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

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Introduction

Isocyanate is a very reactive functional group with a rich chemistry which shows a wide range of possible reactions. Being an electrophile it reacts with nucleophilic groups such as water, amines and alcohols (1). The reactions are shown below:

R-N=C=O + H_2O → R-NH-COOH → R-NH_2 + CO_2

R-N=C=O + R-NH_2 → R-NH-CO-NH-R

R-N=C=O + R^I-OH → R-NH-CO-O-R^I

These reactions involving active hydrogen groups are very important for the study of the interaction of isocyanate containing compounds and metals. That is because it is known that metal surfaces are made by an oxide which contains absorbed water and hydroxyl groups. The aim of this work is to understand the nature of the chemical interaction which occurs between methylene diphenyl diisocyanate (MDI) and metals.

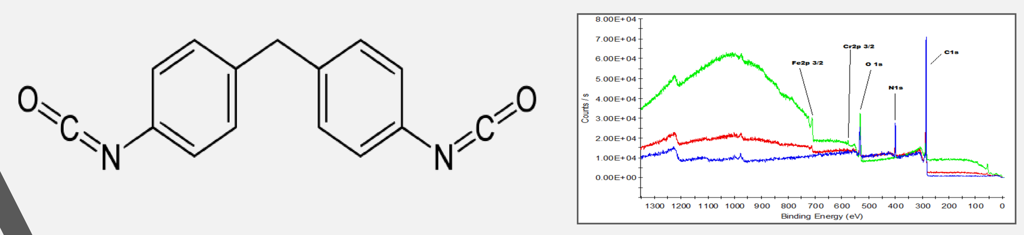


Figure 1: MDI molecule and Survey XPS spectrum of blue) MDI; Red) MDI on steel; green) steel.

Benzene

Experimental

Stainless steel 316L, iron, molybdenum, chromium and nickel samples were used as substrates. Solutions with different concentrations of MDI in acetone were prepared. Samples of metal coated with MDI were produced by drop coating.

XPS analyses were achieved by using a Thermo Scientific Theta Probe spectrometer.

A TOF.SIMS[5] system was employed for ToF-SIMS analyses using static conditions.

O

References:

1) D. Randall and S. Lee, *The Polyurethane Book*, John Wiley & Sons Ltd (2003).

2) K. Shimizu *et al.*, *Surf. Interface Anal.*, **42**, 1432-1444 (2010).

3) J. F. Watts *et al.*, *J. Adhesion Sci. Technol.*, **6**, 337-393 (1992).

4) R.G. Dillingham *et al.*, *J. Adhesion*, **79**, 269-285 (2003).

Results and Discussion

1

MDI, MDI on 316L stainless steel and steel **survey XPS spectra** are shown in Figure 1. The comparison of the fitted high resolution spectra gives information on the reactions occurring at the interface between MDI and steel. The **C1s peak**, at the interface, shows a characteristic carbidic component (not present in the carbon peak of pure MDI or steel), indicative of interfacial bonds (Figure 2).

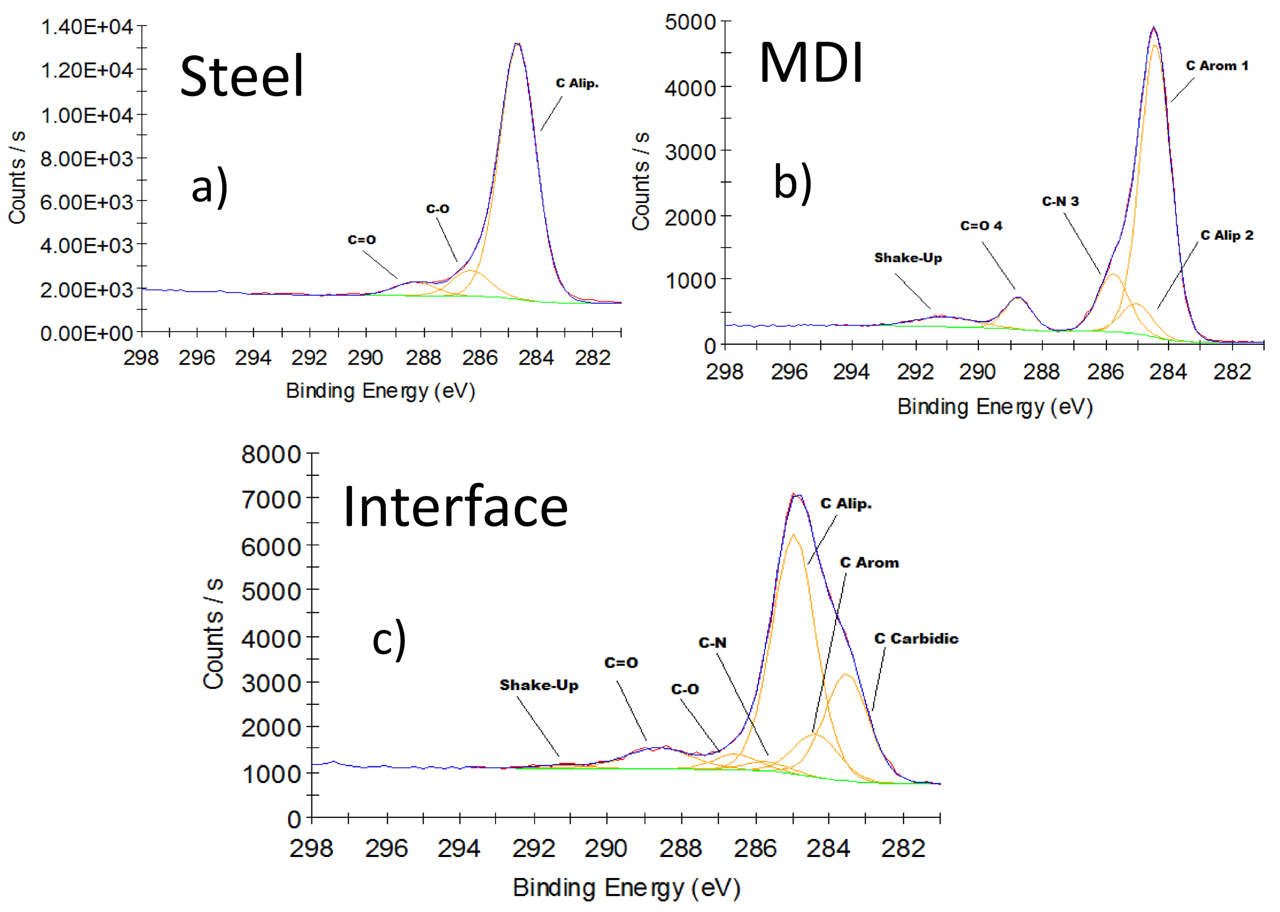


Figure 2: C1s high resolution spectrum of a) Steel, b) MDI C) MDI on stainless steel.

This observation matches with the data obtained by ToF-SIMS, where new peaks appear at the interface sample (Figure 3), and suggests the formation of an organometallic compound.

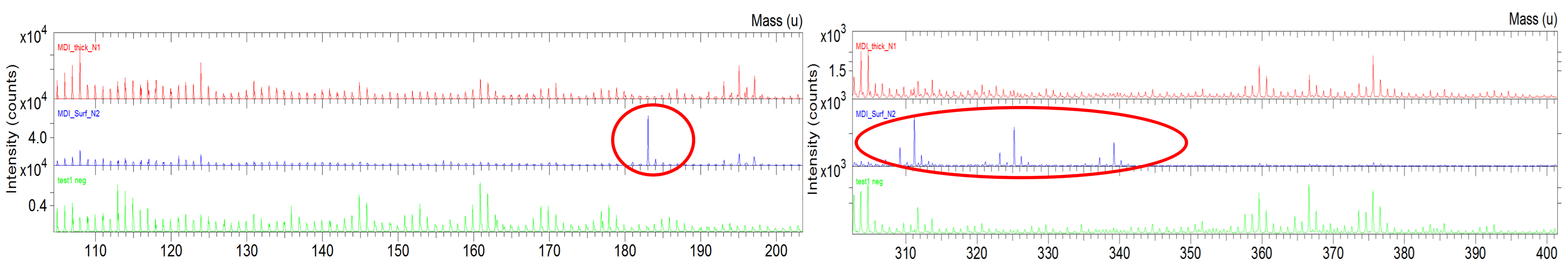
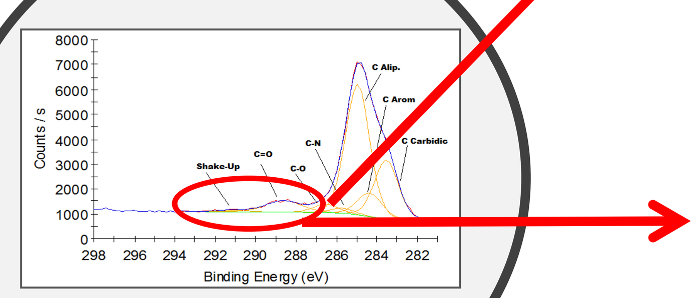


Figure 3: SIMS negative spectrum section of red) MDI, blue) MDI on stainless steel, green) steel.

3

The formation of this bond between substrate and coating seems to be confirmed by the components visible in the C1s peak at the interface in the **N=C=O binding energy region** (Figure 5). The formation of such bond has been already established with Al substrates (2) and has been suggested, (3) and (4), for iron based alloys.



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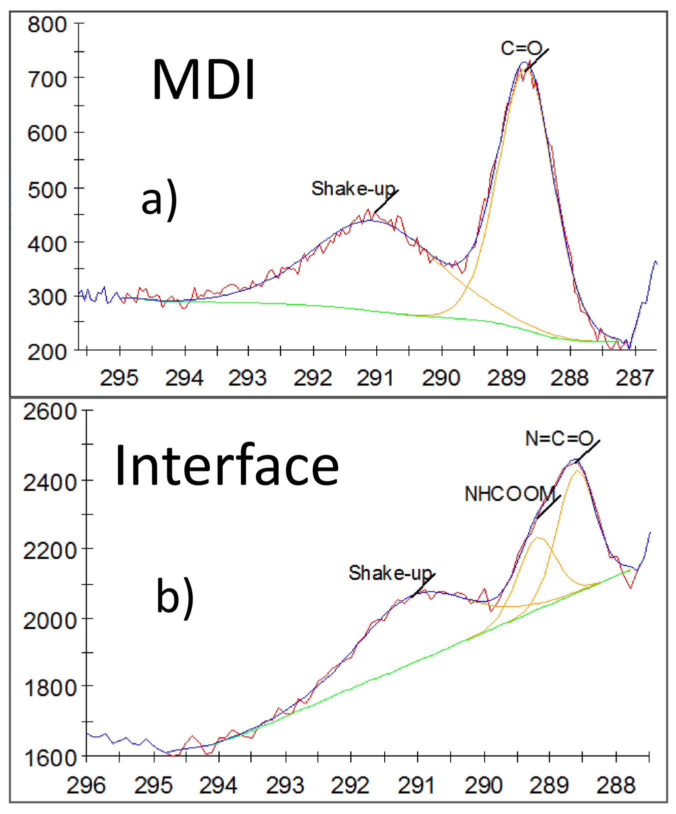

Figure 5: C1s N=C=O high resolution spectrum of a) MDI b) MDI on stainless steel.

N

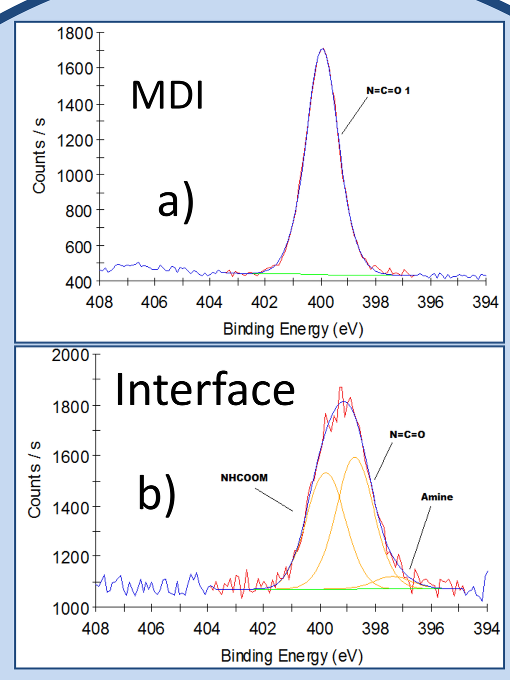

Figure 4: N1s high resolution spectrum of a) MDI b) MDI on stainless steel.

2

The **N1s peak** (Figure 4) at the interface exhibits three components; one of them can be attributed to a urethane link obtained by the reaction of the isocyanate with the hydroxide present on the surface of the metal to give: R-NH-CO-O-M.

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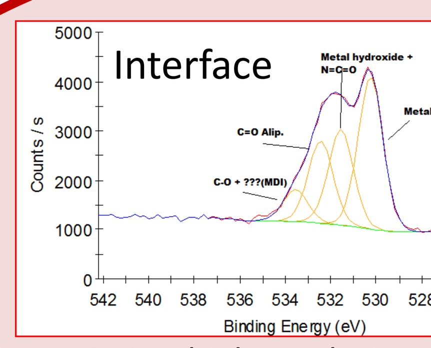

Figure 6: O1s high resolution spectrum of MDI on stainless steel.

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Very little information can be obtained from the O 1s peak (Figure 6) as the MDI peaks mix with the metal oxide ones and the carbon contamination present on the steel.

5

Other metals

Also with pure Fe the "carbidic" peak and the second C=O component appear at the interface!

With Mo the "carbidic" peak does not appear at the interface, however in the Mo3d region a new doublet appears at the interface in a position which could be attributed to an interaction with nitrogen (Figure 7). The same interaction is observed with the Ni substrate.

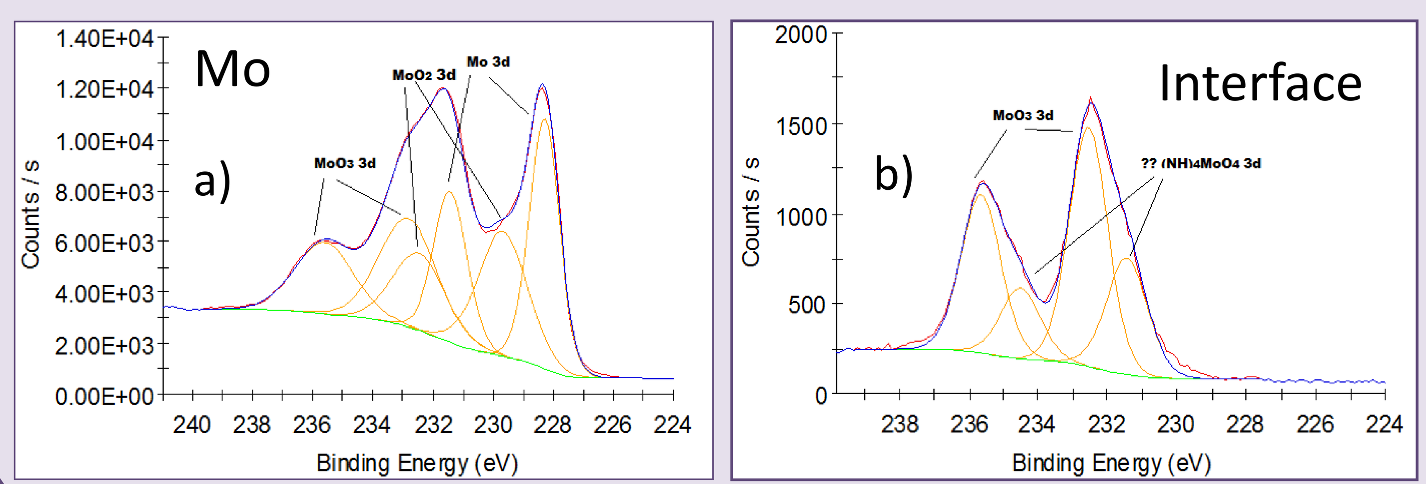


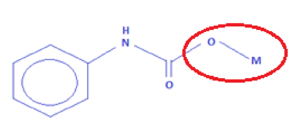
Figure 7: Mo 3d high resolution spectrum of a) molybdenum b) MDI on molybdenum.

Fe

Conclusions

At the interface between MDI and steel and pure iron two kinds of interactions seem to occur:

- The appearance in the thin film of a peak at a BE of 283.6 eV suggests the formation of an organometallic complex or equivalent species.
- The appearance on the thin film of a second peak in the N=C=O region seems to suggest the formation of a bonding like: (see layout!)



At the interface between MDI and pure molybdenum and nickel the appearance of a new doublet seems to suggest an interaction with nitrogen.