Gubala, D. M., Fox, L. J., Harniman, R. L., Hussain, H., Robles, E., Chen, M., & Briscoe, W. H. (2021). Heads or tails: Nanostructure and molecular orientations in organised erucamide surface layers. *Journal of Colloid and Interface Science*, 590, 506-517.
<https://doi.org/10.1016/j.jcis.2021.01.087>

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[10.1016/j.jcis.2021.01.087](https://doi.org/10.1016/j.jcis.2021.01.087)

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Heads or tails: Nanostructure and molecular orientations in organised erucamide surface layers

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Abstract

Hypothesis: Despite the widespread industrial usage of erucamide as a slip additive to modify polymer surface properties, a controversy appears to have persisted regarding the nanostructure of erucamide surface layers, particularly the molecular orientation at the outermost layer. The erucamide nanostructure and molecular orientation, along with its surface coverage, hydrophobicity, and adhesive response, can be tuned by simply varying the erucamide concentration in the solution from which the spin coated layer is prepared.

Experiments: Synchrotron X-ray reflectivity (XRR) allowed a comprehensive characterisation of the out-of-plane structural parameters (*e.g.* molecular packing and thickness) of the erucamide layers prepared *via* spin coating from nonaqueous solution on silica. Complementary Atomic Force Microscopy (AFM) imaging with high lateral resolution revealed localised in-plane structures. Contact angle measurements provided information on the wettability of erucamide-coated surfaces. Peak Force Quantitative Nanomechanical Mapping (QNM) allowed a correlation between the erucamide nanostructure with the surface nanomechanical properties (*i.e.* adhesive response).

Findings: Our results reveal erucamide surface nanostructures on silica as patchy monolayers, isolated circular bilayers/rounded rectangle-like aggregates and overlapping plate-like multilayers as the erucamide concentration in the spin coating solution was varied. In all the cases, XRR and AFM results were consistent with the picture that the erucamide tails were oriented outwards. The QNM adhesion force mapping of all the observed morphologies also supported this molecular orientation at the outermost erucamide monolayer. The wettability study further confirmed this conclusion with the observed increase in the surface hydrophobicity and coverage upon increasing erucamide concentration, with the macroscopic water contact angle $\theta = 92.9^\circ \pm 2.9^\circ$ at the highest erucamide concentration of 2 wt%.

Introduction

Fatty acid amides have been widely used since the late 1960s as slip additives in various industrial applications [1-4], and their efficacy in friction reduction without significantly compromising material bulk properties (*e.g.* stress and strain) has been confirmed in many studies [5-10]. These slip additives can modify the surface structure of different materials, from model substrates such as silica [5] or mica [11] to raw industrial materials such as polyolefin films [9] or fibres [12]. The additives can be introduced to the material externally *via* physical adsorption using different methods, *e.g.* Langmuir-Blodgett deposition [7], drop casting [5], or being smeared in its solid state over the material surface [13]. Alternatively, for polyolefin products, slip additives are often added to the polymer prior to extrusion, and subsequent molecular migration of the slip additives to the polymer surface (a process termed “*blooming*”) is driven by the incompatibility between the amphiphilic additive molecules with the nonpolar polyolefin. The blooming process also allows the surface additive layer to “self-heal” through further diffusion of the additive molecules to the polymer surface over time (*i.e.* *aging*). In general, the structure of the surface slip-additive layer can be controlled *via* parameters such as the additive concentration, substrate hydrophilicity, blooming temperature, and aging time.

Erucamide (13-*cis*-docosenamide, $C_{22}H_{43}NO$; Figure 1) is one of the most widely used fatty acid amide slip additives in polyolefin manufacturing [9, 11, 12, 14-16], reportedly reducing the coefficient of friction (CoF) down to 0.2 [9, 17]. Its stability, low toxicity and transparency, along with its extraordinary slip properties attainable at low concentrations, find erucamide used as an antifouling [18], antifogging [19], angiogenic [20, 21], antiviral [22], dispersing [23-26], or scratch resistant [27-29] agent in a wide spectrum of applications ranging from food packaging, automobile and textile industries to hygiene and healthcare products.

Erucamide migration [6, 14, 30], distribution [11] and nanomechanical properties [5, 9, 12, 17], along with the effect of the erucamide concentration [15, 31] and ambient temperature [32, 33] on its surface structure [9], has been widely studied. From these studies, it is clear that the slip-additive surface assembly and the resultant performance depend on the additive deposition method and concentration as well as the substrate surface chemistry. It is generally accepted that erucamide lubrication performance could be driven either 1) through the formation of a thin film, changing surface properties (*i.e.* surface chemistry and roughness) and reducing friction compared to the uncoated material; or 2) alternatively through the detachment and sliding of the erucamide surface layer, which does not require a uniform surface coverage for friction reduction. In the first case, one could expect that a high and uniform erucamide surface coverage is desirable for optimal lubrication performance. In the second scenario, the lubrication performance is likely driven by erucamide rheological properties as well as the interactions present between erucamide layers. It is thus critically important to understand the nanostructure of the erucamide surface layers, particularly the molecular orientation at the outermost layer.

Recently, it has been reported that drop-cast erucamide formed single-crystalline 2D structures on silica, consisting of 4 nm thick erucamide bilayers with the hydrophobic tails vertically aligned on the substrate. Such a surface layer facilitated an ultralow friction force down to 0.4 nN at a normal load of tens of nN [5]. In another study on multiscale characterisation of single synthetic fibre properties, erucamide was identified as a potential modifier of single fibre tactile properties, with implications to fibre applications in personal care products (*e.g.* babies' nappies and female sanitary pads) and medical products (*e.g.* swabs and surgical masks) [12].

Figure 1 Erucamide chemical structure.

Despite numerous reports on erucamide assembly and performance, a controversy appears to have persisted over the structure of the erucamide surface layers formed on the polymer surface as a result of the blooming process, particularly in terms of the molecular orientation of erucamide in the layer, which hampers our understanding of the molecular mechanism of erucamide as a widely-used slip additive to tailor lubrication properties of polymer products. Chen *et al.* [11] in their study on erucamide as a slip additive in low density polyethylene (LDPE) reported that, for the bulk loading of 2200 ppm, the erucamide migration to the polymer surface resulted in ‘crystal domains’ of a few nm in thickness. Consequently, the surface wettability increased, with the water contact angle (θ) reducing from 104° to 94° , implying that the amide headgroups were located at outermost layer. This particular molecular orientation however was not clearly acknowledged in the schematic representation of the surface layer in the report. Ramirez *et al.* [15] studied the relationship between the CoF and the erucamide concentration in linear low density polyethylene (LLDPE), similarly reporting a change in the surface wettability upon erucamide addition, with the water contact angle reducing from $\theta = 103^\circ$ for the pure polyolefin to $\theta = 91^\circ$ for LLDPE loaded with 5000 ppm erucamide. This relatively small variation in the surface wettability was consistent with the lack of molecular alignment in the erucamide surface from their complementary AFM imaging.

In a study on the effect of erucamide addition in high-density polyethylene (HDPE) bottle closures, Dulal *et al.* [14] reported higher water contact angle ($\theta = 107^\circ$) with erucamide

coating (at bulk loading ~2000 ppm), compared to bare HDPE ($\theta = 93^\circ$), in contrast to the opposite trends observed by Chen *et al.* [11] and Ramirez *et al.* [15] as discussed above. SEM and AFM revealed hundreds of nanometres thick placoid-like erucamide layers on the surface, pointing to a multilamellar structure. The results suggested that erucamide formed stratified surface layers with the hydrophobic chains oriented outwards, responsible for lower surface wettability. In a follow-up study, Dulal *et al.* [16] further showed three growth stages of the slip additive surface layer: starting with a discontinuous monolayer, developing to form bilayers and finally multilayers. In all cases, the erucamide molecules were presumed oriented with the hydrocarbon chains pointing outwards, whilst the surface layer was not well-ordered.

The above erucamide blooming mechanism reported by Dulal *et al.* is consistent with that reported by Allan *et al.* in their work on oleamide used as an additive in the polyethylene (PE) film [7]. It was observed that the water contact angle decreased from $\theta \sim 90^\circ$ to 70° over a few hours after the initial film extrusion, followed by an eventual increase to a few degrees higher after prolonged aging. It was deduced that the initial erucamide migration resulted in an incomplete monolayer with the hydrophobic chains still embedded within the polymer and amide headgroups projected outwards, causing higher friction than that on bare polyolefin (CoF > 0.4). This conclusion could be related to the study by Bowers *et al.* [34] on lubrication of nylon ($[-OC-(CH_2)_4-CO-NH-(CH_2)_6-NH]_n$), where the presence of nylon polar groups, resembling the primary fatty acid amide headgroup of erucamide, led to the friction between nylon specimens almost twice as high as that for the nylon coated with a monolayer of a boundary lubricant (*e.g.* oleamide and stearamide) with the hydrocarbon tails pointing outwards.

In our previous study [12] on polypropylene (PP) fibres with 1.5 % (15000 ppm) erucamide per fibre, AFM imaging revealed overlapping plate-like erucamide multilayers of 4 ± 1 nm on

the fibre surface, which significantly affected fibre nanomechanical properties, decreasing the fibre adhesive response towards the AFM tip. The static contact angle measurement using a custom-designed “spray-on” method showed that the erucamide-coated fibre remained highly hydrophobic ($\theta = 122^\circ$), compared to $\theta = 126^\circ$ for the PP fibre, again suggesting that the hydrophobic tails were oriented outwards in the erucamide multilayer densely packed on the fibre surface. Correlation of AFM height and adhesion maps further showed that the adhesion force experienced by the AFM tip was lower on the erucamide layers than on the surrounding amorphous polypropylene. In another study by Huang *et al.* [5], it was reported that erucamide bilayers formed upon drop-casting from a 0.01 wt% erucamide nonaqueous solution on bare silica surface, with the hydrophobic chains vertically aligned on the substrate. This was inferred from the layer thickness of 4 nm obtained using AFM as well as with an ultralow value of the friction force, presumably facilitated by hydrophobic tails. Despite these studies, it remains somewhat controversial regarding the nanostructure of organised erucamide surface layers, in terms of molecular packing, layering, surface coverage, and particularly the molecular orientation of the outermost erucamide layer, which would determine wettability and ultimately the material functionality and performance.

In this work, synchrotron X-ray reflectivity (XRR) has been performed for quantitative characterisation of the structural parameters (*e.g.* molecular packing and thickness) of erucamide layers prepared *via* spin coating from its nonaqueous solution on hydrophilic bare silica. Such out-of-plane structural information, averaged over a relatively large footprint illuminated by the X-ray beam $\sim 10^6 \mu\text{m}^2$, was complemented by AFM imaging which probes more localised topography over an area of size $\sim 10 \mu\text{m}^2$. Adhesion force mapping with Peak Force Quantitative Nanomechanical Mapping (QNM) technology allowed a correlation between the nanostructure with the nanomechanical properties (*i.e.* adhesive response) of the erucamide surface layer. Such comprehensive characterisation provides unprecedented

nanostructural insights for organised erucamide surface layers, valuable to our fundamental understanding of the surface properties facilitated by slip additives, important to tuning tactile qualities in a wide range of applications.

Experimental methods

Materials

Erucamide (*cis*-13-docosenoamide) was purchased from Sigma Aldrich (UK). Silicon wafer (orientation: <100>; thickness: 1 mm) used as a substrate was obtained from University Wafer (US). The silicon wafer was first cut to smaller pieces (10 mm × 10 mm), and then cleaned *via* sonication for 10 min each in acetone (Sigma Aldrich, 99.5%), MilliQ[®] water (resistivity of 18.2 MΩ.cm at 25°C), and ethanol (Sigma Aldrich, 99.5%). Cleaned silica pieces were then rinsed with ethanol, dried with nitrogen flow and UV-ozoned (UVO CLEANER[®], Jelight Company Inc., US) for 20 min prior to spin coating. Erucamide was first re-crystallised from acetone (Sigma Aldrich, 99.5%), and then dissolved in isopropanol (Sigma Aldrich, 99.8%) at four different concentrations: 0.01, 0.1, 1 and 2 wt%. The solutions were then deposited *via* spin coating (2000 rpm, 30 s) of 10 μL on bare silica surfaces, which were then dried in the in a laminar flow hood (Bassaire, UK) naturally for 3 days prior to measurements. The samples on **bare silica (BS)** are denoted as **BS(*n*)** with *n* = 0.01, 0.1, 1 and 2 corresponding to the erucamide concentrations in wt% used for spin coating.

Experiment methods

X-ray reflectivity (XRR) The experiment was performed at beamline I07 at Diamond Light Source, Didcot, UK, using an X-ray beam with the energy of 14 keV ($\lambda = 0.886 \text{ \AA}$), with an integration time of a few seconds at an angle of incidence θ in the range of 0.06 – 2.6°, corresponding to a momentum transfer vector along the direction perpendicular to the sample

surface, $Q = \frac{4\pi \sin \frac{2\theta}{\lambda}}{\lambda}$ (cf. Figure 2A) in the range $1.49 \times 10^{-2} - 6.44 \times 10^{-2} \text{ \AA}^{-1}$, with the angular resolution of 10 milidegrees ($\delta Q = 0.00248 \text{ \AA}^{-1}$). The measurements were performed using an XRR cell [35, 36] adapted for flat silica surfaces at room temperature in air. The reflected intensity was detected at each angle using a Pilatus 100K 2D detector. The experimental setup is shown in Figure 2A. The 2D images were processed, with the azimuthal integration over 487×195 pixels to generate 1D reflectivity curves plotted as reflectivity (a.u.) vs $Q (\text{\AA}^{-1})$. The XRR curves were fitted using Motofit in IGOR Pro (WaveMetrics, Portland, USA) with the least χ^2 optimisation method using a multi-slab model characterised with different layer thickness (t_n), scattering length density (SLD, ρ_n), and roughness (σ_n). The detailed description of the fitting procedure can be found in Supporting Materials SM.01. The Bragg peaks in the XRR profiles were fitted to a Gaussian using the IGOR Pro Peak Fitting operation (Figure 2), obtaining the peak position Q_n (for the n^{th} -order diffraction) and the Bragg peak full width half maximum (FWHM) ΔQ . The characteristic layer thickness within the multilayer (*i.e.* lamellar d -spacing) could be ascertained as $d = \frac{2n\pi}{Q_n}$ [37, 38]. The coherence length L_a , defined as the lower limit of the crystalline domain size normal to the surface, could be analysed using Scherrer's equation [38-46], $L_a = \frac{2\pi K}{\Delta Q}$, where K is the Scherrer constant (*i.e.* a shape factor) of order unity depending on the actual shape of the crystalline (here $K = 1$). The lower limit of the number of erucamide bilayers in the domain could thus be estimated as $m = \frac{L_a}{d}$. Lattice spacing fluctuations (paracrystalline disorder), evident from characteristic peak broadening upon the increasing diffraction order n ($n = 1, 2, 3$) were taken into consideration by plotting the peak broadening defined as $(\Delta Q)^2 / (2\pi)^2$ vs the fourth power of diffraction order (h^4) for a plane of the Miller index ($h00$) [37, 38, 41]. The degree of disorder (g) together with coherence length L_a were obtained from the slope (a) and intercept (y_0) of the linear fit ($y = y_0 + ah^4$) as $g =$

$\frac{1}{\pi}(ad^2)^{1/4}$ and $L_a = y_0^{-1/2}$. The obtained parameters at different erucamide concentrations were compared to allow for a semi-quantitative comparison of the layer nanostructure.

Figure 2 (A) Schematic representation of setup for X-ray reflectivity experiment; (B) an example experimental XRR curve obtained for BS(2); (C) An enlarged view of the second order ($n = 2$) Bragg peak (black circles) with the background fitted to Q^{-4} (green dashed line)

and the Bragg peak fitted to a Gaussian (solid blue line); (D) The residual Gaussian fit after background subtraction.

Atomic Force Microscopy Each sample was mounted with a circular double-sided sticky carbon pad on a steel sample stub. Height images together with the adhesion force mapping of BS, BS(0.01) and BS(0.1) were taken under the non-resonant Peak Force feedback control (Bruker, USA) using SCANASYST-AIR-HR cantilevers with a spring constant of 0.5 - 0.8 N m⁻¹ (Bruker, CA, USA) and a hydrophilic silicon nitride (Si₃N₄) tip. For the adhesive response measurements, the AFM probe was calibrated (deflection sensitivity: 18.565 nm V⁻¹; spring constant: 0.6427 N m⁻¹). Height images of BS(1) and BS(2) were taken using Nanoscope Multimode III microscope with a Nanoscope V controller (Bruker, UK), and NuSense SCOUT cantilevers were used, of a typical spring constant of 42 Nm⁻¹ (NuNano Ltd., UK). All the data were collected using the tapping mode, which allows high-quality imaging without sample damage. Each sample was analysed at multiple regions of 4µm × 4µm in size. The obtained images were processed using the Nanoscope Analysis 1.7 and ImageJ software [47]. Plane and flatten correction functions were applied to account for any sample tilt; contrast/brightness alterations and false-colouration were applied to the final data representation shown below.

Contact angle measurement The measurement of static contact angles was made at temperature of 20 ± 0.5 °C using a Drop Shape Analyzer – DSA100 (KRÜSS) operated with KRÜSS ADVANCE 1.9.0.8 software, using 10 µL of MilliQ[®] water (resistivity of 18.2 MΩ.cm at 25°C) as a probe liquid. The image of the drop was recorded for 60 s in 2 s intervals and at least two repeat measurements per sample were made.

Results and discussion

Nanofilm structure at lower erucamide concentrations

Figure 3A shows the XRR curves (*i.e.* reflectivity *vs* Q) of erucamide films on bare silica, spin coated from nonaqueous solutions at four different erucamide concentrations (0.01, 0.1, 1 and 2 wt% for BS(0.01), BS(0.1), BS(1) and BS(2), respectively). The mild reflectivity oscillations (*i.e.* the Kiessig fringes) of the BS(0.01) and BS(0.1) XRR curves are indicative of erucamide nanofilm formation, whilst BS(1) and BS(2) XRR curves showed Bragg peaks up to the 3rd ($n = 3$) order, characteristic of erucamide multilayers at these two higher erucamide concentrations. The qualitative differences in the XRR curves suggest that the erucamide layer structure, thickness and packing could be tuned by varying the erucamide concentration in the spin coating solution.

Figure 3 (A) Experimental XRR curves (open circles) and fits (solid black lines) of the erucamide layers from spin coating from nonaqueous solutions at four different erucamide concentrations (0.01, 0.1, 1 and 2 wt%) on silica. For BS(0.01) and BS(0.1) at lower erucamide concentrations, Kiessig fringes were observed, whilst Bragg peaks up to the 3rd ($n = 3$) order for BS(1) and BS(2) indicate the presence of well organised erucamide multilayers at these two

higher concentrations. The XRR curve for bare silica (BS) is also shown for comparison. (B) Three- and seven-slab model for BS(0.01) and BS(0.1) and the multi-lamellar structure for BS(1) and BS(2), with a lamellar lattice spacing d and a coherence length L_a (the lower limit of the domain size perpendicular to the lattice plane); blue blocks represent erucamide bilayers in the multilayer, also shown in the enlarged view. (C) Schematic representation of hydrogen-bonded erucamide molecules constituting the lamellae.

The XRR curve for BS(0.01) at the lowest erucamide concentration (Figure 3A) could be well fitted to a three-slab model (Figure 2B; $\chi^2 = 0.02\%$), assuming an erucamide monolayer with the hydrocarbon tail pointing outwards and the headgroup in contact with the hydrophilic silica (slab 3; water contact angle $\theta \sim 10^\circ$), with the fitting parameters listed in Table 1. Slab 1 ($s = 1$) consists of the hydrophobic tail layer (T) proximal to solid-air interface, with a thickness $t_1 = 14.5 \text{ \AA}$ and a relatively high roughness $\sigma_1 = 6.5 \text{ \AA}$. Compared to the fully stretched C21 saturated hydrocarbon chain length of $28.1 \text{ \AA}$ [48], this implies that erucamide hydrocarbon tails were likely tilted with respect to the surface normal, due to a relatively low packing density at the low surface concentration. Such molecular tilting has been previously observed in surfactant bilayers [36]. This interpretation is also consistent with a recent study by Toledano *et al.* [49] which observed tilted phases in fatty acid Langmuir monolayers at large molecular areas. The *-cis* double bond (C13-C14) in the erucamide molecular structure could also contribute to “kinking” and thus an overall shorter chain length than that for a fully stretched saturated hydrocarbon chain [48]. Slab 2 ($s = 2$) for the hydrophilic headgroup layer (H) was fitted with a thickness $t_2 = 4.7 \text{ \AA}$ which falls within the theoretically estimated range of $4.0 - 6.6 \text{ \AA}$ based on the mass density [50] and the topological polar surface area [51] calculated for formamide molecule (HCONH_2) which closely resembles the erucamide polar headgroup. The theoretically estimated SLD for a fully packed erucamide layer, *i.e.* $\rho = 7.8 \times 10^{-6} - 8.5 \times 10^{-6} \text{ \AA}^{-2}$, falls within the range of fitted SLDs of the tail and the headgroup. The fit considering an

alternative molecular orientation of the erucamide monolayer with the headgroup pointing outwards and the hydrocarbon tail in contact with the hydrophilic silica was unsatisfactory ($\chi^2 = 0.20$ %, Supporting Materials SM.01).

Table 1 Fitted structural parameters for bare silica (control; BS), BS(0.01) and (BS0.1) obtained by spin coating from nonaqueous solutions of erucamide at 0.01 and 0.1 wt%, respectively: layer thickness (t_n), scattering length density (ρ_n) and roughness (σ_n) of the n^{th} layer. Errors in the fitting parameters determined using minimization of χ^2 are <0.05%.

Sample	s^{th} slab	Slab	Parameter		
			t_n (Å)	ρ_n (10^{-6} Å $^{-2}$)	σ_n (Å)
BS	1	SiO $_2$	19.7	18.8	7.4
	2	Si	-	19.9	2.0
BS(0.01)	1	T	14.5	7.7	6.5
	2	H	4.7	9.8	2.0
	3	SiO $_2$	19.7	18.8	7.4
BS(0.1)	1	<i>o</i> -T	21.1	7.6	8.3
	2	<i>o</i> -H	5.5	9.7	5.0
	3	<i>m</i> -H	4.5	9.8	2.0
	4	<i>m</i> -T	12.2	7.6	11.8
	5	<i>i</i> -T	15.1	7.6	9.4
	6	<i>i</i> -H	4.6	9.8	1.7
	7	SiO $_2$	14.0	18.8	5.5

The packing density of erucamide molecule was theoretically estimated as 0.7 Å 2 suggesting rather limited possibility of formation of uniform monolayer suggested by XRR results. Reflectivity measurements typically average over an area of a large footprint ($\sim 10^6$ μm 2), whilst AFM imaging provides local topography (*e.g.* over an area of ~ 4 μm $\times$ 4 μm in this study) with $\sim$ nm lateral resolution. AFM imaging of BS(0.01) showed a relatively low surface coverage (Figure 4B), consistent with a relatively large roughness value obtained from the XRR data fitting ($\sigma_1 = 6.5$ Å and $\sigma_2 = 2.0$ Å; Table 1). A number of erucamide patchy domains,

with a lateral size of *ca.* 10 to 30 nm and thickness from 3 to 5 nm, consistent with that for an erucamide bilayer [5, 12] were observed (Figure 4C and E) atop the smooth bare silica surface (RMS roughness ~ 0.2 nm; Figure 4A). In addition, a few rounded rectangle-like structures *ca.* 7.5-20 nm in thickness and a length *ca.* 40×220 nm were observed (Figure 4C and E, Supporting Materials SM.02). This result differs from that of a previous study, which reported that parallelogram, overlapping plate-like domains of size *ca.* 2-10 μm constituting 4 nm erucamide layers were formed on silica [5]. We attributed this discrepancy to the different deposition method used in that study, *i.e.* drop casting of isopropanol solution containing 0.01 wt% erucamide, with the driving forces for the layer formation likely dominated by the capillary flow and surface tension upon evaporation of the sessile drop [52-55].

Figure 4 AFM height profiles (1st column), height images (2nd column) with dashed white lines corresponding to height profiles, adhesion images (3rd column) with the dashed white lines corresponding to the adhesion profiles (4th column) of: (A) BS and (B) BS(0.01); (C) Height and (D) adhesion images showing silica surface covered with multiple erucamide aggregates; (E) An enlarged view of the square region in (C); (F) An enlarged adhesion image of the square region in (D). The white arrows indicate erucamide aggregates with higher adhesion at the

aggregate core. (G) An enlarged view showing a 3D adhesion image of the square region in (F); (H) Schematic representation of different erucamide aggregate morphologies on silica surface. The direction of all the line profiles is from left to right.

The geometric packing of erucamide molecules in its self-assembled structures can be considered *via* the packing parameter $P = \frac{V}{a_0 L_{max}}$ [56], where $L_{max} = 1.5 + 1.265n_c$ is the maximum length of a fully extended hydrocarbon chain of n_c carbon atoms [48]. The molecular volume V for erucamide can be estimated with the *mass density approach*, i.e. $V = \frac{MW}{\rho_m * N_A}$, where MW is molecular mass, ρ_m is mass density, and N_A is Avogadro's number. Alternatively, the *Tanford approach* [48] gives $V = V_{CH_3} + V_{CH_2} * n_{CH_2}$, where $V_{CH_3} = 27.4 \text{ \AA}^3$ is the volume of methyl group and $V_{CH_2} = 26.9 \text{ \AA}^3$ the volume of ethyl group, and $n = n_c - 1$ is the number of the $-CH_2$ groups. Both approaches would predict $P \sim 1.03 - 1.13$ (Table 2) for erucamide, pointing to lamellar or inverted structures. Such a large P value can be rationalized by the small hydrophilic erucamide headgroup and its unsaturated hydrocarbon chain (C21) with the *-cis* double bond, shorter but larger than a linear chain. With the likely presence of the aggregates in the spin casting solution, it is conceivable that it would not lead to the formation of a uniform, planar monolayer of tightly densely packed molecules, despite the templating effect from the substrate which could restructure the aggregates. As such, it is likely that the XRR monolayer model was a result of averaging the inhomogeneous surface structures formed *via* deposition from erucamide solution of the lowest concentration (BS(0.01)), whilst the patchy erucamide surface layers comprised multiple aggregates of different morphologies as revealed with the AFM imaging.

Table 2 Calculated erucamide molecular parameters: molecular mass MW , density ρ , area a_0 , volume V , the maximum hydrocarbon chain length $L_{\max}$, and packing parameter P .

	Molecular formula	MW (g mol ⁻¹)	ρ (g cm ⁻³)	a_0 (Å ²)	V (Å ³)	$L_{\max}$ (Å)	P
Headgroup	HCONH ₂	45.0	1.13 [50]	^a 19.6 43.1 [51]	^a 66.0	-	^a 1.13
Tail	-(CH ₂) ₂₀ CH ₃	294.6	0.79 [57]	-	^b 617.9 ^c 565.4	28.1	^b 1.03

^{a,b} Based on mass density ρ of (a) HCONH₂ and (b) C₂₁H₄₄

^c Based on the Tanford equation [48]

Quantitative nanomechanical (QNM) AFM mapping of BS(0.01) allowed one to correlate the topography and the nanomechanical properties (*i.e.* adhesive response) of the erucamide structures. This showed that the observed aggregates exhibited a lower adhesive response towards the AFM silicon tip, when compared to that between AFM tip and bare silica (Figure 4D and F), consistent with the molecular orientation of the erucamide hydrocarbon tails exposed outwards (Figure 4H). Furthermore, the adhesive response was found to differ within a single aggregate, with the core section showing a higher adhesive response (light blue) than its sheath (dark blue; Figure 4F). This adhesive response variation could be attributed to AFM scanning-induced partial collapse of the hydrophobic tails. This interpretation is also consistent with a slight change of the thickness observed in the height profiles (Figure 4 B), which shows a slightly higher thickness on the edges (sheath) than in the middle (core) of the structure. In general, the erucamide presence led to a decrease in the adhesive response, demonstrating its efficacy to tune surface nanomechanical properties – making it less “sticky” – even at a concentration as low as 0.01 wt%.

For BS(0.1) at 0.1 wt% erucamide concentration, the Kiessig fringes were more pronounced (Figure 2A), which could be fitted to a seven-slab model (Figure 3B; $\chi^2 < 0.05\%$), corresponding to a tri-layer erucamide structure, referred to in Table 1 as the *o*-, *m*-, and *i*-layer for the *outer*-, *mid*-, and *inner* monolayer, respectively. The thickness of *outer*- ($t_2 = 5.5$ Å),

mid- ($t_3 = 4.5 \text{ \AA}$) and inner- ($t_6 = 4.6 \text{ \AA}$) hydrophilic headgroup layers is within the theoretically estimated value ($4.0 - 6.6 \text{ \AA}$). The thickness of the erucamide monolayer atop the silica substrate with the headgroup down (slab 5 and 6), $t = 19.7 \text{ \AA}$, is smaller than that for a fully extended chain ($t = 28.1 \text{ \AA}$) [48], again suggesting relaxed packing and tilting of the erucamide molecules. The top two monolayers (slab 1-4) had an overall thickness of $t = 43 \text{ \AA}$, which is consistent with that for an erucamide bilayer [5, 12]. We attribute the differences between the thickness of the outermost hydrophobic chain ($t_1 = 21.1 \text{ \AA}$) and middle and inner chains ($t_4 = 12.2 \text{ \AA}$ and $t_5 = 15.1 \text{ \AA}$) to different molecular packing in these monolayers. The fit considering an alternative molecular orientation was unsatisfactory ($\chi^2 = 0.15 \%$) and is shown in the Supporting Materials SM.01

AFM imaging of multiple areas across the surface of BS(0.1) revealed complex structures consisting of three types topographical features, all of a lower adhesive response than that of silica (Figure 5). The discontinuous film *ca.* 1.5 nm in thickness formed atop bare silica was identified as erucamide monolayer (Figure 5A), with its thickness close to that fitted for the erucamide monolayer from XRR ($t = 19.7 \text{ \AA}$). Adjacent to the erucamide monolayer, bilayers of $t = 4.5 \pm 0.5 \text{ nm}$ (Figure 5B) and overlapping few-layers labelled as L1, L2, and L3 in Figure 5C were observed, resulting in a characteristic plate-like pattern.

Figure 5 AFM characterisation of BS(0.1): height profiles (1st column), height images (2nd column) with dashed white lines corresponding to the height profiles, adhesion images (3rd column) with the dashed white lines corresponding to the adhesion profiles (4th column) for (A) monolayers, (B) bilayers, and (C) few-layers of erucamide. The direction of all line profiles is from left to right.

Multilayer structure at higher erucamide concentrations

For the two samples BS(1) and BS(2) of higher erucamide concentrations at 1 and 2 wt%, respectively, highly ordered multilamellar structures were observed, evident from the presence of the Bragg peaks up to 3rd ($n = 3$) order (Figure 3). Multilayers present on BS(1) exhibited polymorphism evident from the presence of two different lattice spacings, with the second order diffraction peak ($n=2$) fitted to two peaks (Figure 6A) with $d = 45.2 \text{ \AA}$, $L_a = 429 \text{ \AA} \pm 32$

and $d = 47.5 \text{ \AA}$, $L_a = 271 \text{ \AA} \pm 83$, respectively. Multilayers on BS(2) appeared monomorphic, with each Bragg peak fitted to single Gaussian peak (Figure 2D). The peak position ($Q_{n,(1-2)}$), d -spacing, coherence length (L_a) and number of multilayers (m) are listed in Table 3. For both samples, one could observe peak broadening upon increasing diffraction order n . Figure 6B represents the peak broadening as a function of the fourth power of diffraction order for a plane of Miller index ($h00$), obtained for peak position at $Q_{n,1}$ for both samples. The comparison of the results obtained for the finite domain size and the paracrystalline disorder parameter g are listed in Table 4. The g values were similar for both samples: 0.0274 ± 0.0003 for BS(1) and 0.0273 ± 0.0012 for BS(2), indicative of little fluctuations of the bilayer thickness within the erucamide film. The obtained L_a values are only slightly higher than those obtained from Scherrer analysis, resulting in a comparable overall number of multilayers $m \sim 10$. The erucamide lamellar assembly is likely facilitated by the primary amide headgroup with a dual donor and acceptor capacity; the tendency of the $-\text{NH}_2$ group to achieve the maximum number of hydrogen bonds leads to intermolecular network formation of hydrogen-bonded erucamide molecular packing (Figure 3C) [48, 59].

Close packing of the unsaturated hydrophobic chains makes it less likely for the erucamide layers to be disturbed by the solvent penetration [58], yet the limits of the contribution from trace amounts of water from the ambience or residual isopropanol from spin coating to inter-layer H-bonding were taken in consideration as follows. The fitted headgroup SLDs for the tri-layer structure in Figure 3B were 9.74 (outer, slab 2) $9.83 \times 10^{-6} \text{ \AA}^{-2}$ (mid, slab 3) and $9.78 \times 10^{-6} \text{ \AA}^{-2}$ (inner, slab 6), respectively. Comparing these with the theoretical value for the headgroup of $9.84 \times 10^{-6} \text{ \AA}^{-2}$ and those for water ($9.45 \times 10^{-6} \text{ \AA}^{-2}$) and isopropanol ($7.56 \times 10^{-6} \text{ \AA}^{-2}$), we could estimate the following volume fractions ϕ : 1) Outer monolayer (slab 2): 26% (water) or 4% (isopropanol); 2) Mid-monolayer (slab 3): 3% (water) or 0.4 % (isopropanol); and 3) Inner monolayer (slab 6): 15% (water) or 3% (isopropanol). These values should only

be considered as an indication as it is likely that both water and isopropanol might have intercalated in the layer. Furthermore, the d -spacing of 44.1 – 47.5 Å for BS(1) and 43.6 – 44.7 Å for BS(2) corresponds closely to the erucamide bilayer thickness reported in literature (40 – 50 Å) [5, 12]. This suggests the very small amount of the inter-lamellar water or solvent, if present, did not cause significant swelling.

The AFM analysis (Figure 7) shows that upon increased concentration the size of erucamide domains was larger, leading to a significantly higher surface coverage.

Figure 6 (A) An example experimental XRR curve obtained for BS(1); (B) An enlarged view of the second order ($n = 2$) Bragg peak (black circles) with the background fitted to Q^{-4} (green dashed line) and the Bragg peak fitted to a Gaussian (solid blue line); (C) The residual Gaussian fits after background subtraction. (D) Peak broadening $(\Delta Q)^2/(2\pi)^2$ as a function of the fourth power of diffraction order h^4 for erucamide multilayers found on BS(1) (green) and BS(2)

(blue). Based on the linear fit ($y = y_0 + ah^4$) the paracrystalline disorder parameters g were calculated from the slope a and the coherence length L_a were calculated from the intercept y_0 . The results are listed in Table 4. The errors for y were calculated *via* propagation method based on the uncertainty for $FWHM (\Delta Q)$.

Table 3 Fitted structural parameters for erucamide multilayers found on BS(1) and BS(2): peak position ($Q_{n,(1-2)}$), d -spacing (d), coherence length (L_a) and estimated number of layers (m). Errors were $< 0.2 \%$, for the position of the peak $Q_{n,(1-2)}$ and $< 0.2 \text{ \AA}$ for the d -spacing (calculated *via* the error propagation method based on the uncertainty of the peak position and considering the angular resolution of the instrument). The errors for L_a were calculated *via* the propagation method using the uncertainty for $FWHM (\Delta Q)$. The errors for m were calculated as a combination of uncertainties for d and L_a .

Sample	Parameter	Diffraction order n		
		1	2	3
BS(1)	$Q_{n,1} (\text{\AA}^{-1})$	0.1426	0.2783	0.4211
	$d (\text{\AA})$	44.1	45.2	44.8
	$L_a (\text{\AA})$	442 ± 13	429 ± 32	371 ± 5
	m	10 ± 1	10 ± 1	8 ± 1
	$Q_{n,2} (\text{\AA}^{-1})$		0.2643	
	$d (\text{\AA})$		47.5	
	$L_a (\text{\AA})$		271 ± 83	
	m		6 ± 2	
BS(2)	$Q_{n,1} (\text{\AA}^{-1})$	0.1440	0.2815	0.4214
	$d (\text{\AA})$	43.6	44.6	44.7
	$L_a (\text{\AA})$	470 ± 32	432 ± 15	382 ± 8
	m	11 ± 1	10 ± 1	9 ± 1

Table 4 Comparison of fitted structural parameters for erucamide multilayers found on BS(1) and BS(2): average d -spacing (d), coherence length (L_a), estimated number of layers (m), paracrystalline disorder parameter (g) calculated for finite size and paracrystalline disorder effects from all three orders ($n = 1, 2, 3$) at $Q_{n,1}$ peak position. The errors for d -spacing were

estimated as standard deviation from values obtained for three diffraction orders ($n = 1, 2, 3$). The errors for g and L_a were calculated *via* propagation method using the uncertainty from the slope and intercept y_0 of the linear fit ($y = y_0 + ah^4$), respectively.

Sample	d (Å)	^a L_a (Å)	^a m	g	^b L_a (Å)	^b m
BS(1)	44.7 ± 0.5	414 ± 38	9 ± 1	0.0274 ± 0.0003	445 ± 3	10 ± 1
BS(2)	44.3 ± 0.6	428 ± 45	10 ± 1	0.0273 ± 0.0012	462 ± 12	10 ± 1

^a Based on finite size (Scherrer equation)

^b Based on paracrystalline disorder

Figure 7 AFM height images of erucamide multilayers from (A) BS(1) and (B) BS(2).

The nanomechanical properties (*i.e.* the adhesive response) of BS(0.1) were studied with Peak Force QNM mapping, as its surface structures consisting of monolayers, bilayers and

multilayers were representative of different erucamide surface morphologies. Figure 8 shows the correlation between the height and adhesion data, together with the height and adhesive response profiles, allowing for a layer-by-layer analysis. Regardless of the layer thickness, the adhesive response towards the AFM tip was found to be lower on the erucamide layers (dark blue) than on silica (light blue; $F_a = 1.54 \pm 0.04$ nN; Figure 8C). The adhesive responses were $F_a = 1.23 \pm 0.01$ nN for the erucamide monolayer of 1.5 nm in thickness, and $F_a = 0.95 \pm 0.04$ nN for the erucamide bilayer of 4-5 nm in thickness (Figure 8E). The adhesive response of erucamide multilayers was close to that of the erucamide bilayer at $F_a = 0.98 \pm 0.06$ nN, confirming the bilayer being the repeating structural unit for the multilamellar structure.

The adhesive response for erucamide monolayer was likely affected by the underlying silica surface, thus slightly higher than that obtained for the bilayers or multilayers, for which the adhesive properties became dominated by the erucamide layers. This is consistent with report by Balzer *et al.* in their AFM adhesion study on different layers of thin polymer films supported by silica [60], as well as the study by Li *et al.* on the adhesion of Langmuir-Blodgett phospholipid layers atop mica [61]. The adhesion of erucamide multilayers appeared to depend on the local curvature, with a higher value obtained on the bilayer edge than on its top, resulting in pronounced adhesive response peak (marked as an asterisk) in the adhesive response profile (Figure 8D), possibly as a consequence of a higher adhesive response between the silicon AFM tip and the exposed erucamide hydrophilic headgroups at the edges of the multilamellar structure (Figure 8F). It is possible that the exposure of hydrophilic headgroups facilitated condensation of the molecular layers of water from ambient environment, resulting in a more pronounced adhesive response of hydrophilic AFM tip. Alternatively, this could result from a greater contact area between the AFM tip and the layer edge [12, 62].

(A) Height

(C) Adhesion

(B)

(D)

(E)

(F)

Figure 8 (A) AFM height image for BS(0.1), with the dashed white line corresponding to the height profile (B) (an arrow indicates the profile line direction), and the asterisk indicating the step between a monolayer and a bilayer; (C) Adhesion image with the dashed line corresponding to the adhesive response profile (D), and the asterisk indicating the bilayer edge; (E) Bar chart with adhesive response values obtained for bare silica and erucamide layers. The uncertainties were determined as the standard deviations of five scanned areas of 100 nm × 100 nm in each case. (F) Schematic representation of erucamide assembly on silica, with the asterisk indicating bilayer edge.

The wettability study further confirmed the overall erucamide molecular orientation deduced from the XRR measurements and AFM imaging, *i.e.* with the hydrophobic tails pointing outwards at the outermost layer. It revealed an increase in the surface hydrophobicity upon increasing erucamide concentration in the spin coating solution, with the water contact angle rising from $\theta = 30.5^\circ \pm 0.5^\circ$ for BS(0.01) to $\theta = 92.9^\circ \pm 2.9^\circ$ for BS(2) (Figure 9). The contact angles for BS(0.01), BS(0.1) and BS(1) were $< 90^\circ$, probably due to low surface coverage as confirmed by the AFM imaging, which showed isolated aggregates for BS(0.01) (Figure 4) and overlapping multilayers for BS(0.1) (Figure 5) and BS(1) (Figure 7A), exposing the underlying hydrophilic silica surface ($\theta = 10.2^\circ \pm 1.2^\circ$). As expected, the higher surface coverage facilitated by the concentration of 2 wt% (BS(2); Figure 7B) resulted in higher hydrophobicity ($\theta = 92.9^\circ \pm 2.9^\circ$).

Figure 9 Wettability study results for BS, BS(0.01), BS(0.1), BS(1), and BS(2): (A) Table listing the contact angle results. The uncertainty was calculated as the standard deviation of the measurements from two separate contact angle experiments for each sample. (B) Microscopy images of 10 μL water droplet deposited on each sample; the scale bar represents 1 mm and is applicable to all the images. (C) Variation of contact angle with erucamide concentration, with the uncertainty shown as shading in the data, and schematic representation of increasing hydrophobicity with increasing erucamide concentration.

Conclusion

Here we report a systematic study of the effect of the concentration on the erucamide nanostructure formed *via* spin coating from nonaqueous solution on model hydrophilic silica substrates. Previous reports on the molecular orientation of the erucamide outermost layer has been limited to contact angle measurements and the conclusions from these sometimes contradicted each other [11, 14, 15]. Here, the correlation of synchrotron XRR, AFM imaging, and wettability experiments have allowed us to gain unprecedented evidence for the molecular orientation within erucamide surface layers, supported by a combination of results from investigation of surface morphology, adhesive properties, and wettability.

Using synchrotron XRR and AFM imaging and adhesion force mapping, we have observed erucamide surface nanostructures as patchy monolayers, isolated circular/rounded rectangle-like aggregates and overlapping plate-like multilayers. The morphological features were tuneable by the erucamide concentration in the nonaqueous spin coating solution. In all cases, our results consistently pointed to the molecular orientation at the outermost layer, *i.e.* with the hydrophobic tails pointing outwards. This was also confirmed by the wettability on these surfaces. Furthermore, XRR and AFM have revealed nanostructural details of the erucamide surface aggregates.

XRR results shed light on the molecular packing and thickness of the erucamide layers at four different concentrations on silica. At the lowest erucamide concentration of 0.01 wt%, the XRR curve was fitted to a three-slab model, consistent with an erucamide monolayer of ~ 19.2 Å in thickness. At 0.1 wt% erucamide concentration, a seven-slab model was used, consistent with an erucamide tri-monolayer of a total thickness 63 Å. At higher erucamide concentrations of 1 and 2 wt%, multilamellar structures comprising erucamide bilayers, presumably facilitated by

hydrogen bonding, were observed, with a bilayer *d*-spacing of 43.6- 47.5 Å, consistent with the literature value [5, 12].

Complementary AFM imaging revealed localised nanostructures with high lateral resolution. At the lowest erucamide concentration of 0.01 wt%, isolated surface aggregates of various shapes were observed, with a thickness in the range 3-8 nm. The presence of erucamide tri-layers was observed at 0.1 wt% and multilayers at 1 and 2 wt%. The surface coverage by the erucamide aggregates generally increased with the concentration. The high-resolution correlation between adhesion force mapping with the surface morphology confirmed that the observed nanomechanical properties were consistent with the hydrophobic chains pointing outwards.

We have also investigated the spin coated erucamide surface structures on a hydrophobic substrate, to be reported in a follow-up publication. These results, with details of erucamide surface layers, are relevant to their widespread application as slip additives, the molecular mechanisms for which are still under debate. It will also be very useful to correlate the frictional behaviour of these surfaces with the structure and adhesive mapping, which is the focus of our ongoing research.

Acknowledgements

D.G. is supported by the UK Engineering and Physical Sciences Research Council (EPSRC) and Procter and Gamble Industrial Case Award. L.J.F. was supported by the Bristol Centre for Functional Nanomaterials (BCFN, EPSRC EP/L016648/1). W.H.B. would like to acknowledge funding from the EPSRC (EP/H034862/1), European Cooperation in Science and Technology (CMST COST) Action CM1101 “Colloidal Aspects of Nanoscience for Innovative Processes and Materials”, and Marie Curie Initial Training Network (MCITN) on “Soft, Small, and Smart: Design, Assembly, and Dynamics of Novel Nanoparticles for Novel Industrial

Applications” (NanoS3; FP7 Grant No. 290251). We acknowledge Dr Bhaveshkumar Bharatiya and Dr Gang Wang for their help with the XRR measurements as well as beamline I07 at Diamond Lightsource (UK) for beam time (experiment no. SI22176) and the staff there for their help during the experiment.

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