Interfacial Studies of Crosslinked Urethanes: Part IV. Substrate Effect on Film Formation in Polyester Waterborne Polyurethanes

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INTRODUCTION

Although recent studies on solventborne urethanes (PURs) examined the effect of surface tension on reorientation and molecular interactions at the film-substrate (F-S) interface,[1,2] and these data showed that urethane H-bonded C=O groups exhibit preferential orientation which is a function of substrate surface tension, there are other factors to be considered. As a matter of fact, in the early 90s we showed[3] that a substrate surface tension may significantly influence stratification processes in coatings and migration of molecular entities during the film formation.[4,5] These issues are particularly relevant for aqueous-based coatings systems, as numerous latex studies indicated their importance in surfactant mobility,[6-10] film formation of waterborne coatings,[11,12] and high solids.[3] Because urethanes may exhibit excessive hydrogen-bonding characteristics, especially in waterborne systems, it is essential to understand their behavior in a context of external factors, such as surface tension of a substrate. In view of these considerations and to expand the scope of previous urethane studies,[18,19] we examined how waterborne PUR crosslinking can affect their film formation. While recent waterborne (WB) studies[20,21] examined isocyanate (NCO) concentration changes as a function of crosslinking, in this study we attempted to elucidate how substrate surface tension may influence stratification processes. These issues are particularly important for WB PURs since crosslinking reactions and orientation of surface species may affect many interfacial properties.[20] Utilizing attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy, combined with other surface techniques, we attempted to analyze interfaces and orientation effects that occur during film formation of WB PUR.

These studies examine the effect of substrate surface tension on crosslinking reactions in waterborne polyurethanes (PUR) applied to tin-plated steel, steel, polypropylene (PP), thermoplastic olefin (TPO), and glass. The results show that, relative to tin-plated steel, removal of tin-plating from a steel substrate increases isocyanate (NCO) consumption by 42% near the film-substrate (F-S) interface. When PUR is allowed to crosslink on steel, PP, TPO, and glass, the NCO concentration is greater at the film-air (F-A) interface. Furthermore, crosslinking reactions result in a greater amount of urea-hydrogen bonded species near the F-S interface for all substrates. While an increase of substrate surface tension decreases the amount of urea-hydrogen bonded carbonyl groups near the F-S interface, TPO was found to exhibit different behavior due to talc stratification near the surface. In this case, the presence of talc in WB-PUR coatings or thermoplastic substrates decreases the amount of hydrogen-bonded species and increases NCO consumption.

EXPERIMENTAL

A polyester resin dispersion (XP-7093) and a hydrophilically modified aliphatic (HDI) polyisocyanate, 1,6-hexamethylene diisocyanate (NCO) (XP-7063) were supplied by the Bayer Corp. Typical properties of XP-7093 resin are as follows: average acid number is 51, OH number is 49, and pH 7-8. An additive based on polyester modified dimethylpolysiloxane (BYK-346) was supplied by BYK-Chemie. The two-component waterborne polyurethane was formulated at an NCO:OH equivalent ratio of 2:1. The polyester resin dispersion was mixed with the flow agent additive 2-methoxymethylethoxypropanol (0.1 w/w%) at 48 rpm. Isocyanate and 2 mL of double deionized water were added incrementally until a uniform dispersion was obtained after seven minutes of mixing. The formulation was allowed to settle

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for five minutes before casting onto tin-plated steel and steel panels, glass, polypropylene (PP), and thermoplastic olefin (TPO) at a wet film thickness of 75 µm. TPO and PP injection-molded plaques were supplied by Ford Motor Co., magnesium silicate (talc, $3MgO{\cdot}4SiO_2{\cdot}H_2O$) was obtained from Mallinckrodt, and tin-plated steel panels were purchased from Q-Panel Lab Products. Steel panels were prepared by rubbing tin-plated steel panels with a cotton, which removed a portion of the tin, exposing the bare steel. The films were allowed to crosslink at 25°C under 65% relative humidity (RH) conditions. Samples were removed periodically from the substrate for spectroscopic analysis either by peeling or using an Hg amalgamation method. An approximate dry film thickness was 19 µm ± 2 µm.

Spectral acquisition and analysis were described elsewhere.[20] Scanning electron micrographs (SEM) were acquired on the surface of the substrate using a scanning electron microscope (JEOL 6300 V) which was fully integrated with an energy dispersive X-ray (EDX) (Noran Voyager II) microanalysis system. Atomic force microscopy (AFM) data were obtained using contact AFM (Eastern Michigan University).

RESULTS AND DISCUSSION

The first step in this analysis was to identify relevant spectral features responsible for the PUR film formation. *Figure* 1 shows transmission FTIR spectra of 2-methoxy-

Table 1—Tentative FTIR and FT-Raman Band Assignments for Waterborne Polyester, HDI Isocyanurate, 2-Methoxymethylethoxypropanol, Polyurethane and Polyurea

Band	Wavenumber (cm^{-1})							
Assignment	Waterborne Polyester		HDI Isocyanurate		2-methoxymethyl-ethoxypropanol		Polyurethane Polyurea	
	IR	Raman	IR	Raman	IR	Raman	IR	Raman
C-OH str.	3530				3440		3530	
N-H str.	3430						3370	
Overtone C=O	3214	3214						
ν_a C=C–CH_2		3082						3081
ν_a CH_3	2961	2967			2954	2966		2963
ν_a CH_2		2945	2939	2937	2933	2936	2936	2936
R_3C–H				2909		2909		
ν_s CH_2	2890	2890	2864	2861	2876	2876	2863	2870
C–H str. aldehyde					Shoulder	2829,2731		
NCO out-of-phase			2271				2271	
Free C=O str.			1760	1762			1780	1760
Free C=O str.	1729	1729					1726	1729
Free C=O str.			1690				1690	
C=O aldehyde					1658	1650		
C=C vinyl ether	1610	1613		1606			1610	1611
δ NH^{+2} salt	1580	1594						
δ N–H & ν_a C-N amide II (urea)			1511				1535	
δ CH_2	1464	1465	1465	1460	1455	1459	1464	1461
NCO in phase str.			1430	1435			1427	1442
C–H rock aldehyde					1415	1413		
δ–$C(CH_3)$	1386	1380	1374	1382	1375		1374	1374
δ N–H & ν_s C–N			1357		1352	1352		
NCO in-phase			1340	1336			1335	1330
CH_2 twist	1302	1312	1304	1314	1302	1293	1304	1307
(O=)C–O–C str.	1241	1248	1249	1241	1260	1264	1241	1245
ν_a C–N–C	1146		1143	1153				1156
C–C str.				1124		1124		
ν_a C–O–C		1083	1108	1099	1108	1126,1096	1097	1098
C–C ske.l vib.	1055	1056	1048	1043			1058	1069
C–C–O out-of-phase	996	1008				1005	994	1006
C–C skel. vib.		943	952		954	968	942	942
C–C–O in-phase		919		901		912		919
ν_s C–N–C			861	855			856	856
ν_s C–O–C	829	834	842	844	844	842	828	843
C–C–O in-phase		775	767		757	757	766	776
CH_2 in-phase-rock	729		732				731	
ν_s C–C_4		660		701,640		692,645		697,648
δ NCO			583					
δ C–O–C			431	438			428	438

ν_s = Symmetric stretch.
ν_a = Asymmetric stretch.
δ = Deformation.

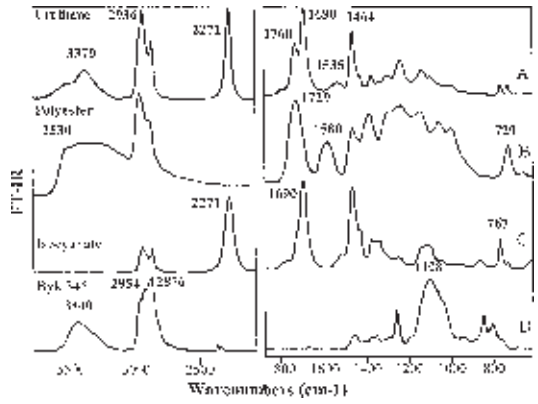

Figure 1—FTIR spectra of waterborne polyurethane (Trace A), polyester resin dispersion (Trace B), HDI isocyanurate (Trace C), and 2-methoxymethylethoxypropanol (Trace D).

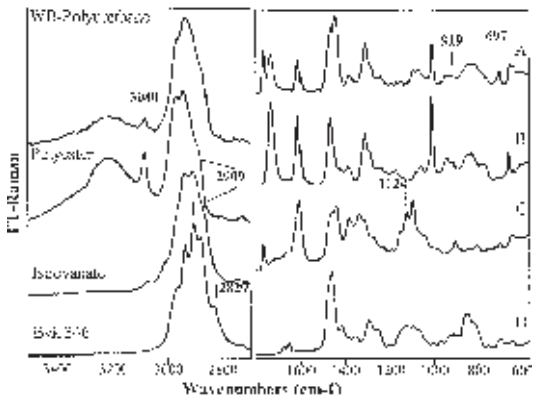

Figure 2—FT-Raman spectra of waterborne polyurethane (Trace A), polyester resin dispersion (Trace B), HDI isocyanurate (Trace C), and 2-methoxymethylethoxypropanol (Trace D).

methylethoxypropanol, HDI isocyanurate, polyester resin dispersion, and an ATR spectrum of WR PUR. Several bands of particular interest are labeled and their assignments are summarized in *Table* 1. Because FT-Raman spectroscopy provides complementary information to FTIR measurements, FT-Raman spectra of these components were recorded and are shown in *Figure* 2. Tentative band assignments are summarized in *Table* 2. The band assignments and changes of vibrational modes responsible for urethane crosslinking reactions have been detailed elsewhere.[20]

As shown in previous studies,[1,20,21] crosslinking reactions leading to PUR formation can be quantified by the decrease of NCO band intensity detected at 2271 cm^{-1}. This can be accomplished using the previously determined absorption coefficient of 822.9 L/mol•cm for the NCO band.[20,21] As we recall previous studies, polyester-based PURs exhibit higher concentrations of isocyanate at the F-A interface.[20,21] Thus, the presence of tin-plating may influence the crosslinking reactions at the F-S interface. To determine if the tin-plated steel substrate exhibits an effect on the distribution of isocyanate, the top layer of tin was removed from the substrate. As illustrated in *Figure* 3, removing the tin layer and exposing bare steel changes the rate of crosslinking reactions. It appears that after 15 hr, for films crosslinked under 65% RH, at 0.92 µm from the F-S interface on tin-plated steel and steel substrates, the NCO concentration on the steel substrate is smaller than that of tin-plated steel. The removal of tin increases the consumption of isocyanate by about 42%. Although one could suspect that the presence of bare tin may accelerate crosslinking reactions, this is not the case.

Table 2—Approximate Surface Tension Values of TPO, PP, Tin-Plated Steel, and Glass

Substrate	Surface Tension (mN/m)
Thermoplastic olefin (TPO)[26]	26
Polypropylene (PP)[23]	28-30
Tin-plated steel[19]	~30
Glass[19]	~70

In an effort to elucidate the origin of NCO changes on steel and tin-plated steel substrates, and relate them to substrate surface morphology, scanning electron microscopy (SEM) and energy dispersive X-ray micro-analysis (EDX) were performed. *Figures* 4a and b illustrate SEM micrographs of steel with and without tin-plating. While the surface of tin-plated steel appears relatively uniform, when tin is removed, the surface exhibits a significantly larger surface area and different composition. To probe the surface topography and extent of surface roughness, contact atomic force microscopy was employed. *Figures* 5a and b illustrate AFM of tin-plated steel and steel. The scale magnitude of AFM images shown in *Figures* 5a and b indicates that tin-plated steel is significantly smoother with the range of 500 nm, whereas steel is about eight times rougher at the 4 µm range. Because roughening the surface of steel generates a larger surface area, the extent of reactions near the F-S interface

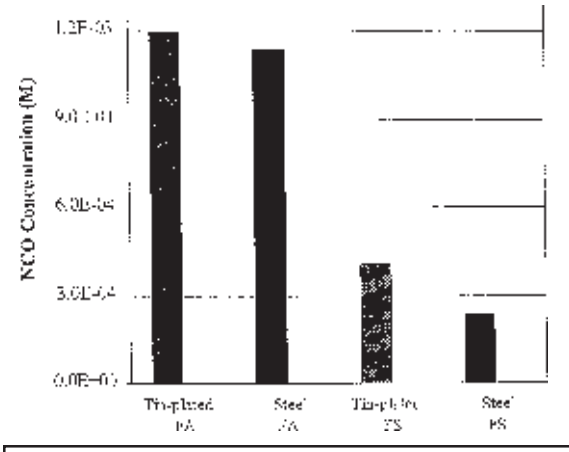

Figure 3—Isocyanate concentration changes near the F-A and F-S interfaces on tin-plated steel and steel substrates.

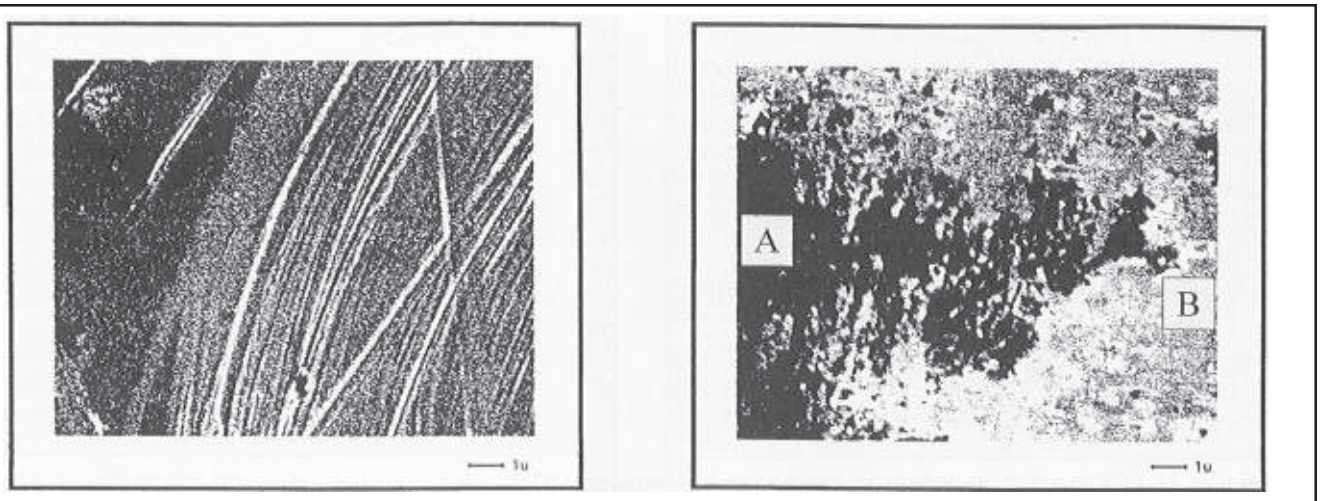

Figure 4a—A scanning electron micrograph of tin-plated steel; Figure 4b—Scanning electron micrograph of steel: A denotes steel and B denotes partial tin-plating.

increases. As we recall the results shown in *Figure* 3, there is a significant difference in isocyanate concentration among the substrates. Greater surface area allows for an increase in NCO consumption relative to tin-plated steel.

Although surface area effects may contribute to increased NCO consumption,[22] other factors should also be considered. For the purpose of this study, EDX was utilized to identify the makeup of surface species. While tin-plated steel panels are composed of C (48%), Sn (49%), and Fe (4%) atom %, washed steel panels contain 71% C, 19% Sn, and 10% Fe atom %, thus suggesting that crosslinking reactions may also be influenced by higher levels of iron and carbon, which may alter reactions with NCO.[17]

Since the substrate surface composition defines surface tension which may affect consumption of NCO, other substrates with a spectrum of different surface tensions were examined. While an approximate surface tension of the WB PUR is about 36 mN/m,[23] *Table* 2 summarizes the examined substrates and their surface tension. Analysis for NCO in WB PUR deposited on PP, TPO, and glass substrates showed no differences and was found similar to tin-plated steel, exhibiting a higher concentration of isocyanate at the F-A interface. Since surface tension does not seem to play a critical role on the NCO distribution, other functional groups were examined.

For that reason let us focus on the C=O region of the spectra, with the band at 1687 cm^{-1} attributed to free C=O groups of urea. Although it appears that this band remains unchanged at the F-A interface, when the F-S interface is examined, the situation changes. *Figure* 6 depicts the C=O region of WB PUR film crosslinked at 65% RH and cast onto glass, PP, TPO, and tin-plated steel substrates. The spectra were recorded 0.92 µm from the F-S interface using TM polarization. As seen, the band at 1687 cm^{-1} decreases as the surface tension of substrates increases. However, the exceptions are TPO, which does not follow the trend, and PP, which is the major component of TPO. In view of the data, let us first focus on these two substrates. Unlike TPO, PP exhibits an intense band due to isocyanate urea free carbonyl. This behavior is somewhat surprising since both sub-

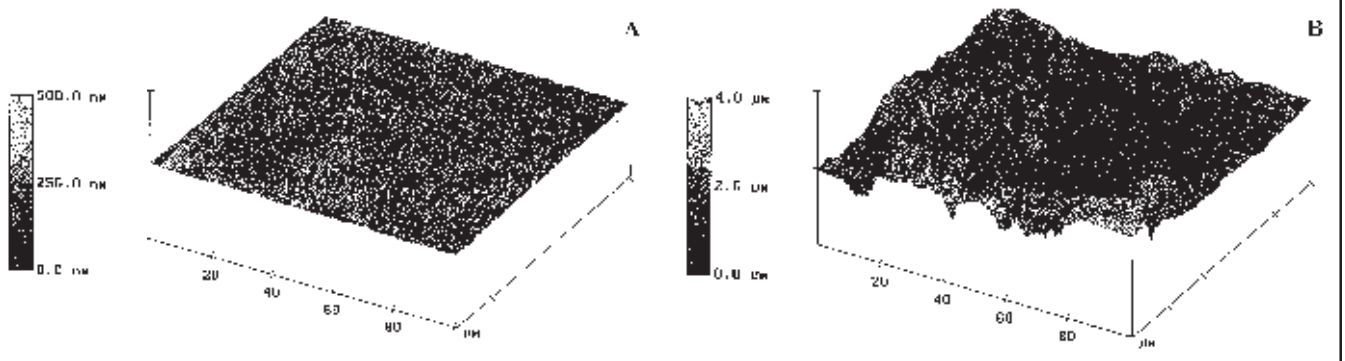

Figure 5a—Contact AFM of tin-plated steel: scale 0 to 500 nm; Figure 5b—Contact AFM of steel: scale 0 to 4 µm.

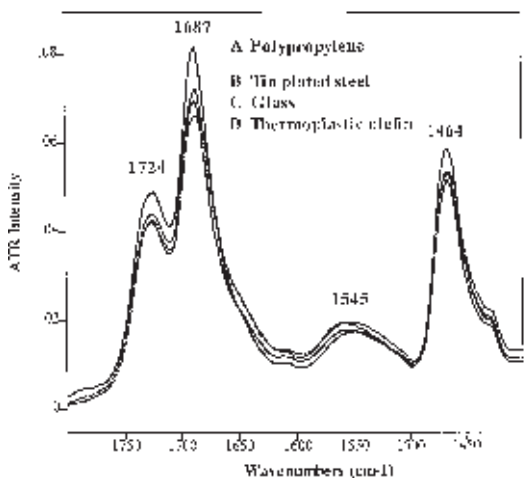

Figure 6—FTIR spectra of C=O region of waterborne polyurethane coated on polypropylene (Trace A), tin-plated steel (Trace B), glass (Trace C), and thermoplastic olefin (Trace D) substrates at the F-S interface, 0.92 µm depth, TM polarization, and 65% RH.

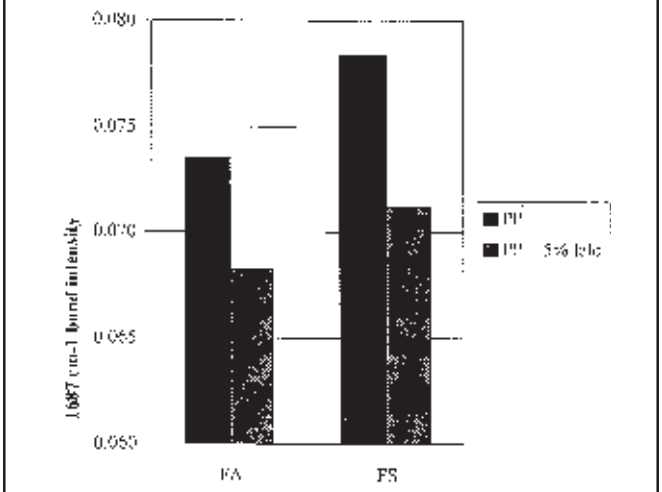

Figure 7—Intensity changes of the 1687 cm^{-1} band plotted as a function of F-A and F-S interface for waterborne polyurethane coated on polypropylene and propylene + 5% talc substrates.

strates exhibit similar surface tensions (PP, 28-30 and TPO 26 mN/m).[23,26] However, previous studies using photoacoustic (PA) FTIR spectroscopy identified stratification of components within TPO,[24] and showed that talc, which is one of the TPO components, stratifies near the surface layer within the first few µm from the surface.[24] Below the talc-rich surface, a crystalline PP region is present, followed by ethylene propylene rubber (EPR) and PP bulk regions.[24] This data suggests that talc stratification causes diminished intensity of the urea carbonyl in the WB PUR. This is illustrated in *Figure* 6, Trace D. Interestingly enough, the presence of talc stratification in TPO results in crosslinking of NCO groups similar to that of glass substrate (Trace C).

In an effort to confirm the effect of talc on crosslinking reactions near the TPO surface, PP substrate was doped with five percent talc, and PUR crosslinking reactions were compared on PP and five percent PP-talc substrates. Again, WB-PUR was cast onto these substrates, and the hydrogen-bonding carbonyl, isocyanate, and urea were monitored. *Figure* 7 illustrates the band intensity of the free carbonyl urea/isocyanate at 1687 cm^{-1} at both interfaces. It appears that reduction of urea/isocyanate is observed when talc is added to PP. This behavior is similar to TPO, illustrated in *Figure* 6, where talc stratifies near the surface and affects hydrogen bonding characteristics. Furthermore, the extent of urea/isocyanate is greater at the F-S interface, and adding talc minimizes this difference between the interfaces.

If indeed the presence of talc affects the extent of H-bonding, the next question is what is the effect of talc on isocyanate consumption. *Figure* 8 illustrates the NCO concentration differences for WB PUR cast onto PP and PP containing five percent talc substrates. As seen, the NCO concentration is greater at the F-A interface and its consumption is significantly higher for a PP specimen containing five percent of talc. These results are consistent with the decreasing intensity of the 1687 cm^{-1} band, and show that, although talc is incorporated into the PP substrate, its presence affects the NCO concentration at the F-A interface. Examination of the band due to urea at 1545 cm^{-1} revealed an increase of these species near the F-S interface, which results from five percent PP talc substrate.

Because the presence of talc exhibits a substantial influence on the NCO reactions, the effects were examined further. For that reason five percent of talc was formulated into WB PUR and similar analysis was performed. *Figure* 9 illustrates that the presence of talc alters NCO concentration levels at the F-A and F-S interfaces. As expected from the results presented in *Figure* 8, the

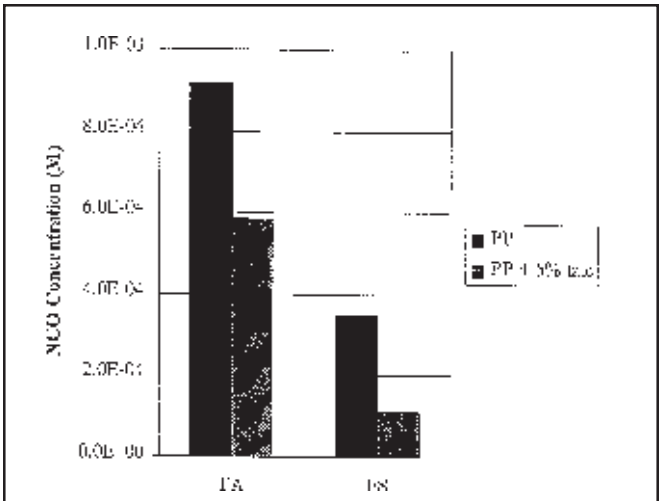

Figure 8—Isocyanate concentration of waterborne polyurethane coated on polypropylene and polypropylene + 5% talc substrate at the F-A and F-S interfaces.

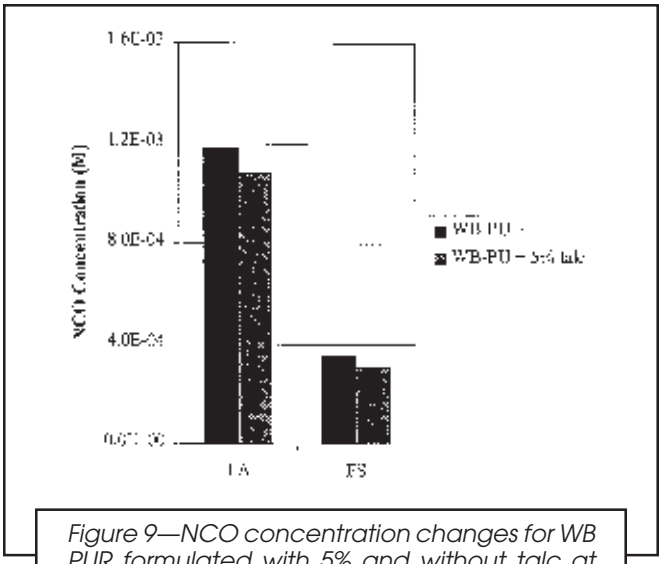

Figure 9—NCO concentration changes for WB PUR formulated with 5% and without talc at the F-A and F-S interfaces.

presence of talc enhances consumption of isocyanate reactions near the F-A and F-S interfaces, which most likely result from NCO reactions with OH and/or H_2O species on talc resulting in polyurea formation. This is supported by ATR FTIR surface depth profiling[25] experiments which revealed that, between 0.6 and 1.2 µm from the F-S interface, the 1687 cm^{-1} band intensities decreases, indicating that less urea is present while going deeper into a PUR film.

CONCLUSIONS

These studies show that substrates may significantly influence reactions and film formation near the F-A and F-S interfaces of organic coatings. Altering tin-plated steel surface decreases the NCO concentration near the F-S interface, thus accelerating crosslinking reactions due to larger surface area and likely catalytic effects of carbon in direct contact with the waterborne polyurethane coating. When crosslinking reactions are conducted on TPO, PP, and glass, which exhibit different surface tension, the extent of NCO reactions is also lower at the F-A interface. Consequently, a greater urea/isocyanate near the F-S interface is detected. For substrates with higher surface tension, a decrease of the urea/isocyanate groups appears to be apparent, with an exception of thermoplastic olefin, the latter being attributed to talc stratification near the TPO surface. For WB PUR formulated with talc, accelerated NCO consumption and increased urea concentrations are observed, thus the effect of pigment appears to be significant on urea/isocyanate ratio. Although it is quite apparent that additional studies are needed to fully understand substrate-coating interactions, especially the effect of surface tension and surface roughness, these experiments demonstrate that crosslinking reactions of waterborne polyurethanes are affected not only by a chemical makeup of a liquid polymer before crosslinking and environmental factors, but also substrate surface morphology and chemistry.

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References

(1) Kaminski, A.M. and Urban, M.W., "Interfacial Studies of Crosslinked Polyurethanes: Part I. Quantitative and Structural Aspects of Crosslinking Near Film-Air and Film-Substrate Interfaces in Solventborne Polyurethanes," JOURNAL OF COATINGS TECHNOLOGY, *69*, No. 872, 55 (1997).
(2) Ludwig, B.W. and Urban, M.W., "Quantitative Determination of Isocyanate Concentration in Crosslinked Polyurethane Coatings," JOURNAL OF COATINGS TECHNOLOGY, *68*, No. 857, 93 (1996).
(3) Urban, M.W. and Evanson, K.W., *Polymer Comm.*, 31, 279 (1990).
(4) Hirayama, T. and Urban, M.W., *Prog. Org. Coat.*, 20, 81 (1992).
(5) Tebelius, L.K., Stetz, E.M., and Urban, M.W., *J. Appl. Polymer Sci.*, 62, 1887 (1996).
(6) Tebelius, L.K. and Urban, M.W., *J. Appl. Polymer Sci.*, 56, 387 (1995).
(7) Thorstenson, T.A., Evanson, K.W., and Urban, M.W., *Advances in Chem. Series 236*, Urban, M.W. and Craver, C.D. (Eds.), American Chemical Society, Washington, D.C., 1993.
(8) Chu, A.P., Tebelius, L.K., and Urban, M.W., ACS Symposium Series, Glass, J.E. (Ed.), American Chemical Society, Washington, D.C., 1997.
(9) Niu, B.-J., Martin, L., Tebelius, L., and Urban, M.W., *Film Formation in Waterborne Coatings*, Provder, T., Winnik, M., and Urban, M.W. (Eds.), ACS Symposium Series 648, American Chemical Society, Washington, D.C., 1996.
(10) Niu, B.-J. and Urban, M.W., *J. Appl. Polymer Sc*i., 60, 379 (1996).
(11) Niu, B.-J. and Urban, M.W., *J. Appl. Polymer Sci.*, 60, 389 (1996).
(12) Niu, B.-J. and Urban, M.W., *J. Appl. Polymer Sci.*, 60, 371 (1996).
(13) Srichatrapimuk, V.W. and Cooper, S.L., *J. Macromol. Sci.-Phys.*, B15(2), 267 (1978).
(14) Ishihara, H., Kimura, I., Saito, K., and Ono, H., *Macromol. Sci. Phys.*, B10, 591 (1974).
(15) Estes, G.M., Seymour, R.W., and Cooper, S.L., *Macromolecules*, 3, 579 (1970).
(16) *Polyurethane Handbook*, Oertel, G. (Ed.), Hanser Publishers, Munich, Germany, 1985.
(17) Saunders, J.H. and Frisch, K.C., *Polyurethanes Chemistry and Technology*, Vol. 1, Interscience, New York, 1962.
(18) Dvorchak, M.J., "Using High Performance Two-Component Waterborne Polyurethane Wood Coatings," JOURNAL OF COATINGS TECHNOLOGY, *69*, No. 866, 47 (1997).
(19) Bui, H., Dvorchak, M., Hudson, K., and Hunter, J., *European Coat. J.*, Vol. 5, pp. 476-481 (1997).
(20) Urban, M.W., Allison, C.L., Finch, C.C., and Tatro, B.A., "Interfacial Studies of Crosslinked Urethanes: Part III. Structure-Property Relationships in Polyester Waterborne Polyurethanes," JOURNAL OF COATINGS TECHNOLOGY, *71*, No. 888, 75 (1999).
(21) Kaminski, A.M. and Urban, M.W., "Interfacial Studies of Crosslinked Urethanes: Part II. The Effect of Humidity on Waterborne Polyurethanes; A Spectroscopic Study," JOURNAL OF COATINGS TECHNOLOGY, *69*, No. 873, 113 (1997).
(22) Katti, K. and Urban, M.W., in preparation.
(23) Brandrup, J. and Immergut, E.H., *Polymer Handbook*, Third Edition, John Wiley & Sons, New York, 1989.
(24) Pennington, B.D. and Urban, M.W., *Polymer*, 1999, in press.
(25) Urban, M.W., *Attenuated Total Reflectance Spectroscopy of Polymers, Theory and Practice*, American Chemical Society, Washington, D.C., 1996.
(26) Ryntz, R., private communication.