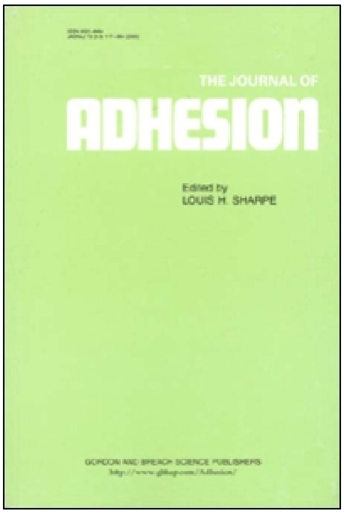

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The adhesion of isocyanate-based polymers to steel

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THE ADHESION OF ISOCYANATE-BASED POLYMERS TO STEEL

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Isocyanate-based materials have been used for decades as the basis for high performance adhesives, coatings, and primers. The origin of the excellent adhesion of these materials to metals such as steel has been generally assumed to derive from the condensation of isocyanates with metal hydroxyls to form metal oxide-cyanate esters analogous to urethanes. In this work Fourier transform infrared reflection (FTIR) was used to demonstrate that these esters do indeed form, but that the esterification is preceded by the formation of carbamate salts between the isocyanate and the hydrated metal oxide.

Keywords: Isocyanate; pMDI; Polyurethane; Steel; Adhesion; Interface

INTRODUCTION

Polyurethanes have been recognized as superior adhesives for metal bonding since the 1940s [1]. This characteristic of excellent adhesion to metal oxide surfaces has resulted in successful application of urethanes as structural adhesives, as primers for rubber to metal bonding, and as vehicles for high performance paints.

The high reactivity of isocyanates with active hydrogens is the basis of urethane synthesis. Polymerization proceeds by the reaction of a diisocyanate and a diol to form a carbamate (or urethane) linkage:

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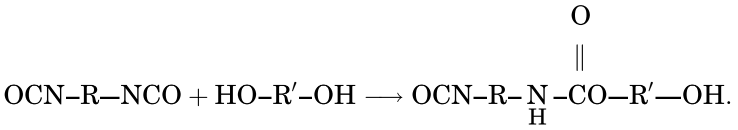
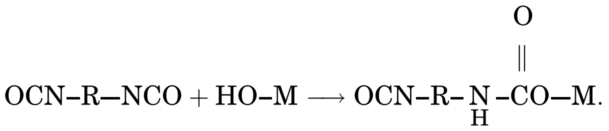


$$\mathrm{OCN{-}R{-}NCO + HO{-}R'{-}OH \longrightarrow OCN{-}R{-}\underset{H}{N}{-}\overset{\overset{O}{\|}}{C}O{-}R'{-}OH.}$$

The resulting polymer is rich in polar functional groups that are potentially capable of strong interaction with a metal oxide surface to provide excellent adhesion. However, it has been proposed [2–4] that isocyanate groups are also capable of condensation with metal hydroxyls to form a carbamate ester and that this reaction could be at least partially responsible for adhesion of prepolymers containing unreacted isocyanate to metal hydroxides:



$$\mathrm{OCN{-}R{-}NCO + HO{-}M \longrightarrow OCN{-}R{-}\underset{H}{N}{-}\overset{\overset{O}{\|}}{C}O{-}M.}$$

Analytical results supporting this mechanism of isocyanate-metal adhesion are difficult to find in the literature. One study [4] used X-ray Photoelectron Spectroscopy (XPS) to analyze the structure of the interface formed between polished steel and a moisture-cured polyurethane resin. There was evidence for strong interaction with the metal surface. Fe (0) was oxidized to Fe (III) and was incorporated into an interphase several nanometers thick. Although the data were not unequivocal, the C(1s) spectra were consistent with formation of a metal carbamate ester in this interphase region.

One of the most commercially important diisocyanates is diphenylmethane 4, 4′-diisocyanate (MDI). It is typically synthesized *via* a two-step process beginning with the condensation reaction between aniline and formaldehyde, yielding diphenylmethane diamine. A subsequent phosgenation gives the aromatic isocyanate MDI. Typically a mixture of MDI and various dimeric and trimeric isomers is formed, which is called polymeric MDI, or pMDI. Figure 1 shows the composition of a typical pMDI. This product is used with appropriate comonomers for manufacture of rigid and semirigid polyurethane foams. pMDI also sees wide application as a high-performance binder for products such as oriented strand board (OSB). Pure MDI distilled from the reaction mixture is mainly used for reaction injection-molding, thermoplastic elastomers, and adhesives.

During the manufacture of OSB, wood flakes are sprayed with pMDI and then pressed at elevated temperature. Under these conditions, pMDI reacts with hydroxyls in the cellulose to form urethane linkages.

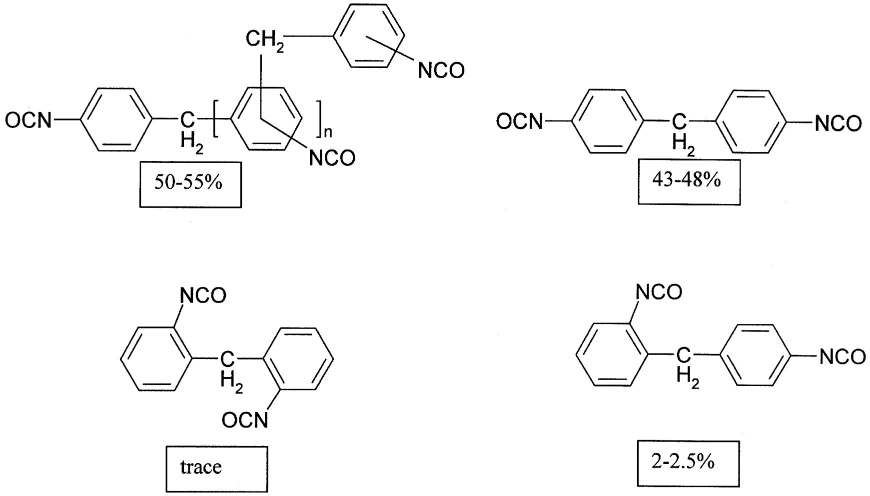
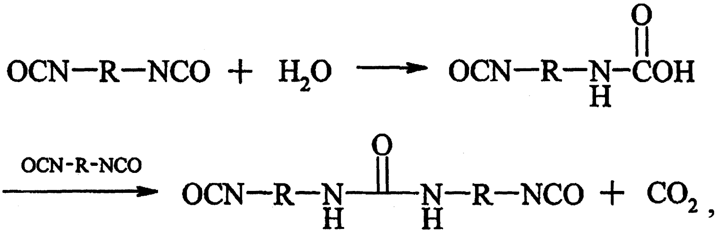


FIGURE 1 Composition of typical polymeric diphenylmethane 4, 4′-diisocyanate (pMDI).

Moisture present in the wood flakes also results in hompolymerization of the pMDI to form urea polymers through the following reaction:



$$\mathrm{OCN{-}R{-}NCO} + \mathrm{H_2O} \longrightarrow \mathrm{OCN{-}R{-}\underset{H}{N}{-}\overset{\overset{O}{\|}}{C}OH}$$

$$\xrightarrow{\mathrm{OCN\text{-}R\text{-}NCO}} \mathrm{OCN{-}R{-}\underset{H}{N}{-}\overset{\overset{O}{\|}}{C}{-}\underset{H}{N}{-}R{-}NCO} + \mathrm{CO_2},$$

and the resulting engineered wood product contains both urethane and urea linkages [5–8]. Mold release technology is critical in the manufacture of these materials, as adhesion of the wood composite to the mold platens can be substantial.

In the current study, we have been interested in developing an understanding of the interactions between pMDI and the oxide on steel surfaces that occur during a typical molding cycle in OSB manufacture. There are several possible mechanisms of interaction between oxides on steel and pMDI that could result in strong adhesion:

1. *Strong dipole-dipole interactions between pMDI and the oxide*. This is a physisorption mechanism that would result in no permanent chemical change to the pMDI, but could produce measurable band shifts in the Fourier-transform infrared (FTIR) spectra due to changes in the bond force constants. With this mechanism, sorption could occur through the isocyanate end-groups. As some urethane linkage is detected in the as-received pMDI, sorption could potentially occur through these groups as well. Any adsorbed isocyanate groups would remain chemically unaltered.
2. *Degradation of the pMDI followed by chemisorption or physisorption of the degradation products*.
3. *Condensation of the isocyanate group present in pMDI with hydroxyls in the iron oxide*. Given the reactivity of isocyanates with active hydrogens, this is the mechanism most often cited in the literature [2–4]. However, until now it has not been conclusively demonstrated to occur.

Distinguishing between these three potential mechanisms of adhesion in the residue left on a mold surface is difficult due to the necessity of separating reactions occurring within the bulk of a film of pMDI and pMDI/wood reaction products (many molecular layers thick) from those occurring immediately next to the oxide surface. This is compounded by the fact that pMDI is a complex technical-grade mixture of isomers. Because of this, unequivocal interpretation of the spectra of reaction products within thin films of pMDI on metal surfaces is difficult. To aid in understanding these interactions, sorbed films of appropriate low molecular weight model compounds were chosen to probe the reactivity between the oxide on polished steel and specific functional groups. To this end, clean, reflective steel surfaces were exposed to solutions of these compounds at various temperatures. Grazing angle reflection infrared spectra of these substrates were obtained before and after exposure to probe the nature of the chemical interactions. The results showed that aromatic amines and ureas sorb to the iron surface with no detectable chemical interaction. However, isocyanates chemisorbed to the oxide at low temperatures through the formation of a carboxylate salt. Additional heat during sorption resulted in the formation of detectable amounts of urethane, probably from addition of the isocyanate to the metal hydroxide. These results suggest that the strong adhesion of isocyanate-based urethanes to steel may result at least in part from the chemisorption of isocyanate to form both ionic and covalent bonds with the oxide surface.

EXPERIMENTAL

Model compounds obtained from Aldrich Chemical Co. (Milwaukee, Wisconsin, USA) included 4-ethyl aniline, diphenyl urea, and 4-ethylphenyl isocyanate. The pMDI used was a fresh sample obtained from Huntsman Polyurethanes (West Deptford, New Jersey). The container was stored in a desiccator after opening to prevent reaction with atmospheric moisture. Samples for transmission FTIR spectra were obtained by pressing a pellet composed of a small amount of the model compound blended with KBr.

Reactions between model compounds and polished steel coupons were investigated at several temperatures. Room temperature interactions were studied by immersing freshly polished steel in dilute solutions of the model compounds for approximately 15 min. The coupons were then thoroughly rinsed with fresh solvent prior to analysis. Interactions at elevated temperatures were studied by refluxing the coupons in dilute solutions of the model compounds. Interactions with isocyanate at temperatures above the solvent boiling point were studied by heating the coupons to 150°C while immersed in pure model compound. The coupons were then Soxhlet extracted for at least 1 h to remove any unreacted compound.

HPLC toluene was used as the solvent for 4-ethyl aniline and 4-ethylphenyl isocyanate; diphenyl urea was dissolved in acetonitrile, as it is insoluble in toluene.

Fresh glassware was thoroughly washed until it passed the water wetout test. Cleaned samples were handled only with stainless steel tweezers. Fresh disposable polyethylene gloves were worn at all times by the analyst.

Steel substrates were prepared by degreasing 1” × 3” (2.5 × 7.6 cm) 1018 steel coupons in acetone, then polishing through 1200 grit SiC abrasive paper and deionized water and blowing dry with compressed air after rinsing. This provided a highly reflective surface that was water-break free. XPS analysis of coupons prepared in this manner confirmed the cleanliness, and typically showed about 15 at% carbon. These were used immediately after polishing to minimize contamination from airborne hydrocarbons. In some instances, polished coupons were further cleaned using a 30 sec/30 watt air plasma in a Harrick Scientific PDC-3XG inductively coupled plasma cleaner (Hartick Scientific Corp., Ossining, New York, USA).

Infrared spectra were obtained using a Nicolet 760 FTIR (Nicolet, Isenburg, Germany) equipped with a FTS-85 grazing angle reflection accessory. All spectra were collected at 4 cm^{-1} resolution and were obtained by averaging 1024 scans. The reflection spectra are presented as difference spectra, representing the spectral difference between the freshly prepared bare steel substrates and the same substrates after exposure to the compound of interest.

RESULTS AND DISCUSSION

4-Ethyl Aniline Interaction with Polished Steel

4-Ethyl aniline was chosen as a model for potential reaction intermediate in pMDI polymerization or as a product of urethane hydrolysis. Amines are capable of significant interaction with steel and are known corrosion inhibitors. Figure 2 shows the FTIR transmission spectrum of this compound. Because of the lone pair of electrons on the nitrogen atom, interaction with a hydroxylated metal oxide such as found on steel would be expected to be through hydrogen bonding. This would affect the strong bands near 3435 and 3360 cm^{-1} (the asymmetric and symmetric NH stretching modes) or the strong band near 1624 cm^{-1} (the NH_2 deformation mode).

Figure 3 is the reflection spectrum obtained from the steel surface after exposure to 4-ethyl aniline in toluene followed by thorough rinsing. This spectrum shows no significant absorbance, indicating little sorption and little, if any, interaction between aniline and the oxide on steel under these conditions.

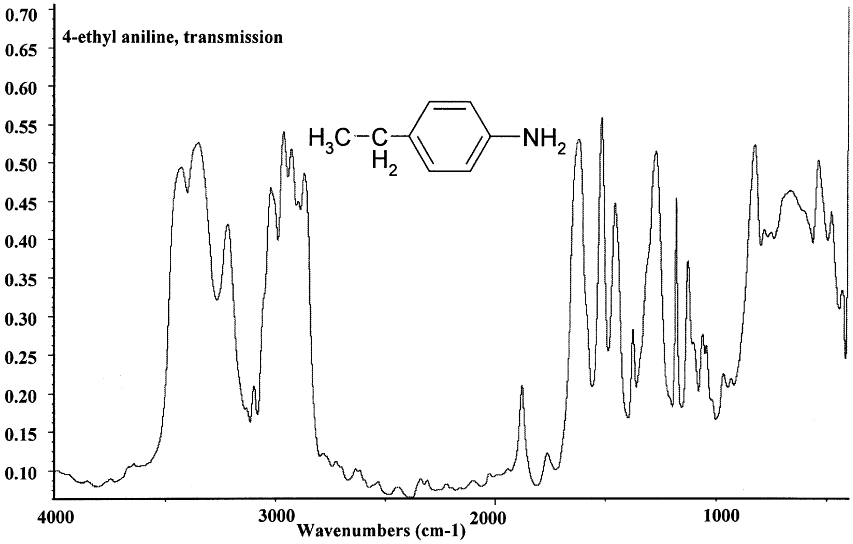


FIGURE 2 Transmission FTIR spectrum of 4-ethyl aniline.

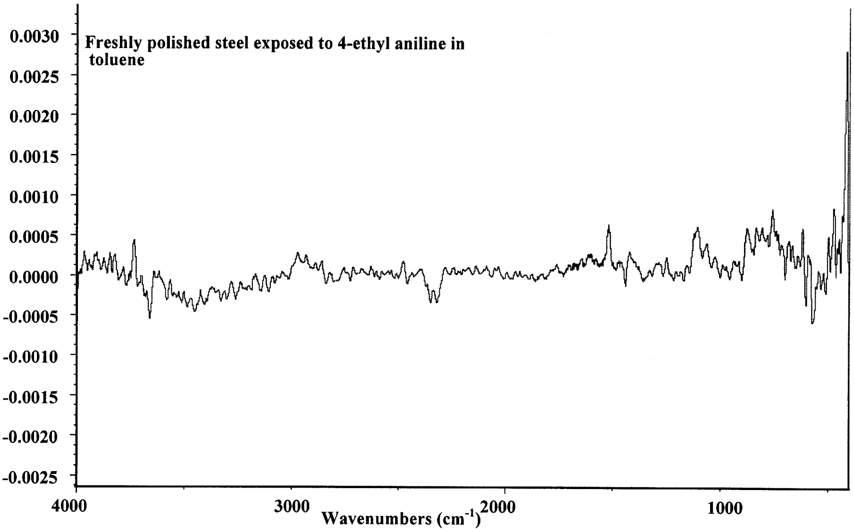


FIGURE 3 Reflection FTIR spectrum of steel exposed to dilute 4-ethyl aniline in toluene followed by rinsing.

Diphenyl Urea Interaction with Polished Steel

Ureas are a reaction product found in wood-pMDI composites, mold surface residues, and the surface residue on steel heated in pMDI. Figure 4 shows the transmission FTIR spectrum of diphenyl urea. The presence of two N–H bands (3330 and 3282 cm^{-1}) shows that this material is intermolecularly hydrogen bonded in the liquid state. The strongest band in the spectrum (1650 cm^{-1}) is due to the urea carbonyl.

Figure 5 is the spectrum obtained from freshly polished steel exposed to dilute diphenyl urea/acetonitrile (20 mg/100 ml). The strong characteristic bands are still readily identifiable and, although the relative intensities are different, the peak positions remain unchanged. The urea carbonyl band at 1650 cm^{-1} is weaker while the N–H band at 1570 cm^{-1} is now the strongest band in the spectrum. The C–N stretching band near 1239 cm^{-1} is likewise increased in intensity. While these changes in relative intensity suggest that the urea is adsorbed to the oxide with a preferential orientation, the frequencies remain unchanged. Although a significant amount of diphenyl urea remains adsorbed to the oxide surface, neither degradation nor chemisorption has occurred.

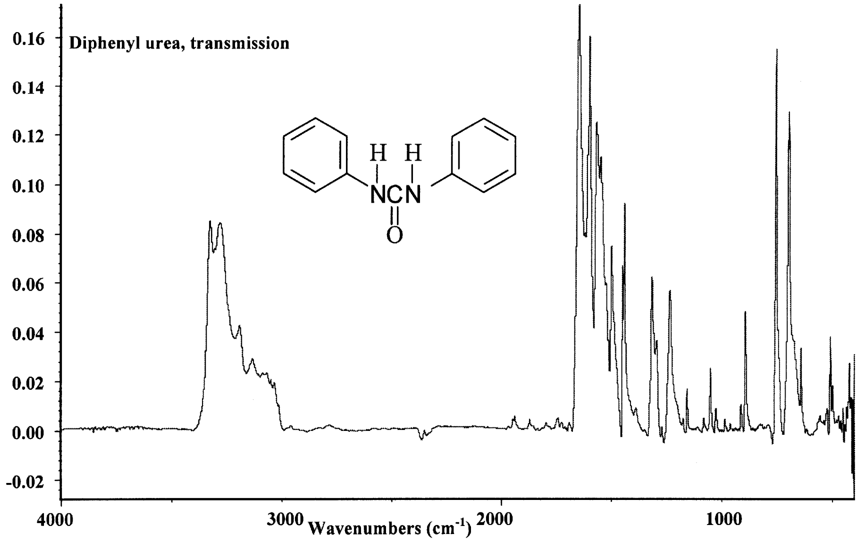


FIGURE 4 Transmission FTIR spectrum of diphenyl urea.

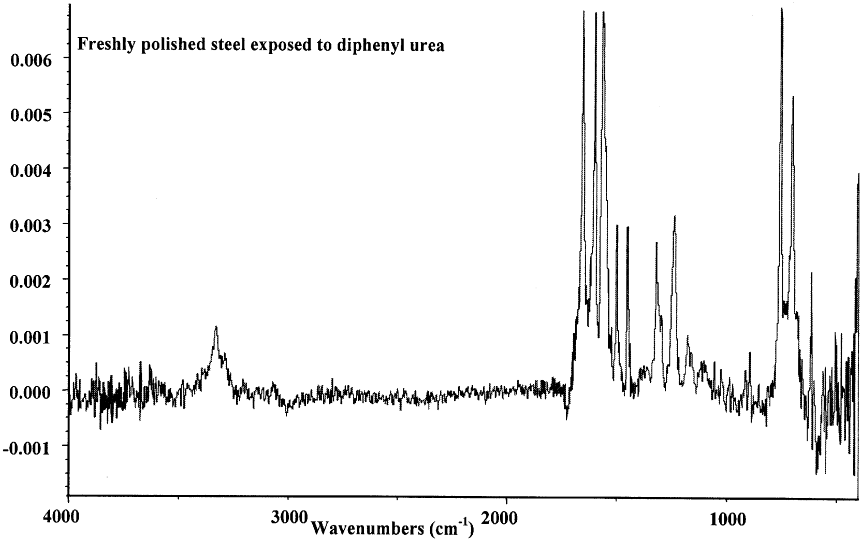


FIGURE 5 Reflection FTIR spectrum of steel exposed to dilute diphenyl urea in acetonitrile followed by rinsing.

4-Ethylphenyl Isocyanate Interaction with Polished Steel

Room Temperature Sorption

Figure 6 shows the transmission spectrum of 4-ethylphenyl isocyanate, and Figure 7 shows the transmission spectrum of pMDI for comparison purposes. The similarity of the spectra confirms the utility of 4-ethylphenyl isocyanate as a model compound. The most noticeable difference between the spectra of the monofunctional model compound and the polymeric material is the band near 1740 cm^{-1} in the spectrum of pMDI of a due to carbonyl functionality. Reference to Figure 1 shows that no carbonyl should be present in this material, however.

The 1740 cm^{-1} peak in neat pMDI is at the right frequency to represent condensation of some of the isocyanate to form urethane. However, because many isocyanate-derived compounds such as biuret and uretonimine absorb in this region peaks between 1640 and 1745 cm^{-1} can be difficult to assign.

Notice the relatively weak bands near 1460 and 1376 cm^{-1}. These are due to the CH_2 and CH_3 asymmetric and symmetric deformations, respectively. The sharp, weak band between these two bands near 1421 cm^{-1} is a band characteristic of substituted phenyls.

Some interaction between 4-ethylphenyl isocyanate and steel is evident after a room temperature exposure. Figure 8 shows the reflection spectrum obtained from a polished steel mirror that was

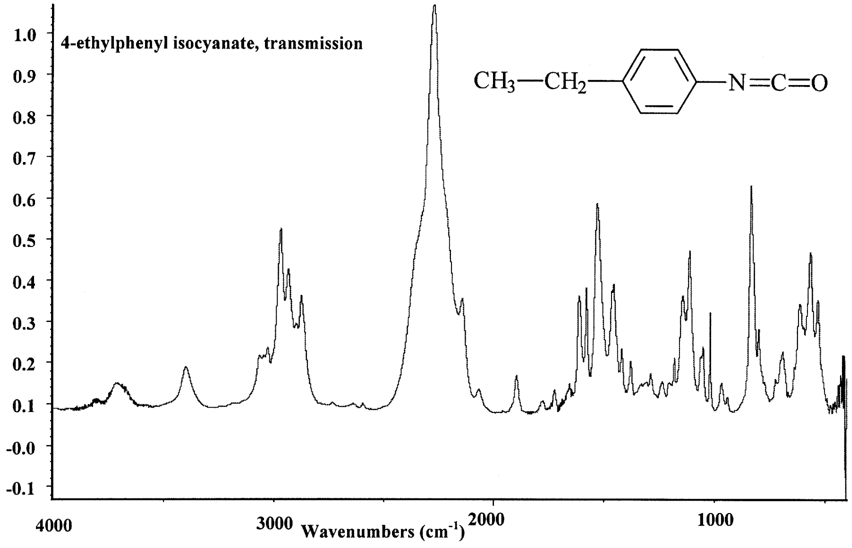


FIGURE 6 Transmission FTIR spectrum of 4-ethylphenyl isocyanate.

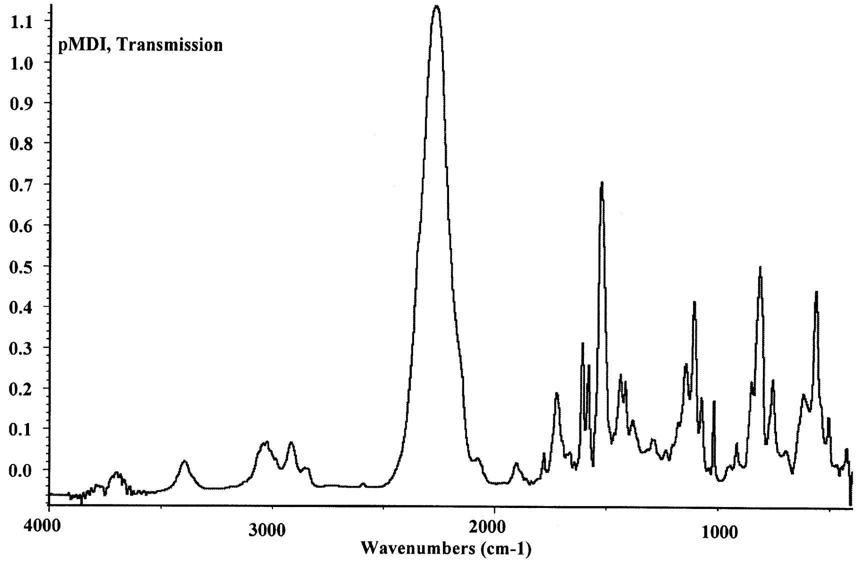


FIGURE 7 Transmission FTIR spectrum of pMDI.

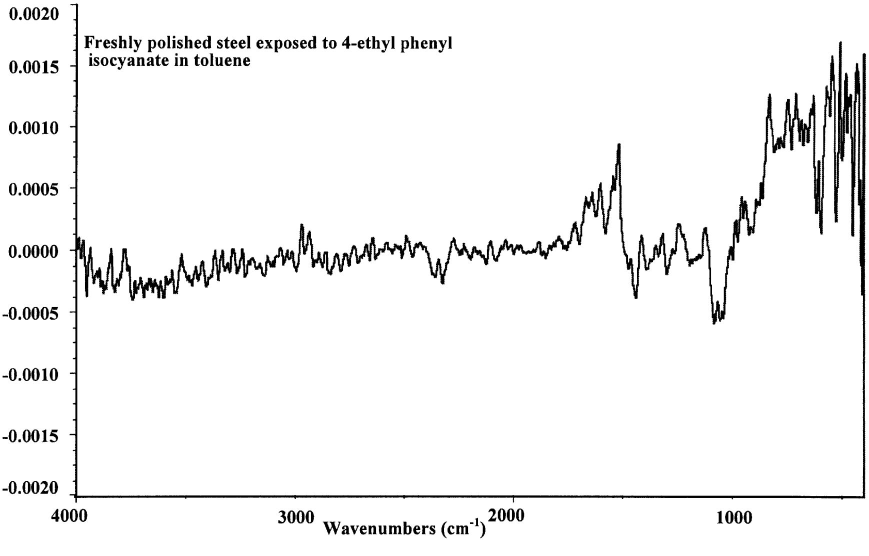


FIGURE 8 Reflection FTIR spectrum of polished steel exposed to dilute 4-ethylphenyl isocyanate in toluene followed by rinsing.

exposed to a dilute solution in toluene and then rinsed. The strongest phenyl band near 1525 cm^{-1} is visible, showing that there has been some adsorption. But there is no evidence of residual isocyanate groups at 2273 cm^{-1}. This is the strongest band in the transmission spectrum. The compound appears to have chemisorbed to the oxide surface with loss of the isocyanate. The amount of adsorbed material is very small, and the products resulting from reaction of the isocyanate are not readily identifiable from this spectrum due to low signal-to-noise ratio.

This sorption experiment was repeated on polished steel that had been plasma cleaned to ensure that residual contaminants were not preventing sorption. The results are shown in Figure 9. This spectrum is essentially identical to the spectrum shown in Figure 8. Very little sorption occurred, and the sorbed species contains no isocyanate.

Sorption of isocyanate-containing compounds at higher temperatures increased the amount of sorbed material and permitted identification of the reaction products, as discussed below.

Sorption at Reflux Temperature (110°C)

To determine if higher temperatures affected the sorption process, a polished steel coupon was immersed in a dilute solution of 4-ethyl isocyanate in toluene and refluxed for 30 min at the boiling point of

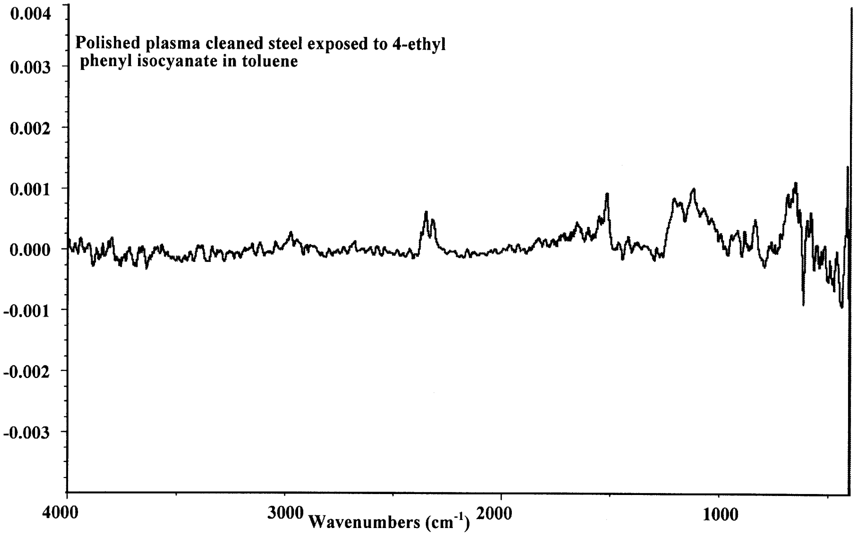


FIGURE 9 Reflection FTIR spectrum of polished, plasma-cleaned steel exposed to dilute 4-ethylphenyl isocyanate in toluene followed by rinsing.

toluene (110°C). The reflection FTIR spectrum of this sample is shown in Figure 10. The spectrum is qualitatively similar to that obtained after room temperature exposure, but the features are slightly stronger, giving better clues as to the structure of the adsorbate. Notice the bands at 1424 cm^{-1} and 1550 cm^{-1}. These are not present in the transmission spectrum of the isocyanate (cf. Figure 6) and are characteristic of the in-phase and out-of-phase C–O stretching of the carbonyl in a metal carboxylate salt. These bands suggest that the chemisorption has occurred through formation of a carboxylate. Further experiments at higher temperature and with pMDI support this assignment and suggest that this is the primary chemical interaction between isocyanate and the oxide on steel.

Sorption at 150°C

To investigate the effect at higher temperatures, polished steel coupons were placed in a petri dish, covered with neat 4-ethylphenyl isocyanate, then heated in a convection oven at 150°C for 30 min. Samples were then removed from the petri dish and Soxhlet extracted in toluene for 1 h. The reflection FTIR spectrum from the resulting sample is shown in Figure 11. The higher signal-to-noise ratio of the spectrum shows that more organic material was retained on the

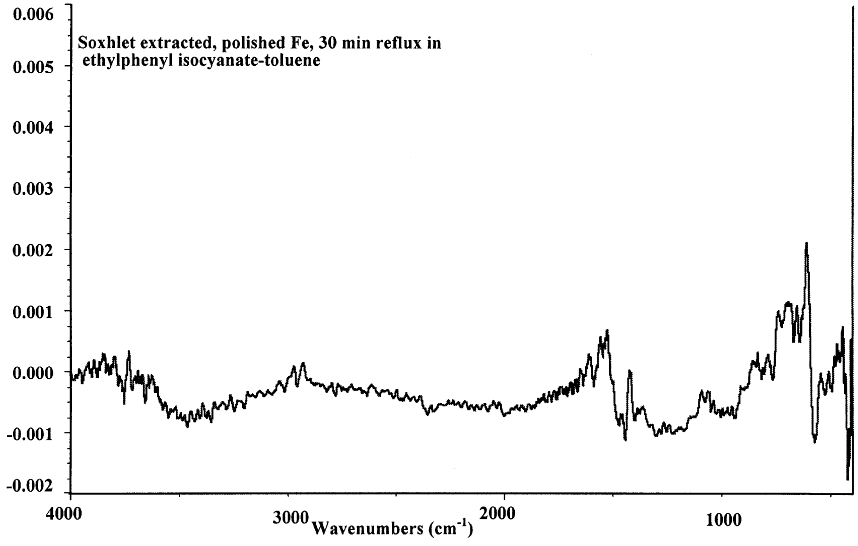


FIGURE 10 Reflection FTIR spectrum of polished steel refluxed in dilute 4-ethylphenyl isocyanate in toluene for 30 min followed by rinsing.

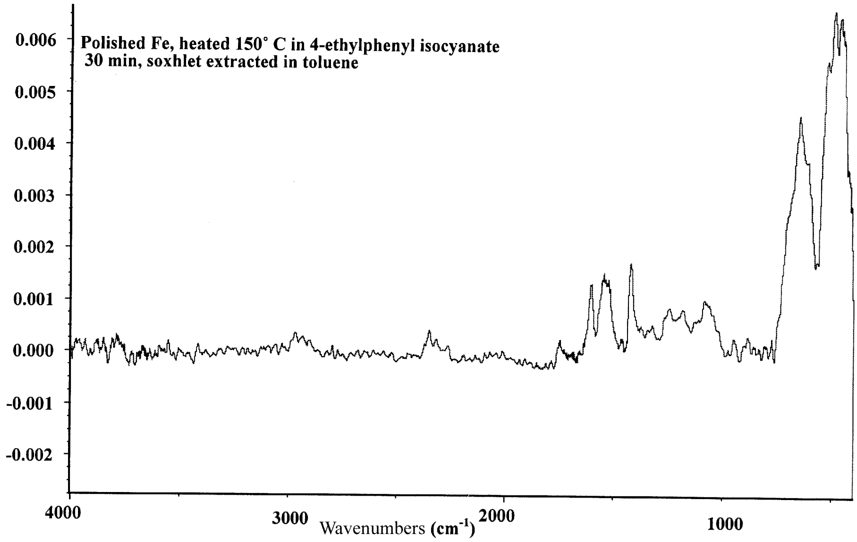


FIGURE 11 Reflection FTIR spectrum of polished steel heated to 150°C in neat 4-ethylphenyl isocyanate in toluene for 30 min followed by Soxhlet extraction.

surface than in the sorptions from dilute solution. There is a small amount of residual isocyanate present (2274 cm^{-1}), as well as a small peak near 1754 cm^{-1}, perhaps due to urethane formation. However, the strongest bands are the new absorbances near 1550 cm^{-1} (out-of-phase CO_2) and 1425 cm^{-1} (in-phase CO_2). This spectrum supports the conclusion that sorption is accompanied by carboxylate salt formation.

Reaction between pMDI and Polished Steel

To confirm that similar reactions can occur between steel and pMDI, polished steel coupons were refluxed for 20 min in a dilute solution of pMDI in toluene, then rinsed in fresh toluene. The resulting spectrum is shown in Figure 12. The strong band at 2274 cm^{-1} shows that there is much unreacted isocyanate in the residue. The strong band near 1730 cm^{-1} is suggestive of urethane carbonyl, a component seen in pMDI but also formed during sorption to some extent. As in the case for 4-ethylphenyl isocyanate, carboxylate salt formation is very prominent. These results show that similar reactions occur between pMDI and steel as well as between 4-ethylphenyl isocyanate and steel.

This sample was then Soxhlet-extracted in toluene to evaluate the extent of sorption. Figure 13 shows the resulting reflection FTIR spectrum. Soxhlet extraction has reduced the relative amount of

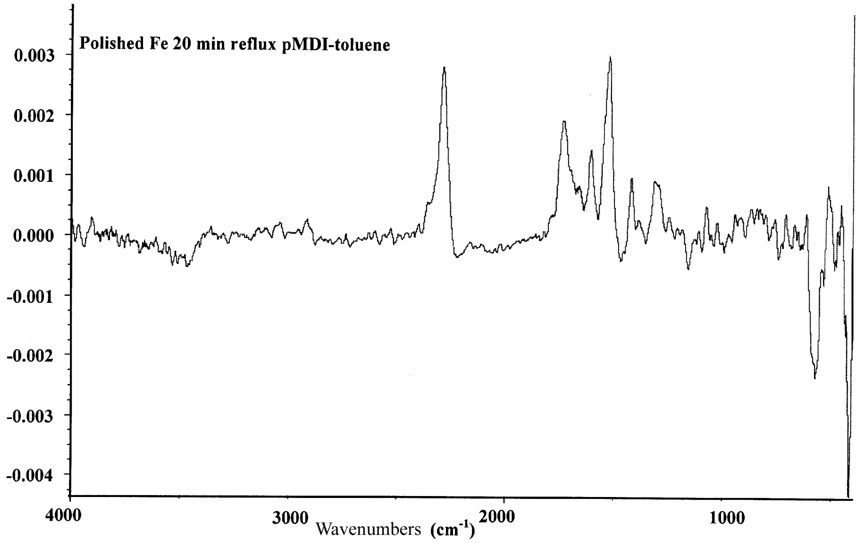


FIGURE 12 Reflection FTIR spectrum of polished steel refluxed at 110°C in dilute pMDI in toluene for 20 min followed by thorough toluene rinsing.

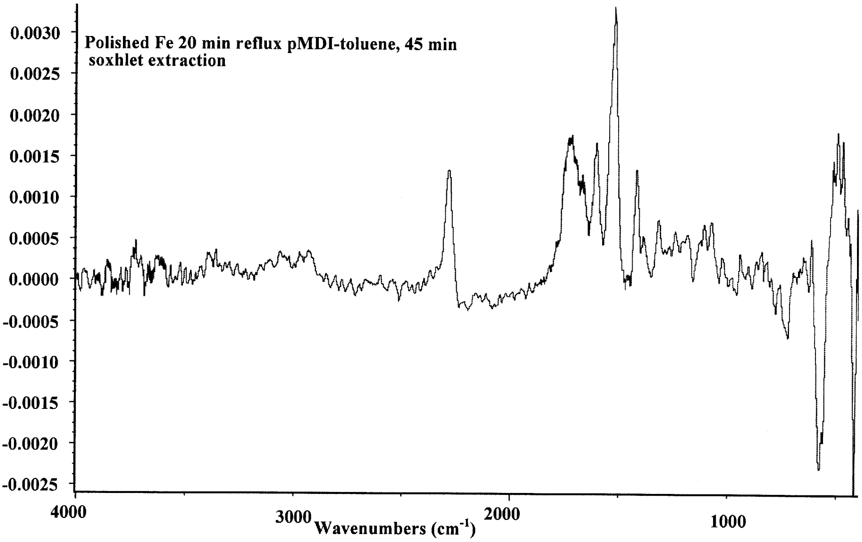
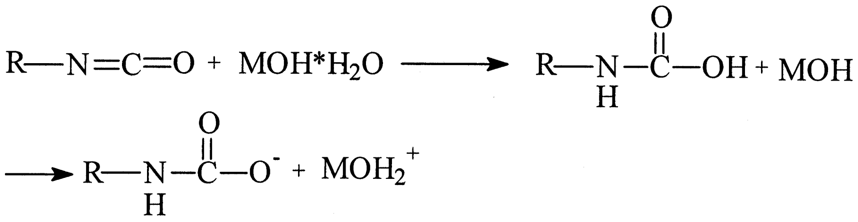


FIGURE 13 Reflection FTIR spectrum of polished steel refluxed at 110°C in dilute pMDI in toluene for 20 min followed by 45 min Soxhlet extraction in toluene.

unreacted isocyanate by 50%, while the relative amount of carboxylate has increased slightly. The extraction process removed additional unreacted pMDI and/or drove the reaction further towards completion by the additional time at elevated temperature.

These data allow us to draw a relatively detailed picture of the reaction between isocyanates such as pMDI and the oxide present on steel surfaces. The exposure of steel surfaces to isocyanates under a variety of conditions produces a carboxylate species at the interface. Metal carboxylate formation can be readily explained based on known isocyanate chemistry. Metal oxides such as those found on steel always have at least a monomolecular film of water adsorbed to the surface. This adsorbed water contributes to the formation of carboxylate according to the scheme shown in Reaction 1 below. Reaction of the isocyanate with adsorbed water of hydration creates a carbamic acid. In the presence of additional isocyanate, this carbamic acid could react further to form urea. However, close to the metal surface, the carbamic acid preferentially reacts with surface hydroxyls to form a carboxylate anion associated with a protonated metal hydroxide.



$$R{-}N{=}C{=}O + MOH{*}H_2O \longrightarrow R{-}\underset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}OH + MOH$$

$$\longrightarrow R{-}\underset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}O^{-} + MOH_2^{+}$$

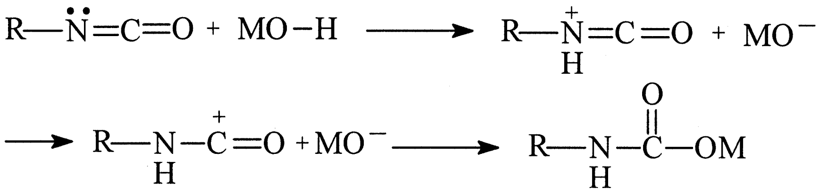
REACTION 1 Carboxylate salt formation between an isocyanate and a hydrated metal oxide.

Similar reactions between metals and organic acids are well known. For example, polyimide films are frequently deposited by spin-coating polyamic acid precursors onto desired substrates, followed with heat-treating to condense the acids to the corresponding polyimide. When the polyamic acids are spin-coated onto aluminum, the interface consists of a carboxylate salt formed by condensation of the acid with the metal hydroxide [9].

Condensation of the carbamic acid with other isocyanates to form ureas is the predicted reaction in the presence of water. However, ureas are not detected in these very thin films. There are at least two factors that favor a carbamic acid-metal hydroxide reaction over the carbamic acid-isocyanate reaction at the interface. Both phenyl isocyanate and pMDI are large molecules owing to the phenyl rings. Physisorption to the oxide (which must precede chemical reaction) would tend to sterically exclude other isocyanate molecules from the vicinity of the isocyanate group. This would favor reaction of the carbamic acid with the hydroxide over reaction with other isocyanates. Furthermore, the acid is formed through reaction with the oxide; it is physically close to the oxide and, therefore, in a favorable location to react with it.

The salt formation is kinetically favored as well. Formation of a carboxylate salt requires reaction of the isocyanate with water of hydration followed by protonation of the hydroxide, a two-step reaction. Formation of urea requires protonation of isocyanates followed by transport of additional isocyanate to the interface and transport of CO_2 away from the interface. This pathway has more steps and would be kinetically much less favorable.

The condensation reaction between metal hydroxide and isocyanate to form the corresponding ester (Reaction 2) is the expected reaction of isocyanates with metals, and as discussed above has been proposed in the literature to explain urethane-metal adhesion.



REACTION 2 Carbamate ester formation between an isocyanate and a metal hydroxide.

However, in the current study this product is not detected on iron oxide exposed to isocyanates until after the appearance of the carboxylate species. Reaction 2 is known to be suppressed in the presence of water, and may not occur near the interface until after the water of hydration has been consumed in the salt formation of Reaction 1.

CONCLUSIONS

Reflection FTIR has shown that the adhesion of isocyanate-derived polymers to steel does not result from simple addition of isocyanate to metal hydroxide. Two primary products result from exposure of steel to isocyanates, apparently in a sequential manner: carboxylate salts are formed initially from the reaction of isocyanate with hydrated oxide. Water of hydration plays a critical role in this reaction. With higher temperatures, formation of this salt is followed by the formation of covalent metal oxide-urethane linkages. This may be promoted by consumption of the water of hydration by salt formation. The presence of this type of organic-metal covalent bond can help explain the excellent strength and durability of isocyanate-based adhesives, coatings, and primers.

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