Perfluoropolyether Impregnated Mesoporous Alumina Composites Overcome the Dewetting-Tribological Properties Trade-Off

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Abstract

Conventional omniphobic surfaces suffer from wear-sensitiveness due to soft apolar coatings or substrates and protruding surface features, that are eroded even for mild abrasion treatments leading to the loss of dewetting properties after wear. Evidently, there was a trade-off between dewetting and tribological properties. Here, we will show the establishment of self-healing slippery properties post severe abrasion by utilizing perfluoropolyether impregnated mesoporous Al₂O₃ (MPA) composites. The hard polar alumina matrix provides the optimal tribological properties and the liquid lubricant in the porous network contributes to both tribological and self-healing dewetting properties. These composites sustained normal pressures up to 350 MPa during reciprocating sliding contacts. The severely abraded surfaces are capable of self-replenishing in ambient environment, driven by capillarity and surface diffusion processes and regained their slippery properties towards water and Hexadecane post 15 h self-healing. Eventually, a *dewetting-tribology* diagram has been introduced in order to show different regimes namely—optimal slippery properties, optimal tribological properties and a mixed regime. We found out that the microstructural expression

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$\left(\frac{\text{Open porosity}}{\text{Total porosity}} \times \frac{\text{surface roughness}}{\text{grain diameter}}\right)_{MPA}$ is a robust guiding tool to predict the regime of interest.

This *dewetting-tribological* diagram may be marked as an inception to designing abrasion-resistant slippery liquid impregnated composites for overcoming the *dewetting-tribological* properties trade-off. Such surfaces may potentially find applications in paint industries and as anti-icing surfaces.

1. Introduction

It is well known that the liquid repellency of a surface depends on its chemistry and roughness factors.^{1,2,3} Traditional liquid repellent surfaces, fabricated by biomimicking Lotus leaf^{4,5}, butterfly wings⁶, rice leaves⁷, rose petals⁸ and many other natural surfaces^{9,10} suffer from high wear-sensitivity due to the high aspect ratio filligrane protruding surface structures and the low wear resistance of coatings or soft substrates such as Polytetrafluorethylene or others. On the other hand, the wear-resistance of a material is inversely related to the surface roughness and linearly proportional to Vickers hardness, especially for abrasive type of wear¹¹. Consequently, often liquid repellent surfaces are not wear-resistant and vice versa and therefore, there is a trade-off between these two functionalities. Hence, there is a thrust to obtain anti-sticking surfaces which are wear-resistant and importantly retain their dewetting characteristics post severe abrasion.

There are only handful of reports available to designing and synthesizing liquid-repellent and wear-resistant materials, that retain dewetting properties post abrasion. The design concepts can be classified into two types—(a) a solid composite, obtained with complex chemical treatment involving fluorinated or non fluorinated alkyl-silanes and (b) apolar surfaces consisting of protruding micro or nano features. Few examples include decanethiol hydrophobized compacted Cu metal powders,¹² a composite of

alumina/chitosan/poly[octadecene-alt-(maleic anhydride)],¹³ highly porous gels,¹⁴ solid foams,¹⁵ liquid impregnated anodized alumina¹⁶, PDMS coated alkali treated PET textiles¹⁷, Ethoxysilane coated interconnected and attached to perfluorosilanized silica microspheres¹⁸, micro-micro hierarchical textured PP surfaces¹⁹ and omniphobic aligned carbon nanotubes²⁰ and candle soot²¹. In the former classification, the surfaces either lacked high wear-resistance or mechanical strength or led to the loss of liquid repellency properties after very mild abrasion (maximum normal pressures up to 310 kPa and only few hundred centimeters sliding distances) or a complex chemical treatment was employed. Presumably, the latter material surfaces cannot withstand high normal pressures and will lose the dewetting properties while employing harsh wear treatment. Clearly, there is no single successful design concept that led to the retention of dewetting properties of a liquid-repellent and a wear-resistant material that underwent aggressive abrasion.

In the very recent times, Nepenthes Pitcher plant inspired slippery liquid infused porous surfaces (SLIPS) have shown excellent anti-sticking properties²², high load bearing capacity²³, anti-fouling properties²⁴, anti-frosting²⁵, and anti-icing²⁶ properties. We exploited this design principle to an anomalous material system which is perfluoropolyether impregnated polar mesoporous α -Al₂O₃ (MPA) whose surfaces are devoid of protruding micro or nano features or apolar rendering functionalization treatments. Such impregnated MPA composites overcome *dewetting-tribological* properties trade-off and lead to extremely durable and scratch-resistant surfaces that will regain their dewetting properties by self-healing processes for multiple damages. They may find potential applications in paint industries where substantial amounts of paints are laid waste due to sticky character of oil and water based paints to the underlying substrates, leading to enormous economy losses.

2. Experimental Details

Sample Preparation and Microstructural Characterizations: Mesoporous α - Al_2O_3 green compacts were synthesized by employing slip casting process^{23,27,28}. Both cuboidal and cylindrical shaped green compacts were manufactured to utilize them as a *tribo-pair*. The green compacts were pre-sintered in air atmosphere in a tubular furnace to remove the binder that was utilized to prepare alumina suspensions for slip casting.^{23,28,29} A heating rate of $1\text{ }^\circ\text{C min}^{-1}$ to heat up to $600\text{ }^\circ\text{C}$, followed by 1 h isothermal holding produced $\sim 59\%$ relative density pre-sintered samples. The pre-sintered samples were eventually sintered in air at 1150 ± 5 , 1205 ± 5 , 1250 ± 5 , 1325 ± 10 , $1500\pm 10\text{ }^\circ\text{C}$ in a tubular furnace at $10\text{ }^\circ\text{C min}^{-1}$ heating rate, 1 h isothermal holding at the corresponding highest temperature to achieve 70 ± 3 , 80 ± 3 , 90 ± 3 , 95 ± 1 , $99\pm 0.5\%$ theoretical densities respectively. The density, open pore fraction and total pore fraction of more than 10 samples immediately after pre-sintering and also after sintering were estimated using Archimedes principle by utilizing isopropanol and water as the suspending liquid media respectively. Samples constituting 70% to 90% density majorly contain open porous network with closed porosity as the minor fraction ($\sim 1\%$), while for $\geq 95\%$ density samples, the closed porosity is the majority (see Table S1, Supporting Information). The pore sizes and distributions were measured using Hg intrusion porosimeter for 70% , 80% and 90% alumina samples and the respective average pore diameters are $47\pm 12\text{ nm}$, $34\pm 10\text{ nm}$ and $25\pm 7\text{ nm}$.²⁸ For samples with 95% and 99.5% densities, the pore diameters could not be characterized due to negligible amount of open porosity.

The microstructural investigations of more than ten sintered and polished samples, and all the abraded samples were performed with Hitachi S4800 high resolution scanning electron microscope (HRSEM) in secondary electron (SE) mode at 1.5 keV acceleration voltage and $10\text{ }\mu\text{A}$ beam current. The sample preparation and the resulting microstructures of unworn samples are highly reproducible as discussed elsewhere^{23,27}. Post abrasion, the impregnated

liquid in the composite was evaporated in an oven at 600 °C by holding it for 10 h for microscopic observations. The grain sizes are 150 ± 25 nm, 330 ± 40 nm, and 1580 ± 500 nm for 70-90 %, 95 % and 99.5 % density samples, respectively [see Section S2, Supporting Information], as measured using HRSEM. The sintered samples were polished using 40 μm and 20 μm diamond blades and diamond slurries containing 15 μm , 6 μm , 3 μm , 1 μm and 0.25 μm sized particles at 150 rpm and 215–280 N normal load (0.173 MPa to 0.226 MPa), as obtained from Struers MD Dur™, Switzerland. The mean surface roughness (R_a) measurements of all the polished samples were carried out using AltiProbe Optic® Profilometer according to the standard DIN EN ISO 4287, ASME B46.1. Fomblin® Y LVAC 25/6 oil ($\text{CF}_3\text{O}[-\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_x(-\text{CF}_2\text{O})_y\text{CF}_3$; $\eta=272$ mPa.s) obtained from Sigma–Aldrich, Switzerland, was used for impregnating 70-90 % dense and lubricating ≥ 94 % dense Al_2O_3 samples by simply submerging them in Fomblin® oil at 150 °C for 2 h. Intuitively, they are correspondingly referred to as *impregnated* and *lubricated* respectively.

The macroscopic excess amounts of Fomblin® oil present atop the composite surfaces were removed by tilting the impregnated sample to 90° and holding for 2h, to let the gravity affect slowly, owing to its high viscosity. Any further visibly thick layer was absorbed with optical lens cleaning fiber free tissue with utmost care and subsequently blown with compressed N_2 gas, utilizing mild pressures and left for 2-3 h undisturbed for allowing the oil film to equilibrate atop impregnated surface. The resulting surface state is referred to as *unflooded* configuration. Alternatively, a macroscopic visible thin pure liquid film was retained atop composite surface, that has completely submerged all the surface roughness features, and is referred to as *flooded configuration*. The readers are directed to our earlier published articles for more experimental details on slip casting process^{23,28} and liquid infiltration²³.

Wetting Characterizations: *n*-Hexadecane ($C_{16}H_{34}$; $\eta=3.0041$ mPa.s), Struers MD Dur™, Switzerland and de-ionised water (resistivity = $18\text{ M}\Omega\text{-cm}$; $\eta=1$ mPa.s) were used to evaluate the wetting properties atop severely abraded Fomblin® oil impregnated 70-90 % dense MPA composite surfaces. The equilibrium static contact angles (CAs), dynamic CAs such as advancing CAs (ACAs) and receding CAs (RCAs) of water and Hexadecane drops atop Fomblin® oil impregnated/lubricated MPA composites were characterized with a high speed camera attached to a contact angle goniometer, Digidrop, France. Typical volume of liquid droplets are $\sim 2\text{--}3\text{ }\mu\text{l}$ and all the CA measurements were carried out at $25\text{ }^{\circ}\text{C}$ and $35\pm 10\text{ }\%$ RH. For reproducibility, the CA measurements were performed on every worn surface at three locations.

Tribological Characterizations: The cuboidal Fomblin® oil impregnated and *unflooded* MPA samples were slid in reciprocating sliding contact in flat-on-flat configuration with SRV® III, Optimol Instruments Prüftechnik GmbH, Germany tribometer to obtain temporal friction coefficient (FC) data. The counter body is a cylindrically shaped dry porous alumina or commercially obtained fully dense WC or diamond samples which were held in a special holder²³ that can compensate for small sample tilts or flatness issues between the two sliding surfaces. The normal load varied from 10 N to 220 N for all the oscillating tribological tests. The contact areas for 70–90 % dense samples lie in the range of $36\text{--}42\text{ mm}^2$. Hence the normal pressures range from $0.24\text{--}5.24\text{ MPa}$, $0.27\text{--}5.87\text{ MPa}$, and $0.28\text{--}6.11\text{ MPa}$ for 70 %, 80 % and 90 % dense samples respectively. The frequency and the stroke are 6 Hz or 13 Hz and 4 mm respectively. All the friction tests were carried out in a controlled chamber environment at 30 % RH and $30\text{ }^{\circ}\text{C}$ and were repeated at least twice. The samples were weighed with a high precision (10^{-4} g) weighing balance before and post wear tests to estimate the wear rates and wear coefficients.

The Vickers hardness ($HV_{0.1}$) measurements were performed on at least 3 samples from each densification on the surfaces that would undergo wear treatment. The average hardness values obtained from a total of 30 measurements for each densification are reported. A load of 0.1 kgf (0.98 N) and 15 s dwell time were used for the measurements.

3. Results and Discussion

The scientific storyline of this article is schematically illustrated in Figure 1. We utilized commercially available Fomblin[®] Y LVAC 25/6 perfluoropolyether for generating both *flooding* and *unflooding* configurations (refer to experimental section for preparation) atop impregnated 70-90 % dense MPA samples as depicted in Figure 1(a) and (b) respectively. The flat-on-flat tribological configuration is achieved by employing cuboidal composite and a cylindrical counter body in contact as represented in Figure 1c, for performing severe abrasion tests. The wetting properties employing water and Hexadecane liquids were investigated prior to abrasion in both *flooded* and *unflooded* configurations (Figure 1a-b), immediately after abrasion (Figure 1e) and also after sufficient self-healing time post abrasion (Figure 1f). The scheme of the microstructure immediately after abrasion is shown in Figure 1(d).

Figure 1. (a-b) Schematic diagrams to show the slippery interfaces of water/alkanes with Fomblin® oil impregnated mesoporous Al_2O_3 composites in *flooding* and *unflooding* configurations, respectively. (c-d) The flat-on-flat tribological configuration of an *unflooded* composite and the worn microstructure are schematically illustrated. (e-f) Wetting properties of worn samples immediately after abrasion and after sufficient self-healing time are schematically depicted. The diagrams are not to scale and proportion.

3.1. Dewetting Properties of Fomblin® oil Impregnated MPA Prior to Wear

$\alpha\text{-Al}_2\text{O}_3$ is known to be an intrinsically omniphilic material, i.e. liquids such as water, Hexadecane, Dodecane, Fomblin® oil wet the alumina surfaces.^{23,27} Static contact angles of Hexadecane, Dodecane, water with flat $\alpha\text{-Al}_2\text{O}_3$ are 0° and that of Fomblin® oil is 18° .²³ The wetting efficiency is furthermore increased by the presence of porous network and surface roughness in MPA samples, implying that liquid impregnation process of alumina is thermodynamically driven. Therefore, unlubricated polar alumina alone cannot render dewetting or slippery properties.

In our previous study²³, we have described the successful establishment of slippery properties in 70–99.5 % dense Fomblin® oil impregnated/lubricated, *flooded* MPA composites prior to abrasion tests. Concisely, a variety of fluids such as water, Hexadecane, Dodecane,

high viscosity water based and oil based acrylic paints slipped off the Fomblin[®] oil impregnated/lubricated *flooded* MPA composite surfaces for sample tilts (α) of $\leq 10^\circ$ and an overview scheme is presented in Figure 1a. The retention of the macroscopic *flooded* film may not be always practical and therefore, we have investigated the wetting properties of *unflooded* composites as pictorially expressed in Figure 1b. In the *unflooding* configuration, the water drops impregnated and replaced Fomblin[®] oil from porous network of MPA due to their strong van der Waals forces of attraction with alumina²³. Moreover, higher sample tilts are essential to initiate sliding of deposited liquid droplets as compared to that of *flooded* configuration. Some of the relevant results are graphically summarized in Figure 4 and in-depth scientific analyses can be found in our previously published article²³.

3.2. Tribological Properties of Fomblin[®] oil Impregnated MPA

The *unflooded* surfaces (Figure 1c) were used for generating worn surfaces by utilizing a flat-on-flat tribological configuration in oscillating tribometer, in contrary to the custom built-home made mild abrasion treatments such as abrading with velvet cloth¹³, sandpaper³⁰, leather, cotton swab³¹, sand grains¹⁸ etc. Typical worn areas of $\sim 95 \text{ mm}^2$ were produced, that are essential to evaluate the wetting properties post abrasion.

The tribological measurements were carried out by increasing the normal load from 10 N to 220 N (corresponding pressures of 270 kPa to 6 MPa), in the steps of 10 N. A typical friction coefficient curve of 80 % dense Fomblin[®] oil impregnated MPA composite that was slid against dry 80 % dense MPA is shown in Figure 2a. It can be observed that the kinetic friction coefficient (FC) decreased continuously with an increase in the apparent normal load up to about 110 N and remained almost constant with further increase of the load. Similarly, tribological characterizations were carried out²⁷ for varying alumina matrix density between 70

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2 % and 99.5 %, that were slid against corresponding same density dry MPA samples, and also
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4 for monocrystalline flat sapphire that was slid against diamond counterbody. In Figure 2b, FC
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6 values extracted from similar curves as shown in Figure 2a, are plotted as a function of Al_2O_3
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8 density for three normal loads of 20 N, 120 N and 220 N, suggesting variation in FC due to
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10 varying normal loads.
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14 The 70 %, 80 % and 90 % dense samples comprise similar microstructures i.e. open
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16 connected porous networks and submicron grain sizes (Section S2, Supporting Information).
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18 But, 70 % and 80 % dense samples have higher surface roughness (Figure S2, Supporting
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20 Information), lower hardness values (Figure 2c) and weak grain to grain necking as a result of
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22 weak metallurgical bond formed at lower sintering temperatures, when compared to 90 %
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24 dense samples. Furthermore, these samples are similar to laser surface textured samples
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26 possessing micro dimples or micro pores that led to early transition of lubrication regime in
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28 the Stribeck curve and governed by geometrical parameters of the pores such as pore
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30 diameter, pore depth, pore fraction and spatial arrangement^{32–34}. Hence, it is intuitive in
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32 abrasive type of wear that the FC should be lowest for 90 % density among 70-90 % dense
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34 samples. On the other hand, for samples with 95 % and 99.5 % densities, the open pore
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36 network no longer exists, thus devoid of continuous lubricant supply by capillarity and
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38 additional hydrodynamic pressure. Additionally, the grain sizes are in 95 % and 99.5 %
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40 density samples are much larger than for 90 % dense samples (Table S2, Supporting
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42 Information) which may also have a slight influence. Therefore, 90 % dense Al_2O_3 samples
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44 impregnated with Fomblin[®] oil yielded lower FC values of 0.12 and smaller than other slip
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46 cast Al_2O_3 samples at wide ranging normal loads of 20 N, 120 N and 220 N as observed in
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The wear coefficients (K') were estimated using Archard's wear Equation³⁵ and graphically summarized in Figure 2c as a function of Al_2O_3 density. They lie between 10^{-5} – $10^{-7} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$ for Fomblin[®] oil impregnated 70–90 % dense MPA composites and $\leq 10^{-8} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$ for lubricated ≥ 94 % dense Al_2O_3 samples, indicating mild or low wear, respectively. Also, the wear-coefficients show an inverse relation to the Vickers hardness (see right y-axis of Figure 2c) of alumina matrix. Additionally, these composites can easily withstand normal pressures up to 350 MPa and sliding distances of 2 km, that are three and four orders of magnitude higher values than the literature^{12,17,19,36,37} reported wear-resistant dewetting surfaces, respectively. On an another note, the frictional and wear properties of unlubricated self-mating mesoporous and fully dense Al_2O_3 reveal one to two orders of magnitude bigger wear-coefficients and slightly increased FC values as compared to that of impregnated samples. A detailed discussion on the tribological pproperties and wear mechanisms of these composites can be found elsewhere^{23,27}.

Figure 2. (a) A typical measured FC curve of Fomblin® oil impregnated 80 % dense MPA composite, that was slid against dry 80 % dense MPA as the counter body. The applied normal load varied from 10 N to 220 N (corresponding to 270 kPa to 6 MPa), (b) extracted FC values of Fomblin® oil impregnated 70-90 % dense MPA samples and lubricated samples of 95-99.5 % dense Al_2O_3 and sapphire, plotted as a function of alumina density for three normal loads of 20 N, 120 N and 220 N. The counter body in each case except for sapphire is its corresponding density dry Al_2O_3 , while diamond is counterbody for sapphire, and (c) their corresponding wear coefficients presented as a function of Al_2O_3 density on x-axis and Vickers hardness on right y-axis.

These Fomblin[®] oil impregnated MPA composites outperforms the traditionally available omniphobic surfaces^{12,17,19,36,37} in terms of mechanical durability and yielding low FCs. The wetting properties of these composites after having undergone abrasive wear are indeed interesting for several applications such as in paint industries, anti-icing surfaces, or self-cleaning scratch resistant high precision tracks in micropositioning stages. Hence, we will emphasize the wetting properties of worn surfaces and the establishment of self-healing *dewetting-tribology* diagram in this article.

3.3. Wetting and Microstructural Characterizations Post Abrasion Tests

Two liquids: water and Hexadecane were employed to evaluate the wetting properties of the worn regions of 70–90 % dense Fomblin[®] oil impregnated MPA composites immediately after wear. A scheme showcasing the microstructure of worn samples immediately after wear is portrayed in Figure 1d. Two sets of sister specimens having undergone the same wear treatment (step load experiments, same as in Figure 2a) were left undisturbed for 5 h and 15 h respectively, at 25±5 °C and 30±5 % RH to allow self-healing. During this self-healing time, Fomblin[®] oil replenished dry alumina surfaces either partially or completely, and eventually, wetting evaluations were performed with water and Hexadecane liquids. A schematic picture demonstrating the replenishment of Fomblin[®] oil on all the dry Al₂O₃ surfaces for a sufficient self-healing time is presented as Figure 1e, while the establishment of slippery properties of such healed surfaces is depicted in Figure 1f.

3.3.1. Wetting Properties of Hexadecane

Immediately after Abrasion

When observed with naked eyes, the worn regions are slightly devoid of Fomblin[®] oil as compared to unworn regions suggesting that the liquid film could have been pushed away by the cylindrical counter body. The equilibrium static contact angles (SCAs) of Hexadecane

1 drops atop Fomblin[®] oil impregnated/lubricated alumina and sapphire composite surfaces
2 were measured immediately post wear i.e within 5 mins after the abrasion measurements.
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4 Typically, the worn surfaces of 70–90 % dense based composites exhibited partial wetting by
5 Hexadecane drops as evident from the highly sticky interfaces, even when the samples were
6 turned upside down. Smaller average SCAs of $\sim 28 \pm 3^\circ$ were observed on such a worn surface
7 as compared to that of $53 \pm 5^\circ$ SCAs typically observed in unworn regions of the *unflooded*
8 samples prior to wear (see Section S4, Supporting Information for more details). This highly
9 sticky interface is attributed to the insufficient coverage of Fomblin[®] oil on the Al_2O_3 surfaces
10 that are approached by Hexadecane molecules. Also, the newly formed surfaces of wear-
11 debris may be devoid of Fomblin[®] oil as schematically shown in Figure 1d.
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25 ***After self–healing***

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27 In order to allow the Fomblin[®] oil molecules to replenish Al_2O_3 surfaces that are either
28 dry or devoid of sufficient film thickness, another set of sister specimens having undergone
29 the same wear treatment were given 5 h self-healing time. Apparently, this healing time was
30 inadequate as it again yielded in sticky interface between Hexadecane and worn region of
31 Fomblin[®] oil impregnated MPA samples. Therefore, third set of worn sister specimens were
32 allowed to self-heal for 15 h and the wetting evaluations were performed. Amazingly, the
33 Hexadecane drops slipped off the worn surfaces when the sample was tilted by an angle α ,
34 that typically differed as a function of alumina matrix density. For reproducibility, 10
35 consecutive Hexadecane drops were allowed to slide on the worn surfaces and a temporal
36 image sequence of a 5th drop sliding atop worn regions of Fomblin[®] oil impregnated 70 %
37 dense MPA is shown in Figure 3. A slow speed video demonstrating such a sliding behavior
38 may be accessed as Video S1, Supporting Information.
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Figure 3. Temporal selected image sequence of 5th Hexadecane drop ($\sim 2.5 \mu\text{l}$ volume) among 10 consecutive sliding drops captured using high speed camera, demonstrating its reproducible sliding behavior atop Fomblin[®] oil impregnated 70 % dense MPA sample post wear and after given a self-healing time of 15 h.

To better understand the effect of Al_2O_3 density, the equilibrium SCAs, advancing contact angles (ACAs), receding contact angles (RCAs), contact angle hysteresis ($\text{CAH} = \text{ACA} - \text{RCA}$), and sample tilt (α) at which the Hexadecane and water drops start sliding were experimentally measured and graphically summarized in Figure 4. Insignificant differences in SCAs were observed for varying Al_2O_3 density for *flooded* Fomblin[®] oil composites prior to wear (see Figure 4a, ■) and are due to flat *liquid-liquid* interfaces. One can deduce that the Hexadecane drop makes a SCA of $\sim 47^\circ$ atop flat Fomblin[®] oil film from these measurements. Typically, the roughness (R_a) of Al_2O_3 samples decreased with an increase in the Al_2O_3 density from 70 % to 99.5 % (see Section S3, Supporting Information). According to Wenzel's theory³⁸, the SCAs of Hexadecane drop atop *unflooded* Fomblin[®] oil impregnated MPA composites are expected to decrease from $\sim 47^\circ$ SCA for a decrease in the Al_2O_3 density from 99.5 % to 70 % (refer to Section S5, Supporting Information for details). However, the experimental results indicate an opposite trend (see Figure 4a, ●). This could be because of

chemical heterogeneity arising due to Al_2O_3 regions that may be deficiently covered by Fomblin[®] oil, thus hinting a composite Cassie state instead^{39,40}.

The SCAs of Hexadecane drops in the worn regions (Figure 4a, ▲) are significantly bigger as compared to that of unworn samples. But, corresponding Hexadecane drops slide at relatively higher sample tilts as shown in Figure 4b, when compared to that of unworn samples. Such increased SCAs and higher sample tilts necessary to initiate sliding are mainly due to the strong pinning forces of the wear debris in the form of micro and/or nano particles, as observed in post abrasion electron microscopy studies and evident from varying wear-coefficients (see Figure 2c). Typical SEM pictures of worn regions of 70 % dense Al_2O_3 are shown in Figure 5(d-g) and also representative microstructure of unworn region is shown in Figure 5c for a comparison. Uncontrollable heterogeneously distributed surface wear debris are evident from Figure 5d. The wear debris and some other regions underwent tribosintering as observed at low and high magnifications in SEM and presented as Figure 5(e-g). Such surface heterogeneity resulted in strongly varying SCAs in 70 %, 80 % and 90 % dense worn samples (Figure 4a, ▲). Such dense debris and regions are replenished mainly by surface diffusion process.

The measured R_a values of 70 %, 80 % and 90 % samples post abrasion are 78 ± 7 , 77 ± 9 and 50 ± 5 nm respectively, which match closely to their corresponding unworn regions (Figure S2, Supporting Information). The worn surfaces were heated in an oven and ultrasonicated to remove all the liquids and loosely adherent wear debris and eventually the roughness (R_a) measurements were performed. Hence, these R_a values cannot be directly related to SCAs or α because they do not include contribution from wear debris.

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The contact angle hysteresis (CAH) values were measured by tilting the sample to a minimum angle (α) at which the Hexadecane drop starts sliding⁴¹. For example, the typical sample tilt, ACAs and RCAs of Hexadecane drop atop Fomblin[®] oil impregnated *unflooded* 70 % dense Al₂O₃ composite prior to and post abrasion with 15 h of self-healing are presented in Figure 5(a-b) respectively. Similarly, these measurements were carried out for 80 % and 90 % dense Al₂O₃ based composites and the results are summarized in Figure 4c and also tabulated in Table S4, Supporting Information. Clearly, higher CAH in the worn regions are due to the wear-debris that may result in local pinning. The wetting evaluations post wear were carried out only for those containing open porous network i.e. for 70-90 % (Table S2) dense Al₂O₃ based Fomblin[®] oil impregnated composites. This is because open porous network present in these matrices acts as reservoirs and preserves the impregnating liquid which aids in the self-healing by a capillary transport process.

Figure 4. The measured (a) equilibrium SCAs of Hexadecane drops, (b) minimum sample tilt (α°) for Hexadecane sliding, and (c) CAH (ACA-RCA) of Hexadecane drops atop 70–99.5 % dense Fomblin[®] impregnated/lubricated Al₂O₃ composites and sapphire samples prior to and post wear experiments are presented as a function of matrix density.

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Figure 5. Typical optical images of a Hexadecane drop ($\sim 2.5 \mu\text{l}$) sliding atop Fomblin® oil impregnated 70 % dense, unflooded composite (a) prior to abrasion, and (b) post abrasion that underwent 5 MPa normal pressure and after 15 h self-healing, and their corresponding (c–g) SEM images showing unworn and worn regions. The worn regions constitute many loose debris particles as shown in (d–e) and (f) other heterogeneously formed microstructure, both of which underwent tribosintering. The magnified image of tribosintered region is shown in (g).

3.3.2. Wetting Properties of Water

Immediately after Abrasion

The wetting evaluations were also carried out by utilizing water as the test liquid. Immediately after the wear i.e. within 5 min after the abrasion test, all the Fomblin® oil

1
2 impregnated 70-90 % dense Al_2O_3 composites demonstrated superhydrophilicity, i.e. water
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4 drop exhibited rapid spreading and infiltration within tens of seconds⁴². A typical optical image
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6 of a water drop atop Fomblin[®] impregnated 90 % dense Al_2O_3 composite is showcased in
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8 Figure 6a. Within just 40 ms after the drop deposition, complete spreading and infiltration
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10 occurred, suggesting that the most of Al_2O_3 regions are deficient of requisite Fomblin[®] oil
11
12 coverage as schematically depicted in Figure 1e. These observations are similar to that of
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14 Hexadecane, but more pronounced. Such strongly detectable infiltration and spreading
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16 behaviors are due to much stronger attractive van der Waals forces between Al_2O_3 and water
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18 as compared to that of Al_2O_3 and Hexadecane.²³
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20
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22 ***After 15 h self-healing***

24
25 A smaller healing time of 5 h was given for another set of sister specimens having
26
27 undergone the same abrasion treatment (as in Figure 2a), that yielded an unstable interface
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29 followed by spreading and infiltration. Consequently, a sister sample having experienced the
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31 same abrasion conditions and self-healed for 15 h, yielded an initial SCA of 69° at time of 0
32
33 ms which reached to its equilibrium SCA of 45±3° after 12 s and remained constant for next 2
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35 min as presented in Figure 6b–c. A further slight decrease in the SCA after 3 min post droplet
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37 deposition was observed due to the continuous evaporation of water. The corresponding SEM
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39 pictures of unworn and worn regions are showcased in Figure 6(d-h). Interestingly, this water
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41 drop (in Figure 6b) slipped off for sample tilts of ~25° and resulted in 15° CAH (not shown).
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43 These observations suggests that a *flooding* Fomblin[®] oil is not essential for achieving
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45 slippery liquid impregnated interfaces as commonly believed.
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Figure 6. Optical images of water drops ($\sim 2.5 \mu\text{l}$) atop 90 % dense Fomblin® oil impregnated MPA composite (a) immediately after the wear, and (b-c) after a 15 h self-healing time, demonstrating temporal evolution of contact angles to reach an equilibrium value of 45° and (d-h) their corresponding SEM pictures of unworn and worn regions.

The self-healing process is a result of the combined capillary transport followed by surface diffusion of Fomblin® oil molecules to replenish the Al_2O_3 surfaces to render sufficient coverage.²³ The required self-healing times are ~ 15 h, which could be quite slow for some specific applications. Consequently, we have supplied Fomblin® oil to the worn regions by external means whose outcomes will be discussed as follows. Alternatively, high temperature healing is a viable option that increases the surface diffusivity linearly with temperature²⁷ and thereby dramatically reducing the self-healing time.

Replenishment by external means:

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2 An external source of lubrication is already commercially implemented especially in
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4 heavy machinery whose tribological performance is critical. Similarly, one could imagine that
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6 a continuous or a regular supply of Fomblin[®] oil on the internals of ink rollers in the paint
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8 industries may enhance the slippery properties of oil based and water based ink atop steel
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10 substrates and lead to easy cleaning. Therefore, we have performed this additional
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12 experiment to demonstrate the successful results.
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16 For this, a tribological experiment was performed by applying a constant normal load of
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18 200 N (~10 MPa) for Fomblin[®] oil impregnated 83 % dense Al₂O₃ *unflooded* composite with
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20 WC as the counter body. The sliding frequency of 13 Hz and 4 mm stroke were used. A
21
22 steady state friction coefficient of 0.15 was observed as shown in Figure 7a. The surface
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24 roughness (R_a) increased from 30±4 nm (unworn) to 100±25 nm (worn) due to wear after
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26 ultrasonicing the loose adherent wear debris. The estimated wear coefficient is $\sim 10^{-5}$ mm³
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28 N⁻¹ m⁻¹ by employing Archard's wear equation³⁵ and indicates a mild wear.
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30

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32 Immediately after the wear, naked eye observations reveal that the worn surfaces were
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34 deprived of Fomblin[®] oil macroscopic films as compared to that of unworn sample.
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36 Subsequently, 2 μ l Fomblin[®] oil was deliberately added to the worn region. The wetting
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38 evaluations reveal that such externally replenished worn region exhibited hydrophobic
39
40 property. For example, the equilibrium SCA of water in the unworn region is 45° as shown in
41
42 Figure 7b. And after wear, the worn regions would have resulted in superhydrophilic behavior
43
44 if not replenished by external means. Nevertheless, an equilibrium SCA of 86° was measured
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46 as demonstrated in Figure 7c. This water drop slipped off the surface for sample tilts of $\sim 10^\circ$,
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48 much smaller than that of self-healed surfaces (Figure 4b). The corresponding SEM images
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50 of the unworn and the worn regions are presented in Figure 7(d-f) showcasing an increased
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52 surface roughness due to wear, and also supported by roughness measurements.
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Figure 7. (a) Temporal FC data of Fomblin® oil impregnated 80±3 % dense MPA that was slid against WC as the counterbody for an applied normal load of 200N (~10 MPa normal pressures), 4 mm stroke, 13 Hz frequency and for a 720 m sliding distance, measured equilibrium SCAs of water drops (~2.5μl) atop 83 % dense Fomblin® impregnated MPA composite (b) prior to wear, and (c) immediately post abrasion test after external replenishment of Fomblin® oil, and (d-f) their corresponding SEM images.

Concisely, we report the retention, and in many cases the improved wetting properties whilst using the normal pressures of ~10 MPa, at least 2 orders of magnitude higher than the literature either by allowing to self-heal or replenishing by external means. It is not only limited to 10 MPa, because we have reported earlier^{23,27} that these composites can withstand normal pressures up to 350 MPa, i.e. 35 times bigger. Although the wetting characterizations were not evaluated in these high pressure wear studies, it can be presumed to have retained slippery properties if given a sufficient self-healing time.

4. Dewetting—Tribology diagram for LIMPA

We introduce a novel *dewetting-tribology* diagram of LIMPA which constitutes different regimes namely: optimal self-healing slippery properties, optimal tribological properties and a

transition regime or a crossover regime. Attaining optimal functionalities depend on a complex mixture of interdependent physicochemical properties of Al_2O_3 such as its surface microstructure and topology of bulk porous network and that of impregnating liquid. To list out, open porosity (OP), total porosity (TP), pore sizes, their distributions and morphology on the surface and in the bulk, hardness and grain diameters of Al_2O_3 and similarly, the viscosity, the surface diffusivity, type of lubricant (Newtonian or non-Newtonian) and the molecular dimensions of the impregnating oil dictate the *dewetting-tribo* properties of LIMPA composites.

Here, we will present and discuss the *dewetting-tribology* diagram of Fomblin[®] oil impregnated MPA for varying microstructural properties of Al_2O_3 matrix. FC exhibits same trend as that of surface roughness (R_a) as expected³³, and also depend on the grain diameters (d_{grain})⁴³ and amount of OP²³. Wear-resistance, in addition to aforementioned parameters, is inversely dependent on TP, because the wear-debris in this material are formed by local intergranular and transgranular fracture mechanisms²⁹. This is because, the flexural strength of the MPA samples which strongly influence the wear-debris morphology and amounts, are dictated by the total porosity fraction²⁹. Therefore, lowest FC and smallest wear-coefficients are achievable for smallest ratios of $\left(\frac{OP}{TP} \times \frac{R_a}{d_{\text{grain}}}\right)$. On the contrary, self-healing slippery properties are best achieved for bigger ratios of $\frac{OP}{TP}$. The values of $\frac{FC \times K_f}{CAH}$, $\frac{OP}{TP}$ and $\left(\frac{OP}{TP} \times \frac{R_a}{d_{\text{grain}}}\right)$ of 70-99.5 % dense Al_2O_3 and sapphire samples are presented as a function of alumina density in Figure 8 (a), (b) and (c) respectively all of which follow a similar trend. The values of OP, TP, R_a , grain diameters of Al_2O_3 samples are tabulated in Table S5, Supporting Information.

In Figure 8a, three regimes are expressed in checked green (regime I), yellow (regime II) and striped red (regime III). In the regime I, which is basically for 70-90 % dense MPA samples, the ratio $\frac{FC \times K'}{CAH}$ is relatively higher and shows a sharp transition for increase in Al_2O_3 density beyond 90 %. The higher values of $\frac{FC \times K'}{CAH}$ suggest higher FC and wear-coefficient (K') values as compared to their corresponding self-healing slippery properties characterized by CAH. In these 70-90 % dense samples, the self-healing processes that contribute to the establishment of slippery properties post harsh abrasion are both capillary and surface diffusion phenomena because of the presence of open porosity network as evident by a sharp decreasing trend in $\frac{OP}{TP}$ (Figure 8b). Although, $\left(\frac{OP}{TP} \times \frac{R_a}{d_{grain}}\right)$ shows similar trend as that of $\frac{OP}{TP}$ (Figure 8b-c), the former ratio is a better microstructural expression. This is because differences between 80 % and 90 % density Al_2O_3 matrices are more visible owing to an increased wear-resistance for 90 % density based composite (see Figure 2c) that depend on R_a and grain diameters (d_{grain}).

In the regime III, very small values of $\frac{FC \times K'}{CAH}$ are observed, suggesting that this Al_2O_3 density range is the best for attaining optimal tribological properties. Due to the absence of OP in this matrices, self-healing occurs only by surface diffusion of the liquid, provided that there is some amount of liquid atop. Alternatively, it is feasible to provide external replenishment to the system, whose outcomes are presented in Figure 7. The wetting properties expressed a transition for Al_2O_3 densities between 90 % and 95 % (refer to Figure 4). Therefore, regime II is a transition regime but, on the other hand, tribological properties are also optimal in this densification range (refer to Figure 2). Henceforth, initial estimations

can be performed by obtaining $\left(\frac{OP}{TP} \times \frac{Ra}{d_{grain}}\right)$ values for a given matrix material and a lubricating liquid to predict the regimes in *dewetting-tribology* diagram.

Furthermore, the role of varying matrix-liquid interactions can be added into this equation by a spreading parameter (S), which was earlier indicated to predict the relative thermodynamic stability of these composites in achieving wear-resistant slippery interfaces²³. Spreading coefficient is also a tool to characterize the wettability of a surface by a liquid. Higher the wettability by the lubricant, the more probability of the tribological contact to be either in mixed or hydrodynamic regime of Stribeck curve instead of boundary lubrication regime, where solid-solid contacts exists. Hence, better oil wettability is good to yield low FC values.^{44,45} Similarly, higher the wettability of the impregnating liquid with the matrix in liquid impregnated composites, the lesser is the probability of the test liquids to replace the impregnating liquid from the pores at the locations of insufficient surface coverage by impregnating oil. Therefore, higher wettability of impregnating liquid with the matrix material is beneficial for yielding good dewetting properties too. Also, higher viscosity that governs the wetting kinetics, leads to thicker films and aids in achieving low FC values. Nevertheless, if the oil film is pushed away during sliding contacts, then the surface diffusion of the oil will be very slow, owing back to its high viscosity (Fomblin[®] oil viscosity: $\eta=272$ mPa.s at 23 °C) and thus affecting the temporal behaviour of FC.

Briefly, this study indicates that liquid impregnated composites can replenish their slippery properties given a sufficient self-healing time. The self-replenishing time of the impregnating liquid to completely cover all the dry alumina surfaces depends on several factors such as depth at which the Fomblin[®] oil is present in the substrate porous matrix at a given time, viscosity of Fomblin[®] oil, CA of Fomblin[®] oil with matrix material, tortuosity of the MPA

network, effective pore radius, surface diffusivity of the impregnating liquid, area of the dry Al_2O_3 surfaces and the required surface lubricant film thickness. Quantitative analyses of these influencing parameters were carried out to develop a simple model which will be presented subsequently.

Figure 8. (a) The dewetting–tribology diagram i.e. $\frac{FC \times K'}{CAH}$ values of Fomblin[®] oil impregnated/lubricated Al_2O_3 are presented as a function of Al_2O_3 density. Three regimes namely— best slippery properties (regime I), best tribological properties (regime III) and a transition regime (regime II) are shown in checked green, striped red and yellow colors respectively. (b-c) The values of $\frac{OP}{TP}$ and $\left(\frac{OP}{TP} \times \frac{R_a}{d_{grain}}\right)$ are presented as a function of Al_2O_3 matrix density indicating similar trends as that of $\frac{FC \times K'}{CAH}$, but $\left(\frac{OP}{TP} \times \frac{R_a}{d_{grain}}\right)$ is a better microstructural representation.

5. Conclusion

We report for the first time, the successful establishment of self-healing dewetting properties of surfaces that were subjected to severe abrasion i.e. for applied normal pressures up to 10 MPa, which are two orders bigger than that utilized in wetting-wear research community. Therefore, perfluoropolyether impregnated alumina composites overcome the traditionally *dewetting-tribological* properties trade-off. These composites are highly capable of self-replenishing, driven by capillary forces and surface diffusion process. Although, the worn regions and wear debris initially exhibited superhydrophilicity and partial oleophilicity immediately after abrasion, but eventually regained their slippery properties towards Hexadecane and water drops after 15 h self-healing time. The developed *dewetting-tribology* diagram reveals three regimes namely optimal slippery properties, optimal tribological properties and a mixed regime. By calculating the $\left(\frac{OP}{TP} \times \frac{Ra}{d_{grain}}\right)$ values of matrix material, it is feasible to predict the regime for a given *matrix-liquid* combination.

Supporting Information

The Supporting Information section contains: (i) Open Porosity (OP) and Closed Porosity (CP) in Mesoporous Alumina Samples, (ii) Grain Sizes and Morphology of Sintered 70-99.5 % dense Mesoporous Alumina Samples, (iii) Roughness (R_a) measurements of Unworn and Worn Samples, (iv) Wetting Evaluations of Worn Samples Immediately After Wear, (v) Hexadecane SCAs predictions using Wenzel's theory, (vi) Measured ACA, RCAs and CAH prior to and post abrasion, (vii) List of microstructural parameters of Al_2O_3 samples and a video file.

The supporting information is available free of charge from the publisher or from the author.

Author Contributions

Rowthu Sriharitha conceptualized and performed all the experiments and wrote the complete manuscript. Patrik Hofmann followed the project updates and contributed to the manuscript revisions.

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Conflict of Interest

The authors declare no conflict of interest.

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TOC graphic

Abrasion-resistant and self-healable dewetted liquid impregnated composites

TOC graphic: Abrasion-resistant and self-healable dewetted liquid impregnated composites

254x127mm (300 x 300 DPI)