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J. F. Watts^a; A. M. Taylor^a

^a Department of Materials Science and Engineering, University of Surrey, Guildford, Surrey, UK

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Interphase Chemistry: The Synergy of Surface Analysis, Surface Adsorption and Adhesion*

J. F. WATTS and A. M. TAYLOR

Department of Materials Science and Engineering, University of Surrey, Guildford, Surrey GU2 5XH, UK

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The formation of an interphase zone at the junction between an organic system, such as an adhesive or coating, and an inorganic substrate is considered. Drawing on experimental work for a fully-formulated photocured resin and theoretical models for a simple homopolymer it is shown that such a feature may be the result of preferential adsorption (for a multicomponent system) or conformational changes in the case of a homopolymer. Guidelines for the recognition, cause and prediction of such layers are provided, and their possible effects on the strength and durability of the organic/inorganic couple are discussed. It is suggested that the consideration of these phenomena at the design stage of a new resin may provide a route to optimise hydrolytic stability. The behaviour of an interphase zone of this type as a weak boundary layer is also considered.

KEY WORDS Adhesives; coatings; adhesion; resin design; preferential adsorption; homopolymers; copolymers; weak boundary layers; methacrylate resins; interfacial stability; XPS; ToF-SIMS.

INTRODUCTION

In general, the adhesion community now regards the adsorption theory as the most significant of the mechanisms that have been proposed to account for the various adhesion phenomena observed. One of the most important properties of polymers, that has enabled them to be used widely in adhesion and coatings applications, is their ability to become readily adsorbed on to solid surfaces.¹ The adsorption of macromolecules such as polymers tends to be high, even from dilute solutions. Macromolecules have large surface areas which produce correspondingly high values of surface activity, thus facilitating adsorption,² as a means of reducing surface activity (*i.e.*, the surface free energy of the solid).

In the past, considerable attention has been devoted to the study of how polymer molecules are adsorbed on to surfaces from dilute solutions.³ More recently, the importance of discovering how polymer molecules are adsorbed on to surfaces from the melt has been recognised,² as this is likely to reproduce, more accurately, the conditions encountered during the application of adhesives or organic coatings.

*One of a Collection of papers honoring James P. Wightman, who received the 13th Adhesive and Sealant Council Award at the ASC's 1993 Fall Convention in St. Louis, Missouri, USA, in October 1993.

Previously, adsorption studies have tended to be restricted to very simple systems, where, for example, the molecular weight of the polymer was varied.⁴ Clearly, this is an oversimplification of the situation that exists with fully-formulated adhesives, which, in the majority of cases, are multicomponent systems. Silberberg's work on the adsorption of polymers from the melt revealed that, for multicomponent systems, in the presence of a high energy surface (such as a metal oxide or a ceramic), preferential adsorption of one of the components occurs.² A correlation between preferential (otherwise referred to as selective) adsorption and the surface tension of the adsorbate was reported. This observation is extremely important, as it is a factor which may not have been considered at the formulation stage of the resin and could lead to the formation of a region of instability (or, simply, one of different properties to the bulk), within the adhesive joint. Roe also reported observing preferential adsorption, which appeared to be independent of the solution concentration.¹ Work by Lipatov carried out on multicomponent systems during cure, revealed that selective adsorption could result in the displacement of other polymer species from the interfacial region.⁵

The aim of this paper is to consider the implications, if preferential adsorption of one of the components in an adhesive system occurs, and to show how, using a combination of surface analytical techniques, it is possible to recognise this phenomenon. Finally, we shall indicate how the use of molecular modelling and surface adsorption experiments might aid, during the initial formulation stages, to produce systems in which preferential adsorption is less likely to occur. The basic tenor of this paper is a discussion of the phenomenon of preferential adsorption and its likely role in the level of adhesion achieved between polymeric and inorganic phases. Rather than attempt to provide an exhaustive review of work in this area, a personal perspective of this phenomenon is given; illustrative examples are provided from recent published work on a fully-formulated photocured system of relevance to the microelectronics industry.^{6,7} An indication of the analogous situation that may exist for the case of simple homopolymers is also discussed.

PREFERENTIAL ADSORPTION

The observation of preferential adsorption has been widely documented, for example, by Kipling in as early as 1965.⁸ Kipling's studies, carried out on mixtures of methyl acetate and benzene, indicated that the methyl acetate was selectively adsorbed on to the surface of alumina. This result is explained by the fact that the polar centre of the ester group in the methyl acetate molecule can bind with the polar groups present on the inorganic surface.

In more recent studies, carried out by the authors on the adhesion of photocured polymers to ceramic (predominantly alumina) substrates, a similar phenomenon was observed.^{9,10} The Luxtrak™ series of photocured resins investigated are multicomponent systems based on aromatic methacrylate type oligomers (manufactured by ZENECA Specialties Ltd.). Repeated analysis of the failure surfaces of adhesive joints previously exposed to a hostile environment (water at 50°C for times in excess of 14 days) resulted in near-interfacial failures, with a thin overlayer of polymer, of the order of 1–2 nm, remaining on the failure surface. Subtle differences between this overlayer of

polymer and the bulk resin were observed by X-ray photoelectron spectroscopy (XPS). In both spectra, the C—O and C = O features, seen as shoulders on the main peak or well-defined components in their own right, are present at binding energies consistent with a methacrylate resin. There was an absence of the $\pi \rightarrow \pi^*$ shake-up satellite, characteristic of aromaticity, in the XPS spectrum recorded from the adherend surface with the thin overlayer of polymer, even when the spectrum was expanded to ten times the intensity of Figure 1a. The shake-up satellite was clearly visible in the carbon 1s spectra recorded from both the as-received resin and the opposite side of the joint, as shown in Figure 1. The apparent reduction in resolution of the spectrum recorded from the ceramic substrate is a result of charge-induced broadening, reflecting the difficulty of recording spectra of thin polymer films deposited on insulating substrates.⁷ The result presented in Figure 1 was somewhat surprising, as the molecules which form the base resin (approximately 90% of the formulation) are highly aromatic. This suggested that selective adsorption of one of the minor components present in the resin on to the alumina surface was occurring. When other substrates were investigated (quartz and silicon wafers), the same result was observed, *i.e.* near-interfacial failure with an absence of any aromatic groups within the polymer overlayer. A combination of XPS and time-of-flight secondary ion mass spectrometry, (ToF-SIMS) proved extremely useful in confirming that this was, in fact, the case.

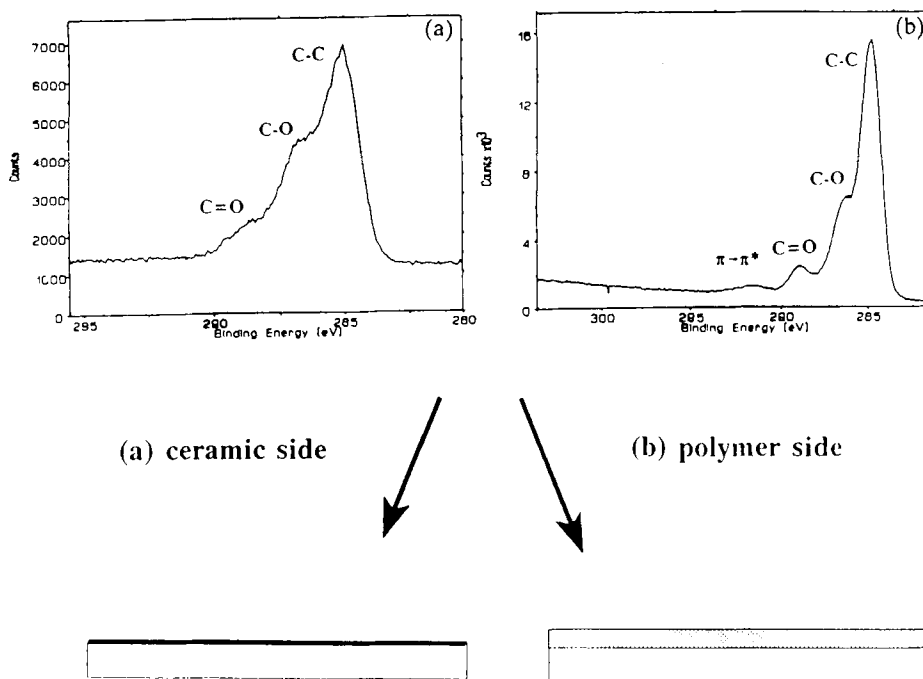


FIGURE 1 XPS C1s spectra obtained from the fracture surfaces of an alumina/standard resin (LCR000) joint. Attention is drawn to the absence on the $\pi \rightarrow \pi^*$ satellite on the ceramic side of the failed joint.

RECOGNITION OF THE PREFERENTIAL ADSORPTION PHENOMENON

In the case of relatively simple bi-component systems, it is possible to carry out adsorption experiments and plot adsorption isotherms for the individual components.¹¹ The concentrations of the various components in the adsorbate can be altered, in addition to the characteristics of the solid surface. When considering systems of technological importance, such as a fully-formulated adhesive or coating, the problem is not quite as straightforward. In the case of the photocured resin/alumina system, the possibility of selective adsorption was first suggested following post-failure XPS analyses of the samples. On the basis of knowledge about the formulation of the LCR000 resin, it was decided that the ethoxylated methacrylate monomer (EMM) component was the most likely to adsorb preferentially on to the alumina surface. In order to test this hypothesis, it was necessary to employ ToF-SIMS, as it was not possible to distinguish unambiguously between the various resin components by XPS analysis. The EMM component seemed to be a likely candidate for the preferential adsorbate, as it comprised about 9% of the formulation and contained no aromatic groups. Silicon wafers were used as substrates for ToF-SIMS characterisation of the EMM component; the loci of failure of the joints when analysed by ToF-SIMS were identical for all three substrates.

Samples were prepared for ToF-SIMS analysis by spin-casting, on to silicon wafers, dilute solutions of the various components of interest in toluene. Both positive and negative ion spectra were recorded from (i) EMM in toluene, (ii) LCR000 resin minus the EMM component, subsequently referred to as ModLCR000 and finally, (iii) the fracture surface of a silicon wafer/LCR000 joint following immersion in water at 50°C for 14 days. The positive ion spectra revealed the most useful information. There were many similarities between the spectra recorded from type (i) and (iii) samples, as presented in Figure 2. The spectra were not identical, although this was not unexpected, as the sample histories were different. There was an absence of any of the high-mass peaks characteristic of the base resin (from (ii) in the spectra recorded from either the EMM or the failure surface of the joint. Although these results from ToF-SIMS analysis are not in themselves conclusive, they are supportive of the preferential adsorption hypothesis. A more complete discussion of the spectra and peak assignment is provided elsewhere.¹⁰ The next stage of the investigation was, therefore, to consider both how and why the EMM component should be adsorbed in preference to the major component of the resin on the alumina surface.

FACTORS LEADING TO PREFERENTIAL ADSORPTION

The precise factors which lead to selective adsorption will obviously vary, depending on the individual components which make up the system. At the simplest level, segregation to a surface or interface may be a result of Gibbsian segregation, the driving force being the tendency of the system to minimise its surface or interfacial free energy by the segregation of the lower energy component. There are, however, a number of other, system specific, general factors which may be considered. An important feature of systems where selective adsorption occurs, is that thermodynamic equilibrium is

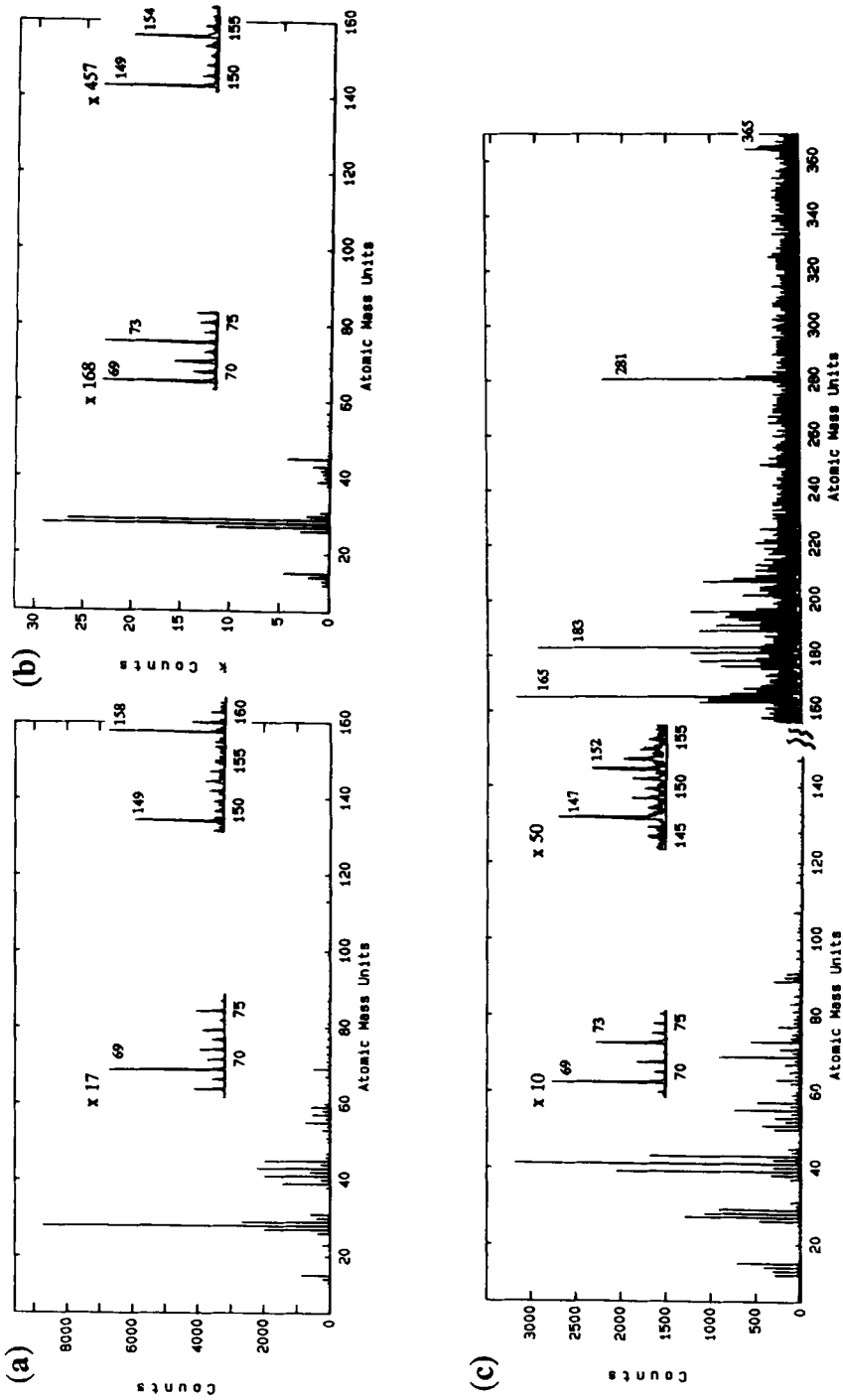


FIGURE 2. Positive ion ToF-SIMS spectra obtained from: (a) EMM component spun-cast onto silicon, (b) the ceramic side of a failed silicon/standard resin joint, and (c) ModLCR000 resin spun-cast onto silicon.

very often not achieved. Additional factors, therefore, need to be taken in to account. For a non-equilibrium system, factors such as chemical potential gradients and transport coefficients are important. The size of a molecule and, in particular, the degree of branching, will affect its mobility, (*i.e.* short, linear molecules will have greater mobility in the polymer melt). The factors described above will affect the kinetics of the arrival of the chains at the interface: but what prevents the molecules from then returning to the bulk?

Selective adsorption of polymers occurs if there are differences in adsorption affinity, once molecules are in close proximity to a surface. In a polymer blend, small differences in surface free energies can lead to pronounced segregation effects. If the polymer molecule has specific sites with which it can bind to groups on the surface, as in the case of the methyl acetate/benzene mixture described by Kipling,⁸ this will be an obvious advantage. One of the most well-documented features of polymer adsorption is the molecular weight dependence.¹² In systems containing polymers of varying molecular weight (but otherwise equivalent), molecules of high molecular weight are adsorbed in preference to smaller ones. This result is a little surprising at first sight, as the smaller and, hence, more mobile species would be expected to reach the interface first. In fact, on arriving at the interface, larger molecules will often displace the smaller ones. This produces an increase in entropy, because it allows larger numbers of small molecules to return to the bulk, each of which has an entropy term associated with it.

Formulation chemists need to be aware of these possible influences, to avoid the deleterious effects which may be caused by segregation occurring within a coating or adhesive. In the case of the LCR000/alumina system, the selective adsorption of the EMM component, which is extremely hydrophilic in nature, left the interphase region particularly vulnerable to hydrolytic attack.

Selective adsorption need not always produce deleterious effects. Knowledge about how various components behave in multicomponent systems could be used to advantage in the final formulation. For example, selective adsorption of compounds which promote interfacial stability could produce improvements in the performance of an adhesive system.

In systems where selective adsorption is believed to occur, several properties are of interest. Firstly, the degree of coverage of the surface. This can be assessed in model experiments by the use of XPS in conjunction with an adsorption isotherm approach.^{13, 14} The geometry of the grafted layer is also important (some molecules tend to adsorb in a preferred orientation). Finally, the sharpness of the interface between the selectively-adsorbed layer and the bulk. All of these properties should be fully characterised in order to optimise the performance of the final product.

PREDICTION OF PREFERENTIAL ADSORPTION

Before deciding on a new resin formulation, it would be advisable to investigate how the various individual components are likely to behave, together, in the melt. The development of powerful molecular modelling packages has provided one possible route to take.¹⁰ Alternatively, it may be possible to carry out simple adsorption-type experiments. The use of a more predictive approach to resin design might help avoid

the need to carry out adhesion trials on formulations which, due to selective adsorption of one of the components present, could never meet the desired specification.

THE SITUATION WITH HOMOPOLYMERS

The situation that exists when a single component homopolymer is cast onto a high energy substrate is, at first sight, more straightforward than that described above for multi-component systems. However, if one ignores chemical segregation effects, which involve selective mass transport of a single component, it is apparent that conformational changes may also occur. In recent theoretical studies, using a kinetic Ising model, Chakraborty and co-workers have studied the poly (methyl methacrylate)/aluminium system.^{15, 16} In elegant simulation studies, they have shown that the near-interface conformation, which is, in general, a balance between enthalpic driving forces and entropic constraints, results in a thin layer of PMMA in which the polymer chains tend to lie in a relatively flat orientation parallel to the metallic substrate. The net result appears to be a thin, diffuse, layer of PMMA between the bulk polymer and the substrate. This concept is shown schematically in Figure 3.

The implications that such a structure have on the mechanical properties of a metal/polymer system are clear. Failure can be envisaged occurring at the junction between the “bulk” and the “diffuse” PMMA regions, leaving the substrate with a very thin layer (several nanometres) of polymer adhering to it. This hypothesis is entirely consistent with experimental observations made by XPS of PMMA on soda-lime glass and SiO₂.¹⁷

A model of this type is perhaps even more relevant to durability studies of polymer/metal systems, where water is known to have a deleterious effect on adhesion and generally results in a near-interface cohesive failure with the ubiquitous 1–3 nm of polymer remaining on the metal substrate.^{18, 19} It is easy to devise speculative models in which the “diffuse” zone has a smaller connected free volume than the bulk material, which results in a reduction of the water diffusion coefficient in this region. Water molecules, therefore, aggregate at the junction between the two regions leading to a reduction of strength. Application of a mechanical constraint leads to failure at this point but the water-induced damage is at least partially reversible,^{20, 21} a phenomenon known as “wet adhesion” in the paint industry.

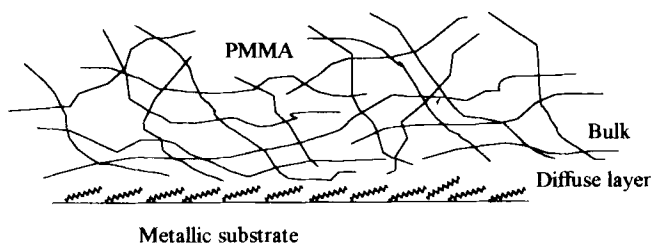


FIGURE 3 Schematic model indicating the formation of a diffuse interphase between aluminium and bulk PMMA. Based on the results of Chakraborty *et al.*^{15, 16}

THE ROLE OF WEAK BOUNDARY LAYERS

The description of interphase formation as a result of preferential adsorption or anisotropic conformation, might, at first sight, seem to refer to examples of the formation of the classic weak boundary layer (WBL) of the type described by Bikerman.²² However, Bikerman's original classification referred to layers of low cohesive strength (*e.g.*, grease on a steel surface prior to coating or bonding) and there is no indication that the thin interphase layers described above have poor cohesive strength; indeed, the reverse may be true. In contrast, the point of weakness is, in fact, at the junction between the two organic layers; an interfacial failure within the polymer phase.

Such ideas go a long way towards resolving the empirical observations and is rather more elegant than the concept of "co-operative" bonding that has been promulgated by Funke.^{23, 24}

CONCLUSIONS

The phenomenon of preferential adsorption has been widely documented. It has also been illustrated as a cause of adhesion failure in certain systems, (*e.g.*, LCR000/alumina). It is possible to recognise the phenomenon, in some cases, by the careful use of surface analytical techniques. With the development of powerful molecular modelling techniques, combined with the use of adsorption studies, the potential exists to be able to avoid certain combinations of polymeric components altogether, or to include compounds deliberately in a formulation, which, by their selective adsorption on to a surface, will promote interfacial stability. In the case of homopolymers, conformational changes at the interface may bring about the formation of a "diffuse" interphase zone. Both situations have the potential to lead to a zone of weakness close to the polymer/metal interface and it is at this point that failure may occur. This is particularly likely following environmental exposure.

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