

***In Situ* Measurement of Metal Ions at the Polymer/Substrate Interface Using Infrared-Active Sensors**

Tinh Nguyen and Eric Byrd

**National Institute of Standards and Technology
Gaithersburg, MD**

Introduction

The transport of metal ions along the polymer/steel interface is believed to be the controlling factor in the cathodic delamination of polymer-coated steel exposed to electrolytes. *In situ* measurement of metal ions at the polymer/substrate interface would provide critical information for understanding and modeling the delamination rate of this material. A number of techniques can be used for measuring metal ions on solid surface or in solution. However, most of these techniques are not suitable for *in situ* investigation at the buried polymer/substrate interface. Infrared (IR) spectroscopy in the internal reflection mode on a suitable substrate is attractive for such study because it probes the interface from the substrate side and can be used at ambient conditions. Although metal ions, such as Na, K, Ca, are not infrared active, their association with an organic group generally alters the spectral characteristics of that group. In this sense, the organic group acts as an IR sensor and may be used for detecting metal ions by IR spectroscopy. Several pieces of data suggest that, with proper organic functional groups, IR internal reflection spectroscopy may be a viable technique for detecting metal ions at the interface. For example, extensive study of the IR spectra of the salts of carboxylic acids indicated that when ionization occurs, the C=O absorption of the acid vanishes and is replaced by bands corresponding to the COO⁻ structure (1). Further, Kimura et al. (2) have shown that IR internal reflection spectra of stearic acid films on germanium have a strong band at 1700 cm⁻¹, while

calcium stearate had two peaks in the 1540-1580 cm⁻¹ region. The disappearance of the C=O band and the replacement by two bands is due to the resonance of the C-O bonds in the ionized COO group (1). This paper presents a technique, which combines the powerful, sensitive FTIR-multiple internal reflection (FTIR-MIR) spectroscopy with carboxylic-based infrared sensors to measure *in situ* metal ions at the interface between a polymer film and a substrate.

Experimental Details

Figure 1 depicts the specimen configuration and experimental setup for measuring metal ions at the polymer/substrate interface using FTIR-MIR technique. The specimen consists of a thin film of an IR sensor depositing between the polymer film and the substrate. Stearic acid was selected as the carboxylic acid IR sensor for this study due to its insolubility in water. The substrates were 3x10x50 mm Si and KRS-5 internal reflection elements (IRE). Polymer films were based on a thermoset epoxy resin. The specimens were prepared by first flooding the substrate surface with a 5% stearic acid in CHCl₃ solution and spun at 2000 rpm for 30 s using a photo resist spinner. A polymer film of sufficient thickness was applied on the stearic-acid coated substrates. After curing, an environmental chamber having a dimension of 10x50 mm and a height of 5mm was mounted on the coated side of the substrate using a silicone adhesive. The chamber has two ports for introducing and removing the cation solution. For some specimens, a 2x10 mm section was cut through

the polymer film (e.g. Figure 1) before mounting the chamber to shorten the transport time of cations from the environment to the polymer/substrate interface.

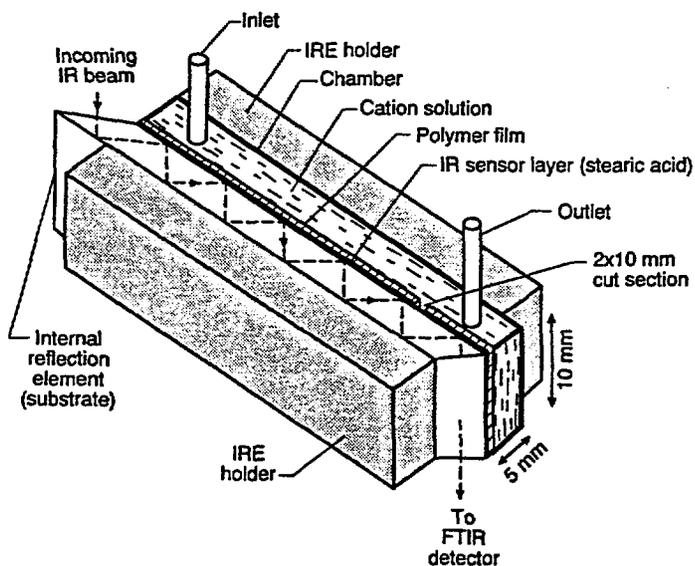


Figure 1. Experimental setup for measuring metal ions at the polymer/substrate interface by FTIR-internal reflection spectroscopy

The specimen with the chamber attached to it was placed in an ATR (attenuated total reflection accessory) holder; the whole assembly was then situated in an FTIR spectrometer. After collecting the initial spectra, electrolyte solution of the desired cation was added to the chamber. FTIR-MIR spectra were then taken automatically every half hour until the experiment was complete. Spectra were collected at 4 cm^{-1} resolution using purged dry air, unpolarized light and at an angle of incidence at 45° . Difference spectra were obtained by subtracting the spectrum of the specimen before exposure from those of the same specimen after exposure for specific time intervals.

Results and Discussion

Figure 2 presents FTIR-MIR difference spectra (exposed-unexposed) in the $1480\text{--}1800\text{ cm}^{-1}$ region taken after three different time intervals exposed to 1 mole/liter NaCl, MgCl_2 and CaCl_2 solutions for a polymer film-free, stearic acid-deposited KRS-5 substrate. In the presence of electrolytes, the intensity of the C=O bands associated with the COOH group at 1700 and 1685 cm^{-1} decreased while the asymmetric bands of the COO^- (carboxylate) structure in the $1525\text{--}1600\text{ cm}^{-1}$ region formed.

Band shapes of cation-coordinated C-O bonds are quite different. For example, after 24h Na-coordinated salt gave a single, sharp band located near 1556 cm^{-1} with two shoulders around 1580 and 1548 cm^{-1} . Mg ion complex produced only a single but very broad band at 1560 cm^{-1} , but Ca coordination resulted in a doublet peaking at 1577 and 1540 cm^{-1} . Resonance stabilization between the two C-O bonds in the COO^- group and structures of the coordinated complex probably contributed to these differences. Using either peak height or peak areas, the rates of decrease and increase of the carboxylic and carboxylate groups for different cations can be followed. For example, the rate for Na and K (results are not shown here) ions was found 2-5 times higher than that for Mg and Ca ions.

Figure 3 displays FTIR-MIR difference spectra of a polymer film/stearic acid/Si specimen (Figure 1) taken after 2, 48, and 170 h exposures to 1 mole/liter KCl. The thickness of the polymer film (a thermoset epoxy) was $150 \pm 9\text{ }\mu\text{m}$. A $2 \times 10\text{ mm}$ section of the polymer film was removed from this specimen, as shown in Figure 1. The intensity of the C=O band of COOH around 1700 cm^{-1} of the stearic acid decreased and the bands due to the COO^- group near 1575 and 1550 cm^{-1} appeared. (The broad band in the 1630 and 1660 cm^{-1} region is due to the water bending mode.) Obviously, K had entered the epoxy film/substrate interface and reacted with COOH group of the stearic acid film to form $-\text{COOK}^+$ compound.

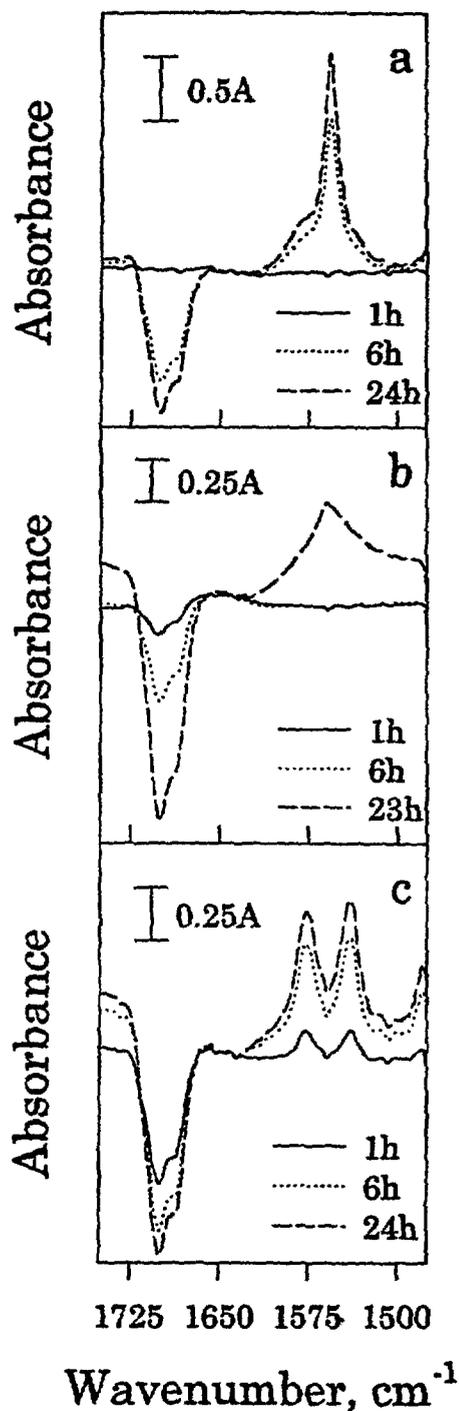


Figure 2. FTIR-MIR difference spectra of a stearic acid layer on polymer film-free KRS-5 substrate exposed to 1 mole/liter: a) KCl, b) MgCl₂, and c) CaCl₂ solutions.

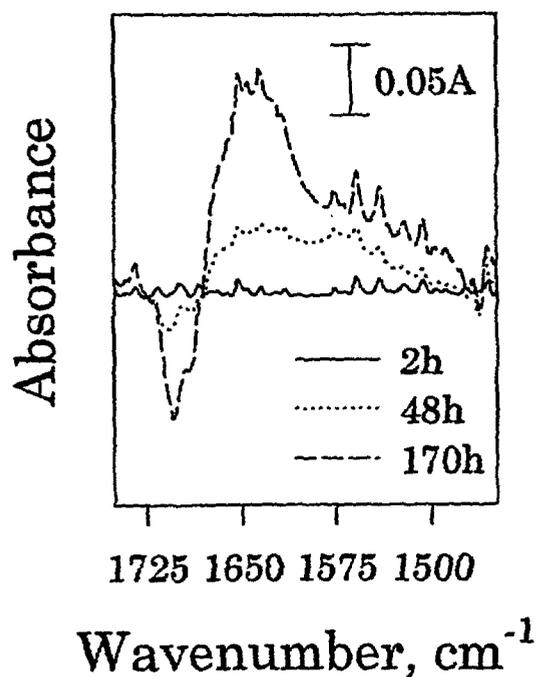


Figure 3. FTIR-MIR difference spectra of stearic acid at the polymer/Si interface after exposure to 1 mole/liter KCl solution.

Conclusions

The results of this study demonstrated that by incorporating an infrared sensor at the polymer film/substrate interface, the transport of cations through and along the interface can be studied *in situ* by FTIR internal reflection spectroscopy.

References

- 1) L.J. Bellamy, *The Infrared Spectra of Complex Molecules*, Chapman and Hall, London, 1975, p.198.
- 2) F. Kimura, J. Umemura, and T. Takenaka, *Langmuir*, 2,96 (1986).