A combined Fourier transform infra-red multiple specular reflectance and inelastic electron tunnelling spectroscopy study of poly(methyl methacrylate) on oxidized aluminium

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The interaction between poly(methyl methacrylate) (PMMA) and oxidized aluminium surfaces has been studied using Fourier transform infra-red multiple specular reflectance (*FT*i.r.-MSR) and inelastic electron tunnelling spectroscopy (IETS). *FT*i.r.-MSR spectra of ultra thin (~ 1 nm) PMMA films show an enhancement of the intensity in the low frequency wing of the carbonyl absorption. The peak is shifted to lower frequency and broadened compared to theoretical predictions. This suggests hydrogen bonding between the PMMA carbonyl species and the surface hydroxyl groups. The relative intensity of the carbonyl mode in the IETS spectrum is very low and its frequency is lowered compared to the i.r. result. In addition, a small band is observed at the position of the $\nu_s(CO_2^-)$ vibration. However, ester bond cleavage and subsequent formation of ionic carboxylate bonds is very unlikely, because it contradicts the *FT*i.r.-MSR results. This suggests an intrinsically low intensity of carbonyl bands in IETS. The inertness of the lead counter electrode in IETS is discussed. The lead electrode may account for the downward shift of the carbonyl vibration in IETS.

(Keywords: inelastic electron tunnelling; Fourier transform infra-red multiple specular reflectance; vibrational spectroscopy; surface analysis; poly(methyl methacrylate); polymer–metal interface)

INTRODUCTION

Both inelastic electron tunnelling spectroscopy (IETS) and Fourier transform infra-red multiple specular reflectance (*FT*i.r.-MSR) are suitable techniques for obtaining vibrational spectroscopic information on polymer–metal interfaces. The IETS technique is restricted inherently to very thin layers (< 2 nm), whereas there is no such restriction on *FT*i.r.-MSR spectroscopy. Recent IETS studies[1–4] have suggested that the interaction between e.g. poly(methyl methacrylate) (PMMA) and an oxidized aluminium surface takes place through cleavage of the ester bond followed by the formation of carboxylate bonds. Generally, IETS spectra are compared to i.r. transmission spectra of thick films or compounds similar to the surface species pressed in KBr discs. However, state-of-the-art *FT*i.r. spectrometers can provide reasonable spectra of even monomolecular layers on metal substrates[5]. Therefore, polymer films in the nanometre range pose no serious problems. In the present work we compare the IETS and *FT*i.r.-MSR spectra of spin-coated PMMA layers on oxidized aluminium substrates. The effect of the counter electrode in IETS has been simulated in *FT*i.r.-MSR spectroscopy by depositing a very thin lead layer on top of a PMMA layer. A comparison is made with calculated spectra for the carbonyl absorption region to avoid misinterpretation due to trivial optical effects. In addition, *FT*i.r.-MSR spectra for various PMMA layer thicknesses are studied.

EXPERIMENTAL

Samples for *FT*i.r.-MSR measurements were prepared by depositing aluminium from a heated tungsten filament on glass slides (20×50 mm^2) at a rate of ~ 0.5 nm s^{-1} to a total thickness of 200 nm in a vacuum system ($< 10^{-1}$ mPa). The glass slides were cleaned prior to use by immersion in chromic acid for 30 min followed by subsequent rinsing with water and ethanol. Samples for IETS were prepared on glass microscope slides, which were cleaned in a similar way. Aluminium strips (1 mm wide) were deposited on to the slides. After metal deposition pure oxygen was admitted to the vacuum system to form a native oxide layer on the metal. Thin films of PMMA (average M_W 81 000) were deposited on these oxidized metal substrates by spin-coating from chlorobenzene solution. The spin-coater operated at 2000 rev min^{-1} for a period of 30 s. Subsequently, the samples were brought into a vacuum system ($< 10^{-1}$ mPa) for ~ 30 min to remove remnants of the solvent. The concentration of PMMA in chlorobenzene (0.006–1% (w/w)) determines the average layer thickness of the polymer film. The preparation of the IETS junction was finished by depositing the lead counter electrode as a crossed bar on top of the aluminium strip resulting in a junction area of 1 mm^2. Conditions similar to those for the deposition of aluminium were applied, except that the lead was evaporated from a molybdenum crucible to a thickness of ~ 100 nm. The thickness of the PMMA layers was measured by ellipsometry. Details of the

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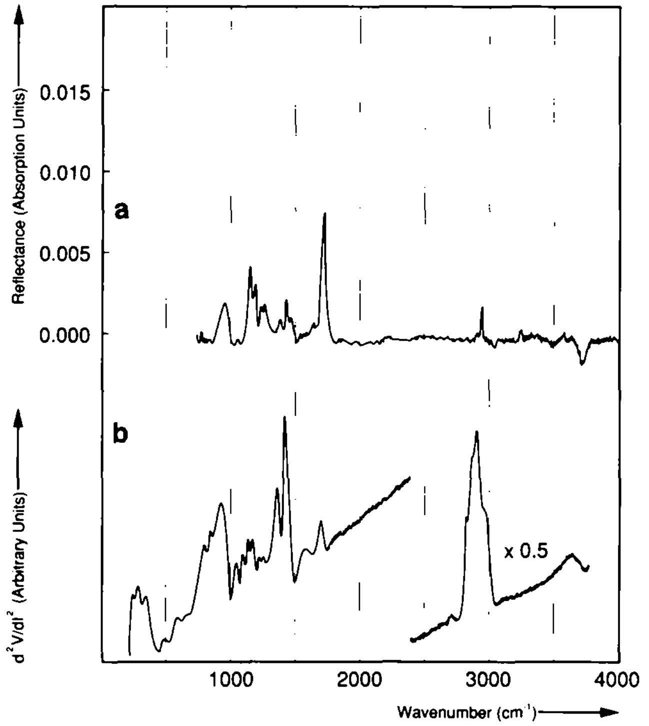

Figure 1 (a) *FT*i.r.-MSR spectrum of a PMMA layer spin-coated from a 0.006% (w/w) solution in chlorobenzene on an oxidized aluminium surface. (b) IETS spectrum of a similar sample

*FT*i.r.-MSR[5] and IETS[6] instrumentation used can be found elsewhere.

RESULTS AND DISCUSSION

The average thickness of spin-coated PMMA layers has been determined on silicon wafers. The continuous growth of the oxide layer on pure aluminium and the rapid contamination of untreated oxidized aluminium substrates prevented direct measurement on aluminium. A linear relationship between the layer thickness and the polymer concentration in the spin-coating process was obtained for concentrations between ~0.05% and 1% (w/w). At concentrations >1% the viscosity of the solution is affected, resulting in relatively thicker layers. At concentrations <0.05% the thickness remains almost constant for the concentration range studied here. In the linear range the layer thickness is ~25 nm $\%^{-1}$ PMMA in chlorobenzene.

An *FT*i.r.-MSR and an IETS spectrum of a very thin PMMA layer, average layer thickness ~1 nm (0.006% (w/w) solution), are displayed in *Figure 1*. The assignments[7,8] of the *FT*i.r.-MSR and IETS bands are given in *Table 1*. IETS spectra could only be obtained using concentrations of <0.05% PMMA in chlorobenzene. The lowest concentration used, however, yielded the best signal-to-noise ratio with IETS.

Comparison of the *FT*i.r.-MSR and IETS spectra in *Figure 1* reveals that the carbonyl band is much more intense in the *FT*i.r.-MSR spectrum. Moreover, the band is shifted to lower wavenumbers in the IETS spectrum (*Table 1*). A weak band is observed at 1595 cm^{-1} in the IETS spectrum. The low intensity of the carbonyl band, together with the observation of a band at ~1600 cm^{-1} in the IETS spectrum, led others[1] to suggest hydrolysis of the ester group by the surface hydroxyl groups. The hydrolysis of the ester would result in the formation of a carboxylate ion. This ion should have absorptions at ~1470 and 1600 cm^{-1} for the $\nu_s(CO_2^-)$ and $\nu_a(CO_2^-)$ modes, respectively[7]. This interpretation seems to be reasonable. However, in the case of PMMA it contradicts the *FT*i.r.-MSR result in *Figure 1*, which is measured on a sample of similar PMMA thickness as that used for the IETS measurement. There is no evidence for the formation of carboxylate ions or for a reduction of the carbonyl absorption in the *FT*i.r.-MSR spectrum in comparison with spectra of thicker layers in transmission or reflection. Carboxylate vibrations would appear as strong bands in the i.r. The low intensity of the carbonyl absorption must therefore be an intrinsic effect of IETS. The lead counter electrode was deposited with the substrate at liquid nitrogen temperature to check the possibility of heat-induced conformational effects. However, the spectrum was shown to be the same as spectra obtained with the lead deposited without cooling of the substrate.

The weak IETS mode at 1595 cm^{-1} may be either an artefact of the strong band at 1440 cm^{-1} due to the superconducting lead electrode[9] or it may be caused by the presence of a small amount of carboxylate groups. The latter suggestion can only be accounted for by assuming a much higher sensitivity of IETS for vibrators close to the aluminium electrode[10]. The IETS band at 1440 cm^{-1} forms no evidence for the formation of carboxylate ions, because CH deformation modes contribute significantly to IETS bands in this region[11]. The possible influence of the lead counter electrode on the IETS spectrum, in particular on the position of the carbonyl mode, will be discussed in the following.

By studying samples with *FT*i.r.-MSR spectroscopy in a series with decreasing layer thickness it may be possible to infer information about the metal–polymer interface. The effects of the interface will become more and more pronounced with decreasing layer thickness. Although ester bond cleavage followed by ionogenic bonding to the surface cannot be proved, the carbonyl

Table 1 Assignments of bands in the *FT*i.r.-MSR and IETS spectra of PMMA on oxidized aluminium

IETS	*FT*i.r.-MSR	Assignment[a]
805(m)		?
850(sh)		$r(CH_2)$
935(s)	963(m)	$r(CH_3)$/Al–O
1055(w)		ν(C–C)
1110(w)		C–(C=O)–O
1150(w)	1155(s)	C–(C=O)–O
1185(w)	1196(m)	C–(C=O)–O
1250(br)	1245(w)	C–(C=O)–O
	1274(w)	C–(C=O)–O
1375(m)	1390(w)	$\delta_s(CH_3)$
1440(s)	1437(m)	$\delta_a(CH_3)/\delta(CH_2)$
	1474(w)	$\delta(CH_2)$
1595(w)		$\nu_a(CO_2-)$??
1715(w)	1736(vs)	ν(C=O)
2850(sh)		$\nu(CH_2)/\nu((O)CH_3)$?
2940(vs)	2956(m)	$\nu((O)CH_3)$
2985(sh)		$\nu((O)CH_3)$

[a] See references 7 and 8

Abbreviations: r, rocking vibrations; δ, deformation vibrations; ν, stretching vibrations. Subscripts a and s denote asymmetric and symmetric stretching vibrations, respectively. Intensity indications: w, weak; m, medium; s, strong; vs, very strong; br, broad; sh, shoulder

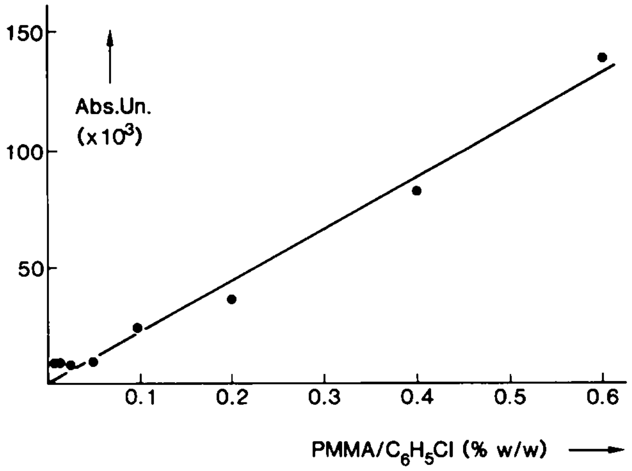

Figure 2 *FT*i.r.-MSR intensity of the carbonyl absorption of PMMA layers on oxidized aluminium as a function of the concentration of PMMA in chlorobenzene

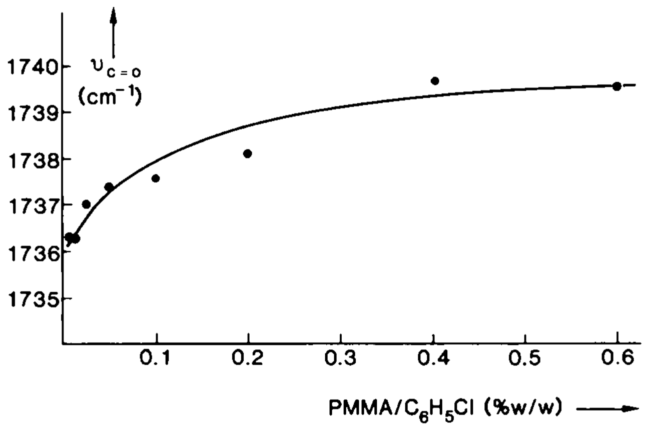

Figure 3 *FT*i.r.-MSR band position of the carbonyl absorption of PMMA layers on oxidized aluminium as a function of the concentration of PMMA in chlorobenzene

species of the PMMA molecule is expected to be particularly sensitive to non-reactive interaction with oxidized metal surfaces. The intensity and band position of the carbonyl band as a function of the PMMA layer thickness (concentration) on an oxidized aluminium surface are shown in *Figures 2* and *3*, respectively. The intensity of the carbonyl band is an approximately linear function of the concentration. The intensity levels off at very low concentrations, i.e. the intensity has an almost constant value in this range. This small deviation from linearity is real and was reproduced several times.

A small shift of the carbonyl absorption is observed in *Figure 3*. This shift is largest at the lowest concentrations. The shift is accompanied by a simultaneous broadening of the band resulting in a band width of $\sim 30\,cm^{-1}$ for the lowest concentration. The band width is $23\,cm^{-1}$ for thick layers. Similar effects, but somewhat less pronounced, have been found for PMMA on an oxidized silver surface. A shift of the carbonyl absorption as a function of layer thickness has also been reported for thin α-cyanoacrylate polymer layers[12,13]. It is important to find out whether the effects observed here can be caused by trivial optical effects[14].

In *Figure 4* a comparison is made between measured and calculated spectra of the carbonyl absorption. The film was coated from a 0.006% (w/w) solution of PMMA in chlorobenzene. The calculation is performed using the Fresnel equations for a four-layer system[15], based on the optical constants for PMMA taken from ref. 14. Optical constants for aluminium and lead were interpolated from literature data[16].

If we compare the solid lines in *Figures 4a* and *b* it becomes clear that the measured band is much broader than the calculated band. In particular a long tail is observed on the low frequency side, giving the band an asymmetric shape. A thickness of 1 nm for the PMMA layer was used to calculate the spectrum. As an example of a thicker PMMA layer, the measured and calculated spectra representing a 0.4% (w/w) solution ($\sim$8 nm layer thickness) are displayed in *Figure 5*. The carbonyl bands in the measured and calculated spectra have similar shapes in this case. Moreover, the bands are quite similar to the band calculated for the thin layer in *Figure 4b*, except for the difference in intensity. Therefore, in this thickness range there appear to be no trivial optical effects, which may disturb band positions and band shapes. Another reason to rule out trivial optical effects is that the ratio of the thickness and the wavelength is well below the limit for the linear approximation[17] of the Fresnel equations to be valid.

To simulate the effect of the lead counter electrode, samples were prepared with 3 nm lead deposited on top

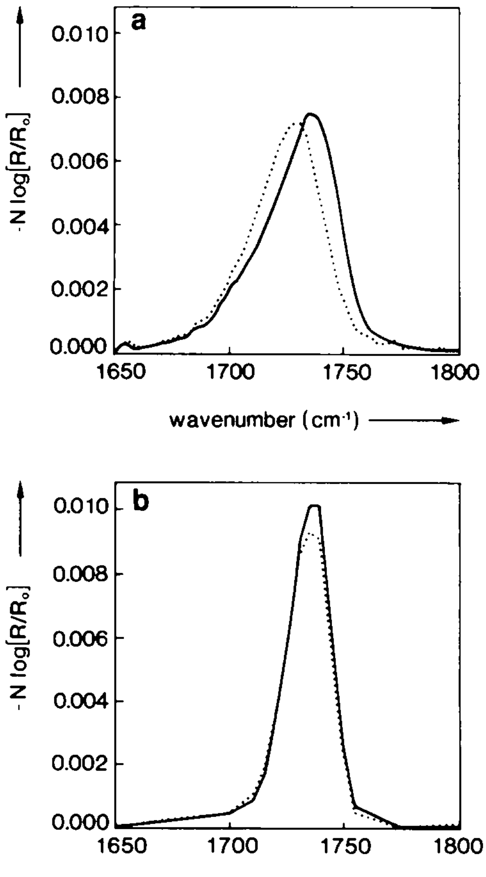

Figure 4 (a) Carbonyl absorption region of the *FT*i.r.-MSR spectrum in *Figure 1* (0.006% (w/w) PMMA in chlorobenzene). (b) Calculated MSR spectrum assuming a 1 nm PMMA film. The dotted lines in (a) and (b) correspond to measured *FT*i.r.-MSR and calculated MSR spectra, respectively, of a similar thin PMMA film covered with a 3 nm lead layer

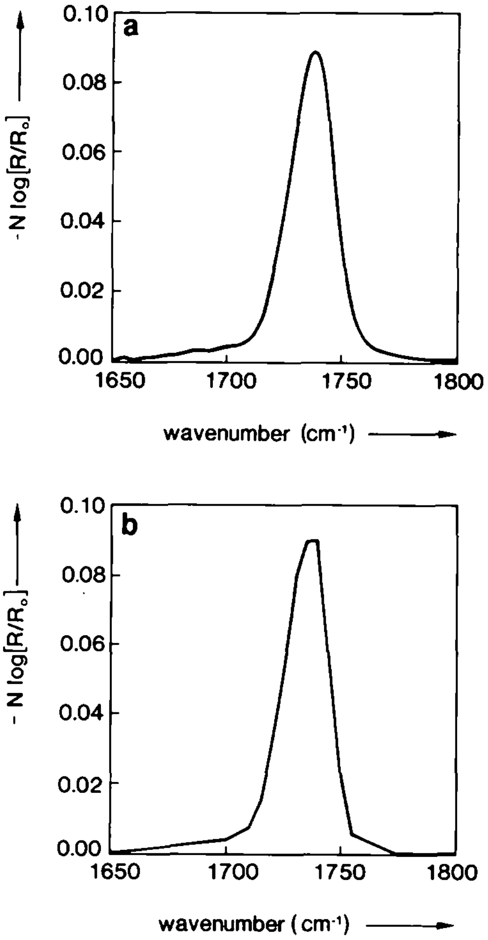

Figure 5 (a) Carbonyl absorption region of an *FT*i.r.-MSR spectrum of a PMMA layer spin-coated from a 0.4% (w/w) solution in chlorobenzene on an oxidized aluminium surface. (b) Calculated MSR spectrum assuming a 8 nm PMMA film

of a 1 nm PMMA film. Such a thin metal layer is transparent to i.r. light. The spectrum of the carbonyl absorption thus obtained is depicted by the dotted line in *Figure 4a*. The line is shifted to lower wavenumbers compared with the uncovered PMMA film. The calculated spectrum in *Figure 4b* does not show any significant shift to lower wavenumbers. The most likely explanation for the observed shift is therefore an interaction between the carbonyl groups of PMMA with the lead layer. A shift of the carbonyl band to lower wavenumbers was also observed for IETS in comparison with *FT*i.r.-MSR (*Table 1*). The *FT*i.r.-MSR spectra of the lead-covered samples are also disturbed in the CH stretching and CH deformation regions but discussion of this phenomenon is beyond the scope of the present investigation.

CONCLUSIONS

The almost constant carbonyl intensity observed for lower concentrations may be an indication of polymer–metal interaction. The layer thickness is no longer determined by the hydrodynamics of the spin-coating technique but by the adherence of an ultra thin polymer film to the oxidized metal substrate. Furthermore, the line shift and broadening observed are in support of such a conclusion. The shift and asymmetry towards lower frequencies suggest the formation of hydrogen bridges between the carbonyl groups of the polymer and the surface hydroxyl groups of the oxidized aluminium. Calculations show that trivial optical effects can be excluded as an explanation for these observations.

There is a remarkable difference between the *FT*i.r.-MSR and IETS spectra. The carbonyl band in the IETS spectrum is comparatively weak and a band at 1595 cm^{-1} is observed which is not present in the *FT*i.r.-MSR spectrum. Cleavage of the ester bonds of the polymer followed by the formation of carboxylate ions may serve as an explanation for the appearance of the 1595 cm^{-1} band. However, in the *FT*i.r.-MSR spectrum there is no evidence for substantial ester bond cleavage. In conclusion, IETS has an intrinsically low sensitivity for the carbonyl absorption.

Evidence has been presented to indicate that the downward shift of the carbonyl mode in IETS may be caused by an interaction of the carbonyl group with the lead counter electrode. The *FT*i.r.-MSR spectrum of a thin PMMA layer covered with a lead overlayer shows a downward shift in comparison with an uncovered PMMA layer.

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REFERENCES

1 Malik, R. R., Pritchard, R. G., Horley, C. C. and Comyn, J. *Polymer* 1985, **26**, 551

2 Comyn, J., Kinloch, A. J., Horley, C. C., Malik, R. R., Oxley, D. P., Pritchard, R. G., Reynolds, S. and Werret, C. R. *Int. J. Adhes. Adhesives* 1985, **5**, 59

3 Comyn, J., Horley, C. C., Malik, R. R. and Pritchard, R. G. *Int. J. Adhes. Adhesives* 1986, **6**, 73

4 Colleti, R. F., Gold, H. S. and Dybowsky, C. *Appl. Spectrosc.* 1987, **41**, 1185

5 Sondag, A. H. M. and Raas, M. C. *Appl. Spectrosc.* 1989, **43**, 107

6 Van Velzen, P. N. T. *Surface Sci.* 1984, **140**, 437

7 Bellamy, L. J. 'The Infrared Spectra of Complex Molecules', Vol. 1, Chapman and Hall, London, 1975

8 Dirlikov, S. and Koenig, J. L. *Appl. Spectrosc.* 1979, **33**, 551

9 Adler, J. G. in 'Tunnelling Spectroscopy' (Ed. P. K. Hansma), Plenum Press, New York, 1982, Ch. 14

10 Kirtley, J. and Hall, J. T. *Phys. Rev. B* 1980, **22**, 848

11 Sondag, A. H. M., Raas, M. C. and Touwslager, F. J. *Appl. Surf. Sci.* 1991, **47**, 205

12 Kusaka, I. and Suëtaka, W. *Spectrochim. Acta* 1980, **36A**, 647

13 Suëtaka, W. in 'Adhesion Aspects of Polymeric Coatings' (Ed. K. L. Mittal), Plenum Press, New York, 1983, p. 225

14 Allara, D. L., Baca, A. and Pryde, C. A. *Macromolecules* 1978, **11**, 1215

15 Heavens, O. S. 'Optical Properties of Thin Solid Films', Butterworth Scientific Publications, London, 1955, Ch. 4

16 Ordal, M. A., Long, L. L., Bell, R. J., Bell, S. E., Alexander, R. W. and Ward, C. A. *Appl. Optics* 1983, **22**, 1099

17 McIntyre, J. D. E. and Aspnes, D. E. *Surface Sci.* 1971, **24**, 417