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A review and comparative study of release coatings for optimised abhesion in resin transfer moulding applications

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Abstract

In this study, a number of abhesion-promoting coatings were considered in terms of their physicochemical and release properties. The techniques used to further this study include; field emission gun scanning electron microscopy, atomic force microscopy (AFM), profilometry, X-ray photoelectron spectroscopy, Auger electron spectroscopy, static secondary ion mass spectrometry, Fourier transform infra-red analysis and contact angle analysis for coating physical and chemical characterisation along with pulsed force mode atomic force microscopy (PF-AFM) and other adhesion and mechanical tests to determine surface release properties. These coatings were applied to metal substrates and were based upon silicone, fluoropolymer or metal–PTFE composite chemistry, all being potentially useful as release films for resin transfer moulding applications. The semi-permanent Frekote B15/710 NC mould release coating system, which is based on PDMS, proved extremely effective in terms of release against a cured epoxide applied under pressure. Although fluoroalkylsilane coatings offer a number of technological advantages for release applications, they generally produce very thin coatings which conform to any existing surface topography and adhesion through mechanical interlocking. The commercial PTFE-based coatings were found to provide poor release properties due to the presence of surface microcracks which allowed epoxide penetration when cured under elevated pressure and temperature. Electroless Ni/PTFE composite coatings comprise a hard nickel–phosphorus matrix containing a very fine dispersion of PTFE particles. The matrix proved sufficiently robust for industrial applications and the low friction and surface energy provided by the embedded PTFE combined with macroscopic-scale surface roughness provided efficient mould release.
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1. Introduction

"Abhesion", a term first used by Zisman [1], is the very antithesis of adhesion. Whilst the majority of reported studies focus on the science and technology used in achieving optimum adhesion, an understanding of abhesion is fundamental to a number of areas. Examples include pressure-sensitive adhesive (PSA) tapes where a silicone backing paper allows easy use of the tape [2], antifouling paints for immersed marine structures, ice-repellent surfaces for aircraft wings, biomedical implants and non-stick bakeware [3,4]. A particularly demanding application, of interest in the present study, are the semi-permanent and permanent externally applied release coatings used in resin transfer moulding (RTM) applications. In this instance, epoxides are cured, under pressure, in contact with the release coating on the inner surface of the mould tool. The role of the release coating is therefore to facilitate removal of the moulded part. Although this is a very specific example of abhesion, many of the conclusions drawn from this study can be applied to other systems.

It is important in the context of the present study to emphasise the fact that RTM processes in the aerospace industry almost exclusively use externally applied, semi-permanent mould release coatings which allow multiple

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moulding cycles to be performed before the release agent has to be re-applied. These will be the focus of the present study. Permanent coatings have also been studied because of their potential advantages. This distinction is necessary because much of the published literature concerning moulding focuses on internal release agents. Internal mould release agents are those added to a polymer formulation that is intended to be injection or compression moulded. Proprietary release agents are used which may be fatty acid esters, metal stearates (often zinc or calcium) and waxes and which are believed to migrate to the surface during the moulding process presenting a weak boundary layer between the moulding and the tool which allows ejection of the part with minimal force [5,6]. Other internal mould release agents operate by forming microcrystals, which increase interfacial stresses [7].

Clearly, the abhesion-promoting properties of release coating need to be understood in order to develop optimised systems. It is important to note at this stage that there are relatively few reported studies relating mould release coating functional chemistry, mechanical properties and performance [8]. However, an understanding of the factors which help to achieve good adhesion is clearly essential in understanding the phenomenom of abhesion. From any review of the literature, it is apparent that for optimum adhesion, surfaces should have high energy, mechanically and hydrolytically stable, and micro- or nano-rough. Intuitively, the corollary is that for minimum adhesion, i.e. abhesion, the surface should have low energy; possibly able to form a cohesively weak boundary layer; of dissimilar solubility parameter to that of the contacting media, to prevent interdiffusion; thermally stable, for some applications; of low molecular mobility, associated with low glass transition temperature; and free from major surface asperities. A consideration of these critical factors follows. Also of importance to the present study are frictional forces acting between the mould and the moulded part. The force required for demoulding must overcome the summation of adhesion and frictional forces. This assumes no distortion of the moulding on ejection.

1.1. The importance of low-energy surfaces

It is well known that low-energy surfaces reduce intermolecular attractive forces. Consequently, the spreading of a contacting medium over a low-energy surface is reduced along with any physical or chemical bonds, resulting in low practical adhesion levels. Packham [9] describes the practical adhesion or fracture energy, G, in terms of a surface energy term G_o and a separate term describing the sum of other energy absorbing processes, φ, where

$$G = G_o + \varphi.$$

With an ideal release coating applied, the G_o term can be regarded as the thermodynamic work of adhesion, W_a, which can be derived from the surface energies in the system, via Young's equation. In practical terms, when there is some mechanical interlocking occurring, there is some cohesive failure of the contacting media and the G_o term contains a contribution due to the work of cohesion, W_c. G is now a complex function of these three interdependent terms. Importantly, for good abhesion, the W_a term should be minimised, this is achieved by having a low surface energy coating. The contribution from W_c is minimised by reducing the surface roughness, as will be discussed later.

Contact angle measurements have been the principal method of calculating surface free energies for many years and their use in comparing different PSAs was pioneered by Gordon and Colquhoun [10], amongst others. Contact angle analysis has been used throughout the present study. The usefulness of the surface force apparatus, in this context, and the analysis by Johnson et al. [11] is also acknowledged.

Fluoropolymer-based systems are well known for their ability to produce low-energy surfaces. PTFE is possibly the best-known abhesion-promoting coating. The closely packed fluorine atoms on the outside of the molecule contribute to the exceptional physical properties of PTFE, which include a very low surface energy, and one of the lowest coefficients of friction of any known material (0.04–0.09) [12]. Unfortunately, PTFE is insoluble in almost all solvents and is difficult to mould or extrude since it has a very high melt viscosity (10^{11}–10^{13} Pa s). It is most frequently encountered in non-stick coating formulations as a dispersed solid phase or emulsion or can be processed in granular form by sintering. Melt processing is possible by modifying PTFE with the introduction of hexafluoropropylene and perfluoroalkylvinyl ether into the polymer chain to give Teflon FEP and Teflon PFA, respectively, both possessing relatively low crystallinity and molecular weight [13].

There are other fluoropolymers that have lower surface free energies than PTFE and these are frequently characterised by possession of CF_3 functional groups rather than the CF_2 groups of PTFE. Zisman [1] found that the surface free energy depends on the constituent groups in polymers, as follows:

$$CH_2(36\,\mathrm{mN\,m^{-1}}) > CH_3(30\,\mathrm{mN\,m^{-1}}) > CF_2(23\,\mathrm{mN\,m^{-1}}) > CF_3(15\,\mathrm{mN\,m^{-1}}).$$

Considering abhesion, the surface of a coating dominates its interaction with other materials and this interaction occurs at a molecular level so that the properties of coatings depend not only on the degree of coverage of a substrate but also on the polymer orientation. Examples of fluorinated polymers possessing low surface energy have been reported in the literature and include perfluoroacrylates [14,15], which are used to increase stain and soil resistance of textiles, perfluoromethacrylates [16,17] and perfluorosiloxanes [7]. Perfluorosiloxanes are used as mould release agents for casting poly(methylmethacrylate)

(PMMA) and fluorochemical elastomer additives are used as release agents for ethylene–propylene, nitrile and fluoroelastomers. They also prevent melt fracturing in film blowing of linear low-density polyethylene [7]. Fluorinated groups in such coatings preferentially migrate to the outer surface since this is favoured thermodynamically because it minimises the surface free energy of the system.

DuPont have recently introduced a range of completely amorphous fluoropolymers based on copolymers of 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole (PDD) and market the products under the trade name Teflon AF [13]. These materials possess many of the desirable properties of PTFE and additionally can be melt processed and are soluble in fluorinated solvents. Processing can be performed from solution, casting, spraying, painting, vacuum pyrolysis and laser ablation [18]. This versatility makes Teflon AF potentially attractive for release applications and it is being used as a low-energy non-stick coating for photomasks in contact lithography in the semiconductor industry [19,20]. This application requires a release coating that is optically transparent and Teflon AF satisfies this since it is completely amorphous. Scheirs [2] gives full details of the properties of these fluoropolymers.

Werner [21] proposed the use of perfluorinated polyethers as mould release agents for high-temperature thermosetting resins. These satisfy the properties that good release agents should possess but are only soluble in highly fluorinated solvents.

Fluoroalkylsiloxane (FAS) molecules possesses a duality of behaviour where one end reacts with a surface and the other end possesses non-wetting functionality. The fluoroalkylsilane molecule is bifunctional with a silane termination which will bond to many different types of substrates whilst a highly fluorinated chain is terminated with a CF_3 group at the other end. After molecular bonding with the substrate, the fluorinated chain, with its tendency to orient itself away from the surface, forms a tightly packed, low-energy release surface. Such molecules are reported to form self-assembled monolayers (SAMs) on substrates [22,23].

Fluoroalkylsilanes are relatively new materials that have been used for hydrophobic [24] and ice phobic coatings [25]. In addition, several recent publications have suggested the potential of fluoroalkylsilanes for adhesion control in micro-electromechanical systems (MEMS) [26]. Burns et al. [27] discuss their application as model lubricants in studies of nano-scale friction investigated using the latest scanning probe technologies.

Fluoroalkysilanes have many interesting tribological properties as non-stick coatings and have been investigated and reported by several authors such as Shanahan et al [28,29]. It was envisaged that, in the present study, these compounds might be used singly or in combination with similar bi-functional chemistries to engineer a suitable barrier between a metal moulding tool substrate and a resin-rich moulded part.

One particular commercially available fluoroalkylsilane is tridecafluoro-1,1,2,2-tetrahydrooctyl triethoxysilane

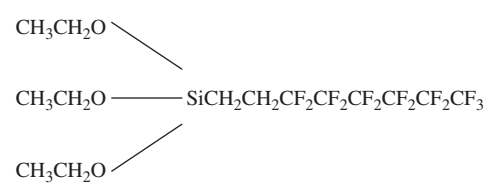

Fig. 1. The molecular structure of Dynasylan F8261.

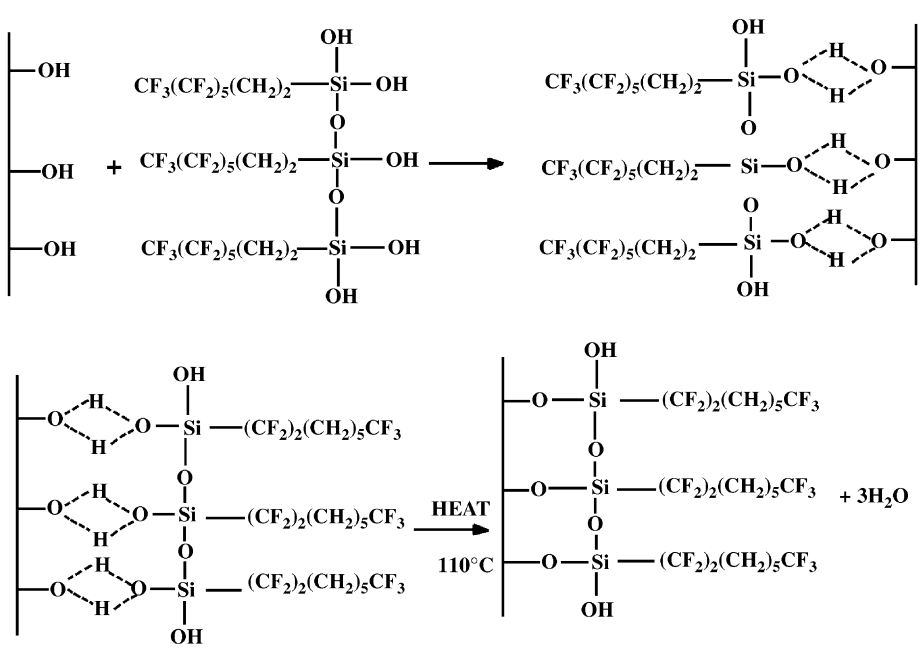

Fig. 2. Reaction and cure of Dynasylan (after Shanahan [29]).

$C_{14}H_{19}F_{13}O_3Si$ (Dynasylan® F8261 hereafter referred to as Dynasylan F8261); see Fig. 1. This was used in the present study.

Dynasylan F8261, reportedly, bonds covalently to the substrate via a hydrolysis and condensation reaction. The application of heat and humidity cures the coating allowing crosslinking to occur with the elimination of water; see Fig. 2.

Many antifouling marine paints are based on polyurethane coatings. Research has shown [30] that, for fluorinated urethanes, the adhesion of marine organisms is a minimum for coatings with surface energies $\sim 25\,\mathrm{mJ\,m^{-2}}$ and actually increases gradually for surfaces with lower energies. The smoothness of antifouling coatings is also known to influence their ability to resist fouling.

1.2. Weak boundary layers

The first external mould release agents used were mineral or ester oils and waxes, such as paraffin, which provided a cohesively weak boundary layer between the moulded part and the moulding tool. Multiple coatings of waxes had to be used and these were buffed to a high gloss [31]. Once a moulding was removed, the mould release had to be reapplied; these were thus termed sacrificial release agents. However, it was found that moulded rubber parts could absorb the oils and waxes during curing processes and this was undesirable. Also it was difficult to obtain a uniform thickness of mould release agent and this led to the use of release agents dissolved in organic solvents that allowed conformal coatings to be applied. Such sacrificial release agents are unsuitable for RTM applications and as such are not considered further.

1.3. Surface mobility

Andrade [32] report that increasing the polymer surface mobility of the molecules comprising a coating reduces the possibility for permanent adhesive bonding and consequently increased abhesion. Brady [33] describes such a molecularly mobile surface as providing "a moving target", making it difficult for a compatible adsorbate functional group to latch onto and bind to a specific site on the mobile molecule bound to the surface. Bonafede and Brady [34] in studying fluorinated urethanes with different levels of PTFE fillers concluded that supple, soft polymers with low glass transition temperatures may be more effective as antifouling materials. The suggestion is that surface roughness and molecular mobility play an important part in the success of a non-stick coating. According to Comyn [7], the viscoelastic properties of a non-stick coating are more important than the surface chemistry.

Some authors such as Owen [35] believe that a definite correlation exists between polymers possessing a low glass transition temperature (T_g) and those making good release agents for PSA tapes since a low T_g is associated with high molecular chain mobility. Ho et al. [36] in his study of minimally adhesive surfaces stated that a low T_g was desirable to minimise mechanical interlocking of adherents. It is perhaps not surprising then that many good release coatings essentially comprise a lightly cured rubbery silicone.

In contrast, electroless nickel/PTFE composite films have excellent tribological properties and a number of studies have evaluated their application as permanent, external mould release coatings [37,38]. In this case, there is little or no surface mobility due to the presence of the hard matrix material. An early electroless nickel/PTFE composite coating system suitable for abhesion promotion was developed by Ebdon [39].

Considering electroless nickel/PTFE composite coatings for mould release applications, dispersions of very fine particles of PTFE are thought necessary. These particles can be in the range of 0.4–1.0 μm in diameter and it is proposed that the low frictional properties of this fluoropolymer are transferred to the coating. The nickel–phosphorus matrix provides hardness and durability to the coating and this is influenced by the volume percentage of phosphorus in the alloy, typically between 4% and 12%. The PTFE particle loading also affects the hardness and volume percentages in the range 15–25% are typical for permanent release coatings. A compromise in final properties of the coating has to be established between lubricity, hardness and wear resistance. Once deposited, the coating can be heat-treated to promote the development of a hard nickel–phosphorus phase (Ni_3P) and to sinter the PTFE to enhance its adhesion to the substrate. The performance of the material at elevated temperatures is limited by the thermal stability of PTFE and this limits its use in practice to 400 °C.

Poeton claim that their Apticote 450 coating has low wear properties at low loading and a bulk hardness of about 250 VPN although this can be increased after heat treatment at 300 °C to 400 VPN. The exceptional properties of the Apticote coating are believed to originate from the high concentration of the PTFE dispersed phase comprising very tiny beads of PTFE with approximate diameter ~200 nm. Stevens [40] discusses the application of Apticote coatings in the moulding of thermoplastic trays and extols their properties as replacements for conventional mould release agents.

1.4. Chemical and temperature stability

The demands of RTM are, however, such that semi-permanent systems are currently favoured. The silicones, or polysiloxanes, mentioned previously have many desirable properties, including good chemical and thermal stability. Possibly, the most commonly used polysilaxane in release applications is polydimethylsiloxane (PDMS); see Fig. 3.

The PDMS structure comprises a long, very flexible inorganic backbone terminated by methyl groups. As a consequence of the long silicon–oxygen bond and flatter

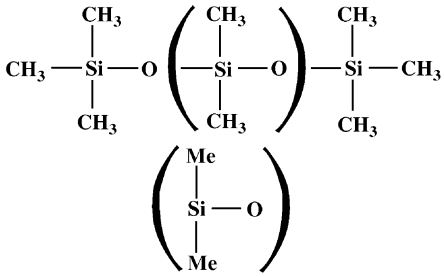

Fig. 3. Structure of PDMS (after Arkles [41]).

bond angles of the backbone, there is no barrier to the rotation of the methyl groups about the backbone. Thus the backbone is very efficient in presenting the methyl groups to an air interface and adopts this molecular conformation since it minimises its surface energy. PDMS can be modified by varying the terminal end groups. Fig. 3 shows termination by a trimethylsiloxy (Me_3SiO) group. These pendant groups effectively shield the strongly polar backbone and since the carbon atoms are fully saturated by hydrogen atoms, intermolecular forces between adjacent polymer chains are very low. This means that they slide over one another easily without any steric hindrance. Measurements of surface free energies for polysiloxanes generally report values in the range 20–23 mJ m^{-2}.

Also of note, Boeing is developing organically modified ceramic coatings called "ormocers" for the high-temperature processing of advanced composite materials where conventional release agents are thermally unstable. These combine the thermochemical stability of a glass with the surface chemistry of a fluoropolymer [42].

1.5. Influence of surface roughness

Packham has reviewed the influence of surface topography on adhesion [9]. The complex interactions between the chemistry and structure, invoking both the adsorption and mechanical interlocking theories of adhesion, are used to explain the generally improved adhesion resulting from micro- or nano-rough surfaces. In the case of the RTM process, assuming little chemical interaction between an epoxide matrix and a low-energy mould surface, it is highly likely that mechanical adhesion will limit the abhesion performance of the system and it therefore follows then that for good abhesion the specific surface area should be minimised.

Packham [43] argues that the degree of penetration of a liquid into a capillary (considered here as a pore) can be derived by equating the spreading pressure of the liquid to the resisting back pressure due to trapped air. At equilibrium, the distance, x, penetrated is given by

$$x = L(1 - \{P_a r/2[2\gamma_2 \cos\theta + P_a r]\}),$$

where L is the pore depth, P_a is the capillary pressure, r is the radius of the pore, θ is the contact angle and γ_2 is the surface tension of the resin. Clearly, the above equation shows that very small pores are more easily filled by the contacting liquid, which in the case of RTM will be an epoxide at elevated temperature, just prior to curing. It is particularly relevant that in RTM the mould will be under pressure so the P_a term is an underestimate. Consequently, a fine-scale morphology will be detrimental for abhesion and we would need to ensure that any fine surface morphology should be filled by a mould release compound. Note that good adhesion is required, however, between the release agent and the metal to which it is applied in order to achieve a durable coating. The proposed condensation bonds which are thought to occur at the metal (oxide)/FAS interface are clearly important; see Fig. 2.

Clarke et al. [44] used atomic force microscopy (AFM) to show that application of a semi-permanent release fills grooves and holes in a metal mould surface and levels the surface topography but does not create a perfectly smooth surface. The single coating thickness was estimated to be approximately 300 nm. The point was made that if the release coating is too thick and the surface too smooth, it becomes unstable due to the high shear forces encountered in moulding and demoulding operations. An optimum coating thickness worked best, which reduces frictional contact with the mould substrate and provides a lubricating effect. AFM, scanning electron microscopy (SEM) and profilometry have been used in the present study to determine the degree of surface roughness following the application of a number of abhesion-promoting coatings.

In a separate, but not completely unrelated field, Bonafede and Brady [34] suggest that the adhesive from marine organisms initially penetrates surface cavities and surface porosities in PTFE and then after chemical bonding has occurred, mechanical interlocking of the crosslinked adhesive contributes to the tenacious attachment of the organism to the surface.

1.6. Summary

In the previous sections, a summary of the critical factors which affect abhesion has been presented along with details of some of the coating technologies which might be used to optimise abhesion. In the present study, we aim to compare the physicochemical properties introduced to metal surfaces by a number of semi-permanent and permanent coatings which are potentially suitable for RTM applications, along with limited adhesion/abhesion data. A number of metal substrates were used in the present study, and the results presented herein focus on nickel, a common tooling material. In terms of coatings, fluoropolymer- and polysiloxane-based materials offer the combination of properties required for ideal abhesion and so a number of these were evaluated. In addition, an electroless Ni/PTFE coating has been studied which shows promise as a permanent external mould release coating.

2. Experimental

2.1. Substrates

Three types of nickel substrate were used. For some experiments, clean, smooth, model substrates were produced by magnetron sputtering 1.1 μm of nickel onto glass slides. These substrates were used in the X-ray photoelectron spectroscopy (XPS) studies. For tapping mode AFM, highly polished nickel was used. Various grades of diamond paste were used with the final particle size being 1 μm. For most studies, industrially relevant, rough, abraded nickel substrates were cut from nickel mould tools. Also, where mentioned in the text, a limited number of mechanical tests were carried out using stainless-steel substrates. These had similar surface texture and surface free energy to the abraded nickel substrates.

With the exception of the sputter-coated nickel samples, all surfaces were thoroughly cleaned prior to release coat application using proprietary chemicals (Isoprep 44, Lea Manufacturing, UK) to remove organic contamination.

2.2. Release coatings

This section provides details of the deposition processes used for the various abhesion-promoting coatings studied, which are listed in Table 1.

2.2.1. Frekote B15/710 NC and Zyvax waterworks

The Frekote B15/710 NC system was applied using the following procedure: substrates were first immersed in Frekote B15 surface sealer and subsequently these were held vertically to drain excess material. The substrates were then allowed to air dry for 30 min at room temperature. A second coating was then applied in the same manner; however, this was dried for 30 min in an oven at 125 °C. The substrates were then double-coated with Frekote 710 NC mould release agent. After each application, the substrates were air dried at room temperature for 15 min and a dwell time of 30 min was used between applications. Finally, a third coat was applied and left to dry at room temperature for 20 min. A similar multi-stage application procedure was employed for the Zyvax Waterworks. Application conditions recommended by the manufacturers were employed for the sealer and the mould release coats.

2.2.2. Dynasylan F8261 FAS

Different concentrations, in the range 0.1–5%, of Dynasylan F8261 solution were prepared and used to coat samples of metal for time periods of 0.5–60 min. The manufacturers recommend preparing a working solution by first mixing absolute ethanol and water in the ratio 95:5. Then by adding 1 part of Dynasylan F8261 to 119 parts of the working solution, a final concentration of 0.5% Dynasylan F8261 is obtained. Stirring then produces a dispersion that has a shelf life of up to 24 h. Acidification was recommended to accelerate polymerisation and it was recommended that acetic acid be used to adjust the solution to a pH between 4.5 and 5.5. Dipping of samples in this solution for a period of at least 1 min allows sufficient material to react with a high surface energy substrate and produce a uniform coating. Heating in an oven at 110 °C for 10 min subsequently cures the coating. Varying these mixing proportions and acidifying each to a pH of 5.0 produced metal samples coated with 0.1%, 0.5%, 1.0%, 2.0% and 5.0% Dynasylan F8261. Although different immersion times were tried ranging from 1 to 60 min, it was subsequently found that reaction times in excess of 10 min did not result in higher water contact angles implying that once the substrate surface had fully reacted with the fluoroalkylsilane, further treatment time did not produce a thicker coating or decrease the surface free energy of the coating.

2.2.3. Oxsilan AL-0501 only and Oxsilan AL-0501 plus Dynasylan F8261 FAS

The theory associated with such coatings has been described by Van Ooij [45] who described their application as replacements for chromate pretreatment of metals. The active silane component in Oxsilan AL-0501 is unknown but is believed to possess a similar chemistry to bis-[triethoxysilyl]ethane (BTSE) as described by Van Ooij and is dispersed in a water °C for 30 min. Some of these coated samples were then immersed in a solution of 1% Dynasylan F8261 fluoroalkylsilane and left to react for 15 min. These samples were then removed and cured according to the procedure previously mentioned. It was thought that a weak boundary layer would be created at the interface between the two cured coatings that would enhance the ease of mould release.

The Oxsilan-treated samples displayed pronounced interference colours in reflected light implying that the thickness of the coating was less than the average wavelength for visible light.

2.2.4. Xylan 8080 and Xylar 2020

Although spray coating was recommended for these coatings, the particle size in the coating was too large for the spray coater available and it was decided to apply coatings using a brush. The Xylan coatings were flash evaporated for 10 min in an oven set at 150 °C and then removed.

For the Xylan 8080, the oven was subsequently reset to 400 °C and the coated samples replaced when the oven had reached this temperature and were left in the oven for a further 5 min. In contrast, the water-based Xylar 2020 was heated in an oven set at 200 °C for 15 min to effect full cure.

The results of these preparations were quite variable. Sometimes, boiling of the solvent during flashing or cure generated a rough surface and these samples were discarded. Only samples where the cured coating was smooth and blemish free were retained for testing and analysis.

Table 1
Summary of release coatings used in the present study

Coating	Supplier	Description
Frekote B15/710 NC	Loctite ltd.	Silicone-based, multiple component, semi-permanent, external mould release
Zyvax waterworks	Zyvax inc.	Water-based, multiple component, semi-permanent external mould release
Dynasylan F8261	Abcr-gelest (UK)	Fluoralkylsilane, semi-permanent external mould release
Oxsilan AL-0501	Chemetall Ltd. (oxsilan)	Oxsilan is an organofunctional silane, developed for use as a pretreatment for aluminium surfaces
Xylan 8080	Whitford plastics Ltd.	Fluoropolymer (PTFE) dispersion with an organic binder, permanent external mould release
Xylar 2020	Whitford plastics Ltd.	Fluoropolymer (PTFE) dispersion in an aqueous solvent with an inorganic binder, permanent external mould release
Apticote 450/460	Poeton industries Ltd.	PTFE dispersion in an electroless nickel matrix, permanent external mould release

2.2.5. Apticote 450 and 460

The Apticote 450 and 460 Ni/PTFE composite coatings were applied to samples of nickel tooling by Poeton Industries Ltd., Gloucester. This is a self-lubricating nickel alloy composite coating comprising a micro-dispersion of PTFE particles. The coating thickness was estimated to be $\sim$20 μm.

2.3. Surface characterisation and mechanical testing

A range of techniques was used to determine the physicochemical characteristics of the uncoated and coated surfaces. Further to this, an attempt, was made to determine the adhesion/abhesion response to these coatings. Brief details of the instrumentation and procedures used are as follows.

2.3.1. Scanning electron microscopy (SEM)

The instrument used was a Leo Gemini 1530 field emission gun SEM (FEGSEM) operated using either a 10×10^3 or 20×10^3 V primary electron beam energy. This instrument also incorporated an energy dispersive X-ray analyser (EDXA).

2.3.2. Atomic force microscopy (AFM and PFM-AFM)

A TA instruments 2990 Micro-Thermal Analyser was used to provide both topographical data and pull-off force information. In the latter case, an attempt was made to quantify differences in adhesion between coatings and the instrument was used in the pulsed force mode of operation.

2.3.3. Auger electron spectroscopy (AES)

A JEOL 7100 Auger Spectrometer was used with a primary electron beam energy of 10×10^3 V and a current close to 1×10^{-6} A. Depth profiling was carried out using argon ion bombardment with a primary beam energy of 3×10^3 eV and a current density of 50×10^{-6} A cm^{-2}. Empirically derived relative sensitivity factors and each rates were used for quantification purposes.

2.3.4. X-ray photoelectron spectroscopy (XPS)

XPS spectra were recorded on a VG Scientific Escalab Mk I instrument operating with an unmonochromatised Al Kα X-ray source (1486.6 eV) and operated in the constant analyser energy (CAE) mode. Spectra were calibrated by assuming a 285 eV binding energy for aromatic and aliphatic carbons. Quantification was achieved by measurement of peak area following subtraction of a Shirley-type background.

2.3.5. Static secondary ion mass spectrometry (SSIMS)

A Cameca 3F SIMS instrument was used to analyse the chemistry of Frekote mould using positive secondary ion detection.

2.3.6. Contact angle analysis

A Data Physics SCA20 Contact Angle Analyser was used to obtain experimental measurements of contact angles using the recently advanced sessile drop method. Using two liquids with known surface tensions allows the calculation of surface free energies (SFE). Triply distilled water and diiodomethane (DIM) were used, these being polar and non-polar liquids of known surface tensions [46]. The approach of Owens–Wendt–Rabel and Kaelble was followed. The SFE values quoted are the mean of at least 10 measurements.

2.3.7. Fourier transform infra-red analysis (FTIR)

Spectra were collected using a Mattson 3000 FTIR spectrometer. The majority of samples examined were liquids and these were prepared by preparing a film of the liquid onto a KBr disc and allowing to dry in air at ambient temperature. This disc was then placed in the spectrometer and spectra collected over the range 300–4000 wavenumbers using 64 scans. The same numbers of scans were used to record the background.

2.3.8. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)

These techniques were used to determine the thermal properties of the Frekote 710 NC. Frekote 710 NC mould release agent is a resin dissolved in dibutyl ether. A volume

of 250 ml of this liquid in a glass beaker was placed in an empty fume cupboard and the solvent allowed to evaporate completely over a 48 h period with the fume cupboard extraction left on for this period. After this period, a rubbery solid remained at the bottom of the beaker. This material was used for subsequent thermal analysis experiments.

For DSC analysis, a mass of 11.05 mg of solid Frekote was placed in an aluminium DSC sample pan, which was hermetically sealed, and then the lid of the pan was pricked to allow volatiles to escape. This was then subjected to a three-stage controlled heating ramp in the furnace of a TA Instruments 2920 modulated DSC. A heating rate of 20 °C min was used which is a standard heating rate for the determination of glass transition temperatures. The heating cycle consisted of a ramp from 30 to 120 °C using nitrogen purge gas to drive off excess solvent and the sample was held isothermally at the latter temperature for 5 min. The second segment of the heating program caused the sample to be cooled to −100 °C using liquid nitrogen cooling. In the final segment, the sample was heated from −80 to 300 °C.

To achieve the stated degree of cooling required, a whole Dewar of liquid nitrogen was used and it was impractical to try to reduce the starting temperature further. At such low temperatures, the heat flow signal in the DSC takes some time before it settles down and becomes steady, after about 20 °C into the run. Thus the recorded data show heat flow from −80 °C to allow for this settling period.

The thermal stability of Frekote was determined using a TA Instruments TGA 2950HR. A mass of 10.011 mg of solid Frekote was weighed into a platinum crucible, which was then positioned inside the TGA furnace. The furnace was purged with dry air at a suitable flow rate (typically 10 ml s^{-1}). The sample was heated from 30 to 300 °C at a heating rate of approximately 3.5 °C min^{-1}. A slow heating rate was chosen to allow excess solvent to be released from the sample. This particular TGA allowed high-resolution data to be obtained whereby the heating rate is reduced automatically when a significant mass change occurs.

2.3.9. Stylus profilometry

Surface roughness measurements to determine R_a and R_t parameters were made using a Talysurf instrument. R_a is defined as the arithmetic mean of the absolute departures of the roughness profile from the mean line. R_t is the maximum peak to valley height of the profile in a given assessment length.

2.3.10. Mechanical tests

Initially, axial butt testing was carried out using 60 mm diameter stainless-steel platens treated with the various release coatings. These were then bonded together using an epoxide-based prepreg laminate. The results obtained were generally unsatisfactory. In some instances, for example with the Frekote B15/710 NC system applied, no repeatable release force could be measured as this force was so small. It was found that a single full application of Frekote B15/710 NC to the steel discs allowed easy release for 20 separate cure cycles for the prepreg laminate. Only slight sticking was noticeable after 20 cure cycles at the periphery of the discs due to bleed out of the resin onto uncoated edges. It was concluded that this rather simple adhesion test method could not provide meaningful data for very small release forces and a new testing methodology was required.

The blister test was then used, using apparatus which was constructed in-house in which the pressure could be varied up to 608 kPa. In this test, a 65 mm stainless-steel disc was machined and cleaned and then treated with release coating prior to application of Cytec Fiberite FM300 epoxide resin sheet. The epoxide was then cured, under pressure, according to the manufacture's recommended procedures for 3 h at 180 °C. The pressure required to delaminate the FM300 or for blister formation was recorded.

Friction coefficient and wear test comparisons were also made on selected coated surfaces using a bi-directional wear test rig manufactured by Teer Coatings Ltd. Each sample was tested at a load of 5 and 10 N for 200 cycles against a 5 mm tungsten carbide–cobalt (WC–Co) ball. The following conditions were used for each bi-directional wear test: 150 mm min^{-1} table speed, 2 mm displacement, 200 cycles.

3. Results

One of the major aims of this research was to evaluate surface coatings that offered potential as mould release agents. A number of candidate systems were selected using the criteria previously detailed in Section 1. For comparative purposes, initial characterisation was carried out on the substrate materials prior to coating application.

3.1. Uncoated substrate characterisation

The following metal substrates were initially studied: sputter-coated nickel on glass, polished nickel and industrially sourced abraded nickel.

3.1.1. Sputter-coated nickel on glass

The SFE of the sputter-coated nickel on glass was not determined, as this was assumed to be clean as care was taken to minimise atmospheric contamination after nickel deposition and prior to release coating deposition. High-resolution SEM and AFM showed no significant features on this sample indicating a very smooth surface topography.

3.1.2. Polished nickel

The polished and then cleaned nickel was examined by SEM and AFM and was shown, as expected, to be relatively smooth over the majority of its surface area; see Figs. 4a and b.

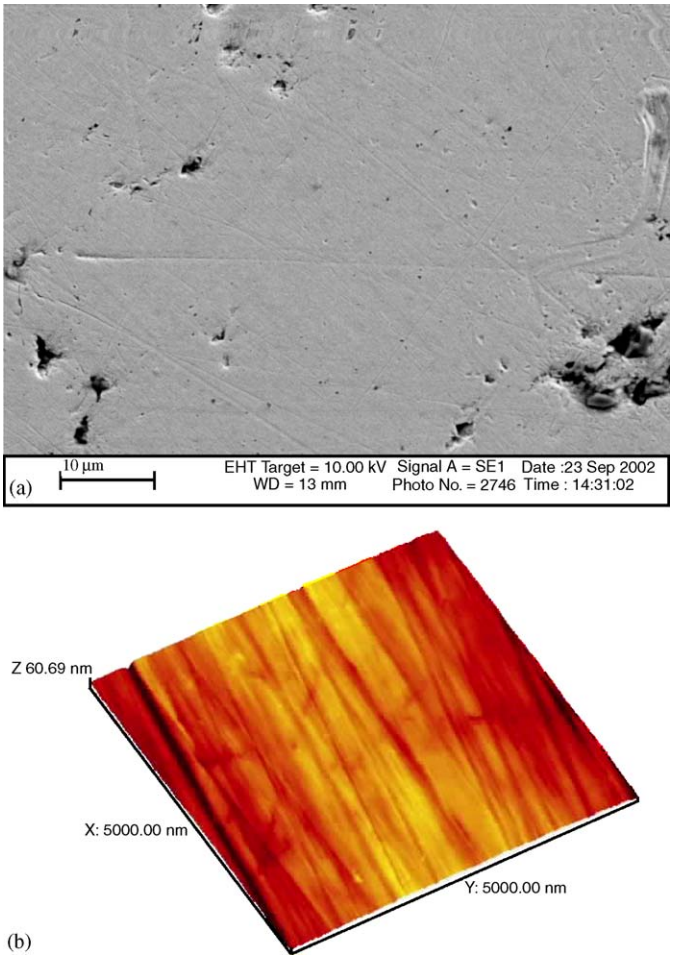

Fig. 4. (a) SEM image of hand-polished nickel tooling. (b) AFM image of hand-polished nickel tooling ($5 \times 5\,\mu m$ area). Vertical scale 60 nm.

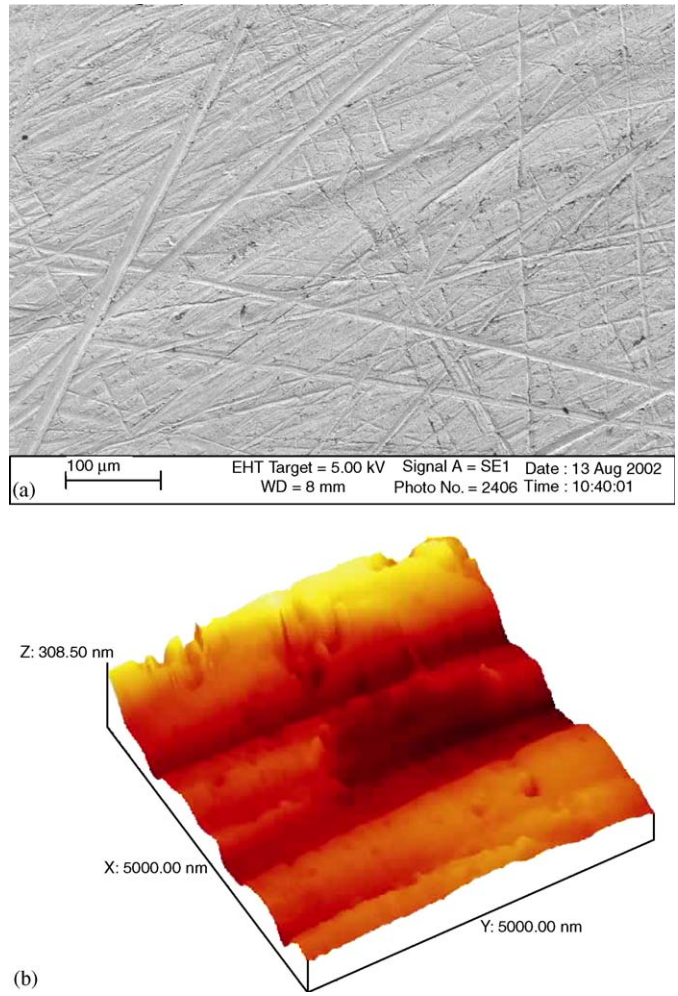

Fig. 5. (a) SEM image of abraded nickel tooling. (b) AFM image of abraded nickel tooling. Vertical scale approximately 0.3 µm.

The roughness, R_a, value was determined to be 0.0240 µm. The polished surface hardness was calculated as $471H_V/150$. An average water contact angle of 35° was measured indicating a reasonably clean surface.

3.1.3. Industrially sourced substrates

Figs. 5a and b show the surface topography of the industrially sourced nickel substrate using SEM and AFM. Mechanical abrasion had clearly resulted in scouring of the surface with many scratches visible, as shown in Fig. 5a. Stylus profilometry results showed an R_a value of 0.405 µm on this surface. An average water contact angle of 32° was obtained from the abraded and cleaned industrially sourced substrate surface, again, demonstrating that a reasonably clean surface was prepared prior to coating application.

3.2. Frekote B15/710 NC release coating

Initial studies focussed on the characterisation of the Frekote B15/710 NC coating system. Using FTIR, the transmittance spectra for Frekote 710 NC mould release agent (Fig. 6a) and Frekote B15 sealer (Fig. 6b) were obtained. The most intense peaks occur at similar positions between 1500 and 500 wavenumbers (cm^{-1}) in both spectra. These figures also show a number of subtle differences in the minor peaks and broadening of the absorption bands. Other peaks common to both samples are clustered in the range ~2700–~3000 cm^{-1}.

Considering the spectrum for Frekote 710 NC, the principal peaks occur at 2931, 2878, 1261, 1095, 1020 and 807 cm^{-1}. Strong absorption peaks assigned to dimethyl- and trimethyl-substituted silicon atoms are reported to occur near 800 cm^{-1} [47]. Also a strong band at 1263 cm^{-1} is assigned to the bending mode for a silicon-bonded methyl group [48]. Absorptions correlated with CH_2 and CH_3 stretching are observed at higher wavenumbers and overall the spectrum resembles that obtained for PDMS. There appears to be a reasonable qualitative similarity between the spectrum for Frekote 710 NC and the Frekote B15 sealing agent and since these are chemically compatible, it is reasonable to assume that this may also be based on PDMS.

In addition, Blanchard [49] used static secondary ion mass spectrometry (SSIMS) to determine that Frekote

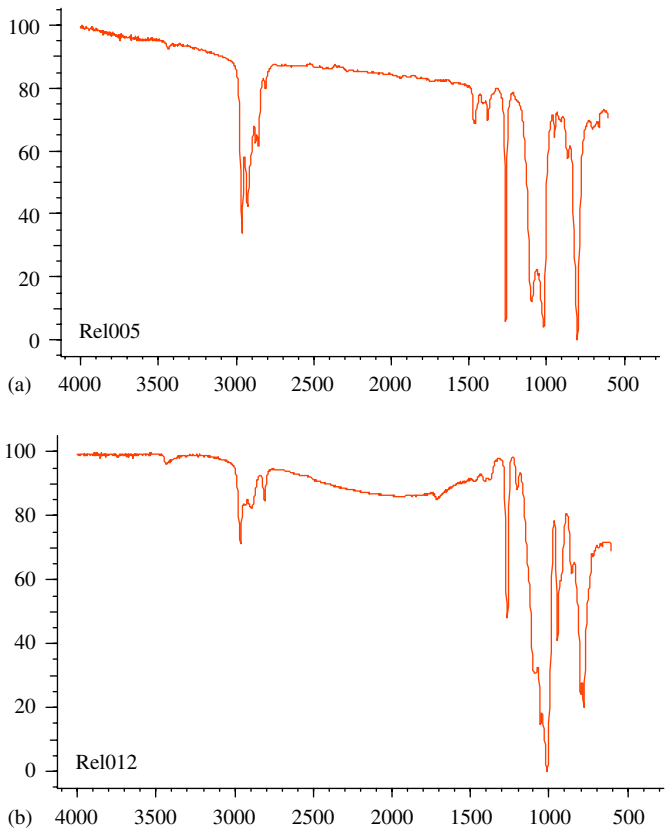

Fig. 6. (a) FTIR transmittance vs wavenumber (cm^{-1}) spectrum of Frekote 710 NC mould release agent. (b) FTIR transmittance vs wavenumber (cm^{-1}) spectrum of Frekote B15 sealer.

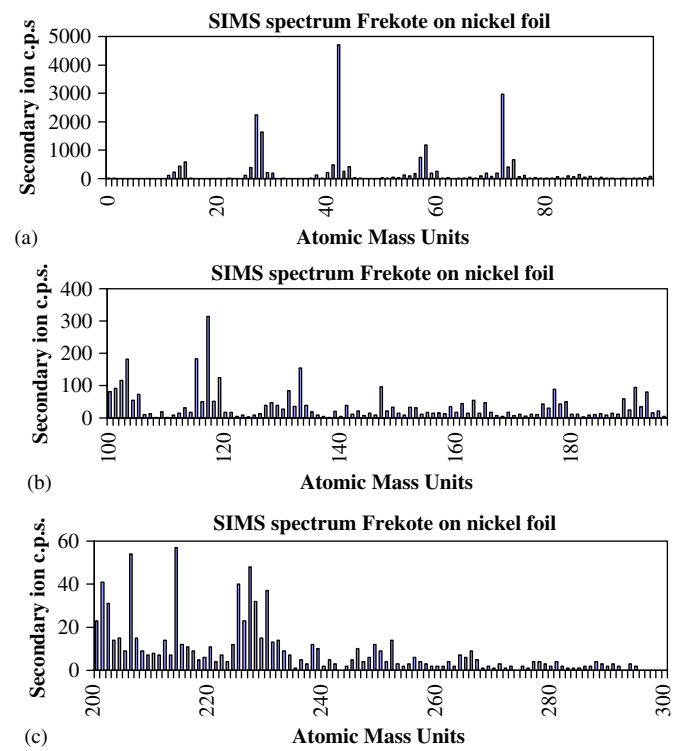

Fig. 7. (a) SIMS positive ion spectrum for Frekote on nickel foil (range 0–100 amu). (b) SIMS positive ion spectrum for Frekote on nickel foil (range 100–200 amu). (c) SIMS positive ion spectrum for Frekote on nickel foil (range 200–300 amu).

710 NC was based on polydimethylsiloxane (PDMS). The positive ion SIMS spectrum of PDMS [50] shows peaks at 73, 147 and 221 atomic mass units (amu) in the order of intensity attributed to $(CH_3)_3Si$, $(CH3)_3SiOSi(CH_3)_2$ and $(CH_3)_3Si(OSi(CH_3)_2)_2$ clusters. Minor peaks also occur at 207 and 295 amu. SSIMS spectra from Frekote 710 NC cured onto nickel foil were acquired in this study and are shown in Figs. 7a–c.

The main peaks at 73 and 147 amu are seen in the above spectra confirming the presence of PDMS although there are many other peaks which cannot be as easily assigned and are likely to be associated with the formulation of Frekote which is a complex product and not a single compound such as PDMS. These results are very similar to those reported by Blanchard.

From simple evaporation experiments, it was apparent that the Frekote 710 NC mould release agent would precipitate out as a transparent, rubbery film once the dibutyl ether solvent had been driven off. This again was consistent with the physical properties of PDMS and an experiment was performed using differential scanning calorimetry (DSC) to determine its glass transition temperature. In this experiment, the calorimeter was cooled using liquid nitrogen to an initial temperature of –100 °C, however, no T_g was measured and it was concluded that the T_g must be very low. This is consistent with the known T_g for PDMS that has been measured as −127 °C. Thermogravimetric analysis of the sample also showed that it is thermally stable with a weight loss of only 2.18% measured from ambient to 300 °C.

The significance of these measurements means that films of the mould release agent will be viscoelastic at the temperatures experienced by mould tooling during a typical heating cycle. Consequently, the molecular mobility of these molecules will tend to lubricate the moulding and the mechanical properties of the film will resist the pressures applied to the tool surface during the cure cycle. The desirability of these properties to obtain good release was previously discussed. These are very different properties to those of fluoroalkylsilanes that cure to form a very thin film on a surface that conforms to the surface topography without sealing porosities or irregularities on the surface.

SEM showed the thickness of the fully applied Frekote B15/710 NC coating to be ~5 μm. The surface roughness for the untreated substrate is significantly less than this. Consequently, a typical application of the Frekote products would be expected to largely fill and mask most of the surface irregularities. This was confirmed by SEM. It is also conjectured that under conditions of elevated temperature and applied pressure commensurate with moulding processes, the Frekote smears and flows over a surface filling in many microscopic substrate irregularities.

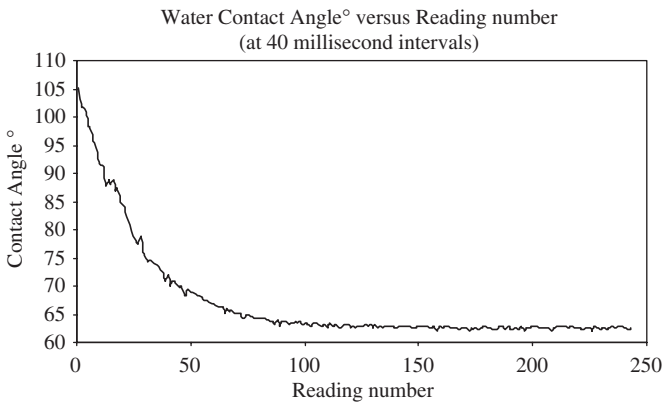

Fig. 8. Spreading of water on Zyvax mould release coating showing contact angle reducing over 40 ms time period.

The role of the sealing component in such mould release products is clearly important.

The SFE of the Frekote 710 NC surface was measured a number of times. Values in the range of 10.7–20.4 mJ m^{-2} were calculated. The lower value was recorded on abraded nickel.

3.3. Zyvax Waterworks

The surface energy of this coating was measured as 24.4 mJ m^{-2}. However, in a pulsed force mode AFM test, the result for the Zyvax-treated surface was interesting in that the AFM tip apparently remained attached to the surface during testing. This was interpreted as implying that this release coating was unstable by virtue of it being hygroscopic. This aspect was further studied by monitoring the water contact angle as a function of time. Results are shown in Fig. 8. The initial water contact angle was 110° but reduced so rapidly that data collection could only be started once the angle had reached 105° as shown. Since the Zyvax demonstrated this instability, it was decided to eliminate it from further studies.

3.4. Dynasylan F8261 FAS coating

It was concluded from preliminary optimisation experiments that a minimum treatment time of 10 min and a solution concentration of 1% of Dynasylan F8261 was optimal for most applications, these conditions giving a surface free energy of ~10 mJ m^{-2}.

Allowing a treatment time of 30 min using a 1% concentration of the chemical in ethanol, a water contact angle of 119° was obtained for an abraded and cleaned sample of nickel tooling with a contact angle of 104° using DIM. A surface free energy of 7.9 mJ.m^{-2} was calculated. This exceptionally low value could be due to the high packing density of the CF_2 and CF_3 groups on the Dynasylan F8261 treated surface. For comparison, measurements were also made on a standard sample of PTFE. An average water contact angle of 116° was obtained and using DIM an average of 82° was recorded. From these values, a surface energy of 16.7 mJ m^{-2} was calculated. The reference value is 18.5 mJ m^{-2}, so the measured value is somewhat low. The reason for this is unknown but even assuming a systematic error of the same order applies to the values calculated for Dynasylan F8261, the surface energies measured for this coating are very low.

The cured Dynasylan F8261 fluoroalkylsilane film was colourless and stable. It did not appear to be susceptible to moisture absorption even after exposure for several weeks to laboratory air. From published work on fluoroalkylsilanes [22,26,28,29] and other silane metal treatments [45], it was believed that the cured coatings were very thin extending to a few nanometres and to investigate the surface morphology of the coating it was apparent that high-resolution microscopy would be required. XPS was used to confirm the estimated coating thickness.

Samples of nickel sputtered onto glass slides were prepared to be utilised for such investigations since the surface roughness values of real tooling were too high to allow clear resolution of the coating. Initially, one of the sputtered nickel slides was treated in a 1% solution of Dynasylan F8261 for 30 min and the coating cured. The sample was then examined using high-resolution SEM without any additional preparation and the images shown in Figs. 9a and b were recorded. These images appear to show that the coating comprises discrete islands of the cured chemical with features up to about 40 nm in diameter.

Published literature [27,51] suggests that AFM can also provide useful topographic and functional images relating to the tribological properties of fluoroalkylsilanes. AFM images were collected from nickel sputtered coated glass slides following treatment with Dynasylan with varying concentrations and treatment times, referenced against an untreated control sample; see Figs. 9c and d. These images show the pull-off force of the surfaces represented in three-dimensional plots and suggest that there is not a great deal of difference in the surface "stickiness" between the treated and control surface. The patterning developing on the treated sample comprising circular patches is difficult to interpret. The features are ~180 nm in diameter and do not correlate with the islands shown in the high-resolution SEM images which were only ~40 nm in diameter. Similar structures attributed to phase separation effects have been reported in the literature. A further consideration of such data is given in Section 3.8.2.

In a subsequent study, a sample was treated with 5% Dynasylan F8261 for 60 min to fully react with the metal substrate. XPS was then carried out to determine the resultant surface chemistry and obtain information about the coating thickness.

The surface survey spectrum showed peaks for oxygen (531 eV) and fluorine (698 eV). Smaller peaks for carbon were also seen (285 and 291 eV). Other elements detected were Si, Mn, Cr and Fe associated with the stainless-steel substrate used in this case. The fact that these elements are

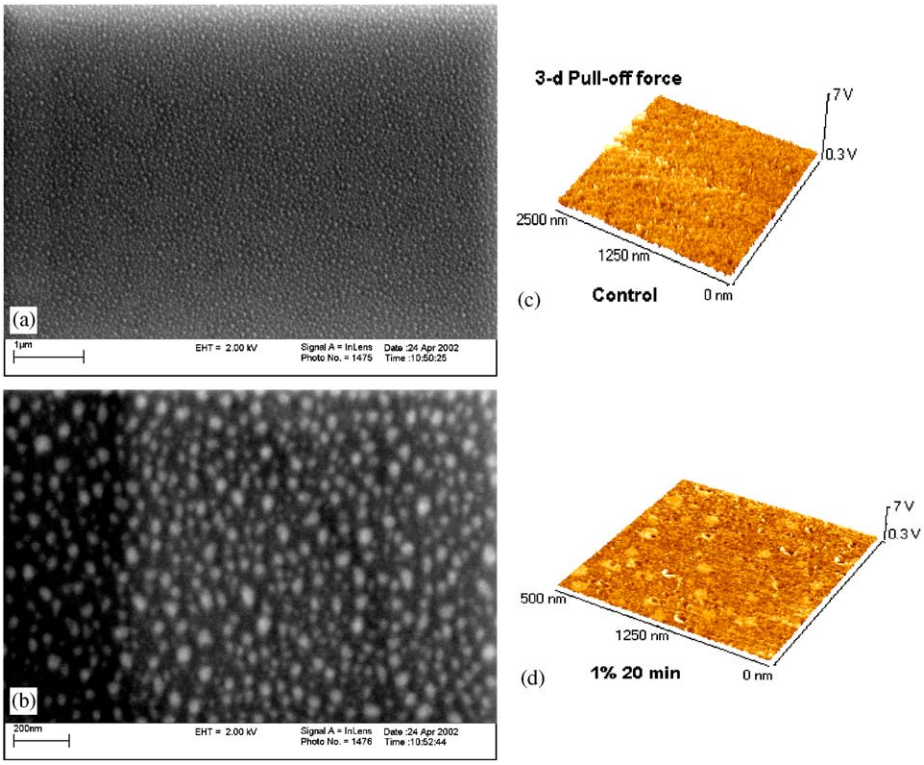

Fig. 9. (a) Low-resolution FEGSEM image of fluoroalkylsilane coating on nickel. (b) High-resolution FEGSEM image of fluoroalkylsilane coating on nickel. (c) AFM image of untreated nickel sputter-coated onto glass (2500 × 2500 nm). (d)AFM image of surface in (c) following treatment with fluoroalkylsilane (2500 × 2500 nm).

detected is evidence that at least part of the fluoroalkylsilane coating is less than 10 nm in thickness.

A high-energy resolution scan was performed for carbon to obtain more accurate information about its binding energy. The binding energy shift between the two carbon peaks was 6.0 ± 0.1 eV. From XPS reference data, the chemical shift in binding energy associated with a CF_2 functional group should be 5.9 eV and for a CF_3 functional group the shift should be 7.69 eV.

The molecular structure of the Dynasylan F8261 molecule is shown in Fig. 1 and has five CF_2 functional groups terminated by a single CF_3 functional group and it is suggested that the 6.0 eV shift seen in the high-resolution scan for the carbon peak implies that the shift due to the CF_2 functional groups dominates and effectively masks the presence of the terminal CF_3 group.

Angle-resolved XPS experiments were carried out on Dynasylan F8261 deposited onto the sputter-coated nickel on glass substrate. The purpose of the proposed experiment was to obtain information about how the fluoroalkylsilane molecules might be oriented on the nickel substrate.

In this experiment, it was appropriate to attempt to produce a coating thickness of only a few monolayers and a low concentration solution of 0.1% Dynasylan F8261 was used to treat a nickel-sputtered slide for a reaction time of 1 min. Data were collected using take-off angles of 20°, 50°, 70° and 90°.

Fig. 10 shows the atomic percentages for carbon, fluorine and nickel plotted as a function of take-off angle.

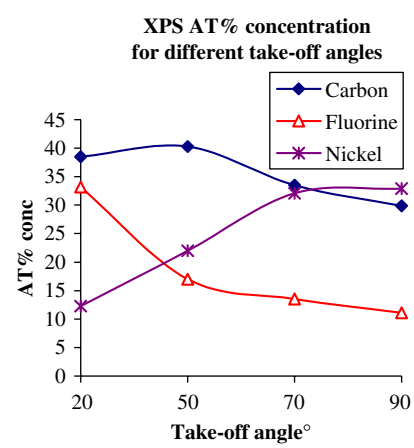

Fig. 10. Carbon, fluorine and nickel concentrations for different XPS take-off angles.

These data can be interpreted either as suggesting an enrichment of fluorine at the surface consistent with the known molecular structure as depicted and comprising a CF_2 tail terminated by a CF_3 group in which the tail orients itself perpendicular to the surface or the data may simply show that defluorination is occurring over the time scale taken to collect the data in each case. Fluorine present on surface coatings examined using XPS can be sensitive to the X-ray irradiation experienced during analysis leading to defluorination. The fact that the fluorine-to-carbon ratio

does not exceed unity is suggestive that defluorination is occurring since if CF_3 were present at the surface, one would expect the ratio to be greater than unity. The possibility of defluorination at the sample surfaces by irradiation over the duration of these experiments severely limits the interpretation of the data albeit a relatively low fluence was used.

It was suspected that to obtain good release properties it was necessary to fill in the asperities and porosities on a rough surface such that mechanical interlocking was denied as a mechanism for adhesion. The thin, conformal coverage provided by Dynasylan F8261 does not achieve this effect. Many widely used commercial mould releases use a sealing agent which is compatible with a mould release coating applied afterwards. In other words, it is usually necessary to use a primer or sealer to treat the surface before producing a low-energy surface. Hence, a combination of Oxsilan AL-0501 plus a Dynasylan F8261 topcoat was studied.

3.5. Oxsilan AL-0501 only and Oxsilan AL-0501 plus Dynasylan F8261 topcoat

The potential use of Oxsilan AL-0501 silane alone or as a sealer followed by the application of a Dynasylan F8261 topcoat was studied. It was thought that this combination might provide a bifunctional coating where a smooth, low-energy outer surface would be produced and, in addition, a weak boundary layer would exist between the Oxsilan AL-0501 and the Dynasylan F8261 coatings to engineer good release properties by a combination of these two mechanisms. Evidence from both ellipsometry and SEM suggested that the Oxsilan AL-0501 forms a sufficiently thick coating to fill in many micro-cavities in a substrate surface.

However, blister tests carried out using discs coated with Oxsilan AL-0501 only and Oxsilan AL-0501 plus Dynasylan F8261 gave essentially the same result with no disbonding of the applied FM300 resin apparent at reasonable applied loads.

It was concluded that Oxsilan AL-0501 alone was not successful at release as this coating is not intended as a release agent and is not optimised for that application. For the combination coating, it was thought that the Dynasylan F8261 coating failed to react sufficiently with an already existing silane-treated surface. In addition, it is possible that an interpenetrating network could form which would reduce the effectiveness of these coatings for release applications. Due to their lack of release properties, these systems were not studied further.

3.6. Xylar 2020 and Xylan 8080 sintered fluoropolymer coatings

Whitford Xylar 2020 and Xylan 8080 PTFE-based coatings were sintered onto different substrates. The contact angles and surface free energies of the prepared coatings were measured, and these are given in Table 2 along with selected SFE values for other coating systems for comparative purposes.

Table 2
Summary of contact angle data for Xylan 8080 and Xylar 2020 coatings

Coating	Water contact angle (°)	DIM contact angle (°)	SFE ($mJ\,m^{-2}$)
Xylar 2020	118	96	10.8
Xylan 8080	126	99	9.0
Frekote B15/710 NC	—	—	10.0–20.4
Zyvax waterworks	—	—	24.4
Dynasylan F8261	—	—	7.9–16.7

The surface of the cured Xylar 2020 coating was examined using SEM and an EDX spectrum obtained; see Figs. 11a and b.

Blister testing was carried out using Xylar 8020 against Cytec Fiberite FM300 epoxide resin. It was found that FM300 tenaciously adhered to the Xylar 8020 coating despite the fact that the Xylar coating possessed a relatively low surface energy of $10.8\,mJ\,m^{-2}$. Figs. 11c and d show areas of the blister test sample in cross-section. In Fig. 11c, the white area on the right-hand side of the image originates from the substrate. A polyethylene terephthalate membrane is present in the FM300 resin sheet as a supporting binder and this is seen as the oval and round, darkened areas on the left-hand side of this image. The Xylar 8020 coating is sandwiched between the two and has sufficient atomic number contrast to be discernable. It seems to be approximately 50 μm thick.

Note from Fig. 11d that there is visible surface roughness which seems to be well wetted out by the FM300 resin.

When the surface of the Xylan 8080 is examined by SEM (see Fig. 12a), a different highly textured morphology is observed. When examined at higher magnification, the porous structure of PTFE is clearly resolved; see Fig. 12b. It is this porosity combined with the pressure and temperature applied to the resin system that causes mechanical interlocking and adhesion despite the low surface energy of the PTFE surface. Again, it is seen that a low-energy surface does not by itself prevent sticking.

The significant factor in this application is the combination of pressure and high temperature (180 °C) applied during FM300 cure. Other non-stick applications of the Whitford coatings are unlikely to have to contend with relatively high-pressure conditions and therefore these coatings satisfy their intended function.

Fig. 12c shows an EDXA spectrum for the Xylan 8080 coating from which it is seen that the coating composition is different from that of the previously studied Xylar 2020 coating with the possibility of barium sulphate and copper chromate present as additives. The role of these additives is unknown, although they could possibly be applied to increase the passivity of the substrate. This again emphasises the difficulty in understanding the observed abhesion performance of a particular system when the chemistry of proprietary coatings is not fully known.

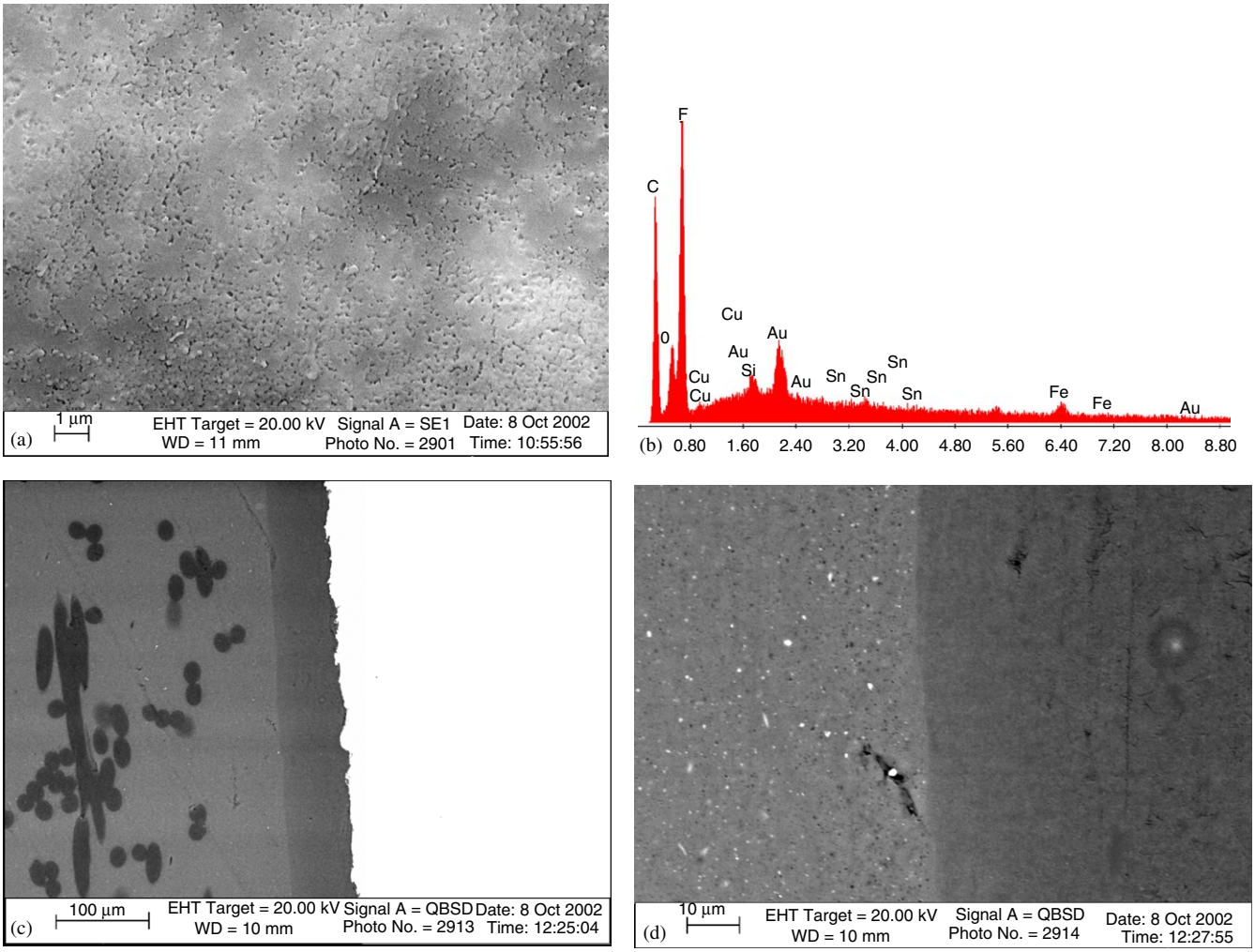

Fig. 11. (a) SEM image of a Xylar 2020-coated surface. (b) EDXA spectrum of Xylar 2020. C, O, F, Si and Fe were detected. (c) SEM cross-section of Xylar 2020/FM300/steel structure. (d) SEM cross-section of the Xylar 2020/FM300 interface.

Further tests were made on the Xylan 8080 coating. In this case, the PTFE coating was sintered onto a piece of stainless-steel foil and Cytec FM300 epoxide resin sheets were laid up onto the coated surface under weighted loading and cured. It was found that the resin could be peeled away from the metal foil substrate with only slight difficulty. It was thus possible to remove the epoxide resin from an area where it had been in contact with the Xylan 8080 coating to examine the failure surfaces using SEM; see Figs. 12d and e.

Fig. 12e shows an image of the underside on the resin where it had been in contact with the Xylan 8080 coating. It is suggested that the asperities seen on this surface may be points where mechanical interlocking has occurred with the Xylan coating giving rise to a level of adhesion making it difficult to separate the two surfaces in tension. The virgin Xylan coating surface possesses fine porosity typical of PTFE. It is suggested that both the Xylar and Xylan coatings resist wetting from the resin in its liquid phase, but that the pressure applied overcomes the surface tension forcing the resin into the porosities in the soft PTFE structure opening them up at the elevated cure temperatures. When the liquid resin crosslinks and cools, a mechanical interlock occurs and the surfaces become difficult to separate in tension.

3.7. Apticote 450/460 coating

Roughness measurements were made on an Apticote 450-coated surface which was deposited onto a piece of nickel tooling plate. The measured surface roughness parameter, R_a, was 1.498 µm. It should be noted that this roughness was of an undulating nature rather than there being deep grooves and scratches present on the surface. Indentation was used to measure the surface hardness. The indentation hardness measurements, measured from the area of the indentation of a stylus or ball bearing under a specific loading, really measure the yield stress of the material, which is dependent on the plastic properties of the material [51]. Hardness measurements were made on the Apicote 450 surface using the Rockwell C scale and measured using an Indentec 8150 ACD tester, which

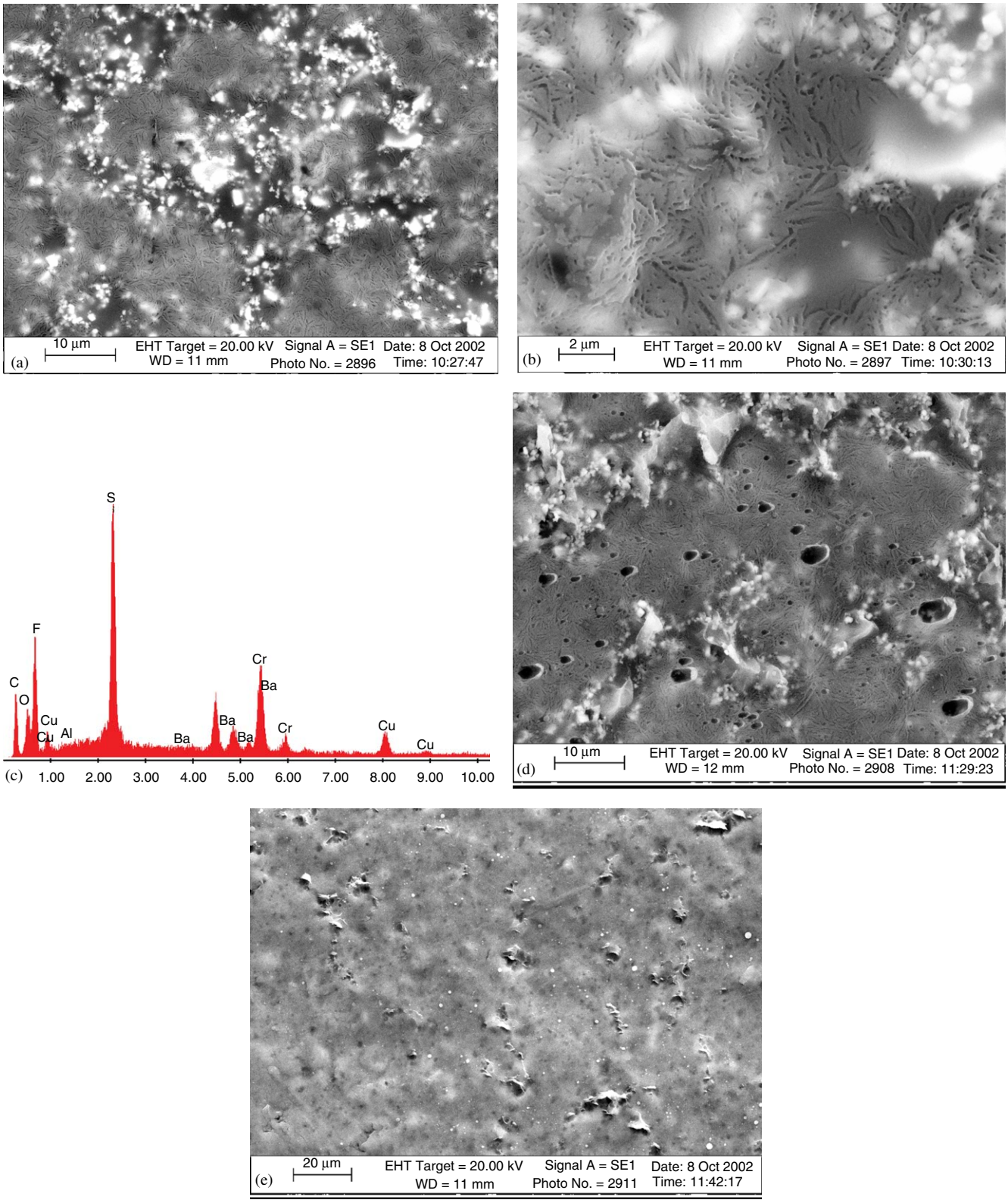

Fig. 12. (a) Low-magnification FEGSEM image showing the Xylan 8080 surface topography. (b) High-magnification FEGSEM image showing the Xylan 8080 surface topography. (c) EDXA spectrum of Xylan 8080 coating. C, O, F, S, Ba, Cr and Cu were detected. (d) SEM image of Xylan 8080 coating following removal of FM 300 resin. (e) SEM image of underside surface of FM300 resin following delamination.

applied a load of 150 kg to a pyramidal-shaped indenter for a dwell time of approximately 8 s. A conversion chart was used to convert the average of three separate readings into the Vickers hardness scale. A hardness of $345H_v/150$ was measured on this surface. Note that some difficulty was encountered in obtaining consistent results for the Apticote

450 sample because the indentations were poorly defined and due to the presence of the softer PTFE phase in the material. As the load is reduced further, the indentation becomes smaller and backlash errors associated with the curtain micrometer in the eyepiece reduce accuracy of measurement of the dimensions of the indentation. Using a 25 g force, the average of three readings gave a hardness of $222H_V/0.025$. The manufacturers quote a bulk hardness of 250HV though no loading is specified.

Physically, the Apticote 450 coating has a brown colouration thought to be due to heating which hardens the coating. Fig. 13a shows an SEM image of the coating and it is seen to possess a shallow dimpled or undulating appearance, as described. Higher magnification reveals the dispersed PTFE phase that contributes to the enhanced release properties of the coating. The coating thickness, measured from a cross-section, was found to be approximately 20 μm; see Figs. 13b–d.

Elemental analysis using EDXA identified Ni, P and F as the major peaks. The size of the PTFE particles is below the resolution limit for X-ray mapping and so it was not possible to produce a map to show the fluorine-rich sites but it is reasonable to assume that the dark, roughly circular features in Fig. 13c are the PTFE phase. These particles have a diameter of approximately 200 nm. The surface free energy of the Apticote 450-treated sample was measured as $16.5\,\mathrm{mJ\,m^{-2}}$, reflecting the presence of this PTFE.

Additional images from the Apicote 450 surface were acquired by AFM; see Figs. 13e and f. No characterisation was carried out on the Apticote 460 surface; this is also a Ni/PTFE composite coating.

3.8. Release performance studies

Studies carried out using either the axial butt or blister geometries indicated that the Frekote B15/710 NC and Apticote 450/460 systems facilitated easy release when FM300 resin was pressed against these surfaces during cure. All other release coatings performed unsatisfactorily to one degree or another. Additional testing was carried out to study the release properties of these surfaces using conventional wear testing and pulsed force mode AFM.

3.8.1. Friction coefficient and wear test comparisons

Friction coefficient and wear test measurements were made on the Apticote 450 and 460 coatings applied to nickel tooling substrates. Both Apticote coatings were compared against cleaned but otherwise untreated nickel tooling and the same tooling that had been treated with Frekote B15/710 NC. Figs. 14a and b show the friction coefficients for 5 and 10 N loadings.

From Figs. 14a and b, it is clear that both Apticote coatings clearly have exceptionally low friction coefficients which was also reflected in their wear test performance; see Fig. 14c. The latter observation is significant if these coatings are to be regarded as permanent release coatings.

An approximate wear depth was measured for the 10 N load tests, as indicated in Fig. 14c. This depth would also include any deformation of the sample. The wear is greatest for the softer Apticote 460 coating. The Apticote 450 coating was heat treated to enhance its hardness. The Frekote system, however, makes little difference to the wear of the untreated tooling so would be considered suitable only for semi-permanent applications.

3.8.2. Pulsed force mode AFM study of adhesion differences

Pulsed force mode AFM (PFM-AFM) is a mechanical property-based AFM imaging method in which a relatively low-frequency (200–2000 Hz) sinusoidal modulation is applied to the z-piezo crystal and hence the probe cantilever. The ultra-sharp silicon tip is therefore pushed onto and pulled off the sample surface at this frequency. The amplitude of modulation is typically a few hundred nanometres. The signals acquired are topography and cantilever deflection (in common with most AFM imaging modes), together with pull-off force (related to tip-to-sample adhesion) and indentation (related to local modulus). Pull-off force is that force imparted by the cantilever required to cause disengagement of the tip from the sample surface. Indentation is the mean gradient of the indenting portion of the probe–sample force distance curve.

The pull-off force results presented in this paper have been left expressed in volts. These voltages can be converted readily into units of force, in this case nN, using the nominal spring constant of the cantilever. It has been found, however, that the spring constant can vary substantially even within the same batch of probes, so that a careful calibration must be carried out to determine its real value. In any case, it is the relative, not absolute, values of pull-off force that are important in this study.

Initially, four nickel mould tooling substrates were hand polished and characterised as previously described; three of these were then release coated prior to AFM and PF-AFM analysis. These were identified as follows: Sample 1—Untreated clean surface; control; Sample 2—Zyvax Waterworks; Sample 3—Frekote B15/710 NC; Sample 4—Dynasylan F8261 (5% solution). Water contact angles were determined to ensure surface cleanliness on the polished nickel substrates prior to coating and, as mentioned, it was found that a drop of water produced an average contact angle of ~35° in this case. For samples 2, 3 and 4, water contact angles of 110°, 107° and 116° were measured, respectively.

For all samples, pull-off force images were obtained from areas measuring $100 \times 100\,\mu\mathrm{m}$. As previously mentioned, with the Zyvax sample, the signal was saturated due to the AFM tip being stuck to the surface. These AFM images indicated that the fluoroalkylsilane coating produces the lowest pull-off force followed by the Frekote-treated surface.

The pull-off force images were then converted into data point distributions that reflect the adhesion of the tip as it is retracted from the sample. As has been discussed, it is difficult to quantify this force since it depends upon many

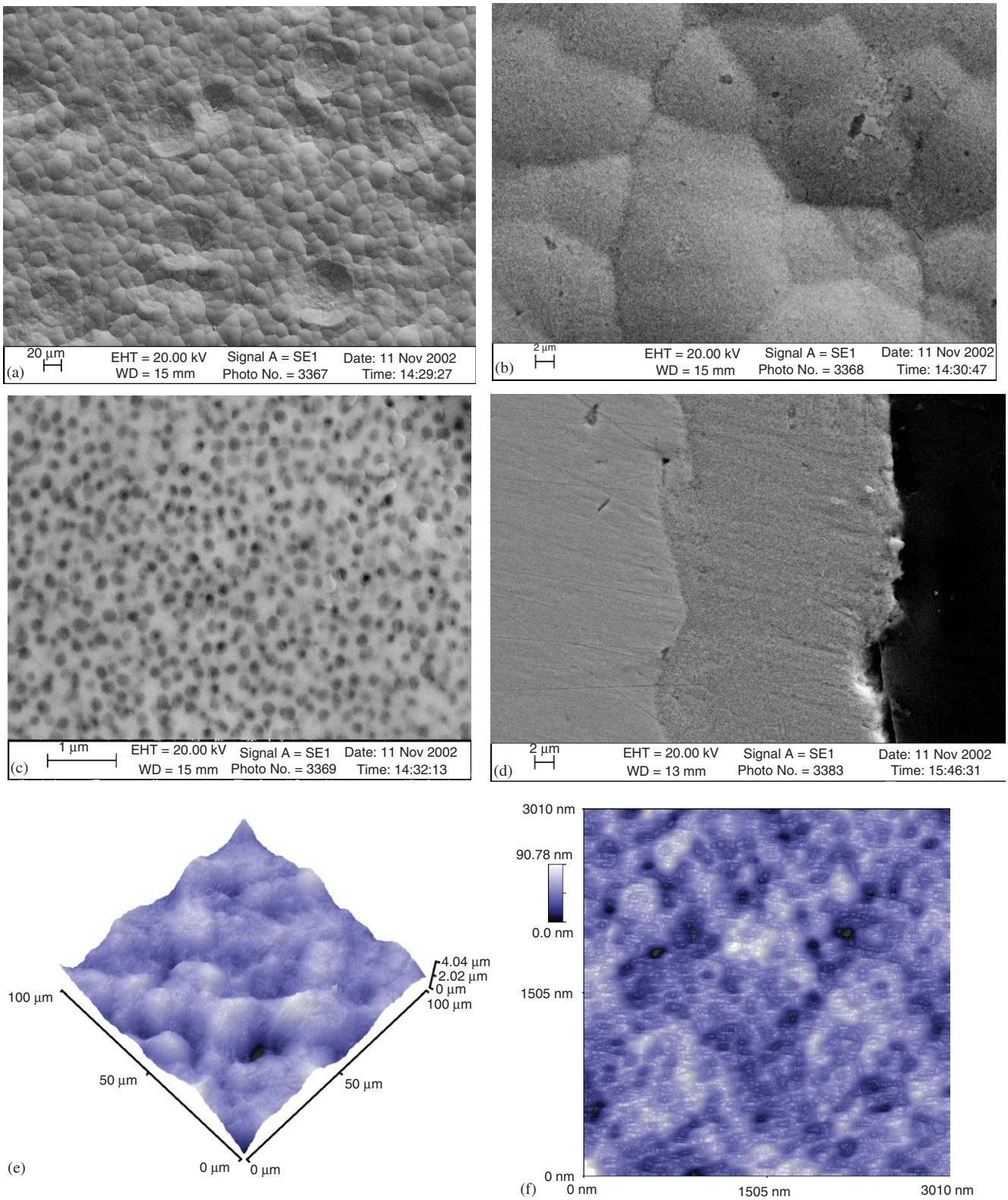

Fig. 13. (a) Low-resolution SEM plan view image of the Apticote 450 coating. (b) High-resolution SEM plan view image of the Apticote 450 coating. (c) High-resolution backscatter plan view image of the Apticote 450 coating. (d) High-resolution SEM cross-section image of the Apticote 450 coating. (e) AFM topographic 3D image for Apticote 450 (area $100 \times 100\,\mu m$). (f) AFM topographic 2D image for Apticote 450 (area $3 \times 3\,\mu m$).

AFM instrumental parameters such as the stiffness and spring constant of the probe. However, presenting the data in this form more clearly illustrates the differences between the samples. It is clear from Fig. 15a that there exists a distinction between the fluoroalkylsilane coating and the Frekote and the untreated control.

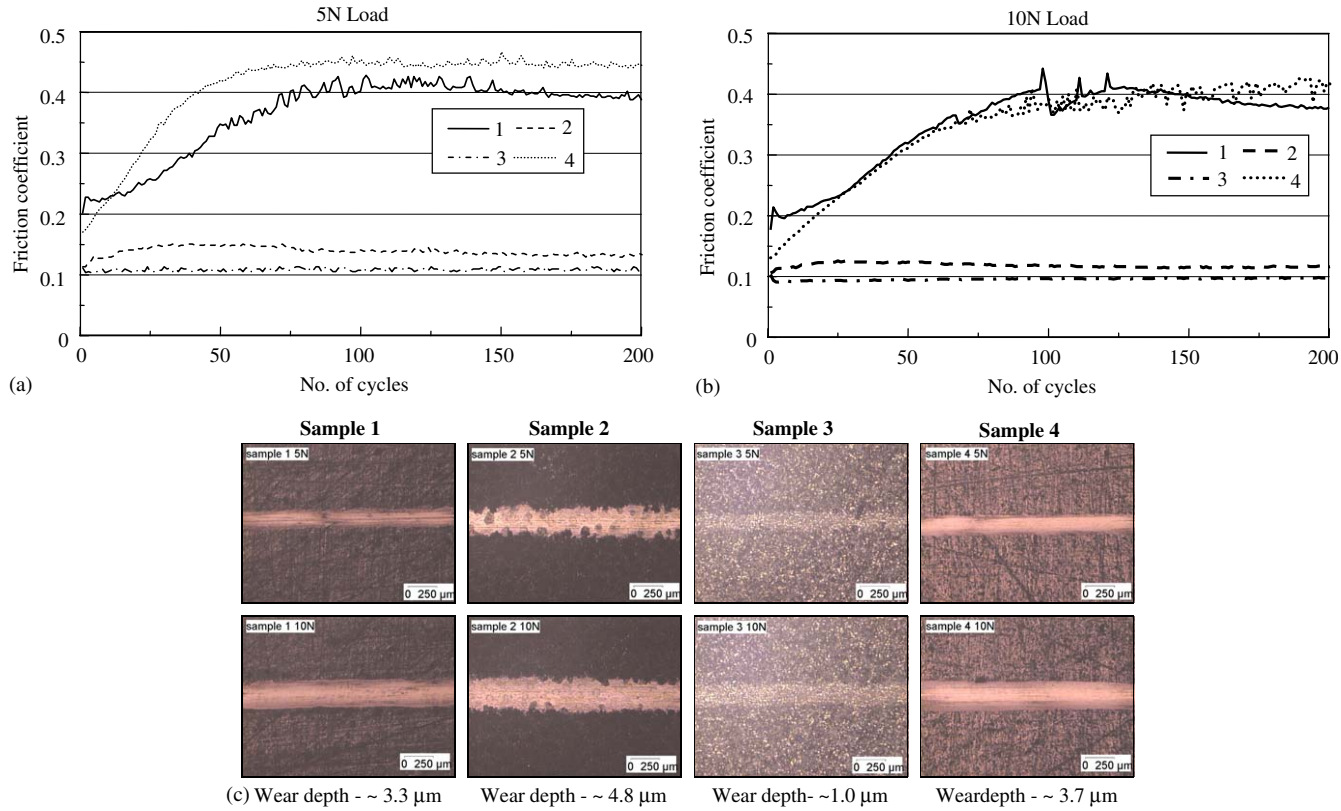

Fig. 14. (a) Friction coefficients for selected surfaces using a 5 N loading. Sample legend is as follows: Sample 1 = Frekote on nickel; Sample 2 = Apticote 460; Sample 3 = Apticote 450; Sample 4 = untreated nickel. (b) Friction coefficients for selected surfaces using 10 N loading. Same legends as for Fig. 14a. (c) Wear test images for sample surfaces using 5 and 10 N loadings.Sample legend is as follows: Sample 1 = Frekote on nickel; Sample 2 = Apticote 460; Sample 3 = Apticote 450; Sample 4 = untreated nickel.

This technique was then used to rank the performance of Apticote 450 coating in relation to Frekote B15/710 NC. Figs. 15b and c show AFM topographic and pull-off force images for the same area on the Apticote 450 surface.

The pull-off force, as discussed previously, is a mixture of the elastic, frictional and adhesive properties of the surface [53]. The adhesion component can be separated using the AFM software and allows images showing differences in adhesion to be displayed. The dark areas in these images represent points where the adhesion is low and conversely the bright areas are those where the adhesion is greatest. The scale of the bright areas in these figures suggests that a correlation exists between these and the dispersed PTFE particles in the Apticote 450 coating as shown using SEM. Note that the pull-off forces are, however, low in these bright areas compared with other surfaces.

Four different surfaces were prepared and compared using AFM, and the pull-off force data are presented in Fig. 15e.

The data in Fig. 15e show clear differences between the adhesive nature of both Frekote and Apticote coatings relative to the control sample comprising a further untreated sample of abrasively cleaned nickel tooling. The data suggest that the Apticote coatings require lower release forces compared with the Frekote-treated surface.

Stevens [40] has claimed that the Apticote coatings already described offer a good solution to the problems of mould users. They possess many of the good attributes of PTFE coatings but offer greater toughness and durability for industrial applications. As has been shown, the microstructure of the PTFE particle phase is very fine but the surface does not contain the same deficiencies, including surface porosity, seen in the conventionally applied PTFE coatings.

4. Discussion

The premise initially adopted was that the release properties of an abhesion-promoting coating for RTM applications were dominated largely by its surface chemistry and the requirement to engineer an exceptionally low-energy surface which would resist the adhesion of any liquid resin. As has been mentioned, the chemistry of mould release formulations is only discussed in general terms in the literature, if ever. Noteworthy exceptions are publications by Clarke et al. [44] and Utz et al. [54]. However, the surface chemistry provided by fluoroalkylsilanes (FAS), such as Dynasylan F8261, suggests that these materials satisfy this requirement; the surface energy of this FAS coating can be lower than that of PTFE.

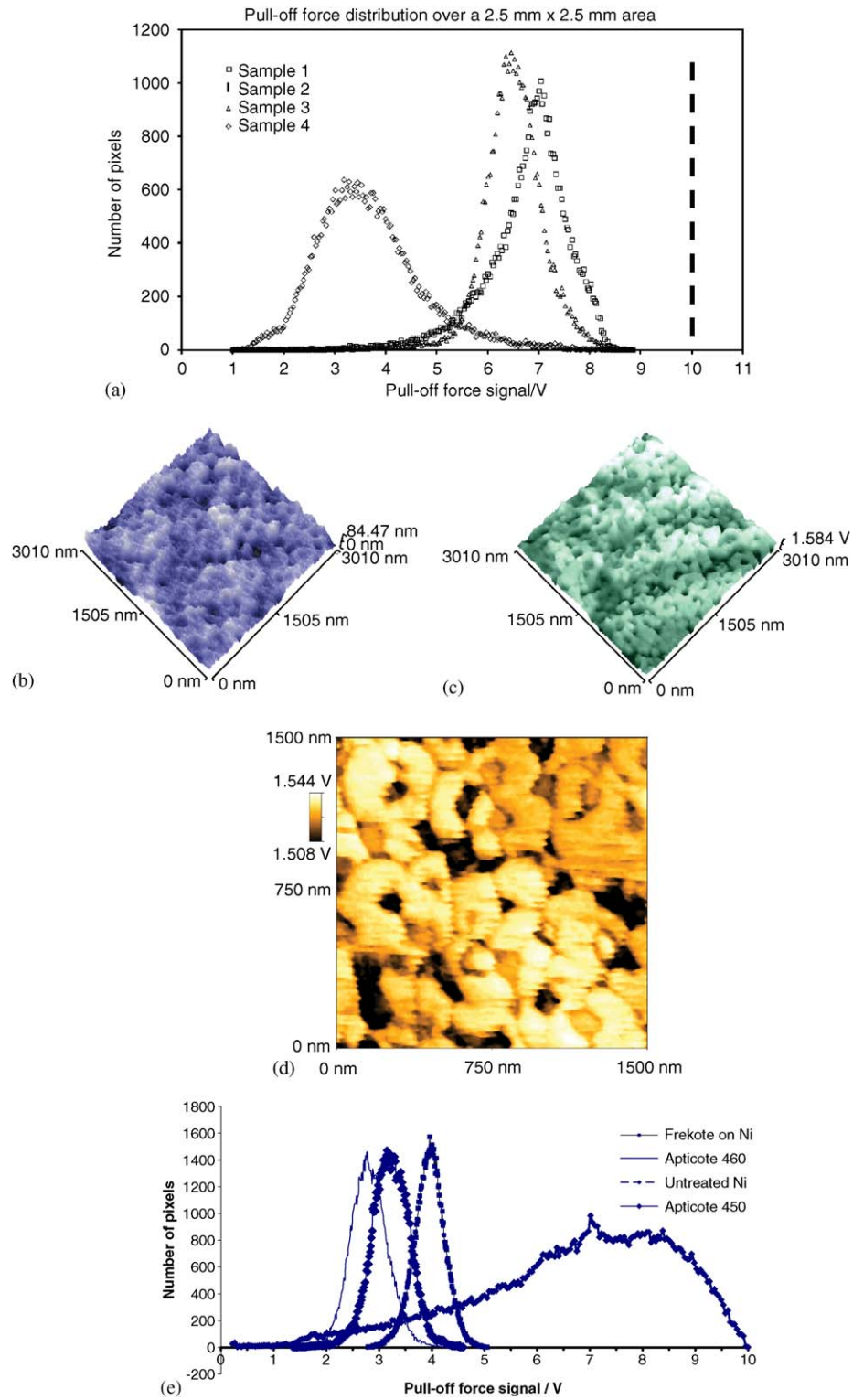

Fig. 15. (a) The pull-off force distributions for clean nickel, Dynasylan F8261, Frekote B15/710 NC and Zyvax Waterworks treated release coatings. (b). AFM topographic 3D image (left). AFM (c) pull-off force image (right) for Apticote 450 (area $3 \times 3\,\mu m$). (d) AFM pull-off force image for Apticote 450 (area $1.5 \times 1.5\,\mu m$). (e) AFM pull-off force comparison for different surfaces.

The FAS compound investigated in this research has been successfully applied to enamelled surfaces to prevent the sticking of food and has also been used successfully as a water-repellent coating for textiles. In both these applications, there is no high applied pressure against the coated substrate. It is also claimed that FAS compounds are effective in mould release for semi-conductor fabrications but in such applications only moderate moulding pressures

are used. The molecular structure of FAS compounds makes it difficult to develop thick coatings; the coating thicknesses are usually only a few monolayers and these are assumed to conform to any substrate topography.

If a water droplet is applied, under pressure, to a FAS-coated surface, clearly it will not intimately wet the surface because the low surface energy resists this but it may well fill some of the irregularities on the surface. Once the pressure is released, the water droplet will return to a roughly spherical bead on the surface because this shape is thermodynamically favoured. If instead of water, a drop of liquid thermosetting resin is applied to the coated surface and deformed by pressure, this will behave similarly to the water droplet. However, if the system is now heated so that the deformed resin crosslinks and hardens, then it will mechanically adhere once the pressure is released. The above scenario is presented as a plausible explanation of the observed facts that, despite engineering a low-energy surface, liquid resin pressed against a FAS-coated surface and cured results in poor abhesion.

Mechanical interlocking has been observed in the case of fluoropolymer (PTFE) coatings but the extreme thinness of the FAS coating makes this difficult to study by SEM. The fact that marine organisms can stick with apparent impunity to such low-energy fluoropolymer surfaces is evidence that abhesion, like its counterpart adhesion, is not a simple phenomenon.

Sintered fluoropolymer coatings based on PTFE perform well in food industry applications but the two systems used in this study did not perform well.

Considering the Frekote B15/710 NC system, the commercially successful PDMS-based mould release agent, evidence has been presented to show that this Frekote system largely satisfies the criteria required for ideal abhesion-promoting coatings. Frekote provide a low surface free energy; thermal and chemical stability; durability, lasting typically for at least 20 releases; mobility at a molecular level, associated with low glass transition temperature; and; a coating that will cover and fill major surface irregularities resulting from abrasive finishing. Bey [55], amongst others confirmed the usefulness of silicones for release applications. In common with many other semi-permanent mould release agents, the Frekote product comprises two resin-based reactive polymers. The manufacturers suggest that a thoroughly cleaned moulding is first primed with two light coats of a sealing formulation. These are followed by the application of further coats of the mould-releasing agent. It is believed that the first sealing component polymerises on contact with air, when applied to a clean metal mould surface, and seals surface pits and porosities in the mould. Heating can accelerate the crosslinking reaction and an open sponge-like structure is created. The second chemically compatible mould release polymer is now applied and it is this polymer that reduces friction between the moulding and the mould.

Frekote release coatings may not form smooth coatings on rough surfaces, such as industrial moulds, and these do not necessarily fill in all the rough contours and irregularities on the surface. Grit-blasted metal surfaces, for example, that have been treated with Frekote B15/710 NC can still feel slightly rough and it may be that a degree of roughness assists separation of a moulding since this will trap air pockets. Also, thin layers of Frekote are easily parted and SEM shows the presence of irregularly shaped platelets overlying surface asperities arising from the grit blasting treatment; these act as weak boundary layers and assist in mould release. For this reason, PDMS-based release coatings are regarded as only semi-permanent.

Apticote coatings also offered good release properties and are durable enough to withstand the aggressive moulding conditions prevalent in the aerospace industry; these are regarded as permanent coatings. In the case of the Apticote 450 release coatings, PTFE particles are uniformly dispersed in a hard nickel matrix that resists the application of pressure applied to a curing resin system. The porosities present in a continuous PTFE coating are not manifest in the Apticote 450 coating. The roughness observed on the Apticote 450 surface is on the macroscopic rather than the microscopic scale. Micro-rough surfaces are known to promote good adhesion with epoxides, but it is possible that macro-roughness could lead to regions where high shear forces are experienced leading to easy release. Thus, the coating combines a low surface energy, derived from the PTFE, with the toughness of a nickel matrix and it is conjectured that these qualities account for its apparent success as a release coating as demonstrated in the present work. This release behaviour is not perhaps surprising in view of the very low friction coefficient measured for the Apticote 450 coating. This surface was characterised in Section 5.1.4.3 for 5 and 10 N loadings. The Apticote 450 coating was used in preference to the Apticote 460 coating, despite its slightly lower friction coefficient, because 450 is temperature hardened.

The desirable properties of mould releases have been discussed previously. Two of these were that the release coating should possess molecular mobility and cohesively weak boundary layers. Clearly, the Apticote coating does not meet these particular properties and yet it appears to be successful at ensuring easy release of parts moulded against it. In discussing the non-stick properties of these coatings, it is necessary to distinguish between "release" and "low friction". Friction results from two surfaces sliding across each other and is measured by the drag force between the sliding parts. Release is different because the separating force is normal to the two surfaces involved and relates to the material properties of the surfaces such as, though not exclusively, surface energy. A release coating for RTM applications requires both low release and low-friction forces. The FM300 resin system used for these tests is an aerospace grade material and therefore the results are very relevant to RTM application.

It should be noted that although established and well-documented testing methods clearly exist for the testing of adhesive bond performance, these generally proved

unsatisfactory in the evaluation of mould release performance, and alternative approaches have been adopted. For example, Percell et al. [56] measured the ejection force required for mould emptying by mounting a piezo-electric device to the ejector rod. Another approach first adopted by Wilkomm et al. [57] was to use a modified rheometer to measure the shear force required to separate a moulded part from a substrate coated with a release agent. A more conventional method for adhesion measurement is the blister test [58] used in the present study. Parry and Wronski [59] and Kinloch and Ferando [60] developed this method and a body of literature and results accumulated over the last 20 years testify to its usefulness in quantifying adhesive fracture energies. In these tests, it was regarded as a useful screening test but not suitable for measuring fundamental adhesion forces. Briscoe and Panesar [61] proposed a method of measuring the release force using the blister test originally developed for measuring low-adhesion interfaces. Although this method proved very successful for Briscoe, it was used to study the effects of external releasants on the adhesion of elastomeric materials such as polyurethane [62], and this research is concerned with thermosetting composites possessing a much higher elastic modulus when cured. Blanchard [49] appraised the blister test and concluded that it was unsuitable for thermosetting compounds. Even in relatively recent publications [42], quantitative measurements of release force seem to be avoided because of the experimental difficulties and qualitative assessments of performance are given instead. New methods of evaluating mould releases continue to be developed [63] which testify to the fact that no single method has yet been accepted as being universally applicable. For this reason, indirect measurements to determine friction forces and PFM-AFM to determine comparative pull-off forces were considered valid in the present study. PFM-AFM did prove itself to be very useful in providing qualitative comparisons of the "stickiness" of surfaces treated with different mould release agents. In PFM-AFM, the tip is attracted to the surface it is tracking, and the oscillating cantilever experiences a damping force if the surface is adhesive which tries to keep the tip in contact with the surface. The amplitude of oscillation is such that it will be sufficient to overcome this and then carries information about the pull-off force required. Effectively, the sinusoidal response of the cantilever will lag behind that of the oscillation impressed upon it and this phase lag can be extracted by operating software and the resulting signal used to modulate an image contrast.

Such phase images can provide information concerning the viscoelastic properties of the sample and adhesion forces. Since the resonant frequency of the cantilever is very high, several thousand pull-off force measurements may be made for a very small area scanned. To use this technique effectively to qualitatively compare the stickiness of different surfaces, resulting from application of different mould release agents, it is necessary to largely eliminate large differences in surface height on a microscopic scale and hence substrates need to be polished to a mirror finish. Quantitative data by this means are very difficult to obtain, relying on the precise knowledge of the spring constant of the cantilever used, a means of calibrating a microscope and a thorough understanding of the complex interactions between tip and surface within the size domain of the technique. Adhesive force measurements can be related to the AFM pull-off force via the Johnson, Kendall and Roberts (JKR) theory of adhesion mechanics [64]. This theory provides a means of calculating the surface energy of a solid directly in terms of the interactions between solid surfaces rather than through the use of contact angle measurements [65–67]. The theory can be used to derive the equation $F_{ad} = 3/2\pi R W_{SMT}$ where $W_{SMT} = \gamma_{SM} + \gamma_{TM} - \gamma_{ST}$ (after Dupré). W_{SMT} is the thermodynamic work of adhesion for separating the sample and tip with associated surface free energies of the sample (S) and tip (T) in contact with the medium (M) and γ is the interfacial surface free energy of the two interacting solid surfaces; F_{ad} is the pull-off force required to separate an AFM tip of radius R from a planar surface. If the two materials in contact are the same, then the work of adhesion is equal to the work of cohesion. This is rather limited, since it is only possible to directly measure the surface free energy for a material which is the same composition as that which the AFM tip is made from but the principle is valid.

It should also be noted that contact angle behaviour can be exceedingly complex and subject to many variables such as surface roughness, chemical heterogeneity of the surface and surface sorption layers to mention but a few. The approach used by Owen and Wendt et al. [66] Kaelble [67] has been used extensively in the present study to calculate the surface energies of treated samples by measuring contact angles using two liquids. The popularity of this analytical approach belies the fact that there is much controversy about whether the geometric mean approximation, used by Owen, Wendt, Kaelble and Uy is the best approach for finding the polar interactions at an interface. Zettelmoyer [68] and Wu [69] separately discuss this approximation in detail. In general, Wu asserts that the geometric approximation gives rather poor results for many organic liquids on organic polymers and that a harmonic mean approximation is preferable. Despite these objections, the Owen, Wendt, Kaelble and Uy approach allows simple and quick measurements of surface free energy to be made. Such is the importance of surface energy values for solids that numerous approximate models [70–72] have been developed and different approaches used to enable their calculation.

The very low surface energy ($7.9\,\mathrm{mJ\,m^{-2}}$) obtained for the Dysalan F8261 FAS coating on a sample of nickel tooling is clearly physically unrealistic. The surface energy of the same coating on an optically flat surface was found to be $12.6\,\mathrm{mJ\,m^{-2}}$. The value obtained is clearly being affected by surface roughness. Surface roughness can affect contact angle by increasing the effective area of the surface [72] and may also give rise to hysteresis [73]. In this case, a

third factor needs to be considered. As a drop advances over a hydrophobic surface, trapped air and porosity mean that the surface must be treated as composite [74]. If the fraction of the solid/liquid interface comprising air is $(1-f)$, then Young's equation may be rewritten as $f\gamma_s = f\gamma_{sl} + (1-f)\gamma_l + \gamma \cos\phi$, where γ_s is the surface free energy of the solid, γ_{sl} the interfacial free energy and γ_l the surface energy of the liquid. ϕ is the observed macroscopic contact angle. The effect of trapped air and porosity is to increase the observed contact angles of both water and diiodomethane over that observed for a flat homogeneous surface, and this will contribute to the lower accepted value for surface energy calculated using the Owens and Wendt method. A value of about 0.1 for $1-f$ would be sufficient to have a significant effect on the apparent surface energy obtained for the Dysalan F8261 FAS-coated nickel tooling.

5. Conclusions

The semi-permanent Frekote B15/710 NC mould release coating system, which is based on PDMS, proved extremely effective in terms of release against a cured epoxide applied under pressure. This system was applied to clean abraded metal tooling and allowed many release cycles to be performed before any fouling problems were experienced. It has proved difficult to find an alternative release that is as effective and offers the same versatility as Frekote B15/710 NC for such an application. The physicochemical properties previously described can be used to explain this result.

Fluoroalkylsilane coatings offer a number of technological advantages for release applications. However, they generally produce very thin coatings which conform any existing surface topography. As such, whilst they provide a low-energy surface, they do not seal any surface porosities present on a substrate and adhesion through mechanical interlocking can occur without impediment. Mechanical interlocking with fine surface features is considered particularly detrimental to abhesion. Whilst there are undoubtedly some specialised applications of these materials, especially in the microelectronics industry, it is considered that they are not suitable for RTM application given the roughness of mould tooling.

The commercial fluoropolymer coating formulations investigated were PTFE based. These were demonstrated to provide low-energy surfaces on metal substrates. With both examples of these coatings evaluated for use with metal tooling materials, it was found that when adhesives were cured under elevated pressure and temperature whilst in contact with the coatings, subsequent release was poor or impossible. It is proposed that the porosities present in PTFE surfaces allow penetration of the resin and, after curing, these bond by mechanical interlocking. The formulations were considered not to be suitable for RTM mould release coatings.

Electroless Ni/PTFE composite coatings comprise hard nickel–phosphorus matrix containing a very fine dispersion of PTFE particles. The matrix is sufficiently robust for industrial applications and the low friction and surface energy provided by the embedded PTFE combined with macroscopic-scale surface roughness provided efficient mould release.

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