

# Effect of the Polyurethane Crystalline Interphase Formed at an Al Surface on Water-Vapor Absorption

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Received 5 June 2002; accepted 2 October 2002

**ABSTRACT:** Water-vapor absorption of polyurethane/Al bonds was studied, and the weight gain of samples after water-vapor exposure was measured to examine the effect of the polyurethane crystalline interphase formed at the Al surface on water-vapor absorption. Water-vapor absorption was found to be independent of the crosslink density of the polyurethanes. Instead, it was found that the microstructural characteristics of the spherulitic interphase, a mixture of crystallites and amorphous material formed on the Al surface, strongly affects water-vapor absorption: As the area

fraction and the size of spherulites for the films increases, the amount of absorbed water vapor initially increases rapidly and then remained constant. The water vapor absorbed and condensed at spherulite boundaries consisting of voids and defects was created due to volume contraction during polymer crystallization. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1417–1422, 2003

**Key words:** polyurethanes; interfaces; spherulites

## INTRODUCTION

Polymer/metal bonding is widespread in various aerospace, automotive, protective food packaging, roofing, etc., applications. Since the materials in such applications tend to be exposed to high humidity, it is useful to evaluate the water-vapor absorption (WVA) characteristics in these bond systems. It is generally reported that water is very detrimental to bond performance, resulting in reduced joint strength caused by water-vapor permeation.<sup>1–4</sup> Dodiuk et al.<sup>3</sup> and Drain et al.<sup>4</sup> proposed an interfacial failure mechanism consisting of the successive processes of water-vapor penetration, condensation, and delamination, and Cognard<sup>5</sup> suggested a water-blistering model for a glass/epoxy adhesive joint. However, these studies did not examine the effect on the WVA of the crystalline polymer interphase often formed at the substrate surface.

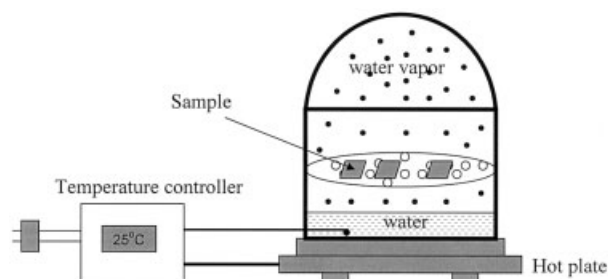
Al-faced rigid polyurethane foam is frequently used as insulation boardstock for roofing and house walls, where the humidity level varies seasonally. Therefore, it is appropriate to investigate WVA with respect to the interfacial properties in polyurethane foam/Al bonds. From a density profile, the skin layer of a foamed polymer bonded to a solid substrate is very

dense and similar to an unfoamed solid polymer. As a result, a thin solid polymer film can be used in adhesion studies of polyurethane foam/Al bonds.<sup>6</sup> This system exhibits a spherulitic interphase formed by substrate-induced crystallization near the Al surface.<sup>6</sup>

There have been few studies of the relationship between WVA and the existence of a crystalline interphase consisting of spherulites at the bond interface. Previous studies attribute bond delamination to the formation of a metal hydroxide, caused by water-vapor uptake, which adheres poorly to the base metal.<sup>7,8</sup> For instance, Ahearn et al.<sup>8</sup> reported that the delamination of a polymer/Al bond, when moisture is present, takes place through the conversion of Al oxide to Al hydroxide; the hydration products exhibit a different morphology from the original adherend oxide and poor adherence to the base metal, which leads to bond failure. Further, long-term durability of the Al adhesive bond was attained by delaying the oxide-hydroxide conversion with hydration inhibitors. This material system did not display the crystalline interphase formed by an interaction between the polymer and the metal. One questions whether these concepts of bond failure upon hydration are still applicable in the case where the polymer/metal bonds display a crystalline interphase.

The present study investigated the effect of the presence of a crystalline interphase, composed of polymer spherulites in the interfacial area of polyurethane/Al bonds, on WVA. The amount of absorbed water vapor is related to the crosslink density, spherulite size, and

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Contract grant sponsor: Air Products and Chemicals Inc.



**Figure 1** Apparatus used to expose specimens to high humidity.

area fraction of the spherulites. In addition, in this study, where the water vapor absorbs and condenses, that is, at the spherulite boundaries, was determined. It was also determined how the polyol OH number, one of the most crucial formulation factors, affects WVA; this OH number determines the crosslink density of the polymer and the microscopic features at the polyurethane/Al interface.

## EXPERIMENTAL

### Sample preparation

The polyether polyols used in this study were provided by Arch Chemicals, Inc. (Norwalk, CT). The polyols had OH numbers of 120, 375, and 600 and molecular weights of 1400, 596, and 374. To form the urethane linkage, these polyols were reacted with diphenylmethane-4:4'-diisocyanate (MDI) (Aldrich, Milwaukee, WI) in the solvent dimethylformamide (DMF). Three polyurethane solutions, PU-120, PU-375, and PU-600, with an isocyanate index of 105, were made at 50°C, with stirring for 1 min. Five percent polyurethane solutions for a microscopic study of the crystalline interphase were then cast at 50°C on approximately 1000-Å-thick Al films, sputtered onto Si wafers. As a sample preparation for the WVA studies, the 5% polyurethane solutions were used to coat 20 × 40-mm pieces of commercial-grade Al foil. The solvent was removed by passing room-temperature air over the film for 1 week. A portion of the samples was aged for 4 h at 170°C and then air-cooled.

### Measurement of water absorption, crosslink density, and X-ray diffraction

Figure 1 shows a diagram of the apparatus used in this study to expose the bonded samples to water vapor. Three nonaged and three aged samples of each polyurethane film were placed on a panel with holes in it and held at 25°C and exposed to water vapor. The weight change of the samples was measured on a Denver Instrument XE-310 balance every 2 h until the weight of the water-vapor-soaked samples was constant to within 1%. The humidity inside the chamber was measured using a Vaisala Inc. HMI41 humidity and temperature indicator with an HMP42 probe at  $100 \pm 2\%$ .

To obtain the sizes and area fractions of the spherulites at the Al interface, the polymer film was peeled from the substrate using 3M double-sided tape. An optical microscope was utilized for the image analysis. The crosslink densities of three polyurethanes were obtained from indentation measurements on the bulk materials using a ball indenter.<sup>6</sup> Table I lists the experimental results from these measurements. Detailed experimental procedures can be found in ref. 6.

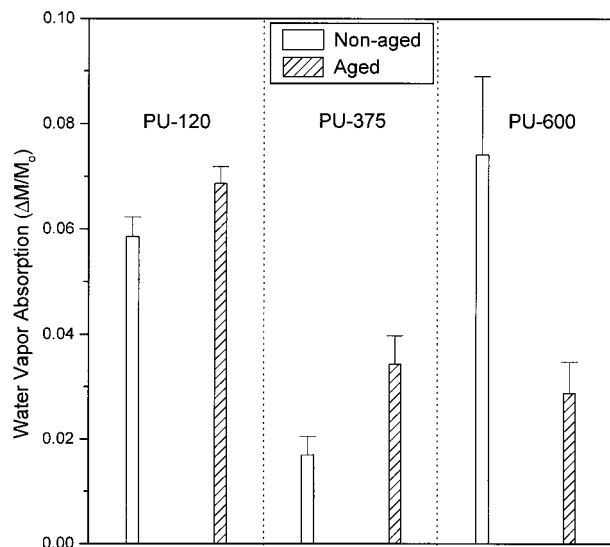
To determine where the water vapor condenses, X-ray diffraction measurements on water-vapor-soaked polymer/Al bond samples were carried out on a beamline X14A at the NSLS, Brookhaven National Laboratory. A cylindrical mirror with variable curvature was used to focus the vertical divergence of the beam at the specimen position. The monochromator consists of a water-cooled flat first crystal and a conically bent focusing second crystal.  $\theta$ - $2\theta$  scans, over the range 10°–50° with  $2\theta$  increments of 0.4°, of the as-cast and water-vapor-exposed samples were made, with a radiation wavelength of 1.54076 Å. In an attempt to detect Al hydroxides, which may form at the polymer/Al film interface, the samples exposed to the water vapor were scanned after the polyurethane film was removed by tape peeling.

## RESULTS AND DISCUSSION

Water-vapor permeability in polymers, conventionally expressed as the product of the solubility and

**TABLE I**  
Microstructural Crystalline Parameters Measured from Tape-peeled Samples for Polyurethane/Al Bonds

Parameters		PU-120	PU-375	PU-600
Area fraction of spherulites (%)	Nonaged	64	0.8	18
	Aged	49	4.5	1.2
Average spherulite size ( $\mu\text{m}$ )	Nonaged	6.6	1.4	2.0
	Aged	4.1	0.9	0.6
Crosslink density ( $\text{mol}/\text{cm}^3$ )	Nonaged	$6.0 \times 10^{-4}$	$9.4 \times 10^{-3}$	$1.2 \times 10^{-2}$
	Aged	$3.4 \times 10^{-3}$	$2.4 \times 10^{-2}$	$1.6 \times 10^{-2}$



**Figure 2** WVA of polyurethane/Al bonded samples, shown as the ratio of the total weight gain to the initial weight,  $\Delta M/M_0$ , after becoming constant to within 1% during water-vapor exposure. Aging results in a significant decrease in the weight gain for the PU-600 sample compared to those for the PU-120 and PU-375 samples.

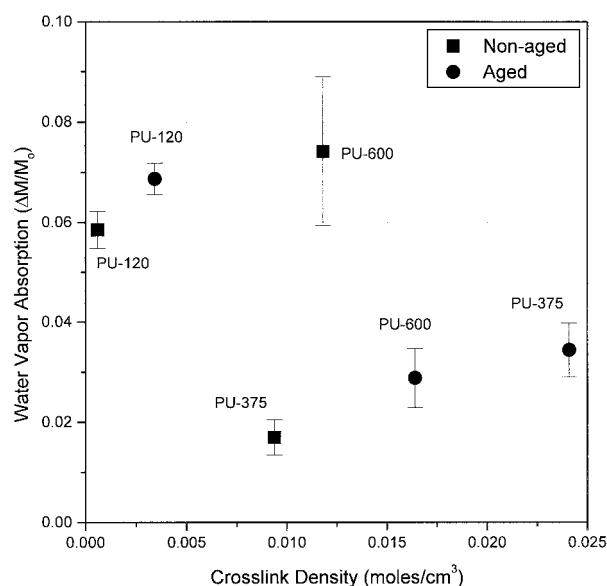
diffusivity of water vapor, is most applicable to the evaluation of water-vapor transmission into a bulk polymer.<sup>9</sup> Water-vapor absorption at a polymer/metal interface is not usually considered, because it is thought that the polymer bulk soaks up most of the water vapor in comparison to the polymer/metal interface. There have been few studies of water-vapor permeation in a polymer/metal bond. Since failure of the bond in humid environments originates mostly at the polymer/metal interface, it is necessary to characterize the water-vapor transmission at the bondline. It has been suggested that water vapor absorbs mostly at defect sites such as pores. For bond systems showing a spherulitic interphase, the spherulite boundaries, where voids are formed, can also be one of the places where water vapor is absorbed. Water-vapor absorption and condensation at the spherulite boundaries is demonstrated in the latter part of this article.

This study used the ratio of the total weight change to the initial weight,  $\Delta M/M_0$ , to represent the WVA in polyurethane/Al bonded samples. Figure 2 shows this weight gain ratio, constant to within 1% after sufficient exposure times, for aged and nonaged samples. The PU-375 samples, both nonaged and aged, exhibited a lower WVA. The response to aging was mixed: The WVA for the PU-120 and PU-375 samples showed increased WVA after aging, while the PU-600 samples exhibited a decrease in WVA upon aging. However, WVA does increase with an increased average spherulite size and area fraction, resulting from a modified crystalline interphase in which the average size of the spherulites and area fraction decreased markedly, as

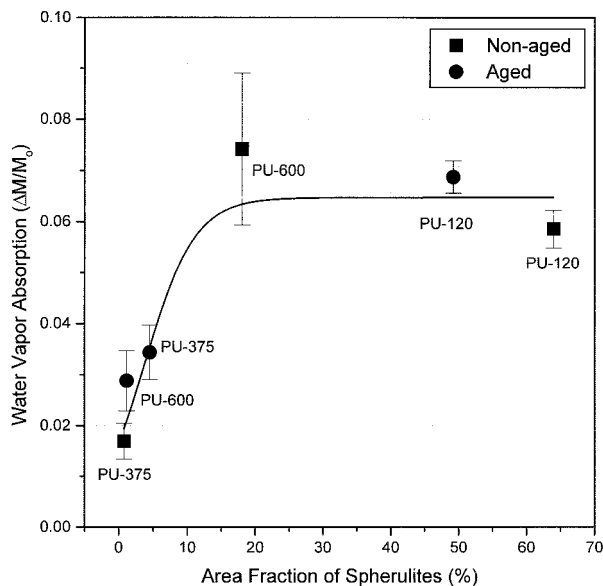
listed in Table I. This change in microstructure at the polyurethane/Al interface had the effect of reducing WVA.

In spite of an increase of crosslink density on aging, the weight gain for the aged PU-120 and PU-375 samples is higher than that for the nonaged samples (see Fig. 3). This is a strong indication that the polymer/Al interface plays an important part in WVA. In general, WVA is expected to decrease with the crosslink density; crosslinking restricts the transmission of water vapor. However, there appears to be no dependence of WVA on the crosslink densities for these three polyurethanes. In fact, the crosslink density is the most important factor in WVA of a bulk polymer only. For a materials system containing a polymer/substrate interface, the microstructural features at the interface tend to be more important.

Polyurethane crystallites on the Al surface were observed utilizing an optical microscope. The size and area fraction of the spherulites on tape-peeled Al surfaces were used to quantify crystalline interphase formation in polyurethane/Al bonds.<sup>6</sup> The WVA values were plotted as a function of the area fraction of spherulites and the average spherulite size (see Figs. 4 and 5). Each curve shows an initial rapid increase followed by an apparent leveling off of the WVA to a fairly constant value. In general, the samples with larger spherulites ( $>2 \mu\text{m}$ ) and more than  $\sim 10\%$  of the bond region covered with spherulites absorb the most water vapor, while samples with smaller amounts of spherulites absorb significantly less. Due to a high volume contraction during polymer crystallization, large spherulites provide a greater number of voids at



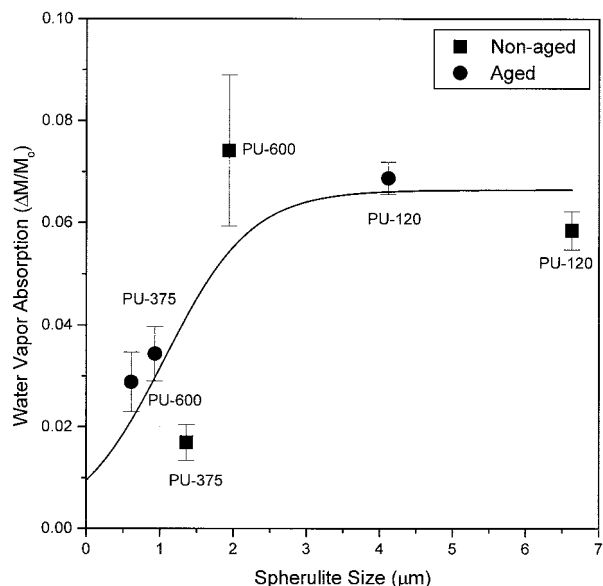
**Figure 3** Effect of crosslink density on WVA. There is no obvious relationship between the amount of absorbed water vapor and the crosslink density, even though it is known that a highly crosslinked polymer absorbs less water vapor.



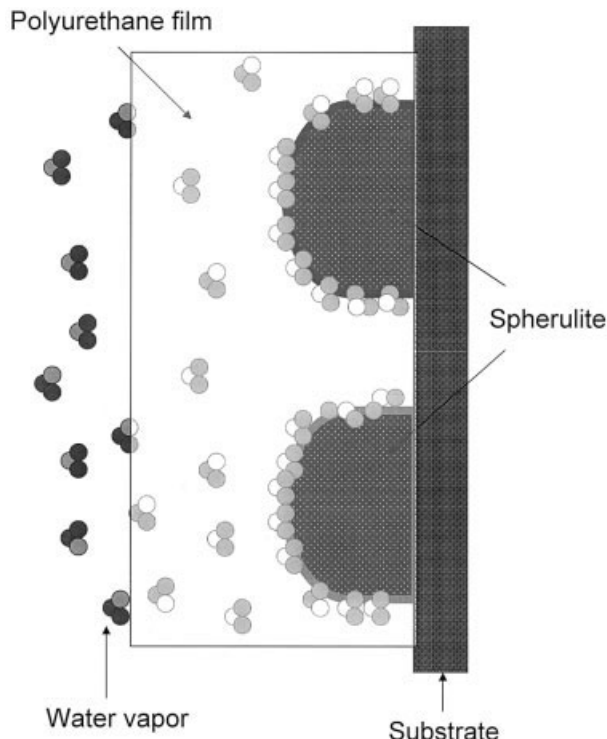
**Figure 4** Relation of WVA to area fraction of polyurethane spherulites at the polymer/Al interface. The WVA increases rapidly with the area fraction until it reaches a maximum at an  $F_A$  of about 20%.

their boundaries where water vapor may absorb and condense. The weight gain was relatively constant for the samples with an average spherulite size greater than 2  $\mu\text{m}$ . This implies that all the water vapor absorbed in the polymer does not condense and contribute to the weight gain.

A location where water vapor resides is shown in Figure 6; the water molecules are retained at the spherulite boundaries. The volume contraction caused by the formation of large spherulites produces a



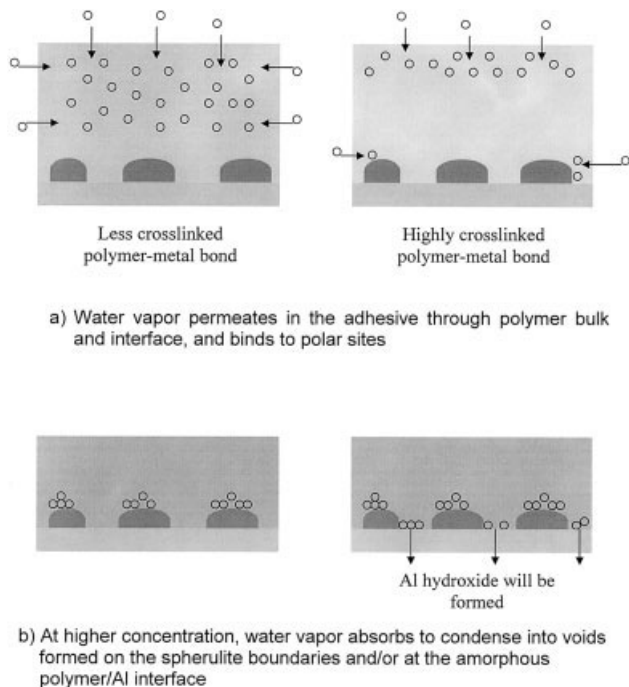
**Figure 5** Relation of WVA to size of the polyurethane spherulites formed on Al surface. WVA attains a maximum at a spherulite size of approximately 3  $\mu\text{m}$ .



**Figure 6** Diagram describing WVA in polyurethane/Al bonds in which a spherulitic interphase has formed. The water vapor condenses at spherulite boundaries where voids and defects are created during crystallization. This model is consistent with the relationship between WVA and spherulite size, etc., as shown in Figures 4 and 5.

greater number of voids than do smaller spherulites, resulting in the dependence of the amount of WVA on the spherulite size shown in Figure 5. The increase of the area fraction of spherulites provides more sites for WVA, and, thus, the weight gain increases, as shown in Figure 4. These results were used to construct the diagrams describing water-vapor permeation for the polymer/metal bond system shown in Figure 7. Figure 7 is based upon Cognard's water-blistering model,<sup>5</sup> showing water-vapor permeation and condensation for a polymer/metal bond system with a spherulite interphase. In less crosslinked polymers, most of the water vapor is transmitted through the polymer bulk to the metal substrate, rather than along the interfacial area. In a highly crosslinked polymer bonded to a metal substrate, the vapor penetrates the polymer bulk regions to some extent, but also permeates along the polymer/metal interface. As the amount of absorbed water vapor increases, the vapor condenses within the voids formed at the spherulite boundaries.

It is also possible for water vapor to be retained at the amorphous polymer/metal interface if there are places unfilled by the polymer at the metal surface. Water-vapor condensing here will cause the formation of Al hydroxides and/or oxides. To investigate this



**Figure 7** Diagram representing WVA in crosslinked polymers bonded to metal substrates in which a spherulitic interphase forms. The water vapor permeates along different routes, but condenses at the spherulite boundaries and/or the amorphous phase/metal interface. The water vapor that permeates to the amorphous phase/metal interface reacts with the Al to form hydroxides.

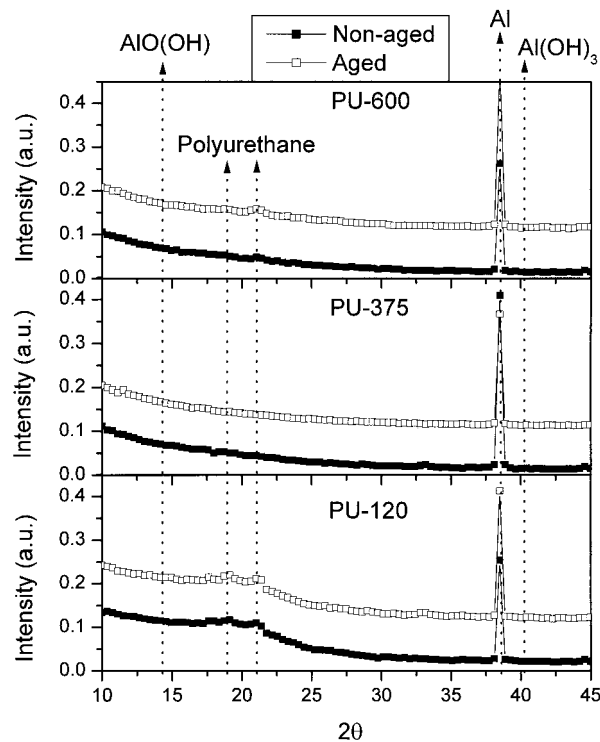
suggestion, samples were exposed to water vapor for 7 days to allow sufficient moisture soaking. X-ray diffraction measurements on the substrate side of these samples, after the polymer film was removed by tape peeling, were performed on a beamline X14A at the National Synchrotron Light Source. From the diffractometer traces (Fig. 8), significant amounts of bay-erite [Al(OH)<sub>3</sub>] or bohemite (AlO(OH)), formed by the reaction of Al with the condensed water vapor, were not found. This suggests that the water vapor condensed only at spherulite boundaries and did not appear to permeate to the amorphous polymer/Al interface. Alternatively, if the water vapor permeated to this interface, the number of vacant sites unoccupied by the polymer at the Al surface was not sufficient for the water vapor to condense and react to form the hydroxides. Although the existence of a very thin Al hydroxide layer, undetected in the X-ray diffraction scans, cannot be ruled out, it seems likely that most of water vapor was absorbed and condensed at the spherulite boundaries. The 7-day exposure may not have been long enough for the water vapor to condense where amorphous polyurethane contacts the Al surface. Nevertheless, it is clear that the water vapor would first choose to condense at the spherulite boundaries. Therefore, the spherulitic features are of great importance in WVA for a polymer/metal bond

system in which a spherulite interphase is formed, particularly in a highly crosslinked polymer.

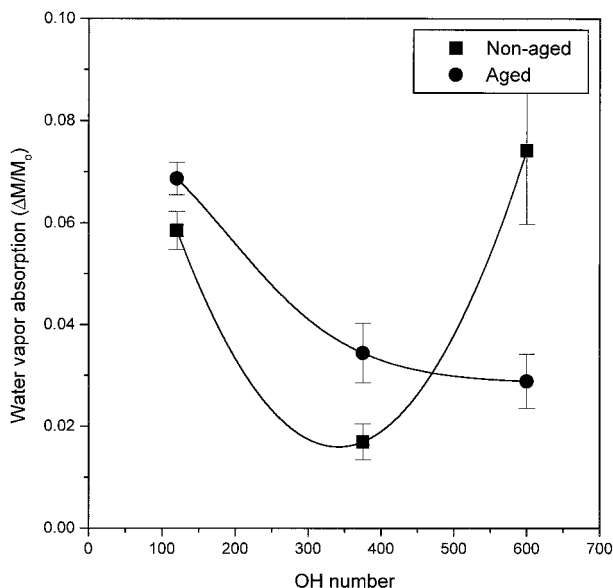
Figure 9 represents the effect of the polyol OH number, which determines the crosslinking level and crystallinity, on the amount of the absorbed water vapor. The weight gain due to WVA decreased with the OH number in the aged samples, but there appears to be an optimum OH number for the lowest weight gain in the nonaged samples. Minimum absorption requires less spherulite formation, that is, a smaller number of sites where water vapor can absorb and condense. The nonaged PU-600 sample displayed the highest absorption, due to greater spherulite formation, and thus a greater water-vapor-absorbing boundary area. Hence, it is likely that while the WVA in aged samples is dependent on the crosslink density the spherulite boundary area determines the amount of absorbed water vapor in nonaged samples.

**CONCLUSIONS**

The weight change due to WVA in nonaged and aged Al/polyurethane samples with OH numbers of 120, 375, and 600 was measured, with the following results:



**Figure 8** X-ray diffractometer traces for tape-peeled polyurethane/Al bonded samples exposed to water vapor for 7 days. Distinct reflections from Al hydroxides were not found for any of the samples, implying that most of the water vapor is retained at the spherulite boundaries, but does not condense at the amorphous polyurethane/Al interface to any significant extent.



**Figure 9** Dependence of WVA on polyol OH number in polyurethane/Al bonds. There is an optimum OH number to reach the lowest weight gain for nonaged samples, while the weight gain decreases with the OH number for aged samples.

1. The total amount of absorbed water vapor was independent of the crosslink density of the polyurethane, because of the existence of additional absorption sites associated with crystalline spherulites formed at the polymer/Al interface. The weight gain was shown to depend upon the spherulitic features such as size and area fraction.
2. The water vapor absorbs and condenses within the voids created at the spherulite boundaries. X-ray diffraction results demonstrated that Al hydroxides were not formed at amorphous poly-

urethane/Al interfaces. Even if an extremely thin Al hydroxide layer was formed, most water vapor apparently absorbs and condenses at the spherulite boundaries.

3. The polyol OH number, which determines the properties of the polyurethane, affected the WVA in such a way that aged samples exhibited a decreased weight gain with the OH number, while there was an optimum OH number for the least WVA in nonaged samples.

This work was supported by Air Products and Chemicals Inc. This research was performed, in part, on a beamline X14A of the National Synchrotron Light Source, Upton, NY. The X14A is operated by the High Temperature Materials Laboratory User Program of Oak Ridge National Laboratory, which is sponsored by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technology, under Contract No. DE-AC05-00OR22725. The NSLS synchrotron facility is sponsored by the Office of Science, U.S. Department of Energy, under Grant No. DE-AC02-76CH00016.

## References

1. Gledhill, R. A.; Kinloch, A. J. *J Adhes* 1974, 6, 315.
2. Kinloch, A. J. *J Adhes* 1979, 10, 193.
3. Dodiuk, H.; Drori, L.; Miller, J. *J Adhes* 1984, 17, 33.
4. Drain, K. F.; Guthrie, J.; Leung, C. L.; Martin, F. R.; Otterburn, M. S. *J Adhes* 1984, 17, 71.
5. Cognard, J. In *Adhesion International 1993*; Sharpe, L. H., Ed.; Gordon and Breach: Amsterdam, 1996.
6. Kim, J.; Ryba, E. *J Adhes Sci Technol* 2001, 15, 1747.
7. Ahearn, J. S.; Sun, T. S.; Froede, C.; Venables, J. D.; Hopping, R. *SAMPE Q* 1980, 39.
8. Ahearn, J. S.; Davis, G. D.; Sun, T. S.; Venables, J. D. In *Adhesion Aspects of Polymeric Coatings*; Mittal, K. L., Ed.; Plenum: New York, 1983.
9. ASTM Standard Designation E 96, Standard Test Methods for Water Vapor Transmission of Materials, 1995.