

An inelastic electron tunnelling spectroscopy (IETS) study of poly(vinylacetate) poly(methyl methacrylate) and poly(vinylalcohol) adsorbed on aluminium oxide

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IETS is used to investigate the adsorption of poly(vinylacetate) (PVA), poly(methylmethacrylate) (PMMA), and poly(vinylalcohol) (PVOH) on aluminium oxide. These polymers are of interest in the field of adhesion science, and until now synthetic macromolecules have not been studied in this way. Both commercially available polymers and those synthesized in our laboratory have been used. On the basis of IET spectra presented here, and existing i.r. spectra it is believed that PMMA and PVA undergo ester cleavage at the oxide surface leading to their subsequent adsorption. For PMMA this is thought to be via carboxylate anions generated on the polymer side groups, while PVA is expected to be adsorbed as PVOH. Bonding of PVOH to the oxide is not fully understood, but may occur by the formation of an Al-O-C bridge. Another possibility for the above polymers, that of intermolecular hydrogen bonding between polar polymer side groups, and adsorbed hydroxyl species present on the oxide surface, cannot be ruled out.

(Keywords: tunnelling; spectroscopy; poly(vinylacetate); poly(methyl methacrylate); poly(vinylalcohol); adsorption)

INTRODUCTION

Inelastic electron tunnelling spectroscopy (IETS) allows one to examine the vibrational spectrum of a monolayer of organic molecules adsorbed upon the metal oxide surface of a metal/metal oxide/metal thin film sandwich—an IET junction¹⁻³. In this work the junctions were aluminium, aluminium oxide, adsorbed organic layer, and lead. If a d.c. bias voltage is applied to the junction, a net current flows due to electrons tunnelling from one metal to the other as indicated in *Figure 1*. Approximately 1% of these electrons tunnel inelastically and so lose energy to molecular oscillators in the oxide or adsorbed layer. This produces a small increase in conductance of the IET junction at a bias voltage V given by the relationship $V = hv/e$ where h is Planck's constant, e is the electronic charge and v the frequency of the oscillator. This increase is more easily seen as a peak in a plot of the second derivative of the voltage with respect to current (d^2V/dI^2) against bias voltage V . IETS is usually performed with the junction at a temperature 4.2 K, mainly to reduce thermal broadening of the IET lines. Both Raman and infra-red (i.r.) vibrational modes may be activated.

IETS is particularly appropriate for the study of organic compounds used as adhesives or adhesion promoters adsorbed on aluminium oxide as aluminium is a widely studied and commercially important material for adhesive bonding. Other workers have used the technique

to investigate both epoxides and their mixtures with aliphatic amines⁴, cyanoacrylates⁵ and silane coupling agents⁶ adsorbed on aluminium oxide. However, none of these incorporated polymers in IET junctions, although in some cases small molecules were used which then polymerized on the oxide surface.

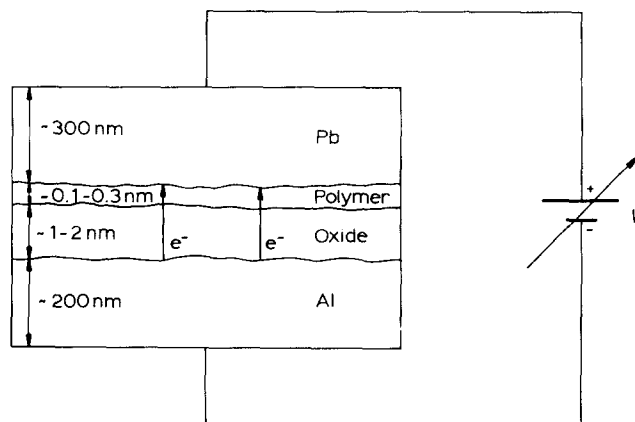


Figure 1 Schematic cross-section through a typical Al/Al-oxide/adsorbed layer/Pb IET junction. When the Pb electrode is biased positively with respect to the Al electrode electrons tunnel from Al to Pb as shown. Approximately 1% of these tunnel inelastically via energy levels in the oxide and/or adsorbed layer

We now report IET spectra for some synthetic polymers directly incorporated into IET junctions, the first time to our knowledge that this has been achieved. The polymers used are poly(vinylacetate) (PVA) which is widely used as an adhesive for wood and paper, poly(methylmethacrylate) (PMMA) which forms the matrix phase in certain rubber-modified reactive adhesives used for bonding metals and other substrates, and poly(vinylalcohol) (PVOH) also used as an adhesive for paper.

By comparing IET, and i.r. spectra of the above polymers, it is possible to investigate the nature of their adsorption on aluminium oxide.

EXPERIMENTAL

Preparation of poly(vinylacetate)

A mixture of 25 cm³ redistilled vinyl acetate, 0.3 g azobisisobutyronitrile (AZBN), and 20 cm³ of acetone was maintained at a temperature of 65°C for 5 h. Acetone acts as a chain transfer agent offering a degree of control of the molar mass. The product was precipitated with water and dried under vacuum.

The molar mass was determined by viscometry from solution in methanol at 25°C in a water bath. Values of K , and α for PVA in methanol at 25°C are $3.80 \times 10^{-4} \text{ cm}^3 \text{ g}^{-1}$ and 0.59 respectively⁹. The viscosity average molar mass was $90\,000 \pm 5000$.

Preparation of poly(methylmethacrylate)

Redistilled methylmethacrylate (MMA) monomer was polymerized under suspension in water. The suspending agent was 0.4 g soluble starch dissolved in 160 cm³ boiling distilled water. This was placed in a reaction vessel fitted with a stirrer, and to it 50 cm³ of MMA and 2 g of AZBN initiator were added. The temperature was maintained at 80°C–85°C for 30 min by means of a water bath. The product was washed in methanol and dried under vacuum. As was the case for PVA the molar mass was determined by viscometry at 25°C but using acetone as the solvent. The viscosity average molar mass was $27\,000 \pm 2500$. The values of K and α used for PMMA in acetone were $7.5 \times 10^{-3} \text{ cm}^3 \text{ g}^{-1}$ and 0.70 respectively⁹.

Commercially available polymers

Three commercially available polymers were investigated; these were:

- (i) PVA supplied by BDH of molar mass 45 000.
- (ii) Poly(vinylalcohol), supplied by Koch-Light of molar mass 72 000.
- (iii) A PVA emulsion sold for bonding wood.

The first two were used as supplied. The PVA emulsion was smeared on a clean glass plate and dried under vacuum. I.r. spectroscopy showed it to be PVA. Its molar mass was determined by viscometry at 25°C in methanol, a viscosity average molar mass of $40\,000 \pm 5000$ was obtained.

It should be noted that PVOH is obtained by the hydrolysis of PVA. I.r. spectroscopy was performed on the Koch-Light material which showed a high degree of hydrolysis as indicated by the absence of carbonyl absorption.

IET spectra

The above polymers were incorporated into IET

junctions by liquid phase doping from solution. A brief description of IET junction fabrication and liquid phase doping is given here as full details appear elsewhere^{2,8}. Firstly, the aluminium base electrode typically ~ 200 nm thick is evaporated onto a clean glass substrate (a microscope slide) through a brass mask, which allows the geometry of the electrode to be defined. This procedure is carried out within a vacuum evaporation chamber at a pressure of $\sim 10^{-5}$ Torr. On removal from the vacuum chamber a thermal oxide approximately 1–2 nm thick is rapidly formed on the aluminium. The slide is then placed on a rotary spinner where a solution of the desired polymer is poured onto the slide and the excess spun off.

The slide is replaced in the vacuum plant and the Pb counter electrode is evaporated typically to a thickness of ~ 300 nm, thus completing the IET junction. The junction is then immersed in liquid helium, and vibrational modes in the range 0 to 500 mV (0 to 4025 cm⁻¹) are investigated with our spectrometer. Details concerning the design, construction and operation of the spectrometer may be found elsewhere^{8,10}.

It should be mentioned at this juncture that the criterion for the choice of solvents for the liquid phase doping of the above polymers was that they should lead to an expansion of the polymer chain; the authors believe that this may lead to a more uniform coverage of the oxide surface. Solutions of approximate concentration 0.05% w/v were found to give optimal spectral sensitivity for the IETS work.

In order to measure the change in conductance of the IET junctions, a small modulation current superimposed upon a slowly increasing current is passed through it. The modulation current produces a second harmonic voltage across the junction which is proportional to d^2V/dI^2 . This small second harmonic voltage is recovered by a lock-in amplifier and tuned pre-amplifier, and plotted as a function of the applied bias voltage V on an X-Y chart recorder. The resulting IET spectrum may also be stored in digital form on a magnetic disc for subsequent manipulation with the aid of an LS1-11 minicomputer. The overall resolution of an IET spectrometer is essentially governed by its signal-to-noise (S/N) ratio, and the combined peak broadening contributions due to thermal, and instrumental effects (ignoring slight shifts in peak position due to superconductivity of the electrodes)^{2,23}. For an Al-insulator-Pb (superconducting) IET junction (Figure 1) at 4.2 K with a modulation voltage of $\sim \sqrt{2}$ mV rms, a spectral line of negligible natural width will be broadened such that the full width at half maximum peak height (FWHM) is approximately 2.7 mV (22 cm^{-1})²³. Under the above conditions, the S/N ratio of our spectrometer is such that with a time constant of 1 s on the lock-in amplifier, and a spectral scan time of ≥ 50 min—as was the case in the present work, peaks approximately 10 cm^{-1} apart can be easily resolved.

In order to test the purity of our 'spectrograde' acetone, two precautionary measures were taken. Firstly, and as a preliminary check, IET junctions were liquid-phase doped with the neat solvent. Resulting IET spectra, and junction resistances were indicative of an undoped device; this is as one might expect since it is known that acetone does not form a stable monolayer on Al-oxide at room temperature by liquid-phase doping¹⁸ (and hence its suitability as a solvent in IETS). Secondly, IET junctions were infusion doped¹⁹ with a $\sim 50\%$ by volume aqueous

solution of acetone; no signs of contamination were apparent in the resulting IET spectra. The cleanliness of our vacuum system is routinely checked by liquid-phase doping of IET junctions with pure water (millipored, and de-ionized to $\sim 10^{-7}$ mho). It has been suggested that reactions at the lead electrode may lead to formic acid contamination. The authors do not believe that this is a serious factor in this context since contamination was not apparent in the resulting IET spectra, and has not been observed in any of our liquid-phase doped IET spectra. However, it is known that such contamination can be a problem in infusion doping experiments^{19,22}, but these are not of direct concern here.

I.r. spectra were recorded on a Perkin-Elmer 683 spectrometer. Solutions of concentration 5% w/v were prepared, which were then spread on a KBr disc, and oven dried at $\sim 60^\circ\text{C}$.

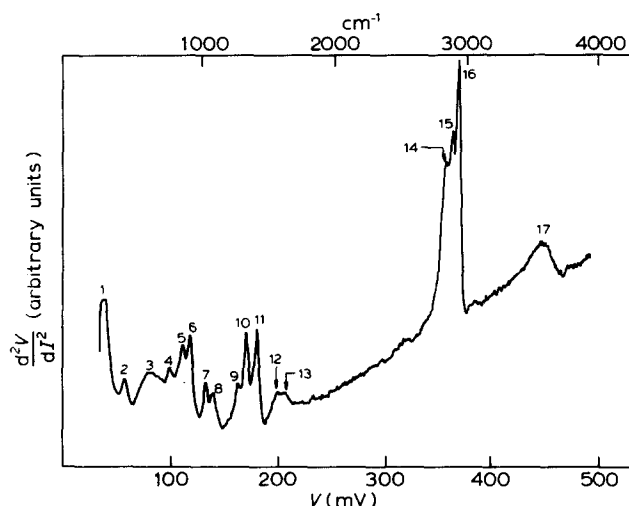


Figure 2 IET spectrum of PVA doped from a $\sim 0.025\%$ w/v solution in acetone

RESULTS AND DISCUSSION

Before discussing the IETS data in detail, the authors feel that a brief qualitative description of the applicability of IETS to the study of surface orientational behaviour is appropriate.

It is believed that chemical bonds whose dipole moment axes lie perpendicular to the oxide surface give rise to a greater change in conductance (and hence IET peak intensity) than those lying parallel to it². This is essentially due to the fact that the bond induces an image dipole in the metal¹¹. The components of dipole moment of the bond and its image normal to the surface are additive, and thus the resultant normal component will be a maximum when the bond is perpendicular to the surface, and a minimum when it is parallel to it. Although the relevant theory is beyond the scope and requirements of this paper, it has been shown that the magnitude of the resultant normal component may vary in quite a complex way as a function of the angle between the chemical bond and the plane of the surface². Thus it is believed that tunnelling electrons couple more strongly with bonds perpendicular to the surface than those parallel to it. One would then expect some degree of correlation to exist between peak intensity, and bond orientation.

Poly(vinylacetate)

Figure 2 shows the IET spectrum for PVA, doped from a 0.025% w/v solution of acetone, and peak assignments are given in Table 1; the IET peak energies have been corrected for the superconducting energy gap of the lead electrode by subtraction of 8 cm^{-1} ².

The most significant feature in the i.r. spectrum is the strong carbonyl peak at 1720 cm^{-1} . The intensity of the IET carbonyl peak is noticeably less, and its frequency is lowered to 1661 cm^{-1} . It has been reported by other workers that such a shift is indicative of intermolecular

Table 1 Assignments for IET and IR spectra of PVA

Peak No.	IETS		i.r. (cm^{-1})	Assignment
	(meV)	(cm^{-1})		
1	37(s)	290		Al phonon
2	56(w)	444		r(COO ⁻)
3	78(w)	621		OH bend
4	98(wm)	782	785	skeletal $\nu(\text{C}-\text{C})?$
5	110(ms)	879	905(w)	$\nu(\text{C}-\text{C})$
6	118(ms)	936	950(w)	Al-O bulk phonon
7	132(m)	1057	1035(w)	r(CH ₃)
8	139(m)	1113	1095(w)	skeletal $\nu(\text{C}-\text{C}-\text{O})$ or $\nu(\text{C}-\text{O})$
9	162(w)	1299	1220(s)	$\delta_s(\text{CH}_3)$
10	170(ms)	1363	1360(s)	$\delta_a(\text{CH}_3)$
11	180(ms)	1444	1430(s)	$\nu_s(\text{COO}^-)$
12	199(w)	1597		$\nu_a(\text{COO}^-)$
13	207(w)	1661	1720(s)	$\nu(\text{C}=\text{O})$
14	356	2863	2920	$\nu(\text{CH}_3), \nu(\text{CH}_2)$ modes
15	362	2912	2960	
16	367	2952	3000	
17	448(m)	3605	3500(w)	$\nu(\text{OH})$

Key to abbreviations and symbols used in assignment tables:

w weak
m medium
s strong

sh shoulder

v very

r rock

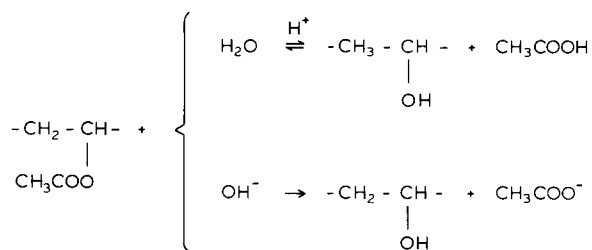
ν stretch, ν_s symmetric, ν_a asymmetric

δ deformation, δ_s symmetric, δ_a asymmetric

hydrogen bonding between the carbonyl group, and absorbed water on the aluminium oxide¹². The reduction in intensity may be attributed either to the orientation of the carbonyl groups relative to the plane of the aluminium oxide surface as outlined above, or a reduction in their number as will now be discussed.

The IET spectrum has two strong peaks at 1444 and 1596 cm^{-1} . These are widely believed to be due to the symmetric, and symmetric stretching vibrations of the carboxylate resonance hybrid COO^- .

A probable explanation for the presence of these peaks is acid- or base-catalysed hydrolysis of ester groups by hydrated alumina to give PVOH and acetic acid or acetate ions as indicated below.



This is possible since aluminium oxide is amphoteric, and hence both basic and acidic sites may hydrolyse the ester. It is known that one of the products; acetic acid is strongly adsorbed on alumina as the acetate ion, which in turn gives rise to the characteristic carboxylate peaks^{13,16}. This would explain the reduction in intensity of the carbonyl adsorption, and also common features in the IET spectra of adsorbed PVA and acetic acid.

In addition to the presence of acetate-like features, very strong aliphatic CH stretching modes are observed *ca.* 2912 cm^{-1} . In a semi-empirical study of monobasic aliphatic acids adsorbed upon alumina, Walmsley and Nelson have shown that some interdependence exists between increasing chain length, and the intensity of the CH stretching vibrations²⁰. A similar effect has also been observed for long chain surfactant molecules²¹. We offer no firm explanation for this observation, but note that in general the IET spectra obtained for polymeric samples in this work exhibit similarly strong CH modes. This may again be due to the orientation of the C-H bonds relative to the oxide surface.

The IET spectrum of adsorbed PVA also shows evidence of low energy polymeric skeletal vibrations of the carbon backbone (see Table 1). The above polymeric features are presumably due to adsorbed PVOH, notwithstanding the inevitable difficulties which arise when comparing the IET spectra of adsorbed PVA and PVOH. As will be seen later, PVOH yields weak, poor quality IET spectra, and in particular the region 550–1120 cm^{-1} is swamped by the Al-O bulk phonon.

We have observed that the IET spectra of the different samples of PVA in acetone, including the PVA emulsion are essentially the same. However, the spectrum of PVA in benzene exhibits a more pronounced carbonyl peak at 1766 cm^{-1} , perhaps indicative of a higher degree of hydrogen bonding between the carbonyl and surface hydroxyl groups.

Further we have found that IET spectra are reproducible for a given solvent, although the spectrum of the polymer in a different solvent may exhibit small changes in peak position and/or intensity. A similar effect has been

observed by other workers⁵. This may open up the possibility of polymer-solvent interactions affecting the adsorption of the polymers on the oxide. However, these slight discrepancies do not seriously detract from the above discussion of the IETS data for the polymers in question. Given the limited range of solvents for polymers in IETS (for reasons discussed in the Experimental section) it is clear that further work is necessary before the nature of this phenomenon can be fully understood.

Poly(methylmethacrylate)

Figure 3 shows the IET spectrum of PMMA doped from a 0.05% w/v solution in acetone, and the relevant peak assignments are given in Table 2. The most significant features are again the strong symmetric and asymmetric stretching vibrations of the carboxylate anion at 1460 cm^{-1} and 1621 cm^{-1} respectively, and a reduction in intensity of the carbonyl peak at 1677 cm^{-1} relative to that of the i.r. spectrum. This would again suggest acid or base-catalysed hydrolysis of the ester groups to the carboxylate. As proposed by Hall and Hansma¹³, it is believed that carboxylic acids dissociate on the Al-oxide surface. They are subsequently adsorbed by the formation of a bidentate symmetrical bridging complex between carboxylate anions and the Al ions in the oxide. As a result, strong carboxylate peaks are observed in IET spectra. Evidence of these peaks in Figure 2 would indicate that carboxylate side groups of the hydrolysed PMMA may also be adsorbed in this manner.

Detection of the methanol by-product would be difficult since it is known that lower aliphatic alcohols are suitable solvents for IETS doping in that they are not strongly adsorbed on aluminium oxide. Presumably, the alcohol would either evaporate from the oxide, or be pumped away in the vacuum system prior to the evaporation of the Pb electrode.

Poly(vinylalcohol)

Figure 4 shows the IET spectrum of a PVOH liquid phase doped from a 0.05% w/v aqueous solution, the corresponding peak assignments are given in Table 3. Although the spectra obtained for PVOH were not particularly strong, tentative evidence exists to suggest the formation of a covalently bonded Al-O-C monodentate bridging complex between alcohol side groups and the oxide surface. For example, Evans and Weinberg^{14,16}

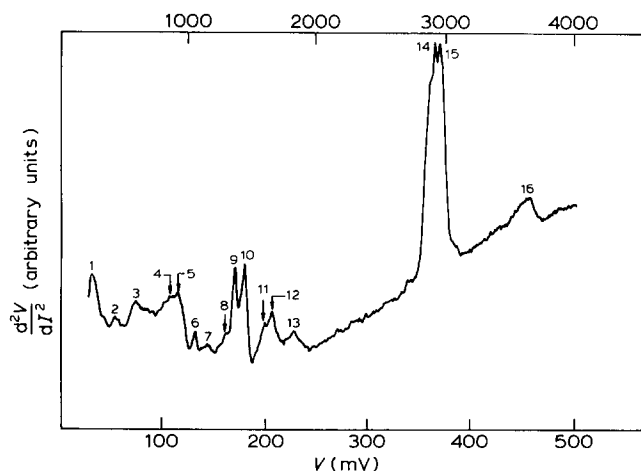


Figure 3 IET spectrum of PMMA doped from a ~ 0.05% w/v solution in acetone

Table 2 Assignments for IET spectrum of PMMA

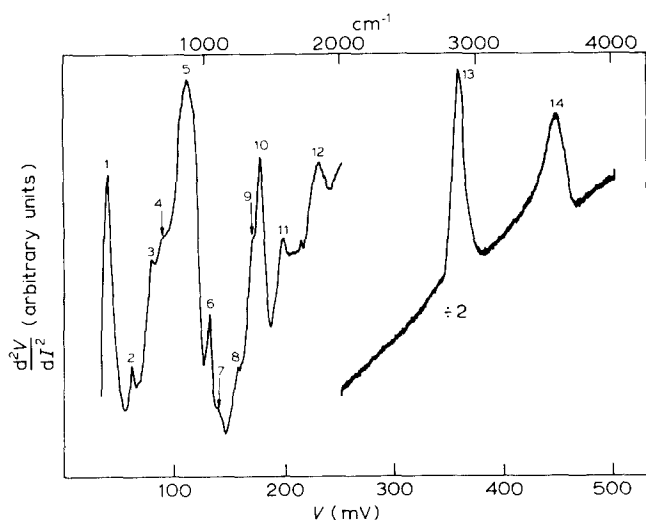
Peak No.	IETS		Assignment
	(meV)	(cm ⁻¹)	
1	35(s) 45(sh)	274 355	Al electrode phonon
2	57(m)	452	r(COO ⁻) in plane
3	77(ms)	613	r(COO ⁻) out of plane and OH bend
4	110(wm)	879	ν (C—C)
5	117(m)	936	Al-O bulk phonon
6	113(wm)	1065	r(CH ₃)
7	147(w)	1178	skeletal ν (C—C—O) or ν (C—O)
8	165(w.sh)	1323	δ_s (CH ₃)
9	173(s)	1387	δ_a (CH ₃)
10	182(s)	1460	ν_s (COO ⁻)
11	202(m)	1621	ν_a (COO ⁻)
12	209(m)	1678	ν (C—O)
13	231(w) 342(vw)	1855 2750	Al-O (2x) overtone and/or Al hydride stretch
14	366(vs)	2944	ν (CH ₂) and ν (CH ₃) modes
15	369(vs)	2968	
16	457(wm)	3678	ν (OH) surface

Key (see Table 1)

Table 3 Assignments for IET spectrum of PVOH

Peak No.	IETS		Assignment
	(meV)	(cm ⁻¹)	
1	39(s)	307	Al phonon
2	60(w)	476	r(COO ⁻) in plane
3	78(w)	621	r(COO ⁻) out of plane
4	90(sh)	718	CH ₂ bend
5	110(s)	879	Al-O bulk phonon and ν (C—C)
6	131(m)	1049	CH bend
7	139(wv)	1113	ν (Al—O—C)?
8	157(w)	1258	skeletal ν (C—C—O)
9	168(w.sh)	1347	δ (CH ₂)
10	177(s)	1420	ν_s (COO ⁻)
11	198(w)	1589	ν_a (COO ⁻)
12	230(w)	1847	Al-O (2x) overtone and/or Al hydride stretch
13	359(vs)	2887	ν (CH ₂) and ν (CH ₃) modes
14	448(ms)	3605	ν (OH)

Key (see Table 1)

**Figure 4** IET spectrum of PVOH doped from a ~ 0.05% w/v aqueous solution

have performed an IETS study of the adsorption of ethanol (and other associated compounds) on alumina over a range of temperatures. At room temperature, as was the case in our work, they attributed the peak at 131 mV (1049 cm⁻¹) to methylene rocking and/or Al—O—C stretching modes, justified by comparison with the bulk i.r. spectrum of aluminium ethoxide. Although the IET spectral evidence is by no means conclusive, it would seem reasonable to assume that the adsorption of PVOH on alumina may be analogous to that of ethanol.

There is also evidence of carboxylate groups in the IET spectrum, for example, COO⁻ rocking, deformation, symmetric, and asymmetric stretching modes are present (see Table 3). The appearance of both Al—O—C, and acetate-like features may be explained in terms of the degree of hydrolysis of the PVA starting material from which the PVOH was prepared. Although the side groups of the PVOH samples are predominantly —OH, a small fraction of acetate groups not having undergone hydrolysis may still remain. This is not consistent with i.r.

data for the PVOH which showed that the PVA had been hydrolysed to a high degree as was indicated by the absence of carbonyl absorption. It is known that the carboxylate anion is strongly adsorbed on alumina; hence, even the presence of a small number of carboxylate side groups in a PVOH sample would give rise to fairly strong IETS lines while the corresponding i.r. absorptions may be weak, or absent.

Another possible adsorption mechanism, that of hydrogen bonding between alcohol side groups and surface OH cannot be ruled out. However, firm confirmation of such hydrogen bonding in IETS is generally quite difficult, based upon small shifts in position and changes in intensity of certain molecular modes involved in the adsorption process and the OH stretch *ca.* 3621 cm⁻¹. The latter is usually broad and of variable intensity, depending much upon the environment and conditions under which the aluminium oxide layer is formed.

CONCLUSIONS

IETS is a useful technique for the study of the adsorption of certain polymers on an aluminium oxide surface. It is not possible to obtain detailed information regarding the configuration of the macromolecules as a whole surface. However, it is possible to gain some insight into the nature of their adsorption, on the basis of reactions involving side groups of the polymers and the reactive oxide surface. The present work has indicated the following.

For the polymers with ester bearing side groups the most probable adsorption mechanism is believed to be ester cleavage catalysed by the Al oxide and/or surface hydroxyl species present on the oxide. For PMMA, subsequent chemisorption of the carboxylate anions generated on the polymer side groups may occur, whereas PVA may be fully or partially hydrolysed to, and then adsorbed as PVOH. Another plausible mechanism is hydrogen bonding of carbonyl groups of the polymer to surface hydroxyls.

The adsorption of PVOH is not well understood, however, it is possible that covalent Al-O-C monodentate bridges may be formed between alcohol side groups and the oxide surface. This is analogous in nature to the adsorption of lower aliphatic alcohols on alumina at room temperature. Also hydrogen bonding of alcohol side groups to surface hydroxyls cannot be ruled out.

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