JOURNAL OF APPLIED POLYMER SCIENCE VOL. 20, 1933–1939 (1976)

Relations Between Solder Dip Resistance and Moisture Permeability of Printed Circuit Adhesives

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Synopsis

By measuring moisture permeability constants of printed circuit adhesive films having different solder dip resistances, a study was made of the relation between moisture permeability and solder dip resistances. Comparisons of poly(vinylbutyral) (I)–phenolic resin with I–epoxy resin, I–phenolic resin with poly(vinyl acetate)–phenolic resin, I–phenolic resin with poly(vinylformal)–phenolic resin and study of the effect of hydroxyl group content of I show that adhesive films of good solder dip resistance have small moisture permeability. The solder dip resistance depends markedly on the mole ratio of formaldehyde–phenol in the phenolic resin, while the moisture permeability is almost independent of the ratio.

INTRODUCTION

Among the characteristics of a copper-clad laminate for printed circuit, solder dip resistance is one of the most important ones and especially becomes a problem to be improved when the insulating board consists of phenolic resin–paper laminate. The solder dip resistance so greatly depends on an adhesive which is used to bond a copper foil to the insulating board that the resistance is one of the main characteristics required for the printed circuit adhesive together with peel strength. But there are only a few reports which deal with relations between adhesive properties and the solder dip resistance. Its relation with thermal decomposition of adhesive was studied by Karakama,[1] and a relation with chemical structure of adhesive components was reported by the author.[2]

When a specimen which shows good characteristics after testing solder dip resistance is observed, a blister is seen at the interface between copper foil and adhesive, and it seems that the copper foil was extended by rapid expansion on account of gasification of a volatile substance. This volatile substance is considered coming from the insulating board or the adhesive. From the point of view that the solder dip resistance becomes a problem especially in case of the phenolic–paper laminate, it is assumed that the causative substance may be water included in the insulating board. If water included in the insulating board is the causative substance for solder blistering, a relation must be recognized between solder dip resistance and moisture permeability of an adhesive film which exists between copper foil and the insulating board.

This investigation is aimed to make clear the mechanism for the occurrence of the solder dip blister. Moisture permeabilities are measured of adhesive films of different solder dip resistance and their relations are discussed here.

EXPERIMENTAL

Materials

Poly(vinylformal) (abbreviated PVF): Vinylec-F of Chisso Corp. Poly(vinylbutyral) (abbreviated PVB): Denka-Butyral #4000-2 of Denki Kagaku Kogyo Co. and material synthesized with hydrochloric acid catalyst from partially saponified poly(vinyl alcohol) (Kurashiki-Poval-217). Poly(vinyl acetate) (abbreviated PVAc): Esnil P-18 (degree of polymerization 1800) of Sekisui Kagaku Kogyo Co. Phenolic resin dissolved in ethyl alcohol: synthesized under conditions of formaldehyde-to-phenol mole ratio (abbreviated F/P mole ratio) 1.5 with ammonia catalyst and under conditions of various F/P mole ratios. Epoxy resin: 70 parts of Epikote-828 of Shell Oil Co. mixed with 30 parts of Lacqamide N-133 of Japan Reichhold Chemical Industries Co. Solvents of extrapure grade were used.

Preparation of Films

For preparation of adhesive solutions, each resin was dissolved in a mixed solvent of toluene–ethyl alcohol (mixing ratio 1:1) or acetone–ethyl alcohol (1:1). After each resin solution was weighed into a glass beaker to obtain a determined solid composition and stirred, the adhesive solution was diluted to 5% of solid content with mixed solvent of acetone–ethyl alcohol (1:1) and poured on mercury in a glass vessel. The glass vessel was covered with filter paper, left at room temperature overnight, and then dried 5 hr by irradiation with an infrared ray lamp. The dried film was then taken from mercury, inserted between Teflon films, pressed by iron clamps, and heated 2 hr in a precisely controlled air oven at 160°C.

Measurement of Moisture Permeability

The moisture permeability constant was measured according to the cup method which corresponds to JIS 0208. An aluminum cup, shown in Figure 1, was filled with granular calcium chloride for elemental analysis and attached with a sample film. Then it was put in a desiccator of 90% relative humidity controlled by sulfuric acid aqueous solution at 40°C and weighed every 24 hr. Temperature was maintained in the range of 40° ± 1°C by dipping the desiccator into a thermostat. Weight gain versus hours was plotted. From the relation between permeated moisture amount and hours at constant value, the moisture permeability constant was calculated as follows[3,4]:

$$Q = \frac{P\,(p_a - p_b) \cdot t \cdot A}{l} \qquad (1)$$

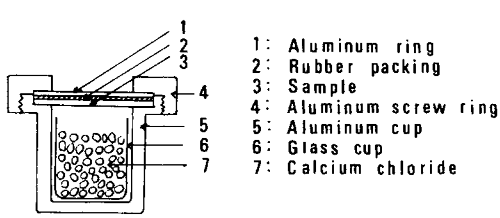

Fig. 1. Permeability cup.

where P is moisture permeability constant; Q is amount of permeated moisture; pa, pb are water vapor pressures of both sides of the sample film; t is time in hours; A is area of the sample film; l is thickness of the sample film; pa of eq. (1) is 4.98 cm Hg water vapor pressure at relative humidity of 90% and 40°C. Though pb is 0.08 cm Hg water vapor pressure dried with calcium chloride at 40°C, it is neglected since it is within the experimental error.

RESULTS AND DISCUSSION

Effect of Adhesive Film Thickness

Although the moisture permeability constant is not expected to change with change of film thickness since it is expressed by a value per unit film thickness, it is known in fact that the constant increases according to increase in film thickness.[5] As it was difficult to obtain equally thick adhesive films in this investigation, it was necessary to study a relation between moisture permeability constant and adhesive thickness before comparing the constants of various adhesive films of different solder dip resistances. In this experiment, moisture permeability constants of adhesive films consisting of 55%

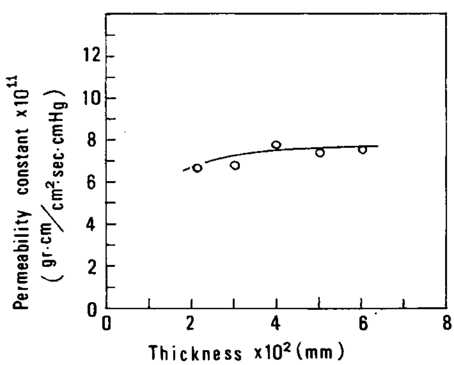

Fig. 2. Effects of thickness on permeability constant.

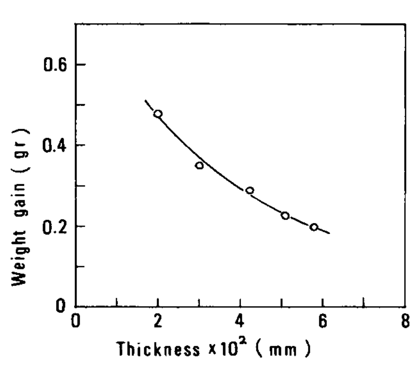

Fig. 3. Relation between thickness and weight gain of permeability cup.

PVB and 45% phenolic resin of different thickness were measured and compared.

As shown in Figure 2, it is clear that the change of moisture permeability constant is very small in this range of adhesive film thickness.

A relation is shown in Figure 3 between film thickness and weight gain of permeability cup of the same area after 120 hr. In Figure 3, weight gain (amount of permeated moisture) decreases according to the increase in adhesive film thickness. This tendency is due to enlargement of diffusion distance of water vapor in the adhesive film and coincides with the increasing tendency of solder dip resistance according to the increase in adhesive thickness.

Comparison of Phenolic Resin and Epoxy Resin

Moisture permeability constants of PVB–phenolic resin adhesives and PVB–epoxy resin adhesives are shown in Figure 4. As seen in Figure 4, PVB–epoxy resin adhesives show larger moisture permeability constants than PVB–phenolic resin adhesives. In case of copper-clad phenolic resin–paper laminate, adhesives based on phenolic resin show good solder dip resistances, but those based on epoxy resin show very low resistances. Therefore, it is considered that there must be a close relation between the difference of solder dip resistance and that of moisture permeability.

In Figure 4, the moisture permeability constant remarkably decreases with addition of phenolic resin in case of PVB–phenolic resin adhesive. It is presumed that this tendency is due to the restraint of molecular chain movement by the increase of crosslinking density since the phenolic resin becomes three-dimensional in structure by heat curing. In case of PVB–phenolic resin adhesive, solder dip resistance increases according to the increase in phenolic resin content. This tendency well coincides with the decreasing tendency of the moisture permeability constant according to the increase in phenolic resin content in Figure 4. On the contrary, in the case of PVB–

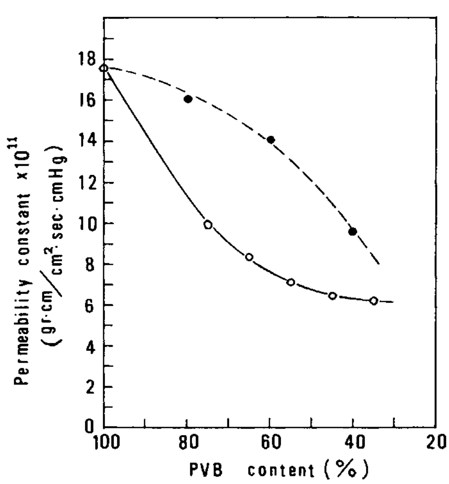

Fig. 4. Comparison of permeability constant of PVB–phenolic resin and that of PVB–epoxy resin: (—O—) PVB–phenolic resin; (- - -●- - -) PVB–epoxy resin.

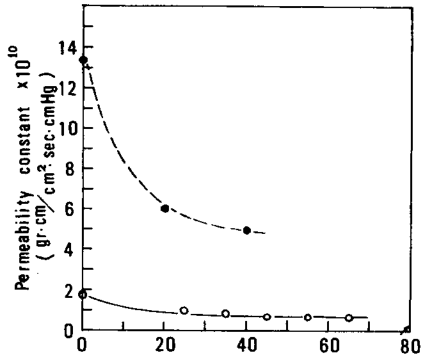

Fig. 5. Comparison of permeability constant of PVB–phenolic resin and that of PVAc–phenolic resin: (—o—) PVB–phenolic resin; (- - -●- - -) PVAc–phenolic resin.

epoxy resin adhesive, the moisture permeability constant does not remarkably decrease with increase of epoxy resin as well as the PVB–phenolic resin, and its solder dip resistance is remarkably low.

Comparison of PVB and PVAc

Moisture permeability constants were measured of adhesive films which were prepared by using PVAc as thermoplastic ingredient and changing its mixing ratio with phenolic resin. The constants are compared with those of PVB–phenolic resin in Figure 5. As seen in Figure 5, PVAc–phenolic resin adhesives show much larger moisture permeability constants than PVB–phenolic resin adhesives. On the other hand, PVB–phenolic resin adhesive shows high solder dip resistance, but the resistance of PVAc–phenolic resin adhesive is very low. It is considered that there must be a relation between this big difference of solder dip resistance and that of the resistance to water vapor permeation in the adhesive films.

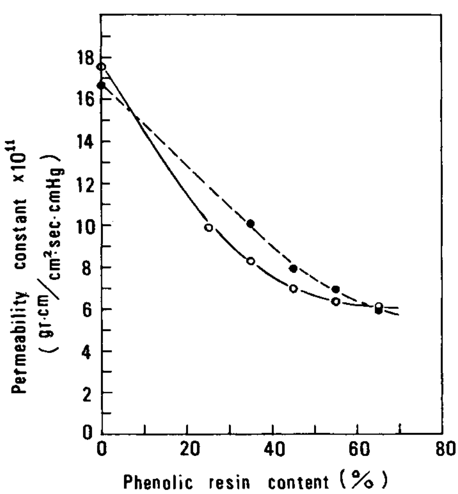

Fig. 6. Comparison of permeability constant of PVB–phenolic resin and that of PVF–phenolic resin: (—o—) PVB–phenolic resin; (- - -●- - -) PVF–phenolic resin.

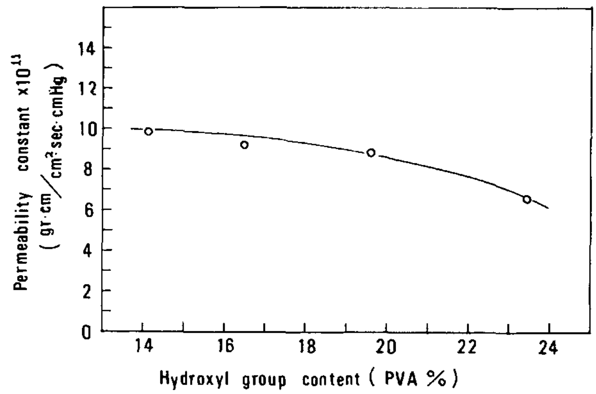

Fig. 7. Effects of hydroxyl group content of PVB on permeability constant.

Comparison of PVF and PVB

Moisture permeability constants were measured of adhesive films which were prepared by changing the ratio of phenolic resin content to PVF. The constants are compared with those of PVB–phenolic resin in Figure 6. In case of PVF–phenolic resin adhesive, the moisture permeability constant tends to decrease according to the increase in phenolic resin content in the same way as does PVB–phenolic resin. But the difference between the constants of these two adhesives at the same phenolic resin content depends on the phenolic resin content. Namely, the moisture permeability constant of PVF–phenolic resin adhesive tends to become almost equal to that of PVB–phenolic resin at 65% phenolic resin content and to become smaller than that of PVB–phenolic resin above 65%. The difference of changing tendencies of moisture permeability constants between PVF–phenolic resin and PVB–phenolic resin mostly coincides with the difference of changing tendencies of solder dip resistances.

Effect of Hydroxyl Group Content of PVB

In case of PVB–phenolic resin adhesive, its solder dip resistance increases according to the increase in hydroxyl group content of PVB. In this experi-

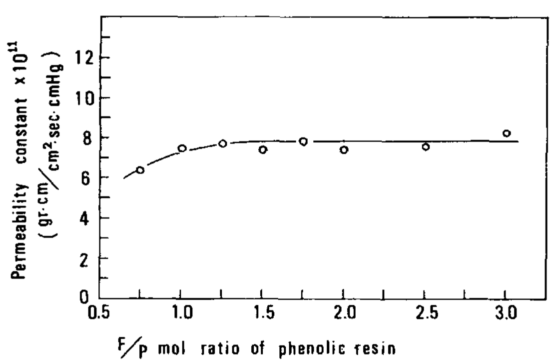

Fig. 8. Effects of F/P mole ratio of phenolic resin on permeability constant.

ment, moisture permeability constants were measured of adhesive films consisting of 45% phenolic resin and 55% PVB of different hydroxyl group content, and the relations were studied between the permeability and the hydroxyl group content of PVB.

In Figure 7, the moisture permeability constant tends to decrease according to the increase in hydroxyl group content. It is generally known[3,4] that moisture permeability in a high polymer is determined by solubility and diffusion constant of water vapor. Though it is considered that the solubility of water vapor increases with increase in polarity of adhesive film, when the hydroxyl group content of PVB increases, the decreasing tendency of moisture permeability seems to be due to the decreasing effect of diffusion constant of water vapor in the film on account of restraint of molecular chain movement by the increase in hydrogen bonds among the PVB molecules and between PVB and phenolic resin.

Effect of F/P Mole Ratio of Phenolic Resin

It was reported[2] that solder dip resistance remarkably changed with change in F/P mole ratio of phenolic resin synthesis. In this experiment, moisture permeability constants were measured of adhesive films consisting of 50% PVB and 50% phenolic resin which were synthesized with 5 mole-% ammonia catalyzed by changing the F/P mole ratio.

As seen in Figure 8, the moisture permeability constant slightly increases in the range of 0.75 to 1.0 of F/P mole ratio and becomes constant above 1.0. On the other hand, solder dip resistance tends to increase remarkably according to the increase in F/P mole ratio[2] in the range of 0.75 to 1.5 and shows a slightly different tendency from the moisture permeability.

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Received July 17, 1975
Revised September 19, 1975