A Study of the Interfacial Interaction between Methylene Diphenyl Diisocyanate (MDI) and Metals by XPS and ToF-SIMS

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Polyurethanes are widely used as adhesives in industry as they show excellent adhesion to metal oxide surfaces.

Often the adhesion is due to intermolecular forces between adherent and substrate: bonds.

The understanding of adhesion phenomena is nowadays investigated by the characterization of the interfacial interaction that occur when the adherent is applied to the substrate.
MDI: a PU monomer

PU polymer chain is formed by urethane linkage. This bond is obtained from the reaction between an hydroxyl group and an isocyanate.

The great majority of di-isocyanate used for the polyaddicion reaction is made by methylene diphenyl diisocyanate: MDI
In order to understand the adhesion of PU on metal substrates the above interaction was analysed.
Isocyanate Reactivity

\[
R - \text{NCO} + \text{H}_2\text{O} \rightarrow R - \text{NH} - \text{COOH} \rightarrow R - \text{NH}_2 + \text{CO}_2
\]

\[
R - \text{NCO} + R - \text{NH}_2 \rightarrow R - \text{NH} - \text{CO} - \text{NH} - R
\]

\[
R - \text{NCO} + R^{\text{I}} - \text{OH} \rightarrow R - \text{NHCOOR}^{\text{I}}
\]

Stainless steel surface is made of metal oxide, metal hydroxide and adsorbed water.

\[
R - \text{NCO} + \text{M} - \text{OH} \rightarrow R - \text{NHCOCOOM}
\]
A sample of 3 nm of MDI on stainless steel.

- **Interface**
- **Pure MDI**
- **Steel (with carbon contam. From protective film)**
C1s High Resolution Spectra

Pure MDI

Steel (with carbon contam.)

Interface:
3 nm of MDI on stainless steel

New peak indicates the formation of a M-C bond:

Organometallic complex??
C1s N=C=O Region

Pure MDI

Interface

Steel (with carbon contam.)

Pure MDI

Shake-up

N=C=O

C Arom 1

C Alip 2

N=O4

C N 3

NHCOOM

N=C=O

C=O
Possible Mechanism of Reaction

Steel surface

**MDI**

Steel surface

![Diagram of the possible mechanism of reaction involving MDI and a steel surface.](image)
N1s High Resolution Spectra

Pure MDI

Interface

Counts / s

Counts / s

Counts / s

Binding Energy (eV)

Binding Energy (eV)

Binding Energy (eV)
The Surface Analysis Laboratory

**SIMS Negative Spectra**

<table>
<thead>
<tr>
<th>Mass (u)</th>
<th>314</th>
<th>312</th>
<th>310</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abundance (%)</td>
<td>40</td>
<td>20</td>
<td>0</td>
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**Isotope pattern**

- Fe\(^{56}\) containing
- Fe\(^{54}\) containing
- Fe\(^{57}\) containing
- Fe\(^{58}\) containing
MDI/Fe: C1s

«Carbidic» peak and NHCOOFe peaks present
When a thin layer of MDI is applied it is not possible to see metallic Mo and MoO$_2$ anymore. Most of the peak is due to MoO$_3$ and a new doublet appears in a position which could be attributed to an interaction with nitrogen.
When a thin layer of MDI is applied, a new doublet appears in a position which could be attributed to an interaction with nitrogen. The nitrogen high resolution spectrum confirms the interaction.
MDI/Cr: C1s

No «carbidic» peak but NHCOOOCr peak present
Summary

M-C interaction $\rightarrow$ Peak at 283.6 eV:
- MDI/Steel and MDI/Fe interfaces

Formation of $\rightarrow$ Peak at 289.2 eV:
- MDI/Steel, MDI/Fe, MDI/Cr interfaces

M-N interaction $\rightarrow$ New doublets in the metal peaks:
- MDI/Mo and MDI/Ni interfaces
Conclusions

- PU is known to show excellent adhesion to metal oxide surfaces.

- PU is formed by polyaddition reaction of MDI with polyols.

- Some adhesive formulations are based on PU monomers, and some prepolymercontaining unreacted isocyanate groups.
Conclusions

• For these kinds of adhesives, the reactions illustrated before between the isocyanate group and the different metals, can partially explain the quality of the adhesion of PUs to metal oxide substrates.

• XPS can be used to differentiate between MDI interaction that are via the C=O or the N=C moieties.
THANK YOU FOR YOUR ATTENTION!

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