Interfacial Studies of Crosslinked Urethanes: Part III. Structure-Property Relationships in Polyester Waterborne Polyurethanes

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INTRODUCTION

Polyurethanes (PURs) are high performance polymers known for their excellent properties among which such properties as abrasion resistance, hardness, flexibility, chemical and solvent resistance, gloss, low temperature film formation, and photostatic stability make them highly attractive for coatings applications.¹,² Many properties are achieved by synthesis with numerous co-reactants,³,⁴ making PURs a versatile class of polymers.¹,³,⁴ Due to increasing environmental concerns, waterborne (WB) PURs with equivalent properties to their solventborne counterparts appear to be of great importance. Although advantages of waterborne PURs are obvious, there are new challenges in synthesizing and formulating these polymers. The presence of water with relatively high surface tension creates difficulty in wetting substrates, and water may react with isocyanate, thus leading to property differences. Although the literature contains some information regarding WB PUR structure-property relationships,⁵,¹⁵ in an effort to understand the factors that influence waterborne PUR film formation and structure-property relationships we initiated studies⁶,¹⁷ on polyacrylate emulsions, which are extended to polyester dispersion polyurethanes. An ultimate goal of these studies is to compare the behavior of polyester dispersion and polyacrylate emulsion polyurethanes in terms of film formation near the film-air (F-A) and film-substrate (F-S) interfaces.

As was identified in our earlier studies,⁶ the following moieties can be formed during PUR film formation: urethane, amine, carbon dioxide, and urea. Thus, we will examine crosslinking reactions and factors influencing waterborne polyurethane film formation near the F-A and F-S interfaces utilizing attenuated total reflectance Fourier-transform infrared (ATR FTIR) spectroscopy,¹⁷ with focus on the formation of polyurethane/polyurea near the F-A and F-S interfaces.

These studies examine crosslinking reactions of polyurethanes (PURs) using attenuated total reflectance Fourier-transform (ATR FTIR) spectroscopy and show that higher relative humidity (RH) accelerates the crosslinking reactions leading to the formation of polyurethane and polyurea. Concentration levels of unreacted isocyanate (NCO) are greater at the film-air (F-A) interface than the film-substrate (F-S) interface. In contrast to the previous studies on polyacrylate emulsion urethanes, no stratification was detected between 0.65 to 1.14 μm near the F-A and F-S interfaces. This behavior is attributed to equivalent weight differences, 3100 g/eq for polyacrylate and 1140 g/eq for polyester. Solvent evaporation experiments show that approximately 10% of the initial water concentration remains in the film for extended periods of time, resulting in reactions leading to the formation of urea near the F-S interface. PUR film formation occurs in two stages, a solvent vapor pressure controlled stage, followed by a diffusion controlled stage. The duration of each stage depends on several factors, including the amount of shear induced on the shear thinning waterborne urethanes, which subsequently affects the exposure of isocyanate aggregates to water. Increased RH significantly affects structure-property relationships of waterborne PURs due to urea formation, which alters the glass transition temperature, storage modulus, crosslink density, and film hardness.

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ethoxypropanol (0.1 w/%) at 48 rpm. Isocyanate and 2 mL of double deionized (DDI) water were added incrementally until a uniform dispersion, 150-300 cp, was obtained after seven minutes of mixing. The formulation was allowed to settle for five minutes before casting onto tin-plated steel panels at 75 µm wet film thickness. The films were allowed to crosslink at 25°C under relative humidity conditions of 20, 40, 65, and 80%. Samples were removed periodically from the substrate for spectroscopic analysis using a mercury amalgamation method. An approximate dry film thickness was 19 µm ± 2 µm.

Analytical Methods

Transmission, ATR, and Circle™ ATR FTIR were collected on a Nicolet Magna 850 spectrometer and purged with purified air (Whatman FTIR purge gas generator). The spectra were collected at 4 cm⁻¹ resolution using a 0.3165 cm/s mirror speed. The ATR variable-angle multiple reflection attachment (Spectra Tech, Inc.) with 45° end cut parallelogram KRS-5 crystal was utilized. The depth of penetration was varied by changing the angles of incidence at 40, 45, and 60°, which correspond to 1.14, 0.92, and 0.65 µm depths of penetration at 2271 cm⁻¹. Polarized ATR FTIR spectra were collected with either parallel, transverse electric (TE; 0°), or perpendicular, transverse-magnetic (TM; 90°) polarization light using a Graseby Specac 12000 polarizer.

In a typical experiment, 60 co-added scans were ratioed against a background of 60 co-added scans of an empty ATR cell equipped with a KRS-5 crystal. ATR spectra of aqueous PUR were obtained by Circle™ ATR equipped with a ZnSe circular crystal at 45° (Spectra Tech Inc.). Liquid PUR was applied directly to the crystal, and the spectra were recorded as a function of time. Due to the fact that ATR spectra are a complex function of refractive index and absorption indexes, the dispersive nature of ATR spectra were corrected using Q-ATR software. Corrected spectra were normalized to the CH₃ stretching modes at 2936 cm⁻¹. FT-Raman spectra were acquired on a Bruker Equinox 55 spectrometer equipped with a Bruker FRA 106 FT Raman accessory. The spectra represent 1000 co-added scans in a liquid cell, at 4 cm⁻¹ resolution using a 415 mW Nd:YAG laser excitation source. Spectral features of overlapping bands were deconvoluted with SS-RES maximum likelihood entropy method.

Viscosity measurements were performed on a Carri-Med double concentric cylinder rheometer with a controlled stress of 2.657 sec⁻¹. Measurements were taken at shear rates of 26, 48, 70, and 90 rpm. Conical mandrel flexibility (ASTM D 522) (Sheen Instruments) was measured by bending the sample over a conical mandrel with the coating side on top. Specimens were bent until cracking occurs at the following intervals: 1, 3/4, 1/2, 1/4, and 1/8 in., where 1/8 in. is the most flexible. In the reverse impact resistance test (ASTM D 2794), a 2.0 lb steel cylinder with a rounded head was dropped through a vertical shaft onto a coated steel panel, film side up. The maximum height at which this weight can be dropped without cracking the film is the impact strength (in.-lb). Knoop Tukon hardness (ASTM-
Table 1—Tentative FTIR and FT-Raman Band Assignments for Waterborne Polyester, HDI Isocyanurate, 2-Methoxyethylhexoxypropanol, Polyurethane and Polyurea

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Waterborne Polyester IR</th>
<th>HDI Isocyanurate IR</th>
<th>2-methoxyethylhexoxypropanol IR</th>
<th>Polyurethane IR</th>
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<tbody>
<tr>
<td>C=O str.</td>
<td>3525</td>
<td>3440</td>
<td>3530</td>
<td>3530</td>
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<tr>
<td>NH str.</td>
<td>3420</td>
<td>3420</td>
<td>3377</td>
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<tr>
<td>Overtones C-O</td>
<td>3214</td>
<td>3214</td>
<td>3080</td>
<td>3080</td>
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<tr>
<td>νs C=O-C=O</td>
<td>3082</td>
<td>3067</td>
<td>2963</td>
<td>2963</td>
</tr>
<tr>
<td>νs CH2</td>
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<td>2937</td>
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<tr>
<td>νs CH2 str. aldehyde</td>
<td>2271</td>
<td>2271</td>
<td>1760</td>
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<tr>
<td>NCO out-of-phase</td>
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<td>1729</td>
<td>1691</td>
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<td>1466</td>
<td>1400</td>
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<tr>
<td>6N-H νs C-N amide I (urea)</td>
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<td>1380</td>
<td>1382</td>
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<tr>
<td>C-H rock aldehyde</td>
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<td>1249</td>
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<tr>
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<tr>
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<td>C=O str. skel.</td>
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<td>952</td>
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<tr>
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<td>732</td>
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<td>a CO-C</td>
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<tr>
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<td>6NH2 νs C-N amide I (urea)</td>
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<td>νs = symmetric stretch</td>
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<tr>
<td>νs = deformation</td>
<td>1146</td>
<td>1143</td>
<td>1136</td>
<td>1136</td>
</tr>
</tbody>
</table>

D 1474 cm⁻¹ was measured by a Tuken® Tester model MO, and the Knop hardness number (KNH) was calculated by the following equation:

\[
\text{KNH} = \frac{L}{\rho C_p} 
\]

where \( L \) is the load applied to the indenter (0.025 kg), \( L \) is the length of the indentation (mm), \( C_p \) is the indenter constant (7.028 x 10⁻³). Dynamic mechanical thermal analysis (DMA) was performed on a Rheometric Scientific DMTA 3E utilizing tension, compression geometry with a 6.2832 rad/sec frequency, 0.5% strain, autotension and a 5.0984 g initial static force. The samples were 5 mm x 9.5 mm and 0.02 mm thick, and measurements were taken from −100 to 250°C at 3°C/min.

RESULTS AND DISCUSSION

The first step in this analysis will be to identify relevant spectral features responsible for PUR film formation. While Table 1 summarizes FTIR and FT-Raman active bands observed in individual urethane components and their tentative assignments, Figure 1 illustrates ATR and transmission FTIR spectra of waterborne polyurethane (Trace A), polyester resin dispersion (Trace B), HDI isocyanurate (Trace C), and 2-methoxyethylhexoxypropanol (Trace D). The band at 2271 cm⁻¹ (Traces A and C)
Due to significantly weaker water bands and minimized fluorescence Fourier transform Raman (FT-Raman) spectroscopy provide complementary information to FTIR measurements\(^{19,21}\) and this method is particularly suited for water-soluble polymers. Figure 2 illustrates FT-Raman spectra of waterborne polyurethane (Trace A), polyester resin dispersion (Trace B), HDI isocyanurate (Trace C), and 2-methoxyethylmethoxypropanol (Trace D). As shown in Figure 2, Traces A and B, asymmetric C=Oâ‰€CH\(_2\) vibrational modes at 3080 cm\(^{-1}\) are detected in polyurethane and polyester dispersions. The bands notated at 2989 and 1124 cm\(^{-1}\) indicate the presence of R\(_2\)C-H and C-C stretching vibrations in isocyanurate (Trace C), and 2-methoxyethylmethoxypropanol (Trace D). Figure 2, Trace D, confirms the presence of aldehyde in the additive, 2-methoxyethylmethoxypropanol, detected at 2829 and 2731 cm\(^{-1}\).

As was shown in the previous studies,\(^ {16,17}\) crosslinking reactions leading to PUR formation can be quantified by following the decrease of the NCO band intensity at 2271 cm\(^{-1}\) along with the increase of the CO\(_3\) (g) band at 2237 cm\(^{-1}\). The primary interest in following these species results from the fact that when NCO reacts with the active hydrogen of a hydroxy-functional compound, a urethane linkage is formed. This is illustrated in Scheme 1. However, in the presence of water, NCO can also react with H\(_2\)O. This is shown in Scheme 2.

When isocyanate reacts with water by condensation, an unstable intermediate, carbamic acid, is formed, which immediately dissociates to evolve carbon dioxide gas and an amine, which continues to react with free isocyanate to form urea. The NCO reaction with water can significantly affect film formation, as the evolution of carbon dioxide gas may result in unexpected property changes. Furthermore, vigorous reactions between isocyanates and amines may cause a rapid increase in molecular weight and viscosity, thus reducing pot life. Since amines are more nucleophilic than OH functional alcohols, urea reactions will occur faster and may predominate the crosslinking process. Under such circumstances, one could conclude that the presence of water is not desirable, especially that its presence may also result in hydrolysis of polyester linkages. However, inclusion of hydrophilic polyether tails surrounding NCO groups minimizes the influence of water and polyurethane formation dominates the process.\(^ {15,28}\)

Since we are interested in quantitative spectroscopic analysis of NCO and CO\(_3\)\(_2\), it is necessary to obtain a calibration curve, where known concentrations of isocyanate and CO\(_3\)\(_2\) (g) are plotted against their respective band intensities. Using Beer-Lambert's law,

\[
A = e \cdot b \cdot c
\]

the molar absorption coefficient of isocyanate and CO\(_3\)\(_2\) can be determined. Figure 3 represents the HDI isocyanurate and CO\(_3\)\(_2\) (g) band intensities at 2271 and 2337 cm\(^{-1}\) plotted as a function of concentration. The slope of the calibration curve is the product of the path length and molar absorptivity, resulting in absorption coefficients of 822.91 1/mol\(\cdot\)cm for NCO and 168.36 1/mol\(\cdot\)cm for CO\(_3\)\(_2\).\(^ {17}\) As crosslinking reactions progress, the isocyanate band intensity detected at 2271 cm\(^{-1}\) de-
creases, while the band at 2337 cm\(^{-1}\) attributed to CO\(_2\) gas formation increases.\(^{17}\) The results presented in Figure 4 show Circle ATR spectra recorded from 10 to 15 min.

As shown in Scheme 2, the presence of CO\(_2\) indicates reactions of water with isocyanate, and amine resulting from these reactions can further react with another free NCO to form urea. Using molar absorptivities determined in Figure 3, NCO and CO\(_2\) concentration changes were calculated at various stages of the reaction. This is illustrated in Figure 5. As seen, the NCO concentration decreases from \(3.93 \times 10^{-3}\) to \(2.48 \times 10^{-5}\) M, while the CO\(_2\) concentration increases from \(2.90 \times 10^{-3}\) M. During this time, from 10 to 50 min, CO\(_2\) increases approximately twice as fast as the decrease of NCO.

The amount of CO\(_2\) generated during polyurethane network formation is influenced by numerous factors, including the amount of water retained in the film at this stage of reaction, relative humidity (RH) of the environment as well as the amount of shear stresses imposed on the system. As shown in Scheme 2, CO\(_2\) is produced when NCO reacts with water. Increasing the amount of water or lowering evaporation rates enables water to be retained within the film, thus increasing the chance of NCO-H\(_2\)O reactions. Since higher relative humidity suppresses water evaporation, reactions shown in Scheme 2 will be favorable. For the matter, higher shear rates imposed on waterborne PUR systems may expose NCO particles to water, thus increasing the likelihood for reactions with water. To account for these features as well as in an effort to improve PUR chemical resistance, waterborne polyurethanes are formulated at 2:1 (NCO:OH) stoichiometry.\(^{25,26}\)

In an effort to compare these results with the studies conducted on polyacrylate emulsions,\(^{23}\) we formulated a polyester-based urethane at 1:1 NCO:OH and followed the decrease of NCO. Figure 6 shows the NCO decrease for polyester and polyacrylate systems formulated at 1:1 stoichiometry and indicates that the rate of NCO consumption in the polyester system is greater, as determined from the slope of \(-9.53 \times 10^{-6}\) M/min. The slope for PUR acrylic is \(-3.05 \times 10^{-7}\) M/min, and this difference stems from the equivalent weight of the two waterborne systems. The acrylic emulsion has an equivalent weight of 3100 g/mol, whereas the polyester dispersion is approximately three times smaller, 1140 g/mol. Thus, when formulating the polyester dispersion as compared to the acrylic emulsion, the polyester requires more isocyanate at a given stoichiometry, which accelerates the crosslinking reactions leading to PUR network formation.

One would also expect that shear rates imposed on both 2K systems may affect the extent of reactions. After all, faster shear rates may expose NCO containing particles to H\(_2\)O, thus promoting reactions illustrated in Scheme 2. Therefore, shear requirements for these two waterborne systems should also be considered. Polyacrylate is an emulsion, while polyester is a dispersion, and this difference is reflected in viscosity behavior. The hydroxy-substituted polyacrylate emulsion exhibits a viscosity of 50-500 cps, whereas the polyester dispersion has a viscosity of 6000 cps. From an applica-

![Figure 4](image1.png)

![Figure 5](image2.png)

![Figure 6](image3.png)
Figure 6—Isocyanate concentration changes resulting from crosslinking reactions in polyester (■) and polyacrylate (○) systems formulated at 1:1 (NCO/OH) ratio.

Figure 7—Viscosity of polyester polyurethanes vs. shearing rate in rpm.

Figure 8—Weight percent of solvent loss at 20% RH of water/2-methoxyethylethoxypropyl (Trace A—■); polyester dispersion (Trace B—○); and formulated polyurethane (Trace C—▲).

Figure 9—Crosslinking reaction time plotted as a function of relative humidity.
	on point of view, this difference leads to different requirements for obtaining a uniform dispersion. The acrylic emulsion can be mixed with the polyisocyanate by creating a vortex with magnetic stirring bar, whereas the polyester dispersion requires a three-bladed propeller set at 48 rpm.

Previous studies have shown that shear rates may also affect particle sizes of isocyanate and polyl.23,24 Because shears imposed on waterborne PUR may have an effect on the resulting chemical reactions and the amount of CO₂ gas evolved during urethane network formation, we conducted a series of experiments on polyester dispersions. The results are shown in Figure 7. As shear forces increase, viscosity decreases, thus indicating shear thinning behavior attributed to structures of NCO-containing particles.25 To disperse NCO in water, it is necessary to have hydrophilic polyester tails attached to the NCO-containing particle which act as a water barrier, minimizing reactions of NCO with water (Scheme 2). Such a structural feature allows the urethane crosslink to predominate over urea formation.

As these studies show, under high shear conditions, urethanes appear to give off more CO₂ gas, which comes from the reactions of NCO functionalities with H₂O. This would indicate increased exposure of NCO to wa-
Figure 10—ATR FTIR spectra at the (A) F-A and (B) F-S interface crosslinked at 80% (Trace A), 65% (Trace B); 40% (Trace C); and 20% RH (Trace D).

Figure 11—SS-RES deconvolution of the F-A interface ATR FTIR spectra recorded after 16 hr: 20% (Trace A); 40% (Trace B); 65% (Trace C); and 80% (Trace D) relative humidities in the 1580-1550 cm⁻¹ region.

Figure 12—Isocyanate concentration changes at the F-A interface recorded from 0 to 50 hr under 20% (Trace A); 40% (Trace B); 65% (Trace C); and 80% (Trace D) relative humidities.

Figure 13—Isocyanate concentration over time at the film-air and film-substrate interfaces at 40% RH.
ter and/or particle size changes as a result of shearing. The latter was suggested in previous studies. Increased shear stresses induced on the NCO particle could either reorient or, under high shear, even remove hydrophilic polymer tails from the NCO-containing particles. Regardless of which process dominates, exposure of NCO particles increases the likelihood of reaction with water, thus increasing the amount of CO₂ gas given off.

Because the amount of water available for isocyanate reactions is critical, we examined how solvent evaporation rates affect chemical reactions. Figure 8 shows weight loss measurements of 2-methoxymethyl ethoxypropanol in DDI water (A), polyester dispersion (B), and waterborne PUR (C), plotted as a function of time at 25°C and 20% RH. These results show that during the first eight minutes, the rate of evaporation of 2-methoxymethyl ethoxypropanol/water (solvent), polyester oligomer, and PUR are the same, thus indicating that this stage is controlled by the partial vapor pressure of the system. After this period, the 2-methoxymethyl ethoxypropanol/water and polyester components continue to evaporate at a rapid rate, while PUR levels off at approximately 55% solids. The slope change indicates a transition from partial vapor pressure to diffusion-controlled evaporation, at which point approximately 10% of the original water concentration remains in the film for extended periods.

Because NCO functional groups can react with water available from the surrounding environment, relative humidity is expected to have a significant effect on the rate of isocyanate consumption. Figure 9 illustrates the effect of relative humidity on reaction times, where reaction times are equivalent to 100% isocyanate consumption. Because NCO is able to react with water contained in the film and also water vapor from the environment, the NCO consumption rate is highest at 80% RH after 16 hr of reaction. Reduction of relative humidity increases the time for NCO to be depleted within the first 1.14 μm from both F-A and F-S interfaces. For example, at 20% RH, it takes 210 hr for all NCO groups to be consumed. At low relative humidities, there are less pathways for the NCO to react, thus prolonging the crosslinking time. It should be remembered that in this study we examine the NCO changes that occur within the first 1.14 μm from the F-A and F-S interfaces. Consequently, NCO concentration levels of the bulk may be higher and thus initiate the crosslinking times presented in Figure 9.

As indicated earlier, ATR FTIR spectroscopy can easily detect urethane and polycrurea formations. Both species exhibit overlapping bands due to the amide II stretching modes, which consist of NH bending and asymmetric stretching modes of CN. Using the maximum band intensity between the 1530-1560 cm⁻¹ region, the relative humidity influence on urethane and urea near the F-A and F-S interfaces was determined. This is illustrated in Figures 10A and B. Figure 10A shows how RH shifts the maximum of the 1552 cm⁻¹ band to 20% to 1559 cm⁻¹ at 80% RH. Similar behavior is observed at the F-S interface (Figure 10B). A shift of the amide II stretching mode reflects a transition from predominately urethane crosslinks at 20 and 40% RH to urea at 65% RH. Other studies have also detected urethane and urea vibrations at these wave numbers.
In an effort to determine relative amounts of polyurethane and polyurea, deconvolution using a maximum likelihood (ML) entropy approach was undertaken. Deconvoluted spectra were normally generated from the best estimation of a maximum probability approach using physical information about spectral features and statistical knowledge of the unknown number of overlapping bands. Figure 11 shows deconvolution of the 1580 to 1500 cm\(^{-1}\) region at the F-A interface after 16 hr under 20, 40, 65, and 80% RH. As the RH increases from 20 to 80%, the band at 1527 cm\(^{-1}\) decreases, while the 1550 cm\(^{-1}\) band increases. While the band at 1550 cm\(^{-1}\) is due to the amide II stretching modes of urea, the band at 1527 cm\(^{-1}\) is attributed to the amide II stretching modes of urethane. These changes are attributed to the formation of urea at higher RHs, resulting from the NCO reaction with water. Because NCO groups react with water at higher relative humidity, reactions with OH functional groups of a resin are suppressed, thus a decrease of the 1527 cm\(^{-1}\) band is observed.

Because solvent evaporation and partial vapor pressure influence crosslinking reactions, the NCO concentration was monitored under 20, 40, 65, and 80% RH as a function of time, distance from the F-A and F-S interface, and polarization spectra were collected to examine possible orientation changes near the interfaces. Figure 12 illustrates the isocyanate concentration changes over time at the F-A interface under different relative humidities. Again, as shown in Figure 9, NCO reactions are accelerated at higher RHs and slow down at low RHs. For example, at 20% RH, only a 28% decrease of isocyanate concentration within 21 to 46 hr is observed. It should be noted that these data were not collected until a coherent film could be removed from the substrate, and 80% RH for seven hours was required. Thus, only a 68% change in NCO concentration was detected. Since no changes in polarization experiments were detected, orientation of the functional groups is preferentially random.

Because PURs are subjected to different external environments, NCO consumption at the F-A and F-S interfaces was examined. Figure 13 illustrates the differences in the NCO concentration at 40% RH. As shown, higher concentrations of NCO are detected at the F-A interface. These results were obtained for all reaction times and agree with the data shown in Figure 10, where the intensity and wavenumber shifts for the amide II stretching modes are greater at the F-S interface, thus resulting in polyurea formation near the F-S interface. When the reactions are monitored between 10 to 36 hr at 40% RH, the NCO concentration difference between the F-A and F-S interfaces decreases from 47 to 9%. Previous studies concluded that the residual concentration of water present within the film enhances plasticization near the film-substrate interface, thus influencing isocyanate consumption.\(^{16,17}\)

Isocyanate consumption as a function of depth within the film at the F-A and F-S interfaces was examined also. Depth of penetration studies can be performed using ATR FTIR spectroscopy by changing the angle of incidence light enters an ATR crystal.\(^{16,17}\) Figure 14 summarizes the results of the depth profiling experiments conducted at the F-A interface under 65% RH. Again, as reactions progress, the NCO concentration decreases; and it appears that within the first few μm from the F-A interface, NCO remains constant. The same behavior was detected at the F-S interface, 0.65-1.14 μm, although the degree of the NCO consumption was different. This behavior examined for the polyester dispersion appears to be different when compared to our previous polycrylate emulsion studies, where a strong dependence as a function of distance from the F-A and F-S interfaces was detected. Relative changes in isocyanate
concentration over time for the polyester dispersion and polyacrylate emulsion are summarized in Figure 15.

At this point it is appropriate to compare waterborne polyester and polyacrylate studies. Previous studies on polyacrylate emulsions revealed stratification within 0.65 to 1.14 μm at both interfaces. However, polyester dispersion does not exhibit this behavior and equivalent weight difference between polyester and acrylate, 1140 and 3100 g/eq, respectively, is attributed for this behavior. As was shown in Figure 6, the rate of the NCO reaction may determine whether stratification is observed on the monitored time scale. Because NCO is consumed faster for the polyester crosslinked PUR, stratification does not occur within the first few μm from F-A and F-S interfaces. On the other hand, slower reacting acrylate system stratification within 0.65 to 1.14 μm at both interfaces is detected.

Figure 16 illustrates the changes in isocyanate concentration as a function of depth and RH after 16 hr of crosslinking. After 16 hr, NCO concentration levels at 40% RH are approximately 51% of the NCO concentration at 20% RH. As shown in Figure 16, the distance from the substrate has no effect on the NCO concentration as a function of RH for the polyester dispersion. All changes observed in Figures 14 and 16 are within the standard deviation for each sample.

Knowing the relative humidity, water retained in the film, and shear rates influence crosslinking reactions of WB PURs, it is appropriate to correlate structure-property relationships for PURs crosslinked at 20, 40, 65, and 80% RH. Conical mandrel flexibility (ASTM D 522) and reverse impact resistance (ASTM D 2794) show no changes as a function of RH, having the highest flexibility and reverse impact resistance at 1/8 in. and 110 in-lb, respectively. However, as illustrated in Figure 17, Tukon hardness reveals the effect of RH. As RH increases, the Tukon hardness decreases from 8 to 2.9, which is attributed to polyurea formation.

Because relative humidity induced structural changes of the WB PUR, dynamic mechanical thermal analysis (DMTA) was conducted. The results of DMTA analysis are illustrated in Figure 18 for a PUR specimen crosslinked at 40% RH. As seen, the maximum of the tan δ peak at 71°C is the glass transition temperature (Tg). The storage modulus (E') minimum in the rubbery plateau region at 100°C, the XLD was calculated as 3.8 x 104 mom/cm². Table 2 summarizes the Tg and XLD recorded for WB PUR films crosslinked at 20, 40, 65, and 80% RH. As expected, higher RH results in lower XLD, which is also reflected in hardness as well as molecular level spectroscopic measurements.

**CONCLUSIONS**

Factors that influence waterborne polyurethane film formation were examined using ATR FTIR spectroscopy at the F-A and F-S interfaces and correlated to macroscopic measurements. These studies show that polyurethane and polyurea are detected and relative humidity significantly influences the time and type of crosslinking reactions. NCO content at the F-A interface is higher than the F-S interface, and the depth profiling experiments from 0.65 to 1.14 μm reveal no stratification of NCO. However, increased polyurea content at deeper depths from both interfaces are detected. Solvent evaporation experiments showed a solvent evaporation-controlled stage within the first eight minutes of reaction time at 20% RH. After this period, the process is diffusion controlled, where approximately 10% of the original concentration of water remains in the film for extended periods.

WB PUR exhibits shear thinning behavior and increased shear rates generate higher CO2 contents during the film formation, ultimately leading to a viscosity decrease. These data suggest that NCO particles have a greater tendency for interactions with water under high shear rates. A comparison of polyester dispersion and polyacrylate emulsion polyurethanes shows different stratification profiles of the NCO. While polyester urethane consumes NCO faster due to differences in equivalent weight, this process may diminish stratification processes observed for slower reacting polyacrylate polyurethanes. Relative humidity also has an influence on macroscopic properties. Although no differences were detected for flexibility and reverse impact resistance tests, most likely due poor sensitivity of these measurements, Tukon hardness decreased for PUR films crosslinked at higher RHs. These results agree with DMTA data, which showed that for films crosslinked at higher RH, the Tg and XLD are lower due to polyurea formation. Since it is

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Table 2 - Tg, and XLD of WB PUR Film Crosslinked at 20, 40, 65, and 80% RH

<table>
<thead>
<tr>
<th>WB-PUR film crosslinked at:</th>
<th>Tg (°C)</th>
<th>Crosslink Density (mol/cm²) calculated at 100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% RH</td>
<td>70.8</td>
<td>5.2 x 10⁴</td>
</tr>
<tr>
<td>40% RH</td>
<td>71.1</td>
<td>3.8 x 10⁴</td>
</tr>
<tr>
<td>65% RH</td>
<td>68.2</td>
<td>3.1 x 10⁴</td>
</tr>
<tr>
<td>80% RH</td>
<td>68.1</td>
<td>1.8 x 10⁴</td>
</tr>
</tbody>
</table>
apparent that urethane film formation is sensitive to environmental effects, our future studies will involve the effect of substrates on their film formation.31

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References
