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Probing the Metal Oxide/Polymer Molecular Hybrid Interfaces with Nanoscale Resolution Using AFM-IR

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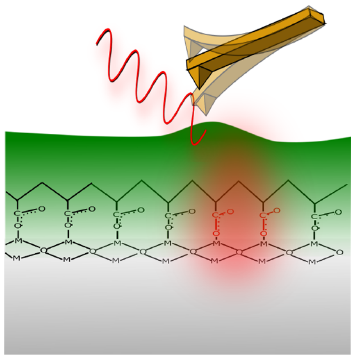
ABSTRACT: Obtaining chemical information from the buried interface of an organic coating is not straightforward. In this paper, for the first time, atomic force microscopy-based infrared spectroscopy (AFM-IR) is used to probe the chemical interactions at the metal oxide/polymer interface. AFM-IR is a novel technique that provides chemical spectra with spatial resolution below the optical diffraction limits. Poly(acrylic acid) (PAA) on aluminum oxide was chosen as a model system. Two different approaches were used: a thin-layer approach and a cross-section approach. The thin layer confirmed the validity of the AFM-IR to look at the buried interface by comparison with results from the literature. Additionally, with a line scan, the exposed interfaces obtained from cross sections of thick coatings on aluminum substrates were analyzed. A semiquantitative analysis of the spectra from the line scan allowed to identify the chemical contribution coming from the polymer/metal oxide interfaces.



INTRODUCTION

Atomic force microscopy-based IR (AFM-IR) is a new technique that allows to detect IR spectra with lateral resolution beyond the optical diffraction limit. This can give an important and innovative contribution to the study of the hybrid polymer/metal oxide interfaces. The study of this region is not straightforward as at most a few nanometers thick is sandwiched between a substrate and an overlayer which can be even hundreds of micrometers thick. Therefore, it is termed buried interface.[1] Understanding the chemistry of the buried interface and its long-term stability in humid or corrosive environments is very important as it largely controls adhesion and delamination. Different techniques and methodologies have been used to characterize the buried interface including X-ray photospectroscopy (XPS), time-of-flight secondary ions mass spectroscopy (ToF-SIMS), Fourier transform infrared spectroscopy (FTIR), and sum frequency generation (SFG) vibrational spectroscopy.[2−5] Although the use of these techniques allows to gain insights into the interfacial chemistry, there are still some limitations associated with them. For example, the chemistry of the surface of "industrially relevant" samples exposed to atmospheric conditions can by modified be the ultrahigh-vacuum environment of ToF-SIMS and conventional XPS. Similarly, in situ ATR-FTIR has been used to look at the buried polymer/metal oxide interface and the effect of water on it,[5−9] but it requires the deposition of a thin metal layer on the ATR crystal by PVD and therefore only mimics "real" substrates. SFG has emerged as a powerful technique for buried interfaces. However, SFG spectrometers are very complex to use such as difficult is the SFG spectra interpretation. Such limitations prevent a wider application of this technology for a greater number of user.[10] Moreover, the low lateral resolution of the above-cited techniques does not allow to study locally the interfacial chemistry in critical points such as defects, precipitates in the alloy, and so on.

In this context, this study reports the first findings toward the establishment of a methodology to look at buried polymer/metal oxide interfaces on a molecular level of industrially relevant samples in nonvacuum conditions via AFM-IR. This promising technique was developed by Dazzi et al.[11−13] to obtain chemical analysis with high spatial resolution by combining atomic force microscopy (AFM) and infrared spectroscopy (IR). The AFM-IR uses a tip of an AFM cantilever as IR detector; the sample is illuminated by a tunable infrared source which is rapidly pulsed (Figure 1a). If the tunable IR light matches an absorbing wavelength of the sample, the thermal expansion due to the absorbance will be detected by the AFM probe in contact with the sample. It has been proven that the deflection of the cantilever due to this oscillation is proportional to the amount of light absorbed, and this in turn is directly proportional to the absorption coefficient. Therefore, plotting amplitude as a function of IR

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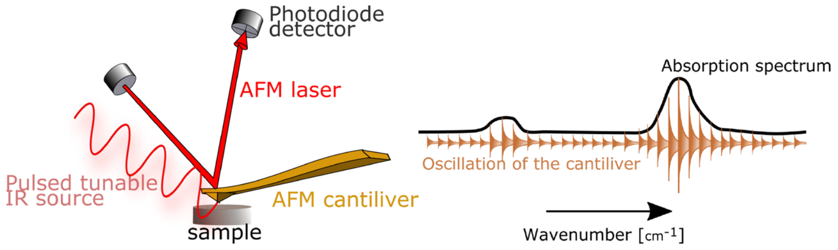
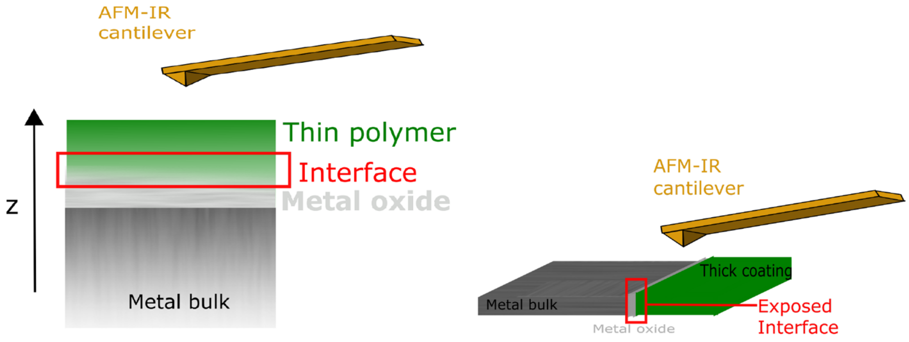


(a) (b)

Figure 1. (a) Schematic diagram of AFM-IR with top-down illumination. (b) Schematic of a local absorption spectrum obtained by measuring the AFM cantilever oscillation amplitude as a function of wavelength.



(a) (b)

Figure 2. Schematic diagram of the two approaches used to look at buried interfaces via AFM-IR. (a) The thin-film approach where a thin layer is deposited on the metal oxide (b) The buried interface of a thick coating on aluminum is exposed via a cross-section polisher.

wavelength gives spectra similar to the ones obtain by macroscopic transmission mode FTIR (Figure 1b).[14−16]

In a recent study from Morsch et al.[17] AFM-IR was employed to look at the interphase area created between an epoxy resin on an iron substrate. In their study they looked at possible formation of organometallics due to diffusion of metal ions during curing in a region 200 nm away from the metal/epoxy interface. However, no study has been done to verify the feasibility to use the AFM-IR to chemically probe the metal oxide/polymer interface, which is only in the order of a couple of nanometers. To do so, in our study a widely studied polymer/metal system has been chosen. Two different approaches were used: a thin film and a cross section. The basic principle of the thin film approach involves the deposition of a layer thin enough (tens of nanometers) so that the thermal expansion of the interface caused by the IR tunable light can be detected by the AFM-IR cantilever from the top. This approach has been already used to look at polymer−metal oxide interfaces of model thin film with other techniques such as XPS and ToF-SIMS.[5,8,18−20] Probing the polymer metal oxide interface from the top via the thin film approach allows to obtain important insights into the chemical interactions of the buried interface and its distribution. Together with the thin film approach the interface between a thick coating and the metal substrate was analyzed via the creation of a cross section. In fact, in industrial applications, a thick polymer coating is usually applied on the metal substrate. The presence of a thick coating rather than a thin layer leads to differences in the mobility and orientation of the molecules near the interface. Therefore, a thin "model" system is not necessarily representative of a thick coating. To access the buried interface of the thick coating on a metal substrate, the cross section was obtained via a cross-section polisher (CSP). Figure 2 illustrates a schematic representation of the two approaches used to reach the buried interface.

For this study, poly(acrylic acid) (PAA) on aluminum oxide was chosen as a model system. PAA contains a carboxylic acid functional group, which is frequently used for different industrial applications.[21,22] Consequently, because of its relevance, the interaction of carboxylic acids with aluminum oxide has been broadly studied in the literature.[2,8,23−28]

EXPERIMENTAL METHODS

Sample Preparation. To study a thin film of PAA on aluminum oxide via AFM-IR, samples were cut from a 0.3 mm thin sheet of commercially pure aluminum (99.99%) and ultrasonically cleaned in ethanol and etched in an aqueous solution of 25 g/L NaOH at 70 °C for 1 min, rinsed for 15 s in deionized water, and then ultrasonically rinsed for an additional 3 min. To provide a AFM suitable substrate and to exclude topographical effects, the samples were electropolished in a solution of 80 vol % (absolute) ethanol and 20 vol % perchloric acid, at current density of 70 mA/cm^2 and 10 °C for 6 min. Subsequently, the sample was rinsed following the procedure described above. After electropolishing the samples were anodized to have a reproducible aluminum oxide layer. Galvanostatic anodizing was performed in a solution of 0.1 M diammonium tartrate to create a oxide barrier layer. The current density was set to 5 mA/cm^2 and a potential of 20 V. The polymer film was deposited via immersion in methanol solution. Two different concentrations of PAA (average M_w = 450000 g mol^{-1}) were used: 0.1 and 0.5 wt %. After immersion in the latter solution the samples were immersed for 2 h in pure methanol solution to look only at the chemisorbed species. To obtain a bulk spectrum of the polymer, a drop of solution of 0.1 wt % PAA was deposited on template-stripped gold chips provided by Platypus Technology (100 nm Au on silicon wafer). The chip was freshly cleaved right before use and therefore free from contamination. The gold was chosen as substrate to obtain a bulk spectrum as it is not expecting to react with PAA. In this way the spectra are representative of the bulk polymer and not of the substrate/polymer interface. For the cross-section polisher, samples were cut from a 0.3 mm thick sheet of commercially pure aluminum (99.99%). The same cleaning and anodizing procedure that was described above has been used. A gel-like PAA solution was formed by dissolving high concentration of PAA in methanol. Subsequently, the gel was spread over the metal substrate and dried in air for 24 h.

Visible Spectroscopic Ellipsometry (VISSE). To measure the thickness of the organic coating on the aluminum substrate, VISSE was performed on the aluminum substrate exposed to 0.1 and 0.5 wt % PAA in methanol solution after rinsing. The measurements were obtained by a variable angle spectroscopic ellipsometer (VASE, J.A. Wollam Co.). The wavelength ranged from 250 to 1000 nm in 10 nm steps. The angles of incidence used were 60°, 65°, and 70°. The spectra were analyzed by using the Complete EASE software (version 4.26) developed by J.A. Woollam Co.

Cross-Section Polisher (CSP). A Jeol IB-09010CP cross-section polisher was used. Prior to the cross polisher a prepolishing step on a cross section of one side of the sample was performed. Polishing occurred with an Ar^+ ion beam at 5−6 keV for 3 h.

AFM-IR. AFM-IR was performed on a NanoIR2-s system (Anasys Instruments−Bruker) in contact mode at a scan rate of 0.5 Hz using a gold-coated silicon nitride probe (0.07−0.4 N/m spring constant, 13 ± 4 kHz resonant frequency, Bruker). For the thin film a pulsed broadly tunable QCL laser with a spectral range 1450−1769 cm^{-1} was used. Spectra were obtained at a single position using 1024 coaverages for each data point. Several points (more than three) were taken to ensure reproducibility. Raw AFM-IR spectra in general show a signal-to-noise ratio lower than for conventional IR spectra. For this reason, AFM-IR spectra are usually smoothed by using the Savitzky−Golay function. For the cross-polished section a tunable OPO laser with spatial range 850−2300 cm^{-1} was used. Spectra were obtained at a single position using 1024 coaverages for each data point. Peak fit and area were measured using the peak fitting option of the software OriginPro version 9.0. A baseline was constructed by connecting the lowest data points on either side of the peak, and peak fitting was done with Gaussian distribution functions. The errors associated with the calculation of the area beneath the fitted peaks were used together with an error propagation procedure to calculate the final error associated with the values of the peak ratios. For the cross section, several line spectra were taken to confirm reproducibility.

■ RESULTS AND DISCUSSION

A comparison of the bulk spectrum of PAA and a thin layer (20 nm obtained with VISSE measurements) of PAA on the aluminum substrate analyzed via AFM-IR is presented in Figure 3. For each spectrum a normalization procedure was applied in which the spectrum was divided by the maximum intensity value recorded and the lowest point of the spectrum was shifted to zero. The bulk spectrum was obtained by depositing drops of solution of 0.1 wt % on a freshly cleaved gold chip. The gold was chosen as substrate to obtain a bulk spectrum as it is a nonreactive metal, and therefore PAA is not expected to be chemiabsorbed on a gold substrates. In this way the spectra would be representative of the bulk polymer and not of the substrate/polymer interface. In the bulk spectrum, the characteristic carbonyl dispersion band (C═O) can be seen at 1700 cm^{-1}. In the spectrum of the thin PAA on aluminum oxide, this peak is slightly shifted toward higher wavenumbers (1718 cm^{-1}) while a new peak can be clearly seen at 1602 cm^{-1}. An AFM-IR spectrum of the uncoated anodized sample is shown in Figure 3 to rule out possible contributions coming from the metal substrate. The interaction between carboxylic acid and aluminum oxide has been extensively studied in the literature. Alexander et al. studied thin deposits of PAA on fully hydrated alumina by means of XPS and FTIR. They identified the formation of carboxylate species at the aluminum oxide/PAA interface due, as well, to the presence of symmetric and asymmetric stretching vibration of the carboxylate functionality assigned at 1560 and 1322 cm^{-1}.[2] Brand et al. studied the interaction of different carboxylic acid-based model compounds with differently prepared aluminum substrates via infrared reflection absorption spectroscopy (FTIR-RAS). In their study it was seen that all the carboxylic acid groups are deprotonated to form a coordinatively bonded carboxylate with the alumina substrate. For all the different carboxylic acid adsorbed on aluminum substrates a broad band in the 1600 cm^{-1} region was assigned to the asymmetric carboxylate stretching vibration COO^-.[23] Pletincx et al. performed 24 h in situ ATR-FTIR in Kretschmann geometry to follow the bonds formed at the interface between a thin layer of Al_2O_3 and 0.01% w/w PAA solution in methanol. During the exposure to the PAA solution, the growth of a peak at 1595 cm^{-1} was assigned to the $\nu_{as}(COO^-)$ carboxylate stretch.[8]

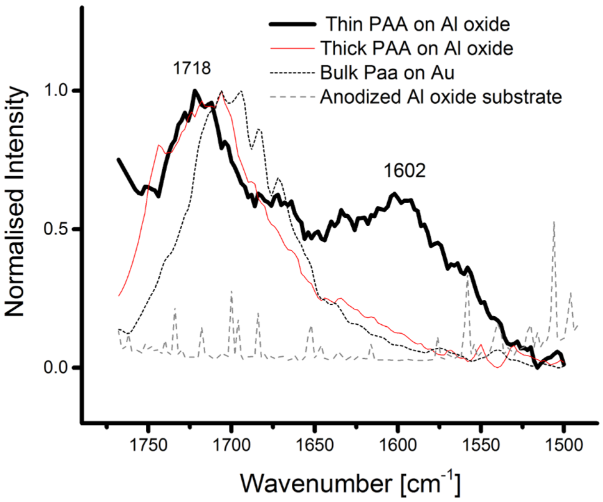
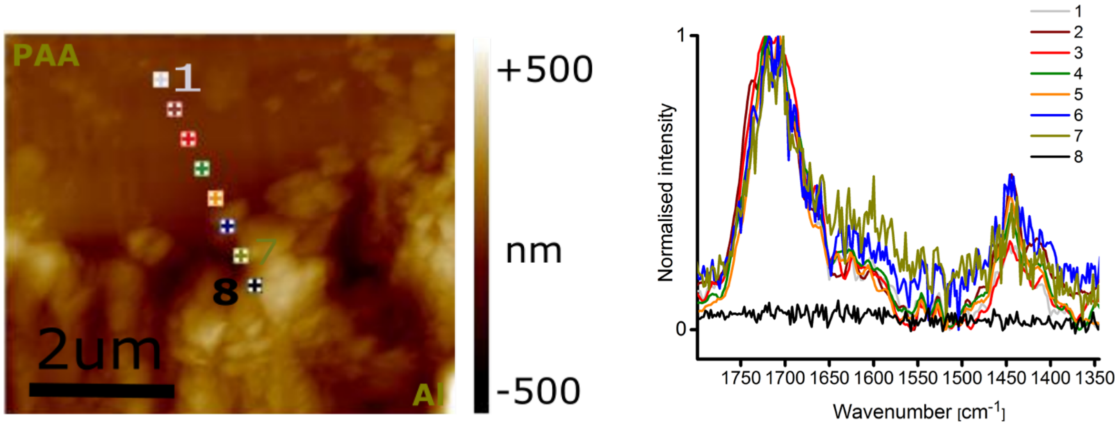


Figure 3. AFM-IR spectrum of bulk PAA (dotted), a thin layer of PAA on Al_2O_3 (black), a thick layer of PAA on Al_2O_3 (red), and the anodized aluminum substrate (gray dotted).

Together with the studies cited above, several other studies used IR-based techniques[24−28] and showed the formation of a carboxylate anion as reaction of a carboxylic acid functional group with the hydroxyl group of the aluminum oxide surface whose asymmetric stretching ν_{as} frequency has been assigned between 1510 and 1685 cm^{-1}. Therefore, we identify the peak present at 1602 cm^{-1} as representative of the carboxylate formed at the PAA/Al_2O_3 interface. It must be noted that some of the mentioned studies show reflection and not

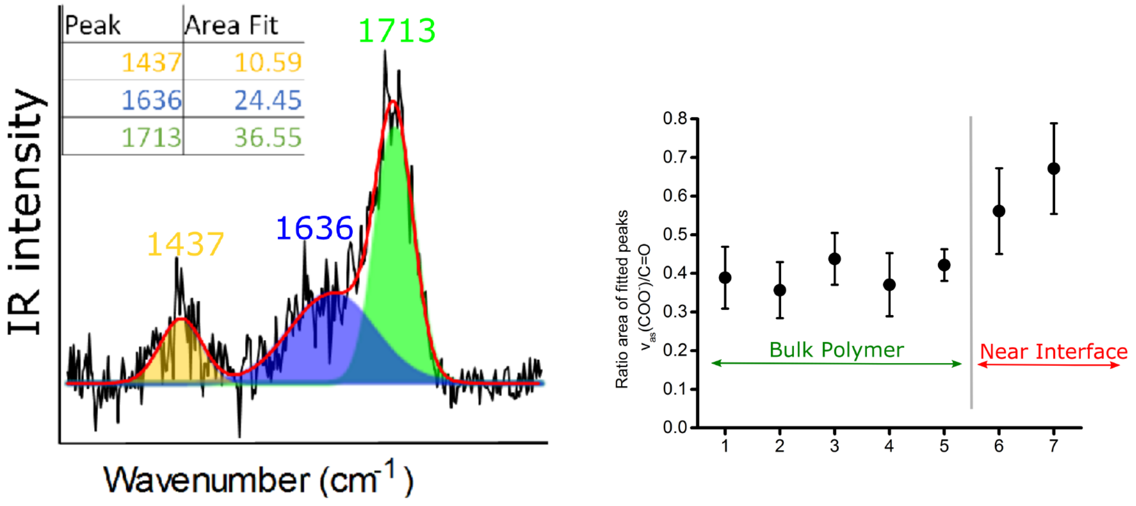


(a) (b)

Figure 4. Cross section of a thick layer of PAA on aluminum substrate obtained via CSP: (a) AFM-IR contact mode height image. (b) AFM-IR spectra of different points as a function of the position.

absorption spectra. According to previous studies,[29] reflection and absorption spectra cannot be directly compared as there might be a discrepancy in the vibrations' peaks. However, in this study only a maximum discrepancy of 30 cm^{-1} wavenumber has been found. In the studies mentioned above, the asymmetric carboxylate band has been reported in a much broader wavenumber range (as mentioned between 1510 and 1685 cm^{-1}). Therefore, the difference between this band in a reflected and an absorbed spectrum is almost negligible compared to the wide range in which it has been found in other works. To have additional confirmation that the peak is due to the interface, a thicker layer (50 nm obtained with VISSE measurements) of PAA on aluminum oxide was analyzed (Figure 3). In this case, the peak characteristic for the carbonyl dispersion band is in the same position as the one of the thin PAA (1718 cm^{-1}). However, the peak that is representative for the formation of carboxylate species is not present anymore. The absence of a peak for the carboxylate species for thicker coating (50 nm) confirms that in the 20 nm coating the peak at 1602 cm^{-1} is actually coming from the interface and is not due to other contributions. It should be noted that the interface itself is on the order of nanometers. Therefore, if the signal coming from such a thin layer is buried beneath a thicker coating, there is a higher contribution coming from the bulk phase polymer rather than the interface, and therefore the latter cannot be detected anymore. The presence of a carbonyl dispersion band ($C{=}O$) for the PAA adsorbed on aluminum oxide indicates the presence of undissociated carbonyl groups. As the band remains present even after the sample has been rinsed for 2 h in the methanol solution, it originates from species strongly bonded to the oxide surface. The shift of the carbonyl dispersion band to higher wavenumber for the thin and thick layer compared to the bulk may be due to the different ordering or morphology of the carbonyl bulk compared to thinner ordered layers. Moreover, it was shown by Keddie et al.[30] that the glass transition temperature (T_g) decreases as the thickness of the film is reduced. Peng et al.[31] proved that the characteristic vibration modes of the same chemical group are to some extent under the influence of the glass transition process of the polymer. According to their studies, polymers with a lower T_g absorb IR light at higher wavenumbers. Therefore, the change in T_g and, consequently in IR absorbance, can explain the shift of the carbonyl dispersion band to higher wavenumbers for a thin compared to a thicker layer.

The second approach consists of analyzing the exposed interface of a cross section of PAA on aluminum oxide obtained via CSP. The AFM height image of this section (Figure 4a) shows a clear distinction between the polymer and the metal oxide phase. A line scan across the interface was taken. It must be taken into account that when taking chemical images, thermomechanical artifacts may have an influence on the intensity of the IR detected as mentioned by Dazzi et al.[13] However, in our study, we are performing single-point measurements, and all the spectra have been normalized; therefore, a possible difference due to thermomechanical properties would be ruled out. Moreover, the high spatial resolution of the AFM-IR decreases by increasing the thickness.[32] In our case the probed polymer part of the cross sections (as seen in the graphical representation in Figure 2b) is relatively thick, thus reducing the lateral resolution. Each spectrum in Figure 4b represents a point of the line scan. Spectrum 7 is closer to the PAA/Al oxide interface than spectrum 1. It can be seen that for all the spectra both a peak characteristic of the carbonyl band (around 1700 cm^{-1}) and a peak representing the carboxylate (around 1600 cm^{-1}) are present. Moreover, an additional peak can be seen in the region around 1450 cm^{-1}, which can be associated with both the symmetric COO^{-1} stretching or the CH_2 bending. The spectrum corresponding to point 8 (which is situated on the aluminum part) shows purely noise as consequence of the absence of PAA. As point 8 was the last one to be recorded for this line scan, these results exclude the possibility of any AFM tip contamination due to organic species adsorption during the measurement. In the cross section, the carbonyl band (1700 cm^{-1}) is present in the polymer phase part (points 1−7) while the presence of the $\nu_{as}(COO^{-})$ is expected only for points very close to the interface. However, from Figure 4b it can be seen how a contribution around 1600 cm^{-1} is present for all the points (with the exception of point 8). This small contribution at 1600 cm^{-1} was seen in all the points probed in the polymer phase for the CPS sample. As we do not expect to have an extensive interphase region, the presence of this small peak could be due to an artifact. The cross section is in fact created by argon ions. It has been shown that the argon ion beam causes chemical damage, especially for polymers.[33,34] Therefore, a damage on the first layer of the cross section due to the



(a) (b)

Figure 5. Example of peak fitting after baseline correction and area calculation (point 7). To quantify the contribution of the interface for the different points, a ratio between the area beneath the $\nu_{as}(COO^-)$ contribution (blue line) and the C═O contribution (green line) was taken. (b) Value of ratios as a function of position (1 further from the interface, 7 closer to the interface).

Ar^+ ion beam may happen and, hence, the presence of these artifacts could be the result of beam damage. Despite this, as the AFM-IR laser causes thermal expansion not only of the damaged layer but of layers underneath it, a contribution coming from the interface will still be probed together with other contributions.

To investigate the contribution in the peak at 1600 cm^{-1} coming from the hybrid interfacial bonding, we looked at the intensity of this peak as a function of position. As AFM-IR produces very noisy spectra, it was necessary to implement a fitting procedure to exclude the contribution of noise. These spectra obtained for the cross-section approach were not smoothed by using the Savitzky−Golay function to avoid any influence of this procedure on the quantification performed through the fitting of these peaks. After fitting, it was possible to calculate the area beneath the peak. However, differences in intensities may be due to variations in topography from one point to another. By taking a ratio of two peaks in the spectrum, the influence of topography can be ruled out. Figure 5b shows the ratios of $\nu_{as}(COO^-)$ and C═O intensities as a function of position. While for the first 5 points the ratios are very similar to an average around 0.39 ± 0.06, points 6 and 7 both show a higher value (0.56 ± 0.11 and 0.67 ± 0.11, respectively). The fact that the relative contribution of this peak in the spectra is always approximately the same together with the fact that the this small peak is seen in all the spectra taken in the polymer phase supports the possibility mentioned above that the peak at 1600 cm^{-1} is due to the presence of an artifact. However, for points 6 and 7, which are closer to the interface, an extra contribution is added as it can be seen from the steplike behavior in Figure 5b. As an interface must be formed between the metal oxide and the polymer and this interface will create carboxylate ions (whose contribution can be seen at around 1600 cm^{-1}), we have strong reasons to believe that the added contribution is due to the interface. The peak around 1450 cm^{-1}, as mentioned above, is characteristic of the COO^- symmetric stretching vibration. However, the same frequency range is characteristic as well for the CH_2 bending vibrations coming from the bulk PAA. Taking a ratio of the area of the peak characteristic of the ($\delta(CH_2)$ + $\nu_s(COO^-)$) and ν_{as}(C═O) shows a different trend than the one seen in Figure 5b. In fact, approximately the same values were obtained for all the points of the line scan. This is due to the fact that the thermal expansion of the bulk is much higher compared to the one of the very thin interfacial region. Therefore, at 1440 cm^{-1}, the contribution of the bulk is overruling the one of the interface.

The results shown above highlight the importance of sample preparation for this technique. CSP is an accessible and easy-to-use sample preparation technique which allowed to obtain preliminary results on the feasibility of the AFM-IR to obtain information from the interface. A next step in our research is to use focused ion beam (FIB) to create a lamella cross section of adequate thickness and exploit at best the spatial resolution of AFM-IR. A combination of FIB lamella and AFM-IR has been already successfully used by Baden et al.[35] to look at the chemical structure of polyimide films on a copper substrate. Furthermore, the confirmation of AFM-IR as a technique to look at the polymer/metal oxide interface opens the possibility to in situ probe the effect of humidity on interfacial interactions of a realistic sample, while the study of the effect of humidity/water on the interface has been done only on model systems so far. In situ AFM-IR has been already used by Morsch et al.[36] to map the water uptake in organic coatings. By placing a sample chamber equipped with a portable temperature and humidity logger, they were able to look at the chemical changes under raised humidity of epoxy−phenolic coatings. Furthermore, in real-life applications, the metal substrates are highly heterogeneous due to, for example, alloying elements or defects presents on the surface. Because AFM-IR is capable of probing the chemical buried interface with high lateral resolution, this will allow to pinpoint the effect of these heterogeneities of the substrate on the adhesion properties of the system.

■ CONCLUSION

To sum up, in this work for the first time AFM-IR was proven to be able to be a suitable characterization technique to probe the buried interface of a polymer/metal oxide using a well-known model system: PAA on aluminum oxide. Two different methodologies were used: a thin film and a cross section. The thin film approach confirmed the possibility to use AFM-IR to probe the hybrid interface to obtain information about the chemical bond present. Therefore, our research opens up the opportunity to use AFM-IR to look at the buried interface by overcoming most of the limitations encountered with other techniques such as the need for ultrahigh vacuum, the low lateral resolution, or limitations in sample preparations. Moreover, because of the high lateral resolution of the AFM-IR, it was possible to probe the interface of an "industrially relevant" thick coating−metal substrate interface on a cross section obtained via CSP. Through a semiquantitative analysis we were able to clearly identify the chemical contribution from the interfacial bonding.

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Notes

The authors declare no competing financial interest.

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