# Quantitative Determination of Isocyanate Concentration in Crosslinked Polyurethane Coatings

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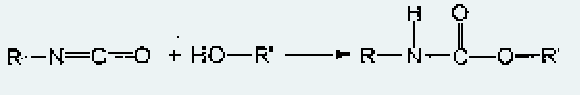
## INTRODUCTION

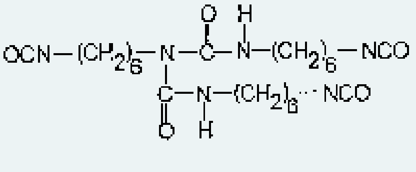
Although it is generally believed that crosslinked urethanes acquire their superior physical properties from the urethane linkages, there are other issues that are not fully understood, which may have a significant effect on polyurethane characteristics. Therefore, the objective of this study is to further enhance our understanding of the urethane chemistry, especially near surfaces and interfaces. However, before we address these issues, let us consider the formation of a urethane linkage, which involves reactions of highly reactive isocyanate functionalities with OH groups of an alcohol.



$$R-N=C=O + HO-R' \longrightarrow R-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-O-R'$$

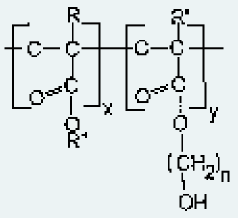
Scheme 1

Ignoring temporarily the presence of $H_2O$, and following the reaction shown in *Scheme* 1, a crosslinked urethane network can be obtained from difunctional polymers that are reacted with crosslinkers containing at least three functional groups. One type of crosslinker containing three isocyanate functional groups is formed by addition of a diisocyanate to urea, forming a biuret linkage. The biuret of hexamethylene diisocyanate (HDI), a useful and commonly used example of such species, is shown in the following:



Structure 1

If such species are reacted with multi-functional polyacrylic or polyester based polyalcohols, such as shown in the following acrylic copolymers:

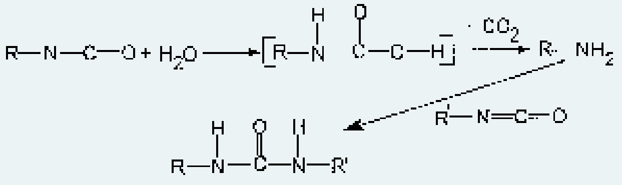


Structure 2

*The influence of relative humidity on the rate of isocyanate functionality depletion at the film-air and film-substrate interfaces of a urethane coating was examined using attenuated total reflectance (ATR) FTIR. The effect of relative humidities (RH) ranging from 0 to 80% on crosslinking reactions was examined. The results indicate that reactions of isocyanate groups with OH functionalities are inversely proportional to the RH. The results are discussed in terms of the reactions which occur between water and isocyanate, as well as the plasticization effects of water and solvent molecules. These studies indicate that the presence of competing reactions within the system may result in various degrees of crosslinking.*

where: R and R´ are either H or $CH_3$, and R˝ is an alkyl group, a urethane network is formed. In such a copolymer, the alcohol groups are randomly distributed along the polymer chain, with $y < x$. Typically the values of n are $\leq 3$.

Although formation of urethane linkages is a key step in the urethane crosslinking, the presence of water may significantly affect these reactions. If water is present while the crosslinking reactions occur, the formation of urea functionalities parallels crosslinking reactions. The reaction proceeds through a carbamic acid intermediate, and the latter dissociates to yield carbon dioxide and an amine, which further reacts with another isocyanate to produce urea.[1,2] This is shown in *Scheme* 2.



Scheme 2

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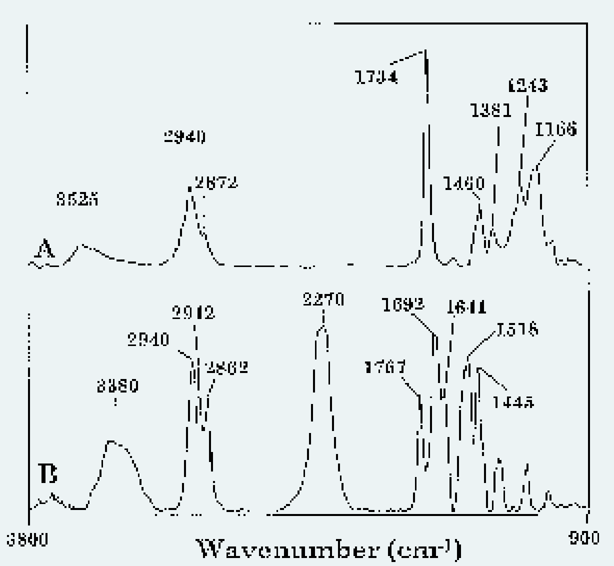

*Figure 1—Identification of the infrared bands in the polyalcohol and biuret. (A) Polyalcohol; (B) crosslinker.*

Following the reactions shown in *Scheme* 2, the presence of water will affect the kinetics of isocyanate consumption and furthermore, it will cause $CO_2$ production during crosslinking. As a matter of fact, recently we[3] reported how crosslinking conditions may affect the rate of $CO_2$ production during urethane network formation, and the consequences resulting from such reactions. These studies demonstrated that decreasing cure temperature extends the time of $CO_2$ production, and its subsequent diffusion out of the system. The focus of this study is a quantitative analysis of the isocyanate consumption in urethane films, crosslinked under controlled humidity environments. Furthermore, following our previous findings on various latex systems,[4-8] we will attempt to determine the differences, if any, in isocyanate group consumption near the film-air (F-A) and film-substrate (F-S) interfaces using ATR FTIR spectroscopy. For that reason, we will employ our recently developed quantitative methodologies for analysis of ATR results.[9,10]

## EXPERIMENTAL

### Sample Preparation

An ambient crosslinked acrylic urethane coating (Sunfire 421) was obtained from The Sherwin-Williams Co. Following the manufacturer's directions,[11] crosslinking was accomplished with the biuret of hexamethylene diisocyanate. Samples were drawn down on tin plated steel panels and crosslinked at 25°C, at 0, 20, 40, and 80% relative humidity, to yield a dry film thickness of 90 ± 10 μm. The glass transition temperature of a typical crosslinked film was approximately 65°C. Relative humidity was controlled using a dessicator containing saturated salt solutions corresponding to specific relative humidity. Portions of each sample were periodically removed from the substrate and spectroscopically examined in order to determine the content of unreacted isocyanate functional groups.

### Spectroscopic Measurements

ATR FTIR spectra were collected on a Mattson Sirius 100 spectrometer. A resolution of 4 $cm^{-1}$ and a mirror speed of 0.3 cm $s^{-1}$ were used. An attenuated total reflectance (ATR) attachment (Spectra Tech Inc.) using a 45° end parallelogram KRS-5 crystal was utilized. Considering the experimental conditions, the intensity of the isocyanate band at 2270 $cm^{-1}$ was determined by the concentration of isocyanate functionalities with 0.9 μm of the surface. All spectra were collected with a perpendicular polarization using an aluminum wire grid polarizer with 0.4 μm grid spacing. All spectra represent 200 co-added scans, ratioed against a background, obtained by co-addition of 200 scans of an empty ATR cell with a KRS-5 crystal. In order to quantify the results, Q-ATR software[9] was utilized to account for refractive index and crystal coverage effects on band intensity. All spectra were normalized to the $CH_2$ deformation vibrations at 1460 $cm^{-1}$.

**Table 1—IR Band Assignments for the Acrylic Polyalcohol, Biuret Crosslinker and Urethane Linkages**

| Band ($cm^{-1}$) | Polyalcohol | Biuret | Urethane | Reference |
|---|---|---|---|---|
| 3525 | $\nu_s$ O-H | | | 12 |
| 3380 | | $\nu_s$ N-H | $\nu_s$ N-H | 12,15 |
| 2940 | $\nu_a$ $CH_2$ | $\nu_a CH_2$ | $\nu_a$ $CH_2$ | 12 |
| 2912 | | $\nu_a$ $CH_2$ | | 12 |
| 2872 | $\nu_s$ $CH_2$ | | $\nu_a CH_2$ | 12 |
| 2862 | | $\nu_s$ $CH_2$ | | 12 |
| 2270 | | NCO | NCO | 12,13 |
| 1767 | | C=O (urea) | | 12 |
| 1734 | C=O | | C=O | 15 |
| 1692 | | C=O | C=O | 15 |
| 1641 | | C=O | | 15 |
| 1518 | | C-N & N-H | C-N & N-H | 12,15,16 |
| 1460 | δ $CH_2$ | | δ $CH_2$ | 12,13 |
| 1445 | | δ $CH_2$ | | 12 |
| 1381 | δ $Ch_3$ | | δ $CH_3$ | 12 |
| 1352 | | C-N | | 12 |
| 1243 | $\nu_a$ C-O | | | 15 |
| 1210 | | C-N & N-H | | 12,15 |
| 1166 | C-O | | | 15 |
| 1145 | C-O | | | 15 |

$\nu_s$=symmetric stretching; $\nu_a$=asymmetric stretching, δ=deformation

## RESULTS AND DISCUSSIONS

In view of the reactions presented in the Introduction Section, we will begin analysis of the spectroscopic data by assigning infrared bands to specific vibrational modes. *Figure* 1, traces A and B, present transmission FTIR spectra of acrylic polyol and isocyanate crosslinker, respectively. While *Table* 1 provides tentative band assignments for all components involved in the urethane crosslinking reactions, several bands are of particular interest because their behavior reflects reactions resulting in crosslinking. Trace A of *Figure* 1 shows the band at 1734 $cm^{-1}$ due to C=O stretching modes, and the bands at 1243 and 1166 $cm^{-1}$ are attributed to the C–O stretching vibrations of acrylic ester groups. The $CH_2$ bending deformation modes are detected at 1460 $cm^{-1}$. The presence of isocyanate functionality is responsible for the band at 2270 $cm^{-1}$ shown in trace B. While the band at 1767 $cm^{-1}$ is attributed to the carbonyl groups of the urea linkages, the bands at 1692 and 1641 $cm^{-1}$ represent asymmetric and symmetric C=O stretching modes of the biuret, respectively. The bands at 1518 and 1445 $cm^{-1}$ are due to amide II and $CH_2$ bending deformation modes, respectively.

With this background in mind, let us go back to our main theme and focus on the spectroscopic changes that occur as the isocyanate functionalities are consumed. Traces A and B of *Figure* 2 illustrate ATR FTIR spectra collected at the F-A interface of the urethane films crosslinked under ambient conditions (average 30% relative humidity and 25°C) for 24 hr and 80 days, respectively. A comparison of the spectra indicates that, as isocyanate groups are consumed, the band at 2270 $cm^{-1}$ due to NCO groups is reduced. At the same time, the bands due to N–H and C–O modes at 1518 and 1145 $cm^{-1}$ due to urethane linkages increase. The urethane carbonyl is expected to absorb at approximately 1715 $cm^{-1}$.[12,13] Although this band does not appear as a separate entity, the intensity of the 1733 and 1692 $cm^{-1}$ bands are significantly increased. This observation is attributed to the formation of urethane linkages containing carbonyl groups.

In an effort to quantify ATR FTIR results, two prerequisites must be met. Firstly, it is necessary to construct a calibration curve which relates the band intensity changes plotted as a function of concentration of a given species. Secondly, ATR FTIR spectra have to be corrected for optical effects. While the second prerequisite has already been established in recently published literature,[9,10] the development of a calibration curve needs to be further investigated. Since we are interested in a quantitative assessment of the isocyanate functionality, hexamethylene diisocyanate (HDI), in amounts ranging from 0.1 to 1.7 N, was added to an acrylic resin, and the plot of the 2270 $cm^{-1}$ band as a function of HDI concentration was constructed. This plot is shown in *Figure* 3 and allows us to correlate band intensities with unknown isocyanate concentration at the F-A and F-S interfaces, thereby allowing quantitative assessments of the NCO groups.

In order to examine the effect of water on urethane crosslinking, urethane films were exposed to 0, 20, 40, and 80% relative humidity at 25°C. The effect of the exposure conditions on the isocyanate concentration is shown in *Figure* 4, which illustrates the changes in isocyanate concentration near the F-A and F-S interfaces as a function of crosslinking time and relative humidity. Because the determination of how relative humidity affects the rate of isocyanate consumption is the goal of this study, let us first examine the rate of isocyanate depletion under conditions free of the influence of water. Curve A of *Figure* 4, obtained from the F-A interface of a specimen crosslinked under 0% relative humidity, exhibits a relatively rapid rate of isocyanate depletion during the first 35 days of crosslinking, which becomes more moderate through approximately 200 days, at which time the isocyanate con-

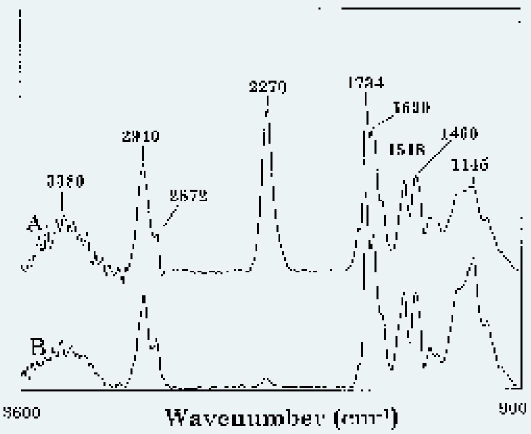

*Figure 2—Changes in infrated spectra with crosslinking of polyurethane coating. (A) Urethane cured one day; (b) urethane after 80 days of cure.*

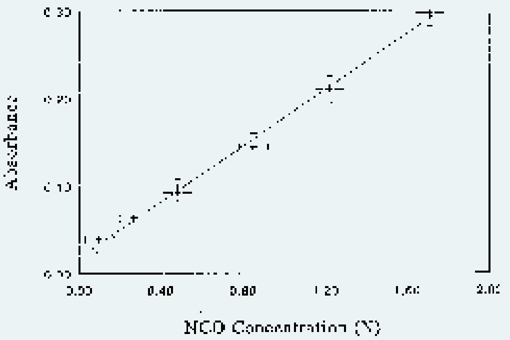

*Figure 3—Calibration curve relating the observed ART FTIR intensity to the concentration of isocyanate present.*

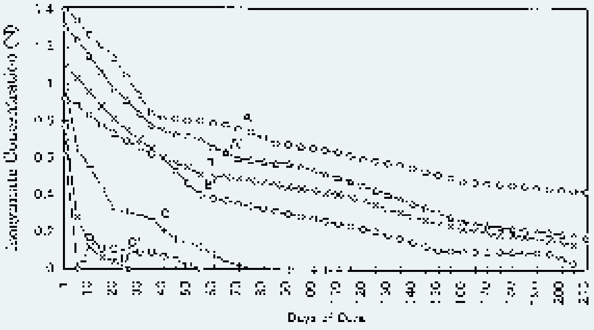

*Figure 4—Concentration of isocyanate functionalities at the film-air and film-substrate interfaces as a function of relative humidity and time. Crosslinking conditions and interface: (A) 0% relative humidity-F/A; (A') 0% relative humidity, F/S; (B) 20% relative humidity, F/A; (B') 20% relative humidity, F/S; (C) 40% relative humidity, F/A; (C') 40% relative humidity, F/S; (D) 80% relative humidity, F/A; and (D') 80% relative humidity, F/S.*

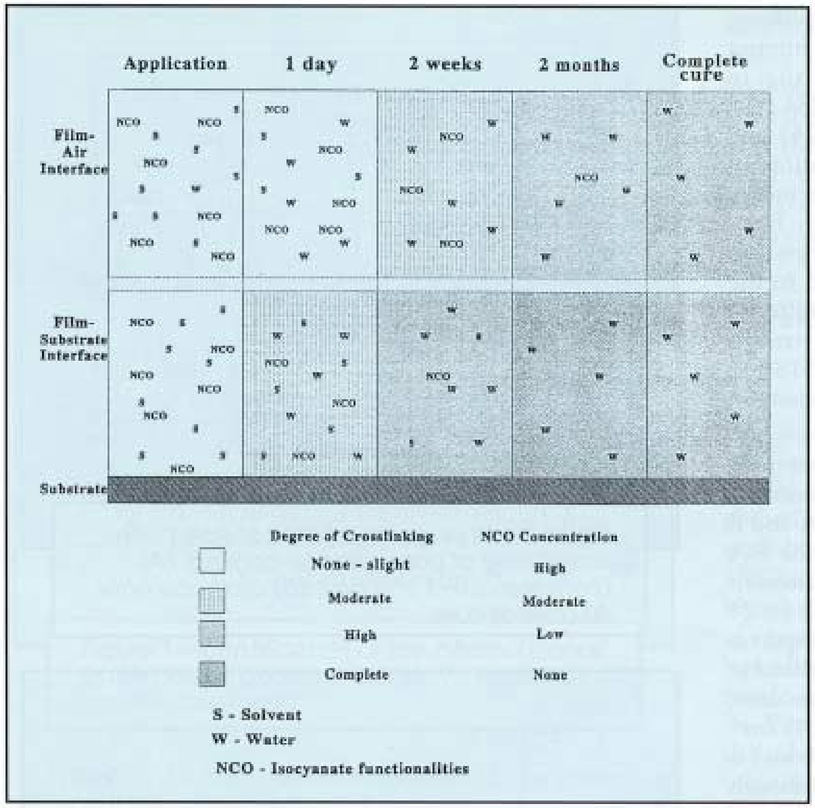

*Figure 5—Schematic representation of crosslink density and isocyanate concentration in ambient crosslinked polyurethane as a function of time.*

centration attains a value of 0.5 N, approximately one-third the concentration detected after the initial 24 hr of reaction.

With these results in mind, let us examine the changes in isocyanate concentration and its mobility during crosslinking, which determine the rate of isocyanate depletion over the course of crosslinking. During the first stage of crosslinking, high concentrations of unreacted isocyanate and alcohol groups are present. Therefore, the proximity of the functional groups results in reactions presented in *Scheme* 1, and the formation of the initial crosslinked network. During that time, solvent molecules evaporate, and as the crosslink density increases, the mobility of the isocyanate and alcohol groups decreases, reducing the rate of further crosslinking reactions.

At this point it is important to realize that the mobility of the reactants is limited by crosslinking due to the oligomeric nature of the polyalcohol and trifunctional isocyanate biuret. In both cases, the diffusion of the molecules is highly restricted due to their relatively large sizes, and following the initial crosslinking reactions, unreacted functional groups are limited in their freedom of motion. At the same time, the concentration of the functional groups declines as the crosslinking reactions proceed. As the functional groups become more isolated, the rate of isocyanate depletion should decrease in the absence of other reactions. The decrease of the rate of isocyanate consumption near the F-A interface over time, observed in curve A of *Figure* 4, is consistent with the increased isolation of isocyanate functionalities which have limited mobility and are unable to approach the equally hindered alcohol groups to undergo urethane formation.

The concentration of isocyanate near the F-S interface of a urethane film crosslinked under 0% relative humidity is shown in curve A´ of *Figure* 4. Although the trends observed in the rate of isocyanate consumption are similar to those detected near the F-A interface (curve A), the rate of consumption diminishes after approximately 35 days of crosslinking, and levels off after approximately 200 days. Furthermore, a lower concentration of isocyanate groups at the F-S interface, relative to the F-A interface, is also detected.

The lower concentration of isocyanate functionalities near the F-S interface relative to the F-A interface results from different solvent concentrations at the F-A and F-S interfaces during the first stage of crosslinking. Initially, the F-A and F-S interfaces contain the same content of solvent molecules. However, as solvent evaporation begins at the F-A interface, and the viscosity of the film increases, the diffusion of solvent from the interior of the film to the F-A interface becomes hindered. This results in a higher concentration of the solvent molecules near the F-S interface, and an increased freedom of motion for the reactive functional groups at that interface. As a result, an increased rate of isocyanate depletion is detected. Thus, the presence of solvent facilitates the early stages of crosslinking by providing desirable mobility of reactive groups, resulting in the lower isocyanate concentration detected near the F-S interface after 24 hr of crosslinking of all the relative humidities examined in this study.

Before we discuss the effect of relative humidity on the rate of isocyanate consumption at the F-A interface, let us examine the anticipated impact of water on the isocyanate reactions. As shown in *Scheme* 2, water can react with isocyanate to yield an amine, which tends to be more reactive towards isocyanate than alcohol.[1] Therefore, it reacts with another isocyanate to form urea. Thus, consumption of two isocyanate groups by each reacting water molecule make the isocyanate concentration highly sensitive to humidity conditions. With this in mind, let us examine the effect of different crosslinking conditions on the rate of isocyanate consumption. Examination of curves A, B, C, and D obtained from the F-A interface of films crosslinked under 0, 20, 40, and 80% relative humidity, respectively, indicates that the amount of unreacted isocyanate groups is inversely related to the amount of water vapor over the film. Because this interface is directly exposed to the water vapor-containing environment, one would expect that the isocyanate consuming reactions depicted in *Scheme* 2 would be accelerated at higher water vapor partial pressures. The inverse relation between isocyanate concentration and relative humidity also supports the argument that the mobility of the isocyanate functionalities has become restricted, since their consumption would be dependent upon reactive species diffusing through the network. Such a diffusion controlled mechanism would favor small reactants, and agrees with the permeability of this network to small molecules such as $CO_2$, which was demonstrated in our earlier studies.[3] Uptake of water by the network was evidenced by the production of $CO_2$ within the urethane network, and is consistent with the reactions presented in *Scheme* 2. Therefore, the inverse relation between the amount of unreacted isocyanate groups and relative humidity comes from the fact that higher partial vapor pressures of water facilitates a higher concentration of water being absorbed by the network.

Curves A´, B´, C´, and D´ of *Figure* 4, represent the isocyanate concentration near the F-S interface for films crosslinked under 0, 20, 40, and 80% relative humidity, respectively. While the urethane films crosslinked under 80 and 40% relative humidity show complete depletion of isocyanate near this interface after 5 and 75 days, respectively, the films crosslinked under 20 and 0% relative humidity achieve stable concentrations within 200 days, which remain unchanged through the duration of the experiment. As we already discussed, curve A´ follows the same trend as curve A, and a comparison of curves A´, B´, C´, and D´ indicates that the isocyanate concentration retained at the F-S interface is inversely proportional to the amount of water vapor over the film. The same trends were detected near the F-A interface. Both observations indicate a loss of mobility, and isolation of the isocyanate reactive groups.

In addition to the time and relative humidity dependence of the isocyanate concentration, one further distinct trend is visible in the data presented in *Figure* 4. When comparing the isocyanate concentration at the F-A and F-S interfaces of film crosslinked under a given water vapor pressure (curve A vs. A´, B vs. B´, C vs. C´, and D vs. D´), the differences are apparent. We can identify the action of low molecular weight species, such as solvents or other additives, which may act as plasticizers, and thus influence the kinetics of crosslinking reactions within a polymer network. The most effective plasticizers are those which result in the increase of free volume. Since free volume can be pictured as the probability of a temporary opening being created in the network as a result of molecular motion, for polymer networks which contain a significant number of polar groups, the interaction of these groups with neighboring polymer chains hinders chain motion and reduces free volume. Therefore, water as a polar solvent may disrupt the interchain interactions through the association of their own polar centers with those on the polymer chains. Thus, in order for a polymer chain segment to undergo a local displacement, it is necessary to overcome energy barriers to assume a new conformation, but not necessarily break numerous polar interactions. The decreased energy requirements for molecular motions result in an increased free volume, and subsequently, a greater mobility of reactive species and higher rates of their depletion.

The inverse relationship between the isocyanate concentration and relative humidity for the F-A and F-S interfaces shown in *Figure* 4 is caused by the increased concentration of water within the films exposed to higher relative humidities. While the reactions shown in *Scheme* 2 account in part for the increased rate of isocyanate depletion, the role of water as a plasticizer is apparent. The plasticizing ability of water results from its ability to form H-bonding with polar groups of the network. Although an approximate energy for H-bonding is 50-7 kcal/mole, the H-bonding between water molecules and H-bond acceptors, such as the C=O groups present in the urethane and urea linkages, as well as the C=O and C–O–C lone pair electrons of the acrylic groups, is among the strongest intermolecular interactions.[14] Water also forms H-bonds with such hydrogen donors present in the network, as the N–H of urea, urethane groups, and the OH of the acrylic polyol, thus further interrupting intermolecular interactions between polar groups on the polymer chains, which results in an increased free volume.

To summarize the discussed results, *Figure* 5 schematically demonstrates the relative extent of isocyanate consumption near the F-A and F-S interfaces as a function of time for a film crosslinked under 40% relative humidity. At the initial stages, both interfaces exhibit identical concentrations of isocyanate groups and high solvent content. As the solvent evaporates from the F-A interface, and progressively diffuses from the F-S interface, the solvent concentration remains nearly uniform through the thickness of the film, until the free volume decreases to the point at which solvent diffusion is hindered. Once solvent diffusion is inhibited, a larger gradient of solvent concentration between the F-A and F-S interfaces is obtained with the highest concentration at the F-S interface. Because solvent molecules act as a plasticizing agent, providing freedom of motion of the functional groups, there is an increased probability of isocyanate and alcohol functionalities undergoing reactions. For that reason, isocyanate groups at the F-S interface, with a higher concentration of the plasticizing solvent, are consumed more rapidly than at the solvent deficient F-A interface. This results in lower concentrations of the isocyanate groups at the F-S interface. However, water uptake results in an increased water concentration in the film, and a more rapid depletion of isocyanate through two primary mechanisms: (1) direct reaction of water with isocyanate functionalities; and (2) plasticization of the network by $H_2O$ molecules, which results in an increased rate of reaction between isocyanate and alcohol functional groups.

## ACKNOWLEDGMENTS

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