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Characterization of the Epoxy-Metal Interphase: FTIR-ERAS and Spectra Calculation for Ultra-Thin Films

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Summary: The interphase between polymers and metal substrates can be elucidated by studying ultra-thin films. In this paper, spin coating films (20 nm – 2 µm) are prepared from a two-part epoxy adhesive on Au, Al and Cu. After room temperature cure, the chemical structure of the epoxy films is studied by FTIR external reflection absorption spectroscopy (FTIR-ERAS) and the results are compared with the state in the polymer bulk as measured by attenuated total reflection (FTIR-ATR). Inevitably, this evaluation of the thin film spectra has to account for the optical situation which is significantly different from bulk measurements. Spectra calculation provides the essential tool for a reasonable comparison between bulk and thin film spectra, thus allowing for a detailed quantitative analysis. Thickness and substrate effects on the interphase can then be separated from the optical situation of the measurement.

The results reveal very specific features caused by adhesive interactions and different cure behaviour in the interphase on different metal surfaces.

Keywords: epoxy adhesive; FT-IR; interphase; spectra calculation; thin films

Introduction

The performance of adhesive bonds depends strongly on the properties of the interphase region between the adhesive polymer and the substrate.[1-9] The interphase region can be elucidated by studying ultra-thin polymer films.[10-12] In this way, it is possible to investigate how the curing process and the resulting network structure differ for polymer films compared to the bulk.[6,8,9,13,14]

Such differences can result from a chemical or a catalytic influence of the substrate. Moreover, components of the reacting system can undergo preferential adsorption and immobilization or the substrate could even initiate phase separation. For ultra-thin films, the dimensional constraint could alter molecular mobility significantly. Up to now, it is almost unknown how these processes affect the emerging macromolecular structure in a curing polymer adhesive.

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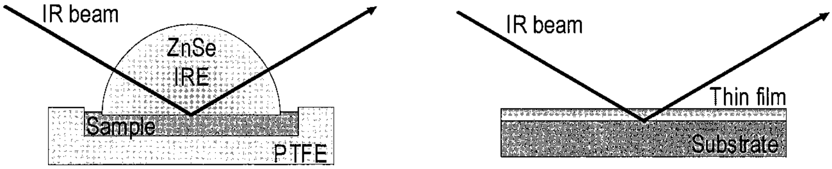
The differences in chemical structure can be investigated by infrared spectroscopy. Inevitably, the evaluation of thin films has to account for the optical situation which is significantly different from bulk measurements.[15]

In this paper, a new combination of infrared spectroscopy and spectra calculation is developed. This method provides the essential tool for a reasonable comparison between bulk and thin film spectra, thus allowing for a detailed quantitative analysis. Effects of thickness and substrate can then be separated from the optical situation of the measurement.

Methodology

The investigation of the polymer bulk is performed using the FTIR attenuated total reflection spectroscopy (FTIR-ATR) as illustrated in Figure 1a. The incident infrared light is totally reflected at the plane interface between the internal reflection element (IRE) and the sample (refractive indices: $n_{ZnSe} = 2.43$, $1.5 < n_{polymer} < 1.6$).



a. Bulk (FTIR-ATR). **b.** Thin film (FTIR-ERAS).

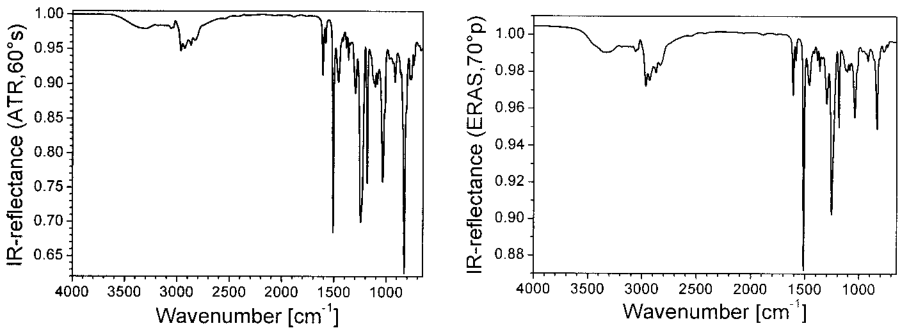
Figure 1. Optical situation for bulk (FTIR-ATR) and thin film samples (FTIR-ERAS).

The penetration depth of the resulting evanescent wave into the sample is a function of the refractive indices, the polarization of the light, the angle of incidence and the wavenumber. In order to receive the bulk properties of the sample with penetration depths in the order of several microns, modest refractive indices of the IRE and incident angles only slightly above the critical angle of total reflection are recommended.

The evaluation of thin polymer films on metal substrates is carried out with the FTIR external reflection absorption spectroscopy (FTIR-ERAS) as shown in Figure 1b.

Infrared spectra of any FTIR experimental technique are not only determined by material properties that are commonly described by the optical function $\hat{n}(\tilde{\nu}) = n(\tilde{\nu}) + i \cdot K(\tilde{\nu})$, i. e. the complex refractive index (real part $n(\tilde{\nu})$: refractive index, imaginary part $K(\tilde{\nu})$: absorption index). The optical situation in the measurement includes other relevant factors of influence, e. g. the angle of incidence, the polarization of light, the optical function of the IRE or the film thickness. Furthermore, ATR spectral intensity is dominated by the wavenumber dependence of the penetration depth of the evanescent wave.

Figure 2 demonstrates that the absolute values as well as the relative intensities of absorption peaks differ significantly in bulk spectra (Figure 2a: ATR, 60°, s-polarization) compared to thin film spectra (Figure 2b: ERAS, 70°, p-polarization), though – in this example – both spectra are calculated from the same optical function (material: epoxy adhesive). In general, the absolute peak heights in thin film spectra are different from bulk spectra as they are a function of film thickness (e. g. phenylene ring stretch at 1510 cm^{-1} in Figure 2). Relative peak intensities in the ATR experiment are different from thin film spectra due to increasing penetration depth with increasing wavenumber (e. g. phenylene 1510 cm^{-1} to 830 cm^{-1} in Figure 2).

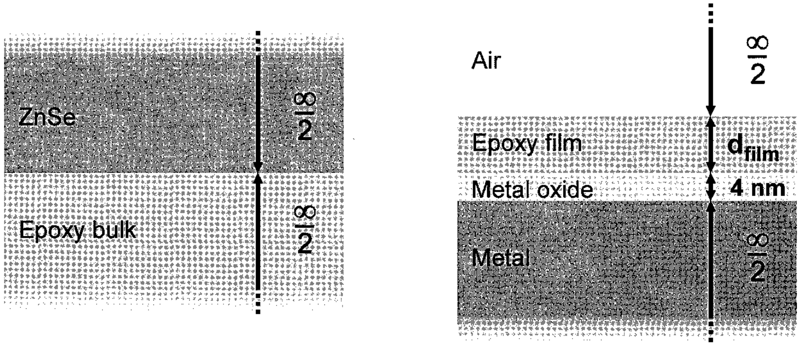


a. Bulk spectrum (FTIR-ATR). **b.** Thin film spectrum (FTIR-ERAS).

Figure 2. IR spectra representing the same material properties but different optical situations.

Therefore, any evaluation of thin film spectra inevitably has to account for the optical situation which is completely different from bulk measurements. Spectra calculation provides the essential tool for a reasonable comparison on a quantitative basis.

In a first step, the optical function of the polymer bulk is calculated from measured ATR spectra. This so called backward calculation requires an optical situation which is simple, well-defined and well-known: the layer stack is shown in Figure 3a; further optical parameters are given by the experimental conditions chosen.



a. FTIR-ATR (2 layers, 1 interface). **b.** FTIR-ERAS (4 layers, 3 interfaces).

Figure 3. Layer stacks as used in infrared spectra calculations.

Unfortunately, the determination of the optical function from ultra-thin film spectra is often more difficult or even incorrect.[16] For this reason, thin film and bulk behaviour are not compared on the basis of optical functions.

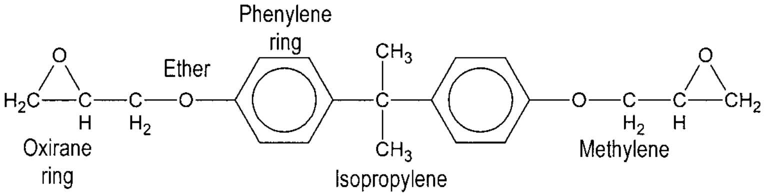
Instead, in the second step, the optical function obtained for the bulk is used to calculate ERAS spectra (forward calculation; see layer stack in Figure 3b). Thereby, the optical situation of the calculated spectra matches exactly the spectroscopic conditions of the thin film experiment with one distinction: The calculated spectrum represents the situation as it would be observed if the polymer would maintain bulk properties in the thin film, while the measured spectrum contains all changes in the sample due to contact with the metal substrate.

The variation of the experimental film thickness from several nanometres to microns allows for the weighting of these substrate effects in the measured infrared spectra. As the depth of substrate influence is limited and as the FTIR-ERAS averages over the whole thickness of the polymer film, bulk properties are expected to dominate the IR spectra of thick polymer films. With decreasing film thickness, polymer – substrate interactions are supposed to affect the spectroscopic results more and more.

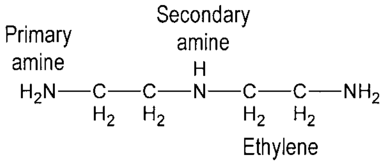
Each calculated spectrum is compared with the corresponding measured ERAS spectrum. Using this method, film thickness and substrate effects can be depicted by a detailed analysis of infrared absorption bands, which are significant for the chemical structure of the polymer.

Experimental

In this paper, spin coating films (20 nm – 2 µm) are prepared from a two-part epoxy adhesive on metal substrates (Au, Al and Cu). The room temperature curing epoxy system (Figure 4) consists of the epoxy resin DGEBA (Diglycidylether of Bisphenol A) and the curing agent DETA (diethylene triamine) in a mixing ratio of 100:14 (by weight).



DGEBA = Diglycidylether of Bisphenol A



DETA = Diethylene triamine

Figure 4. Chemical structure of the 2-part epoxy adhesive system educts.

The curing reaction and the final epoxy network develop as a result of the polyaddition of oxirane (epoxy) groups of DGEBA with primary and secondary amine groups of DETA. The substrates are PVD-layers of the pure metals (Au, Al, Cu) with their native surface chemistry, i. e. oxide / hydroxide on Al and Cu, adsorbed species etc.[17]

The FTIR experiments are performed on a Bruker IFS66v/S spectrometer with a Harrick Seagull reflection unit. After 72 h at room temperature in dry air, the chemical structure of the now cured epoxy film is studied by FTIR-ERAS (incident angle 70°, p-polarized light).

The bulk state of the same adhesive is characterized with FTIR-ATR-spectroscopy (ZnSe-hemisphere IRE, incident angle 60°, s-polarized light).

The software SCOUT 2[18] allows for the calculation of optical functions (oscillator model parameter fit[15,16,18,19]) from these IR-ATR spectra and the calculation of IR-ERAS spectra thus representing the chemical structure of the bulk.

A detailed qualitative and quantitative evaluation of these calculated (bulk properties) and measured (thin film properties) spectra is carried out.

Results and Discussion

According to the literature, chemical reactions between gold as a noble metal and the epoxy adhesive do not have to be expected. Therefore, the inert gold substrates were chosen as an adequate reference in order to elucidate the suitability of the experimental approach and the methodology.

In Figure 5, the measured spectrum of a quite thick epoxy film (d_{film} = 2 μm) on gold is shown together with a calculated spectrum representing bulk properties. Both spectra agree very well.

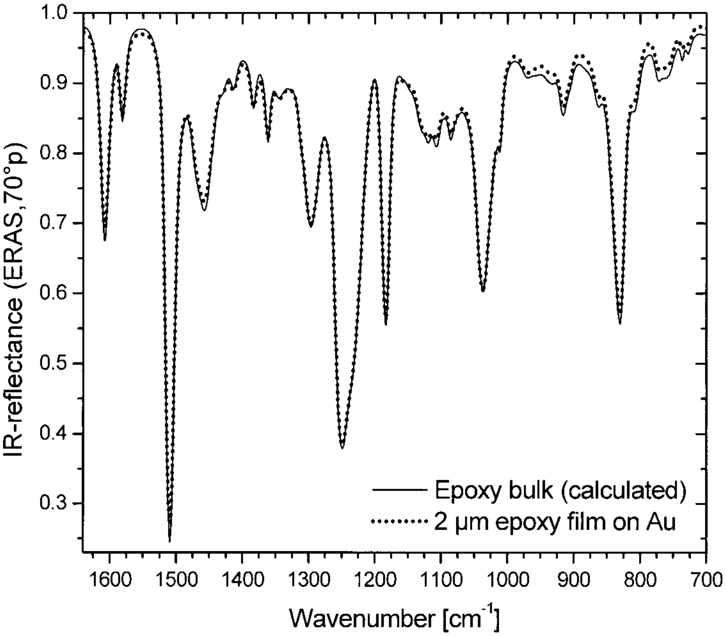


Figure 5. Epoxy film (2 μm) on gold, calculated (bulk) and measured thin film IR spectra.

It is obvious, that the method developed in this paper in fact opens the hoped-for way to directly compare bulk and film properties, thus overcoming effects of different optical situations in the measurements using spectra calculation.

Figure 6 illustrates this method successfully applied on the elucidation of ultra-thin epoxy films (d_{film} = 50 nm) on gold.

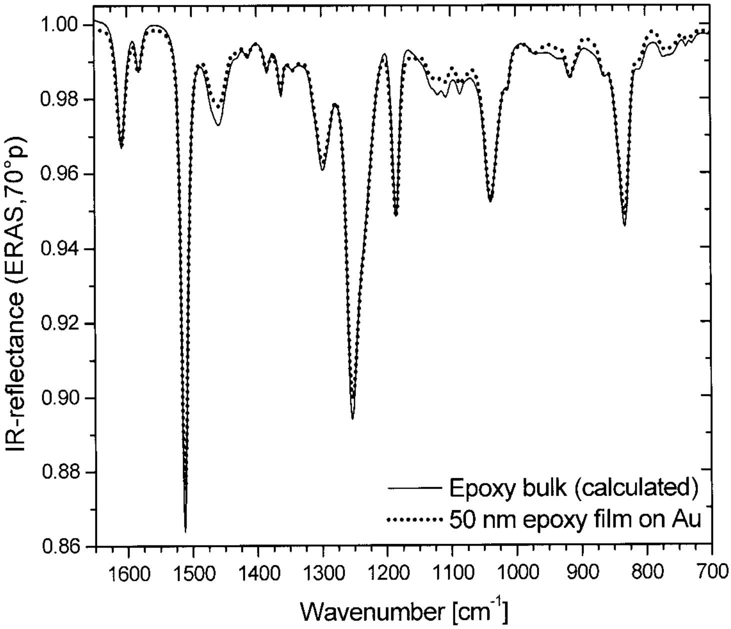


Figure 6. Epoxy film (50 nm) on gold, calculated (bulk) and measured thin film IR spectra.

At the first view, calculated and measured IR-ERAS spectra look very similar (Figure 6). Atom groups that are unaffected by the curing reaction, such as phenylene rings (e. g. 1610 cm^{-1}, 1580 cm^{-1} or 1510 cm^{-1}) or ether groups (e. g. 1250 cm^{-1}), do not show significant differences in ultra-thin films compared to the bulk. However, more oxirane groups (e. g. 915 cm^{-1}) remain unreacted in ultra-thin films.[1]

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[1] The oxirane consumption during room temperature cure stays incomplete even in the bulk due to the vitrification of the adhesive.

The quantitative analysis is based on the spectroscopic degree of epoxy conversion X_{EP}, which is calculated from the intensity I_{EP} of the epoxy ring stretch absorption band at 915 cm^{-1}. The intensity I_{PH} of the phenylene ring stretch band at 1510 cm^{-1} is introduced as an internal standard:

$$X_{EP}\left(t_{cure}=72h\right)=\left(1-\frac{I_{EP,norm}\left(t_{cure}=72h\right)}{I_{EP,norm}\left(t_{cure}=0\right)}\right)\;;\qquad I_{EP,norm}\left(t_{cure}\right)=\frac{I_{EP}\left(t_{cure}\right)}{I_{PH}\left(t_{cure}\right)}.$$

Unfortunately, the initial amount of oxirane groups $(t_{cure}=0)$ that is required for the calculation is not experimentally available for room temperature curing adhesives. Therefore, spectra calculation has to be used.

A simple mixing rule combined with the well-known Lorentz-Lorenz equation[16] is applied on the optical functions of DGEBA and DETA in order to calculate the effective medium optical function of the hypothetical unreacted adhesive bulk prior to curing:

$$\frac{\hat{n}^2_{eff,Mixture}-1}{\hat{n}^2_{eff,Mixture}+2}=p\cdot\frac{\hat{n}^2_{DGEBA}-1}{\hat{n}^2_{DGEBA}+2}+\left(1-p\right)\cdot\frac{\hat{n}^2_{DETA}-1}{\hat{n}^2_{DETA}+2}\;;\qquad p=\frac{V_{DGEBA}}{V_{DGEBA}+V_{DETA}},$$

Volume fraction.

Using this optical function, any IR spectra of the mixture can be calculated. Thereby, their optical situation ought to match exactly the conditions in the experiment.

In Figure 7, the infrared spectrum of the calculated mixture of DGEBA and DETA can be compared to infrared spectra of the reactive adhesive in the early stages (after 11 min.) of the cure.

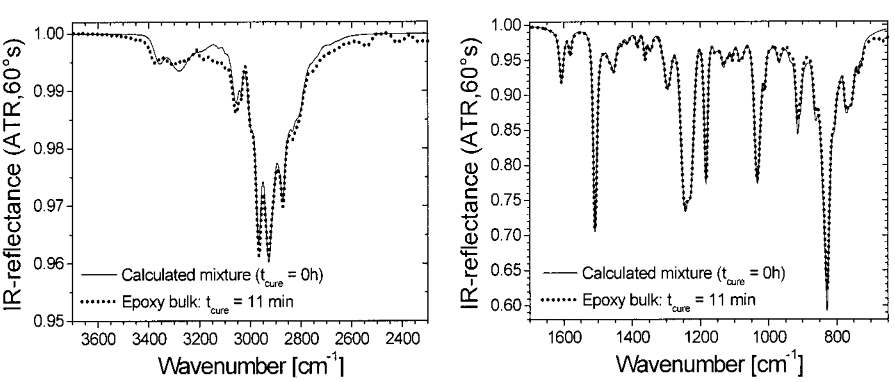

Figure 7. Calculated mixture of DGEBA + DETA compared to the measured epoxy system.

Apart from slight differences, which result from the ongoing chemical reaction in the measurement, the calculated spectrum corresponds excellently with the measured spectrum of the mixture. Therefore, a good representation of the uncured adhesive has been found.

The quantitative analysis of epoxy films on gold substrates in Figure 8 illustrates, that the spectroscopic degree of conversion is a function of the film thickness.

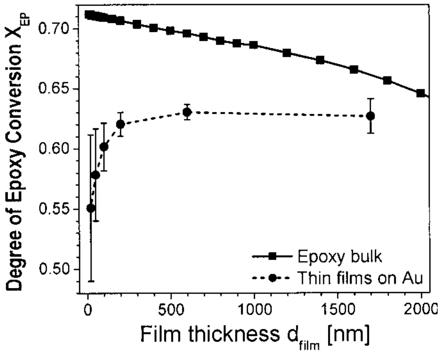

Figure 8. Epoxy conversion in thin films on gold compared to the bulk.

It is important to note, that the *spectroscopic* degree of conversion is not equal to a *chemical* degree of conversion. For that reason, though the chemical degree of conversion in the bulk is constant, the spectroscopic degree of conversion decreases to some extend with increasing film thickness (Figure 8) as a result of optical effects. Despite the reverse trend given by the optical situation, the spectroscopic degree of conversion in spin coating films decreases significantly with decreasing film thickness. Due to this fact, pure optical effects can be excluded. It has been shown instead that the chemical extend of cure is remarkably reduced in the interphase on gold. With increasing film thicknesses, the degree of conversion approaches bulk values, as expected by the model.

Figure 9 and 10 summarize the results for thin epoxy films on aluminium and copper respectively. Unlike gold, these substrates are not inert. As far as spectra calculation is concerned, the oxide / hydroxide layers on these metals have to be taken into account.

The behaviour of epoxy films on aluminium (Figure 9) corresponds to that on gold substrates. Within the sensitivity of the experiment, specific chemical interactions could not be revealed yet.

Copper was chosen as an example (Figure 10) with high potential for interactions with the adhesive. It is well-known, that Cu^{2+}-ions from the oxide / hydroxide layer can form soluble complexes with the amine hardener DETA. Experiments[17] have shown, that – in this way – Cu^{2+}-ions can migrate a few hundred nanometres into the curing adhesive. IR spectra of thin epoxy films on copper support this complexation theory. The significant increase in the degree of epoxy conversion in the film thickness range below 100 nm (Figure 10) is a remarkable proof of catalytic effects and chemical interactions of copper with the epoxy adhesive.

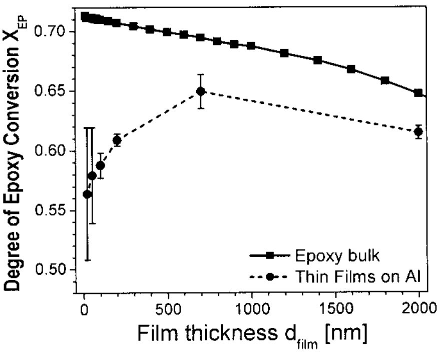

Figure 9. Epoxy conversion in thin films on aluminium compared to the bulk.

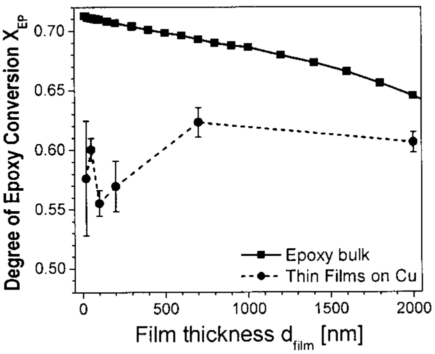

Figure 10. Epoxy conversion in thin films on copper compared to the bulk.

Conclusions

A combination of IR-spectroscopy and spectra calculation has been developed. This method opens a new way to study ultra-thin polymer films on metal substrates compared to the bulk.

In this paper, epoxy adhesive films (20 nm – 2 μm) on different metal surfaces have been elucidated successfully using this method. The results reveal very specific features caused by adhesive interactions and different cure behaviour in the interphase on different metal surfaces.

Acknowledgement

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