CHAPTER I

INTRODUCTION

1.1 General Review

Phenolic resins, polymers formed by the condensation reaction of phenol and formaldehyde, were first found in 1872 by A. Bayer. Baekeland discoverd the commercial exploitation and took out his first patent in 1910. Phenol-formaldehyde resins play an important role in a wide variety of industry. The principal current uses include thermosetting molding powder which are widely used in general purpose electrical moldings, heated appliance, wood adhesive and binder [Saunders, K.J. (1988)]. They show good properties in temperature and humidity resistance, chemical inertness and good electrical insulating. However, they still have some shortcomings such as the emission of volatiles upon curing, the need for strong acid or alkaline as catalysts, poor shelf life and brittleness.

A new class of phenolic thermosetting resins has been developed based on the ring-opening polymerization of benzoxazine chemistry. These resins were first synthesized by Holly and Cope [Holly,F.W. and Cope,A.C. (1944)]. Benzoxazines are made by heterocyclic compounds by Mannich condensation of a phenol with formaldehyde and an amine. Schreiber suggested the potential of the benzoxazines for the preparation of phenolic materials with improved properties [Schreibet, H (1973)].

The polybenzoxazines overcome many of the inherent shortcomings of phenolic resins, while they still maintain their benefits. These new polymers exhibit many advantages, namely, no catalyst needed, long shelf life, no by-product produced, very high char-yield and rich molecular design flexibility. Traditionally, thermosetting resins undergo a volumetric shrinkage during polymerization which causes problems in high precision applications, for example, in dental composite and high strength composites [Allen,D (1993)]. The ring-opening polymerization of these new materials occurs with near-zero shrinkage or even a slight expansion upon curing. The superior mechanical interlocking to a substrate that is possible with zero shrinkage or expanding materials makes them ideally appropriate for high-performance adhesives, sealants and coatings.

The most popular aluminum adhesive is epoxy resin. There are a number of favorable characteristics that epoxy resins exhibit such as absence of volatile by-products during curing reaction, excellent adhesion to metals and many other substrates and high level of mechanical strength. However, they also have some shortcoming, namely, rather high water absorption and volumetric shrinkage [Bansal,R.K and Singh,M (1980) and Shimbo,M and et.al (1984)]. The epoxy resins suffer from volumetric shrinkage of 2-7 % upon curing. Shrinkage of an adhesive can induce the internal stresses. These stresses develope due to the differences in thermal coefficients of expansion between the adhesive and the substrate [Brewis,D.M and et.al (1980) and Bikerman,J.J (1968)]. Polybenzoxazines can overcome this problem because they polymerize with near-zero shrinkage or even a slight expansion upon curing.

It was found that there is an inverse linear relationship between aluminum /epoxy joint strength and the water content of the joint. The water generally enters a joint by diffusion through the epoxy. This is likely to depend on the type of epoxy. Water is a very destructive environment for metal /polymer adhesion system. Once water reaches the interfacial region in sufficient quantity, it causes the loss of strength of metal/polymer system. Since water molecule is a very strong hydrogen bonding agent, it can readily break the bond between the metal and the epoxy resin and form new hydrogen bonds with the hydrated oxide surface of the metal. The result is the displacement of the epoxy resin from the metal and the formation of a weak water layer at the interface. The presence of the weak water layer can greatly reduce the strength of the metal/epoxy system [Croll, S.G. (1982)]. Polybenzoxazines have lower rate of water absorption and lower saturation contents than epoxy resin [Kinloch, A.J.(1977)]. This should make polybenzoxazines a candidate as an adhesive for aluminum and other metals.

The corrosion inhibition for copper in humid environment is also investigated. The technique utilized was Fourier transform infrared reflection-absorption spectroscopy (FTIR-RAS). With this method, the molecular information about surface species including corrosion product can be obtained.

1.2 FTIR-RAS Theory

Reflection - absorption technique is used for surface studies. A smooth surface with high refractive index, such as a metal, is a good substrate for this technique. The high angle of incidence near the grazing angle is used. The specimen is in the form of a very thin film on a polished metal.

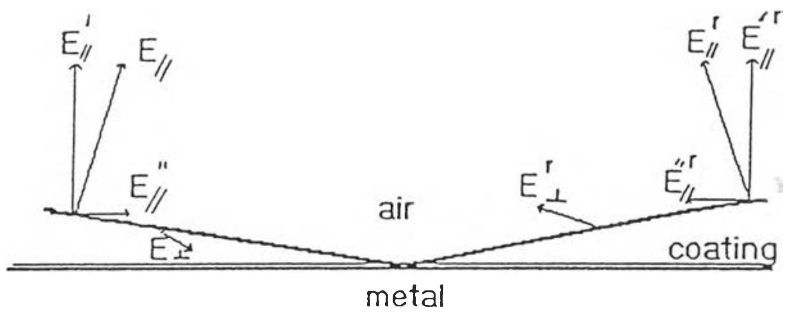

Figure. 1.1 Reflection absorption spectroscopy of a thin coating on a polished metal subtrate.

Electromagnetic waves reflect at any interfaces if there is a difference in refractive indices between the two contacting materials. When an electromagnetic wave arrives at an interface, the radiation penetrates into another phase on the order of its wavelength and returns to its orginal phase. The reflected wave contains the structural information of the reflected interface.

The perpendicular polarized (s-polarized) radiation with respect to the plane of incidence phase shifts by approximately $-\pi$ at any angle of incidence. Conversely, the parallel polarized (p-polarized) radiation has zero degree phase shift at normal incidence. This phase continues until the angle of incidence becomes very close to the grazing angle, where the phase shift quickly approaches $-\pi$. Thus, the electric vectors of the s-polarized radiation cancel at the metal surface, and such near-zero-amplitude radiation is unable to interact with the surface species, whereas the p-polarized radiation has a finite amplitude at the metal surface as shown in Figure 1.2

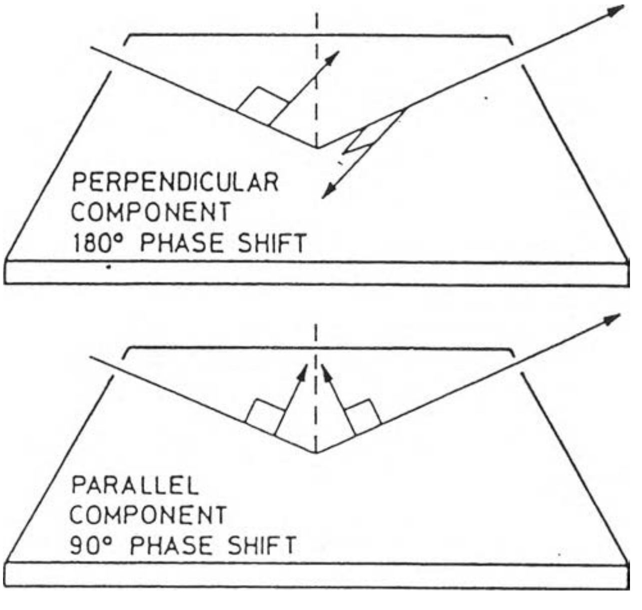

Figure 1.2 Incident and reflected electric vector geometries at the metal surface at grazing incidence.

Therefore, although the s-polarized radiation reflects from the surface, it contains little information about the surface species. On the other hand, the p-polarized radiation has a finite amplitude at all angles except very close to 90 degrees. This vector sum of the electric vectors can interact appreciably only with the dipole moment change of the surface species toward the normal direction of the metal surface. It is for this reason that RAS can provide information on orientation.

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The vector sum of the p-polarized radiation becomes large as the angle of incidence increases. However, when 90° is approached, the electric vectors start to cancel each other due to the phase shift. As a result, the amplitude of the electric vector sum shows a maximum near 88° and at this angle, the highest sensitivity is obtained. However, this optimum angle depends on the substrate and the surface species. Experimentally, it is difficult to use such a high angle of incidence, and typical values ranging from 72° to 82° are used.

If a thin film less than a few hundred nanometers on a metallic substrate is being analyzed, use of a polarizer does not make any difference to the molecular information obtained. However, by blocking the s-polarized component from the sample spectrum and the s-polarized component from the reference sample, one can improve the S/N ratio by a factor of 2. When the thickness of the surface film is large, even the s-polarized radiation yields a spectrum with appreciable intensity. In such a case, the use of a polarizer eliminates this situation of mixed polarization [Ishida, H. (1983)].

1.3 Objectives

The objectives of this research work are to evaluate the potential of polybenzoxazine as an adhesive for aluminum and a corrosion inhibitor.