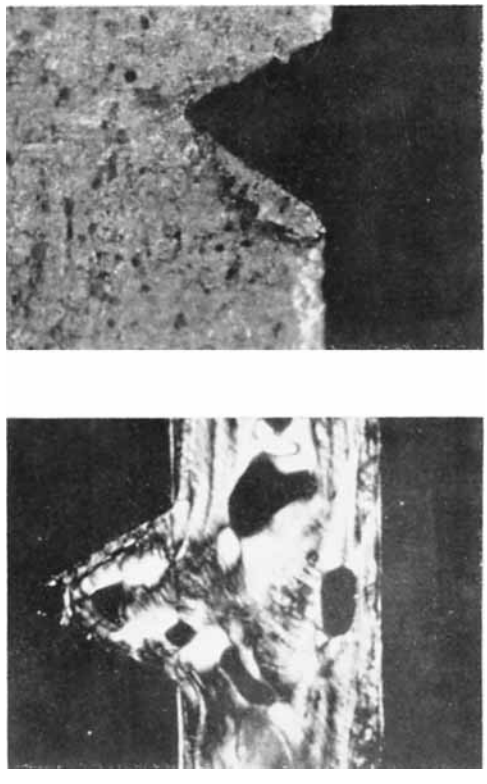

Fig. 6. (Top) Cross section of sheet of aluminum which had an 8-mil groove milled on one surface; (bottom) cross section of liberated adhesive film.

liberated, and a cross section prepared as described in the section on examination of cross sections of films. The ribbon was examined at the same magnification. The groove in the metal corresponds in shape to the hill in the film, although an air pocket was trapped at the bottom of the groove.

The work is still exploratory. Problems of contact may exist, not necessarily because the resin does not eventually wet the adherend, but because the rate at which surface equilibration is attained is much smaller than the rate at which we make our bonds. This kind of approach to studying interfacial contact is obviously very crude. It would be preferable to carry out similar examinations with the electron microscope. Actually, the problem is related to that of obtaining good replicability of surfaces. Conventionally, electron microscopists use dilute solutions of polymers in very fluid solvents. The problem involved with this study is one of obtaining good replicability with an extremely viscous polymer without allowing much time for surface equilibration.

CONCLUSION

Different procedures are described for detecting defects within adhesive bonds. No attempt is made to evaluate the significance of these defects in terms of bond performance; however, from the point of view of the original objective of this work—that of developing a general nondestructive procedure for evaluating glue bonds—the work suggests that no one test will be adequate.

References

1. Nadai, A., *Trans. Am. Soc. Mech. Eng.*, **61**, A-54 (1939).
2. Tadokoro, H., S. Seki, and I. Nitta, *Bull. Chem. Soc. Japan*, **27**, 451 (1954).
3. Griffith, A. A., *Phil. Trans.*, **221A**, 163 (1920).
4. DeBruyne, N. A., *Aero Research Tech. Notes, Bull.* No. 168 (1957).

Synopsis

A technique is described for liberating the adhesive layer from adhesive-bonded aluminum panels. Procedures are described for demonstrating directly the presence of defects within adhesive layers. The presence of a variety of types of defects is undoubtedly responsible for the inability to develop a general nondestructive test for evaluating adhesive-bonded panels.

Résumé

On décrit une technique pour détacher la couche adhésive de panneaux d'aluminium liés à un adhésif. On décrit des procédés pour montrer directement la présence de défauts à l'intérieur des couches adhésives. La présence d'une grande variété de défauts est certainement responsable de l'impossibilité de mettre au point un test géneral non destructif pour évaluer le pouvoir adhésif de ces panneaux.

Zusammenfassung

Ein Verfahren zur Entfernung der Klebstoffschichte von verklebten Aluminiumtafeln wird beschrieben. Massnahmen zum direkten Nachweis der Anwesenheit von Defekten innerhalb der Klebstoffschichten werden angegeben. Zweifellos ist das Vorhandensein verschiedener Typen von Defekten dafür verantwortlich, dass es nicht möglich ist, einen allgemeinen, zerstörungsfreien Test zur Bewertung von Plattenverklebungen zu entwickeln.

Received March 21, 1960