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Novel applications of ESEM and EDX for the study of molecularly thin amide monolayers on polymer films

K.I. Dragnevski[a], A.M. Donald[a], S.M. Clarke[b,*], A. Maltby[c]

[a] Sector of Biological & Soft Systems, Cavendish Laboratory, University of Cambridge, J J Thomson Avenue, Cambridge CB3 0HE, UK
[b] Department of Chemistry and BP Institute, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK
[c] Croda Europe Ltd, Oak Road, Hull HU6 7PH, UK

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ABSTRACT

This work reports novel Environmental Scanning Electron Microscopy (ESEM)/Energy Dispersive X-ray (EDX) measurements on the equilibrium composition and kinetics of alkyl amide adsorption at the polymer–air interface. This experimental approach provides certain advantages over other existing techniques for the study of the physisorbed molecules and offers potential for further development.

1. Introduction

Adsorbed molecular layers are the central feature of many academic and industrial problems including detergency, colloidal stability, catalysis, nanotechnology and photovoltaic applications. Key to understanding and controlling the behaviour of these layers is fundamental data on composition, structure and intermolecular forces—information with both academic and industrial significance [1]. Molecular layers adsorbed to solid surfaces represent only a small fraction of the total material present, but can dominate the observed behaviour. The adsorbed layers are often completely different in terms of structure, dynamics and reactivity to the bulk phases. For example, washing involves the adsorption of particular molecules (surfactants) from a complex multi-component soap solution to solid surfaces (clothes or skin) where they form a link between otherwise incompatible bulk materials (oil and water). The unusual properties of these physisorbed layers usually arise from a delicate balance of forces operating within the layer and between the layer and the substrate, and often result in a complex and interesting phase behaviour. The behaviour of these systems therefore provides insight into the nature and importance of the different molecular-level interactions. Key to understanding the behaviour is the characterization of the thermodynamics, composition and structure of these adsorbed monolayers and the identification of the parameters that control their formation and behaviour [1–3].

Adsorbed monolayers are difficult to study, because, as mentioned above, they contain a very small amount of material, relative to the amounts of the bulk phases present. Monolayers adsorbed at the solid–vapour and liquid–vapour interfaces are relatively accessible, relative to the 'buried' solid–liquid interface. However, even the solid–vapour interface cannot be investigated using conventional surface techniques (such as LEED) which are incompatible with the presence of the vapour which would lead to evaporation of the very molecules we wish to study. As a result, minimal information on surface composition is available for adsorbed monolayers of these types [1,4].

1.1. The importance of alkyl amide adsorption

Primary alkyl amides are an important class of materials with a number of commercial applications that exploit their novel behaviour at interfaces, particularly as friction modifiers in polymers [5–7]. There is a significant body of technical literature discussing the use and formulation of amides in materials, predominantly based on trial and error approaches, but without the underlying fundamental physics and chemistry.

These materials are often derived from plant sources and usually consist of a mixture of several alkyl chain lengths within a single material. Hence it is important to consider the mixing behaviour in the adsorbed layers. In addition, it is usually desirable to have a limited amount of unsaturation (usually a single double bond) to

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* Corresponding author.
E-mail address: stuart@bpi.cam.ac.uk (S.M. Clarke).

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reduce the material's melting point. Many natural materials have a predominance of 'cis-' isomers which can be considered to have a significant 'bend' in the alkyl chain relative to the saturated analogues. However, this difference in shape is expected to have a major influence on the molecular packing in mixed layers.

Individual amides adsorbed from phenyl octane solution on the surface of graphite and MoS_2 at the solid–liquid interface have been experimentally characterized with Scanning Tunneling Microscopy [8]. Under these conditions an ordered array of molecules was observed laying flat on the surface with the carbon backbone parallel to the graphite surface. The amide heads are reported to be hydrogen bonded into dimers and adjacent head groups hydrogen bonded together.

We have also recently performed an exploratory calorimetry study of the solid monolayer formation of alkyl amides adsorbed onto graphite from the liquid and from liquid mixtures for a range of alkyl chain lengths, unsaturation and for different isomers. This study identified that these adsorbates exhibit surprising and unexpected features when adsorbed at the solid–liquid interface—they form the most stable solid physisorbed monolayers yet observed and they exhibit abnormally efficient mixing behaviour. There is also evidence of a number of other calorimetric transitions as yet unidentified, possibly multi-layering or solid–solid transitions [9].

In addition, to their importance at the solid–liquid interface, amides are commercially very important additives for their surface properties at the polymer–air interface [5,7]. Pure polymers can often be very 'sticky' leading to problems—many will be familiar with the problem of blocking of plastic bags. To prevent this tack, amides are added to the polymer prior to formation of the polymer sheet. Once formed the amides are believed to migrate through the bulk polymer to the surface with a consequent reduction in tack and friction coefficient. However, there is only very poor composition data and essentially no structural data on these materials to confirm this picture. In addition, some amides also show a number of unexpected effects such as an initial fall in the friction coefficient with time but followed by a subsequent rise. This behaviour has been suggested to arise from in-plane surface ordering or oxidation of the amides to a non-slip species with time. Also, given that the polymer is hydrophobic as is the 'air', the amide could easily adsorb as a monolayer or a bilayer.

The use of amides as slip agents is particularly important for polymers such as polyethylene and polypropylene. However, an additional complication in the study of adsorbed layers at the polymer–air interface arises from the semi-crystalline nature of these materials. There is no 'flat' surface that will allow the study by new approaches such as X-ray or neutron reflectivity which permit roughness at only an atomic lengthscale. In addition, the distribution of the adsorbate across the polymer–air surface is also significant with interesting questions about the amount of amide on the crystallites compared to the amorphous regions.

There are other related techniques to those described here where samples in an ambient atmosphere can be probed, such as PIXE (particle induced X-ray emission) [10] which is quantitative, and sensitive to trace elements. However, there are significant issues with these approaches for our systems particularly that elements lighter than Ne cannot be easily investigated—hence excluding H, C, N and O of central importance to the present study.

1.2. Novel experimental methods and approaches

Recently we, and others, have been developing a number of experimental techniques to probe the structure, composition, dynamics and phase behaviour of 'buried' adsorbed layers. These approaches have a number of key advantages including, sensitivity to fractions of monolayer, they are non-invasive and they can probe each component of multi-component mixtures. Sensitive calorimetry [4] was used to map the monolayer phase diagram of mixed adsorbed systems [4,11,12], X-ray and neutron powder diffraction [13] were employed in order to obtain detailed information about the state and in-plane structure of a crystalline adsorbed layer and its mixing behaviour and Quasi-Elastic Neutron Scattering (QENS) was used to identify the adsorbed amounts, multi-layers and the formation of rotator phases. QENS is complemented by similar NMR approaches [14].

1.3. Environmental Scanning Electron Microscopy (ESEM)

In the current work we consider the adsorption of amides at the polymer–air interface using electron microscopy. Scanning electron microscopy has a long history of exploitation for the study of surfaces. However, given the very strong scattering of electrons by condensed matter and dense vapours, essentially all surface studies require UHV conditions. This is incompatible with the study of delicate physisorbed layers of interest here: the adsorbate molecules will be 'sucked off' the surface before a measurement can be made. The surface can be cooled to try to prevent desorption, but this is likely to dramatically alter the state of the adsorbed layer we are trying to study.

Unlike conventional Scanning Electron Microscopy, where, as mentioned, high vacuum is maintained throughout the instruments, ESEM [4,15] is based on the use of a multiple aperture graduated vacuum system, which allows specimens to be imaged under water vapour or other auxiliary gases, such as nitrogen or nitrous oxide [16]. In this way, the chamber can be held at pressures of up to 20 Torr [17] while the gun and column remain at pressures of $\sim 7.5 \times 10^{-7}$ Torr. Moreover, by using a correct pumpdown procedure [18] and by controlling the temperature of the specimen, which in the ESEM is usually done by using a Peltier stage, dehydration can be inhibited and hence samples can be imaged in their 'natural state' without the need of conductive coating. The presence of a significant water vapour pressure in the microscope chamber means that our polymer–amide samples will not rapidly lose (or not lose at all) their amides at the surface, which will allow us to study their layers.

At equilibrium the adsorbate will have a non-zero vapour pressure. The external pressure will consist of the 'imaging gas' and evapourated additive (at its saturated vapour pressure for the given temperature). If the additive can maintain its saturated vapour pressure then evaporation will stop (in a dynamic equilibrium). If the external pressure is too low then the evaporation will continue and the additive will keep evaporating. 'Normal' UHV conditions have essentially zero vapour pressure and continued evaporation of the additive would continue until entirely removed. In ESEM the saturated vapour pressure of the additive can be reached and equilibrium established preventing further additive loss.

The presence of the amides at the polymer surface can be addressed by following the appearance of oxygen of the amide at the surface using Energy Dispersive X-ray (EDX) analysis, which can also be carried out in the ESEM [19]. The energy of the emission from the oxygen at the surface gives rise to a characteristic peak, the intensity of which can be measured.

In this initial study we have attempted a proof of concept to see if ESEM combined with EDX analysis can determine the composition of the surface of thin polyethylene (PE) and polypropylene (PP) films, as well as the migration of amide additives to the surface as a function of time. The focus here is to explore the potential of the ESEM technique to observe additives surface selectively (in the presence of bulk species). If successful, as it seems, this approach has the potential to be used in the future to study additives that might not be assessable by related techniques (e.g. that require UHV conditions) and to map 2D distributions of additives at a polymer surface. Structural information on a molecular level still requires other complementary methods.

2. Materials and methods

Polymer thin film samples were prepared for this study, by Croda Europe Ltd., UK, using both polyethylene (LDPE) (Lupolen 2420H) and polypropylene (HPP) (Borealis DH204CF). The rate of migration to the surface is believed to be significantly slower for polypropylene than polyethylene, as determined by the variation of the coefficient of friction with time [20]. Hence we have used polypropylene in the kinetic studies to allow a longer time window to prepare samples and measure the kinetics.

The PE films were produced by blown film extrusion using a 35-mm single screw extruder (24:1, l/d) fitted with a 50-mm annular blown film die. Heater temperatures were 180–200 °C (feed to die). Film thickness was controlled by adjusting nip roller and extruder speed. PP films were produced on a small-scale cast film line through a 150-mm die “coat hanger style” at 190–210 °C onto chilled rollers (15 °C). The amide was dosed in by batch-mixing a pelletized concentrate of polymer-containing 2% additive prior to extrusion. The film thickness was controlled by the draw rate and prepared with thicknesses, 50, 40, 30 and 20 μm. Samples were prepared as pure polymer and with 500 ppm of an alkyl amide (erucamide: $C_{22}H_{43}NO$, $CH_3(CH_2)_{11}CH{=}CH(CH_2)\cdot_7CONH_2$. A C_{22} alkyl chain amide with a single double bond in the nine position, CRODA commercial grade CrodamideER).

Erucamide is typical of an important class of amide surface agents with commercial importance and hence an ideal representative species for this preliminary study. Based on the temperature variation of the boiling points of erucamide under reduced pressure [21] (180 °C, 0.4 Pa and 245 °C, 60 Pa), equilibrium vapour pressure of erucamide at room temperature is expected to be very small, well below that of the ESEM external pressure (approximately 100 Pa). Under much lower external pressures than the ESEM, the desorption of erucamide from polymer surfaces has been reported be complete in approximately 1 day (pressure of 8×10^{-3} Pa and at 70 °C) [22]. Hence we conclude that we do not expect erucamide to desorb in these EDX/ESEM experiments with the particularly low vapour pressure of erucamide at room temperature. However, the EDX signal of erucamide at the surface of the polymer is expected to be very similar to other amide additives where the vapour pressure and desorption at room temperature is more significant and exploration under UHV prohibitive.

The effect of film thickness is to alter the ratio of the bulk volume to surface area of the film. A thick film will be expected to have a larger potential reservoir of amide for a given surface area, compared to a thin film which will only have a small amount of bulk polymer for the same surface area. Hence, we expect that there will be more amide at the surface of thick films than thin films. The full range of thicknesses of PE films was used for the static, equilibrium study. Only 50-μm thick PP samples were used for the kinetic measurements.

The analysis was carried out on an FEI XL-30 ESEM, equipped with an EDAX X-ray analysis system. Small samples (approximately 5 mm across) were placed onto an Al-sample holders in the ESEM chamber and analyzed under water vapour at room temperature, at an operating voltage of 10 kV (spot size 4–5), a commonly used pressure of ∼1.0 Torr and working distance of ∼9.0 mm. The EDX spectra were obtained using a raster scan of areas approximately 30 μm × 30 μm at a scan rate of 1.68 ms. It is obvious that most of the above parameters can be varied significantly, which would undoubtedly have an effect on the final results. It was found that lower operating voltages resulted in lower peak intensities, while higher voltages resulted in significant beam damage, which in both cases would make the interpretation of any results extremely difficult. Pressures of around 1 Torr were required in order to minimize sample charging, whereas higher pressures would most probably result in an increased skirting effect [23] and ultimately increase the experimental error. After the acquisition of the EDX spectra of the studied specimens, the intensities of the peaks were normalised to the intensity of the carbon peak obtained for the specimen without amide additives, by using the EDAX software.

Calculations, using Casino *v.2.42* software, addressing the penetration depth of the beam, and hence the volume over which we are sensitive to the composition are illustrated in Fig. 1. These calculations indicate that the majority of the scattering arises from the top 1.7 μm of the specimen. Furthermore, from the simulated data for the intensity of the X-rays, presented in Fig. 1b, it is also evident that the escape depth of the X-rays is in the region of 600–800 nm.

3. Results and discussion

3.1. Static measurements

Fig. 2 presents the results for specimens with and without oxygen-containing amide additives. These samples have been allowed to age for a period well in excess of that required to obtain equilibrium (in excess of 2 weeks—see measurements below). The appearance of the oxygen signal in the samples with amide relative to that without clearly indicates that EDX can be successfully used

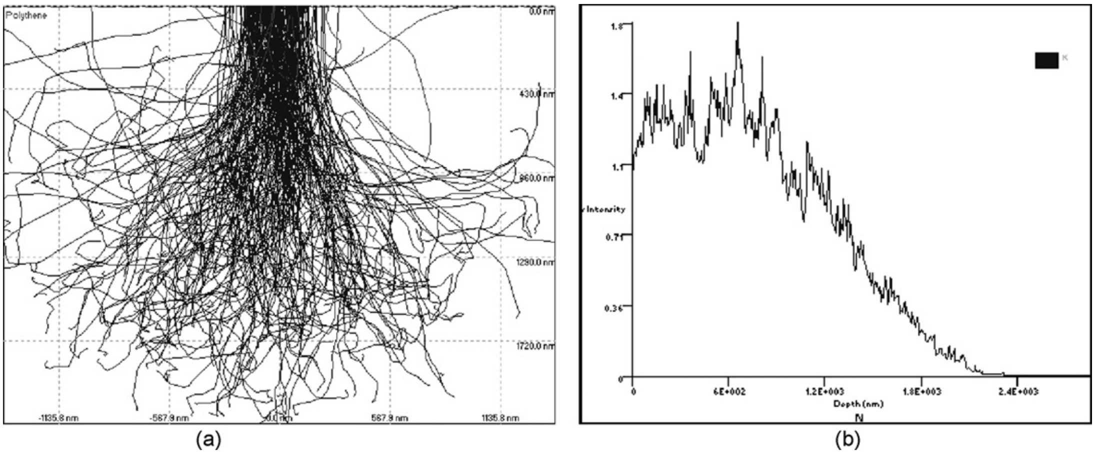

Fig. 1. Casino *v.2.42* simulation showing the interaction volume (a) and (b) X-ray intensity distribution of a 50-μm thick PE sample (beam voltage = 10 kV and penetration depth ∼1.7 μm). Similar results were obtained for the PP specimens.

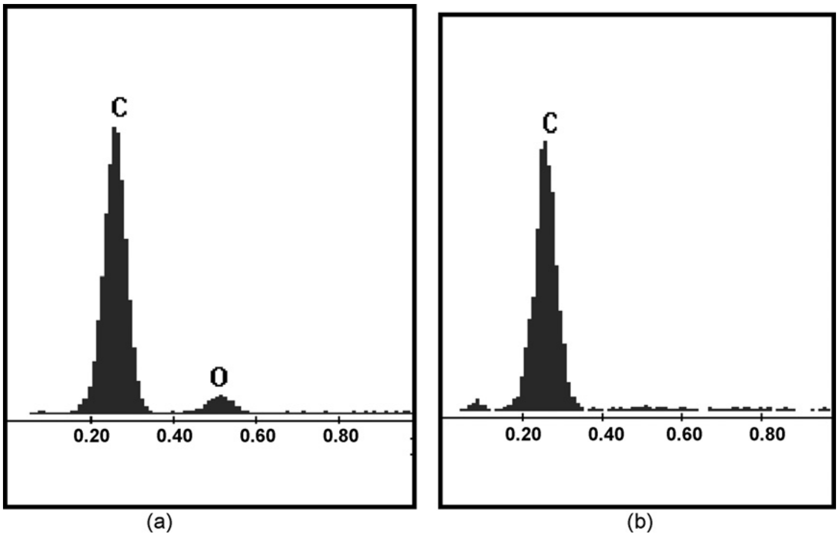

Fig. 2. EDX spectra of 50 μm PE specimens with (a) and without (b) amide additives.

in determining the presence of oxygen-containing species on polythene films. Due to the fact that the intensity of the 'amide' peak is fairly low it will be extremely difficult to give the absolute amide composition at the surface from this data. An alternative approach to obtain quantitative information to compare with the ESEM/EDX approach would be neutron scattering, and this will be attempted in the future.

The variation of amide signal (normalized net intensity) for different PE samples thicknesses is given in Fig. 3. Again these samples have been allowed to age for a period well in excess of that required to obtain equilibrium. It can be seen that the total intensity of the oxygen peak, increases with increasing sample thickness. This would suggest that the thicker the specimen, the more amide present on its surface. This is in good agreement with the results of friction coefficient measurements discussed above.

However, there is some question over the interpretation of the variation of oxygen signal with thickness. If the beam were not strictly surface sensitive, but in fact scattered from the whole thickness of the sample illuminated by the beam of a given cross-section of area, then we would also expect to see a similar increase in oxygen signal for thicker samples relative to thinner sample. For a thicker sample, using a fixed electron beam diameter, the total amide content measured in the sample would be more than for a thinner one.

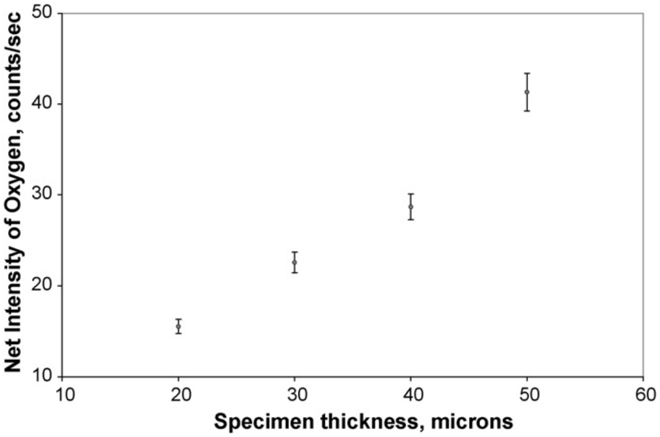

Fig. 3. Intensity of amide signal as a function of specimen thickness.

To address this issue and confirm the surface sensitivity of the ESEM/EDAX approach, we have performed a time dependent study. For a given sample initially prepared with no amide at the surface we expect to see a very weak oxygen signal, if the signals do indeed come from the near-surface region. As the amide migrates to the surface we should see the oxygen signal increase only if the scattering is surface sensitive. If the scattering is from the entire thickness of the sample then the intensity of the oxygen signal should be independent of time.

3.2. Time dependent study

A set of typical spectra obtained in this study for the 50-μm PP amide-containing samples are presented in Fig. 4. In this figure it is clear how the intensity of the oxygen peak increases with time, confirming that ESEM and EDX can successfully be used in determining the presence of oxygen in thin polymer (PP) films. Fig. 5 shows the variation of the net intensity as a function of time indicating the pronounced rise in oxygen with time as expected on adsorption of the amide, over a period of ~12 days, after which the intensity levels off.

There is an issue concerning the possible oxidation of the double bonds at the surface of the polymer–amide film which may also give rise to an increased level of oxygen with time. We have addressed this issue with an adsorption study of saturated amides where this oxidation cannot occur. The results from this study were similar to those obtained for the PP specimens, i.e. the amount of amide increases with time and therefore it can be concluded that if oxidation of the double bond takes place it does not have a significant effect on the EDX measurements.

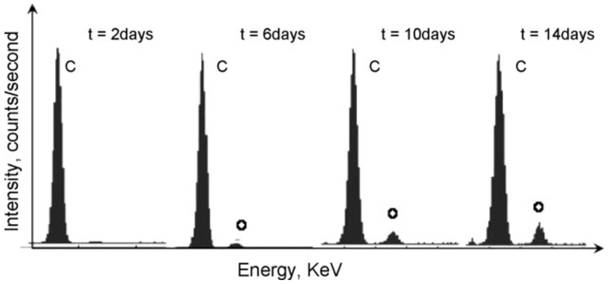

Fig. 4. Set of typical EDX spectra for a 50-μm thick amide-containing PP specimen showing that the intensity of the oxygen peak increases with time.

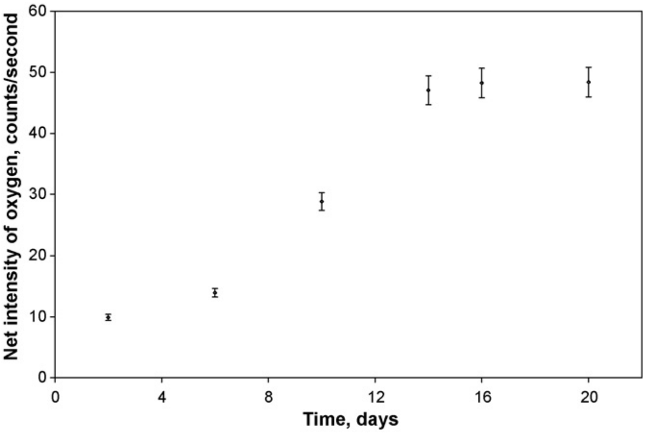

Fig. 5. Net intensity as a function of time for the amide-containing PP specimens.

However, at present we have no explanation for the absence of the nitrogen edge in these samples which should also form part of the amide head group. The reason for this may be insufficient sensitivity of the EDX technique, due to the very small concentration of nitrogen, or some other sensitivity issue. It is clear that this issue is not a feature of the surface science because there is no nitrogen peak in measurements of the pure bulk amide.

These measurements of the bulk amide also proved a crude scaling for the amount of amide adsorbed at the surface of the polymers. The count rate for the oxygen peak from the bulk amide is 45 cps. The saturated surface layer has a count rate of approximately 35 cps. This suggests that the surface layer represents approximately 3/4 of the bulk amide density in the saturated layer. We recognize that this is a very crude estimate until we can establish more precise surface excess measurements to use as more effective standards.

Fig. 6 presents the variation in the static and dynamic coefficient of friction (COF) as a function of EDX intensity (and hence some estimate of adsorbed amide). This figure indicates that these parameters are related as might be expected—higher surface concentrations of amide will give higher EDX intensity and lower coefficient of friction. The static COF is more linearly related to the EDX intensity than the dynamic COF. Although this correlation is as one might expect it is not appropriate at this stage of the ESEM technique development to draw any more significant conclusions at present.

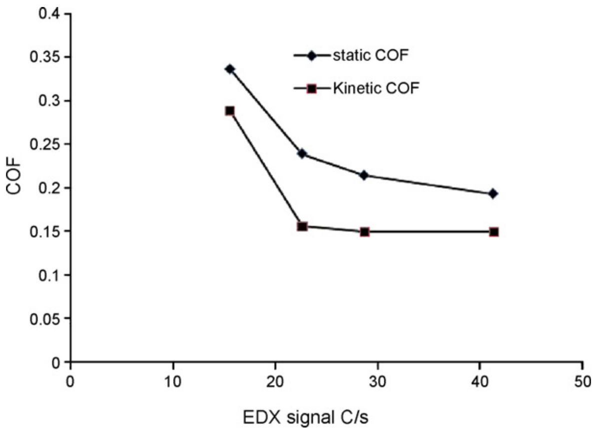

Fig. 6. Coefficient of friction (static and dynamic) as a function of EDX intensity.

4. Conclusions

Environmental Scanning Electron Microscopy, together with Energy Dispersive X-ray analysis can be successfully employed in the study of additive adsorption to the surface of thin polymer films. It was found that oxygen, present in the form of amides on the surfaces of the films can be detected at an operating voltage of 10 kV and water vapour pressure of ~1 Torr. Further analysis revealed that the intensity of the oxygen increases with increasing specimen thickness, which indicates that more molecules are present per unit area in the thick polythene samples. We have also been able to demonstrate that the amount of amide at the surface increases with time from an initially blown polymer film. We have eliminated a number of potential experimental artifacts such that we are confident that the ESEM/EDX results do not simply determine the overall composition of the sample in the cross-section of the electron beam, but are surface sensitive.

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