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Vertical photo-enforced stratification for more damage resistant antifouling coatings

Jimenez Zucchet, D.A.

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Vertical photo-enforced stratification for more damage resistant antifouling coatings

D. A. Jiménez Zucchet

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Abstract

Fluorinated polymers have been proven to be a good option for antifouling coatings. However, these fluorinated coatings are in general very soft. This research proposes an effective method to reach vertical stratification in fluorinated (meth)acrylate coatings that enables an increase of the damage resistance while preserving the antifouling abilities of fluorinated coating. Using photo polymerization with a photo-absorber included in the system, a photo-enforced stratification along the thickness of the coating is obtained. A difference in volume fraction higher than 0.3 between the top and the bottom of the coating was achieved. Thus, this concentration profile enabled to tune the characteristics and mechanical properties in the bottom and the top of the coating. A 4-fold increase in storage modulus for the top of the coating was obtained. In conclusion, by using a light gradient within the coating it is possible to reach a vertical stratification through the thickness of the coating.
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Introduction

There are more than 4000 fouling species, ranging from microorganism, plants and animals, that attach, grow and accumulate in different surfaces building up a biofilm. This process is called biofouling. Biofouling is not only an environmental problem, but also a huge economic problem. In fleets, for instance, environmentally one of the main problems is that organisms attach to the hull of ships and then can be transferred to new ecosystems. In a new environment, these invasive species can affect the food chain, the preexisting water conditions, etc. From an economic point of view, the problems are related with enormous increase in cost due to maintenance and out of service ship time. As well as to ships, buoys and other equipment in contact with water are affected with this problem. Moreover, it has been demonstrated that the fuel consumption can increase due to the drag increase caused by the biofouling. This is also an environmental problem, because higher fuel consumption means higher CO₂ emissions. Another industry where biofouling is a very critical issue is the medical field. Due to biofouling, infections and associated healthcare costs are huge. For instance, in the United States hospitals the healthcare cost derived from infections due to biofouling are about $28 and $45 billion per year. In addition, the production and maintenance costs of equipment and clothes are very high since biofouling can occur in almost any wetted surface and requires sterilized conditions that are very expensive. Furthermore, the cleaning steps of many chirurgical and medical procedures are more time consuming than the procedure itself causing more displeasure in patients. Likewise in these two previously mentioned fields biofouling is an identified problem in many industrial fields such as food processing, paper manufacturing, water purification, etc. Therefore, the development of coating materials for antifouling purposes has been gaining a lot of interest.

In the naval industry, for instance, there are antifouling coatings based on the release of biocides to kill fouling organisms. However, this technique is being banned in some countries, because the substances used like tributyltin oxide and copper oxides are not selective and affect other living organisms and the human food chain,
besides the increasing level of toxins released in the oceans and rivers. This has motivated to search for non-biocidal alternatives. Fluorinated polymers have demonstrated potential for antifouling purposes\textsuperscript{2,9–12}. However, the mechanical properties of these coatings are not always practical e.g. fluorinated coatings can be very soft\textsuperscript{11}. Thus, it is required to improve the mechanical properties to make this kind of coatings more damage resistant and suitable for industrial applications.

Therefore, the purpose of this project is to elucidate an alternative production technique that enables the increase of the damage resistance properties, while preserving the antifouling abilities of these fluorinated coatings.
Theoretical background

Non-biocidal coatings

Using nature as a guide, biomimetic approaches to combat biofouling have been widely investigated\textsuperscript{6,9,13–17}. The type of biofouling depends on the type of organisms, the nature and conditions of the water and the time that the surface stays in contact with water\textsuperscript{1}. Therefore, the attachment mechanisms of the fouling species are very diverse, complicated, and in some cases even unknown or not completely understood. However, it has been proven that the interaction with surfaces and mobility of microorganism and animals cells can be altered at the interfaces by the shape, pitch and aspect ratio of structured surfaces\textsuperscript{18}. Therefore, other approaches of structured surfaces that prevent or reduce biofouling have also been studied\textsuperscript{15,17,19,20}. In addition, trying to improve the antifouling properties against certain organisms relief structures, such as the micro structured skin of sharks, were proposed. Overall these approaches related to the micro topography aim to minimize the surface area where organism can attach\textsuperscript{16,17}. Thus, structured surfaces capable of preventing or reducing the adhesion of fouling organisms on a target surface are required, so that with the natural motion of the entity (e.g. the shark, the vessel, etc.), the hydrodynamic shear will lead to fouling release\textsuperscript{19}.

In the past, some studies have claimed that for better antifouling properties hydrophobic surfaces were the best option while others have expressed the good results of surfaces with hydrophilic features\textsuperscript{17}. However, it has also been proven that they are not sufficient separately\textsuperscript{9}. One of the most difficult factors of biofouling is the high diversity of species and that almost any biomass is conformed of hydrophobic and hydrophilic components\textsuperscript{18}. Moreover, these organisms are capable to adjust in response to the properties of the substrate\textsuperscript{18}. Hydrophobic surfaces have been proven to be effective against several types of fouling organism such as algal and zoospores, but not for other types such as the adsorption of proteins and cells or vice versa with hydrophilic surfaces\textsuperscript{9,18}. Therefore, there has been an interest to exploit the omni- or
amphiphobic properties (ability to repeal both simple liquids like water and more complex like hydrocarbons, blood, etc.) using fluorinated monomers and the resultant fluoropolymer in the structured surfaces to avoid the problem of fouling specificity21-23.

Photo-embossing

Even though structured surfaces appear to be the right approach for non-biocidal and more ecofriendly antifouling alternatives, from a commercial point of view this option is still less popular because the techniques and conditions of production are very complicated. Typically, techniques such as lithography, self-assembly, layer by layer, and mold replication have been used to obtain structured surfaces24. These techniques are not practical or not economically convenient on large surfaces such as the hull of ships because require many steps and/or are very time consuming25. Photo-embossing has opened a new opportunity to circumvent these issues because it is inexpensive, not time consuming and can be done at room temperature24. Using a system of monomers with different reactivity and/or mobility, photo-embossing allows to create a coating with a designed surface relief. The method consist of basically two steps: A polymerization step with exposure of the target surface to an UV irradiation through a patterned lithographic mask, an additional flood exposure to ensure a complete polymerization26.

The mentioned polymerization step of photo-embossing corresponds to a photo induced polymerization process based on a free radical polymerization. The photo-initiator generates radicals that will initiate a chain reaction, producing cross-links between the liquid monomers resulting a solid polymer27. The structured surface is created by a material flux due to the local polymerization in the exposed areas (light areas) next to the covered areas (dark areas)25. The local polymerization creates a chemical potential difference between the areas, which is the driving force for the material flux28. This diffusion relies on a difference in reactivity and/or a difference in mobility. It is therefore important to understand that other entropic effects such as
monomer size and the degree of cross-linking of the polymer network also play important roles in this flux of material\textsuperscript{29}.

Thus, photo-embossing seems to be not time consuming, it can be done at room temperature and it is inexpensive. As generally UV light it is used for the polymerization process, the intensity of the light, the wavelength and the photo-initiator can be modified to tune the final properties of the coating\textsuperscript{26,27}. Moreover, previous studies have demonstrated satisfactorily the possibility of obtain structured surface fluorinated coatings by using the photo-embossing technique\textsuperscript{26}.

However, although this horizontal stratification is an excellent property achieved, the damage resistance of these fluorinated coatings are not completely functional. Fouling release polymers in general are very soft\textsuperscript{11}. Thus, it is required to improve the mechanical properties to make this kind of coatings more damage resistant. Therefore, an increase of the damage resistance properties, while preserving the antifouling abilities of these fluorinated coatings is required.

\textit{Vertical photo-enforced stratification}

Several methods such as wet on wet coating, solvent evaporation and incorporation of low surface energy monomers have been use in the past to create polymers with a vertical concentration gradient\textsuperscript{30–33}. Moreover, previous studies have demonstrated the possibility of obtain photo-enforced stratification in the vertical direction using homogeneous systems like monomers and oligomers or liquid crystal systems\textsuperscript{6,24,31,34,35}. Cook \textit{et al.} reported satisfactory results for a monomer system using a single step process\textsuperscript{32}. The method relies on a free radical polymerization, and a material flux within the coating due to differences on reactivity and/or mobility between the monomers and the local polymerization towards the light source\textsuperscript{29,32}.

When compared to photo-embossing, instead of an alternation between dark and illuminated areas in the horizontal direction, a gradient of light intensity in the vertical direction is required. Therefore, it is no longer possible to use a lithographic
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mask. To obtain the needed light gradient the use of a photo-absorber is implemented. As the relationship between the absorbance and the concentration of the photo-absorbers will determine the light gradient, this is an important factor to be considered. The hypothesis is that with a sufficient light gradient the material flux towards the light source will produce a concentration gradient through the thickness of the coating (Figure 1).

Figure 1. Graphical representation of the light intensity gradient and the resulting concentration gradient.

Because the storage modulus is dependent on the composition it is possible to tune the mechanical properties of the coating and increase the damage resistance.

The Beer-Lambert Law

The relationship between the absorbance and the concentration of the photo-absorbers is a crucial factor to create vertical stratification. The Beer-Lambert Law describes the optical absorption \( A \), attenuation of the light intensity through the medium in which is travelling, proportional to the extinction coefficient \( \epsilon(\lambda) \), the length of the absorbing medium \( l \) and the concentration \( c \) of the absorbing species. Equation 1 describes the Beer-Lambert law. The extinction coefficient \( \epsilon \) is wavelength specific and is usually expressed in \( L \ mol^{-1}cm^{-1} \). High values of \( \epsilon \) are desired to ensure the gradient of light is sufficient to produce a gradient in concentration.

Vertical photo-enforced stratification for more damage resistant antifouling coatings
\[ A = \log \frac{I_0}{I} = \varepsilon(\lambda)lc \rightarrow \varepsilon(\lambda) = \frac{A}{lc} \]

**Equation 1.** Beer-Lambert Law expression. The absorption \( A \) is linearly related to \( \varepsilon(\lambda) \) the extinction coefficient, \( l \) the path length \( l \) and \( c \) the concentration.

Combining **Equation 1** with the relation between absorption and transmission, **Equation 2** is obtained. **Equation 2** states that there is a logarithmic dependence between the transmission through a medium and the product of the extinction coefficient, the path length and the concentration.

\[ T = 10^{-A} = 10^{-\varepsilon(\lambda)lc} \]

**Equation 2.** Beer-Lambert Law expression. The transmission \( T \) is logarithmic related to the negative product of \( \varepsilon(\lambda) \) the extinction coefficient, \( l \) the path length \( l \) and \( c \) the concentration.

**Raman confocal spectroscopy**

Raman confocal spectroscopy was used in this study as the main characterization technique, because it is a non-invasive technique, it requires an easy sample preparation, it offers an adequate spatial and depth resolution and it is suitable for liquids and solid materials. Raman is a scattering vibrational spectroscopy technique. It means that in this technique a monochromatic beam (usually a laser) excites the target sample and the Raman spectrum, measured as inelastically (energy is not conserved therefore there is a shift of frequency) scattered intensity, results from a change in the polarizability of a molecular bond. The **Scheme 1** shows the schematic set up of confocal Raman spectroscopy.
Scheme 1. Typical set up of a Raman process measurement\textsuperscript{36}. 

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Experimental section

Materials

The monoacrylate selected in this study was 1H, 1H, 2H, 2H-perfluorodecyl acrylate (PFDA) and it was obtained from Sigma-Aldrich. The two cross-linkers, perfluoropolyether dimethacrylate (PFPE-DMA 9, Mw=1600 g/mol) and perfluoropolyether dimethacrylate (PFPE-DMA 20, Mw=4000 g/mol), were provided by Solvay Specialty Polymers. The photo-initiator used in this study was 2-Hydroxy-2-methyl-1-phenyl-propan-1-one, Darocure 1173 (D1173), purchased from BASF Schweiz AG. The corresponding molecular structures are shown below (Figure 2). All materials were used without further purification.

![Molecular structures](image)  
**Figure 2.** Molecular structures of (a) Perfluorodecyl acrylate (PFDA) with molecular weight 518.17g/mol, (b) Photo-initiator 2-Hydroxy-2-methyl-1-phenyl-propan-1-one (D1173) with molecular weight 164.2 g/mol, (c) Perfluoropolyether Dimethacrylate (PFPE-DMA 9) with Mw 1600 g/mol, and (d) Perfluoropolyether Dimethacrylate (PFPE-DMA 20) with Mw 4000 g/mol.

Mainly two standard mixtures were used. One corresponding to 49.3 vol% of PFDA, 49.3 vol% of PFPE-DMA (9 or 20) (50:50) and 1.4 vol% of D1173 (1 wt% of the photo-initiator in the mixture). The other mixture with 24.7 vol% of PFDA, 74 vol% of PFPE-DMA (9 or 20) (25:75) and 1.4 vol% of D1173 (1 wt% of the photo-initiator in the
mixture). The naming convention for this study is monomer-cross-linker-vol% e.g. PFDA:PFPE-DMA 9 – 25:75. In general samples containing 1 wt% D1173 were used.

The photo-absorbers selected for this study include: 2-(2H-benzotriazol-2-yl)-4,6-ditertpentylphenol, Tinuvin 328° (T328), and 2- [4-[2-Hydroxy-3-tridecylnoxypropyl]oxy]-2-hydroxy phenyl] -4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, Tinuvin 400° (T400), obtained from BASF Schweiz AG, 2-Hydroxy-4-n-Octoxy Benzophenone, Milestab 81 (Octabenzene), produced by MPI Chemie B.V. as and Bis-(2,3,4,5,6-pentafluorophenyl) methanone (Perfluorobenzophenone) purchased from Sigma-Aldrich.

Maximum solubility for all the photo-absorber was determined by adding different amounts of photo-absorber to several samples of PFDA:PFPE-DMA 9 – 25:75 + 1wt% D1173. The samples were heated to 40°C and mixed at 1200 rpm for 1 hour, and then allowed to cool down naturally. Samples completely transparent to the naked eye were defined as soluble. In general samples containing 0.037M Octabenzene were used.

**Sample preparation**

Glass samples of 3 by 3 cm were used as substrates. To enhance the adhesion and achieve covalent attachment of the polymer layer to the substrates, the surfaces were activated and functionalized as follows: First, a cleaning step was carried through sonication in acetone during 15 minutes. Subsequently, the samples were treated with UV-ozone (Ultra Violet Products, PR-100) for 20 minutes to activate -OH groups at the substrates surface. Following, the substrates are spin coated for 30 sec at 3000rpm with a solution of 1 vol% 3-(trimethoxysilyl) propyl methacrylate in a mixture 1:1 of water and isopropanol. As a final step the substrates were cured for 10 minutes at 110°C. **Figure 3** shows a graphical representation of the substrate preparation process. Glued cells were made consisting of a lower silane methacrylate modified glass slide and an upper cover slip (thickness No. 1, between 130µm to 160µm). The cells were subsequently capillary-filled with a monomer mixture.
Quartz samples of 3 by 3 were also prepared. However, for these only the cleaning step of sonication with acetone during 15 minutes was applied. After this, glued cells were made using a quartz piece for the bottom and one piece for the top or using a quartz piece for the bottom and a cover slip (thickness No. 1, between 130μm to 160μm) on top.

**UV irradiation**

The cells were put inside a nitrogen box with quartz glass on top and irradiated using a Thorlabs LED lamp with nominal wavelength of 310nm and with a dose of 180 mJ/cm² to ensure full polymerization.

**Characterization**

The Raman measurements were performed in a Horiba Raman fibre microscope Olympus BX40, using an oil immersion objective Olympus UplanApo 100x/1.35. Measurements in the vertical direction were done with a z-scan using steps of 0.92μm for 120s. Additionally one spectra measurement was done in the middle of the sample for 120s. The baseline procedure for all spectra was done using the software SpectraGryph from Spectroscopy Ninja by processing the spectra with an adaptive coarseness of 9 and 0 offset.

The ultraviolet-visible light spectroscopy measurements for the analysis of transmittance and absorbance were performed using an ultraviolet-visible spectrophotometer Shimadzu UV-3102 PC (UV/Vis). For the monomer mixture analysis a sample of PFDA:PFPE-DMA 9 – 25:75 using a path length of 1cm was used.
To ensure the validity of the linear relationship from the Beer-Lambert law diluted samples of the photo-initiator and photo-absorbers D1173 (0.0084M), T328 (0.0003M), T400, Octabenzene (0.0005M), Perfluorobenzophenone (0.0007M) on a monomer mixture of PFDA:PFPE-DMA 9 – 25:75 were used. The path length used was 1mm.

**Mechanical properties**

The storage and loss modulus of the fluoropolymers was measured using a TA instruments Q800 Dynamic Mechanical Analyser. Fluoropolymer films of different compositions were made in a PDMS mould of 30x8x1 mm. A temperature sweep between -140 and 150 °C was performed with a constant frequency of 0.2 Hz. Storage and loss modulus that are reported here are at room temperature (22°C).
Results and discussion

To obtain the aforementioned concentration gradient in a vertical plane, a light gradient is needed. Therefore, to calculate the light gradient the Lambert-Beer law was used. Using the UV/Vis spectrophotometer the absorption measurements were done for monomers and for monomer mixtures including photo-initiator and/or photo-absorbers. Figure 4 shows the absorbance spectra of the monomers and the monomers including the photo-initiator D1173.

![Absorbance spectra](image)

**Figure 4.** Absorbance spectra for a monomers mixture PFDA:PFPE-DMA 9 – 25:75 and for a sample with 0.0084M D1173 in a monomers mixture PFDA:PFPE-DMA 9 – 25:75.

Thus, with all the parameters known the extinction coefficients were calculated (Table 1). The specific wavelengths correspond to the wavelengths of the LED lamps used in this study (365nm and 310nm). As can be seen in Table 1 the extinction coefficient is wavelength dependent. Therefore, the values can drastically change from one wavelength to another. However, as was expected, the extinction coefficient of these molecules were not very high for the selected wavelengths.

Then, to be able to create a high gradient of light it was necessary to use a photo-absorber, which correspondingly has a high extinction coefficient. However, in addition to the extinction coefficient values, it is important to remember that the Lambert-Beer law relays also in the concentration of the absorbing species in the sample. This is a very important parameter because the monomer systems used in this study (monomers + photo-initiator) are based on fluorinated monomers, which can lead to solubility problems with many substances.
For this study several photo-absorbers, such as T328, T400, Octabenzone, and Perfluorobenzophenone were used. The maximum solubility of all photo-absorbers in the monomer mixture was determined. The results of maximum soluble concentration are shown in Table 1. From this analysis the photo-absorber T400 was already discarded because it was not soluble in the mixture. Correspondingly, the absorbance measurements (Figure 5) and the calculation of the extinction coefficient values for these components were performed (Table 1). As it was expected the extinction coefficient values were high, which it is necessary to achieve a light gradient through a thin coating.

<table>
<thead>
<tr>
<th></th>
<th>Max. soluble concentration [M]</th>
<th>ε [mol/(L*cm)]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>310 nm</td>
<td>365 nm</td>
</tr>
<tr>
<td>Monomer mixture</td>
<td>-</td>
<td>0.105 0.063</td>
</tr>
<tr>
<td>D1173</td>
<td>&gt;0.091</td>
<td>299 117</td>
</tr>
<tr>
<td>T328</td>
<td>0.011</td>
<td>18721 12013</td>
</tr>
<tr>
<td>T400</td>
<td>Not soluble</td>
<td></td>
</tr>
<tr>
<td>Octabenzone</td>
<td>0.037</td>
<td>9667 2353</td>
</tr>
<tr>
<td>Perfluorobenzophenone</td>
<td>&gt; 0.17</td>
<td>2791 1220</td>
</tr>
</tbody>
</table>

Table 1. Extinction coefficient values of photo-initiator D1173, and different photo-absorbers for two specific wavelengths. The maximum amount soluble in the monomer mixture is also indicated.

Figure 5. Absorbance spectra for different photo-absorbers in a monomers mixture PFDA:PFPE-DMA 9 – 25:75.
By using the Lambert-Beer law (see, Equation 2) and the determined values for extinction coefficient (Table 1) the transmittance as function of the path length was calculated, see Figure 6.

![Figure 6. Comparison of different photo-absorbers for transmittance vs thickness at 310nm.](image)

As can be observed in Figure 6, on a cell with thickness of 30μm, it was expected for T328 and Octabenzone to have about 19% and 7% of light transmittance at the back of the cell, respectively. It is important to highlight that the photo-absorber Octabenzone was able to create a higher light gradient in comparison to T328, due to solubility differences.

In addition to the light gradient, another parameter reported by Cook et al. to be considered is the amount of time available for the diffusion and counter diffusion of the monomers before vitrification; which is related with the rate of polymerization\textsuperscript{32}. If the polymerization is too fast, the diffusion time is too short to get a concentration gradient through the coating. However, although the polymerization process in this case was fast, according to the results of Kommeren et al. it was concluded that the available time for the diffusion was enough\textsuperscript{26}. Additional details about this aspect are shown in the Appendix section A2.

The Raman spectra of the two unpolymerized monomers are shown in Figure 7. For the cross-linkers (PFPE-DMA - 9 or 20) the characteristic peak at 825 cm\textsuperscript{-1} from the vibration of the C-O-C, was used to determine its presence. In the case of the PFDA the characteristic peak at 725 cm\textsuperscript{-1} corresponding to the vibration of CF\textsubscript{3} was used.
The peak corresponding to the vibration of the C=C bond for the methacrylate and the acrylate group was located at 1638 cm$^{-1}$ and it will be used as an indicator for conversion. Notice in Figure 8 that after polymerization the acrylate peak disappears completely indicating complete conversion, as was expected.

![Raman spectra](image)

**Figure 7.** Raman spectra of the unpolymerized monomers: **a.** PFDA and **b.** PFPE-DMA 9.

For further calculations all spectra were normalized using the peak of the OCH$_2$ group at 1451 cm$^{-1}$ as an internal reference (see, Figure 8). An internal reference must be a common parameter between both monomers and its intensity must be constant and independent of the fraction of the materials in the mixture.
Figure 8. Raman spectra of the polymers, a. PFDA. b. PFPE-DMA 9. The characteristic peaks for each one and the common are indicated. The lines are marked to help the reader in the comparison. The spectra for PFPE-DMA 20 is similar to PFPE-DMA 9 (Appendix section A1).

With the internal reference defined, the ratio between the peak integral of one of the characteristic peaks and the internal reference was calculated. In Figure 9 the Raman spectra for different monomer mixture ratios is depicted.

Figure 9. Variation of the peak intensity at 725 cm$^{-1}$, characteristic for PFDA. The selected internal reference, corresponding to the OCH$_2$ group, at 1451 cm$^{-1}$ remains almost constant through the samples of different mixture ratios.
It has to be noted that the analysis of the Raman spectra is quite sensitive to the procedure used to generate a baseline, which has a large influence on the intensity of the peaks. Moreover, the peak intensities are also very influenced by neighboring peaks. In this study, the analysis of the Raman spectra was done using the respective peak integrals and the ratio of the integrals between the characteristic peaks and the internal reference.

The calculated ratios between the peak integral of the CF$_3$ peak and the OCH$_2$ peak for different volume fractions of PFDA in the mixtures are shown in Figure 10. These figures are used as reference curves to characterize the composition of the coatings in the vertical (thickness) direction. Respectively, a high ratio value will be an indicator of a higher volume fraction of the PFDA. Oppositely, a lower ratio will be a reference for lower volume fraction of the PFDA. The hypothesis is that PFDA monomer will move towards the light source and lower values in the opposite direction as can be expected from Kommeren et al.$^{26}$. Furthermore, as was mentioned previously, the diffusion process depends on a balance between reactivity and mobility, and for this case the mobility of the PFDA is higher than the PFPE-DMA 9 or 20. Therefore, it diffuses faster than PFPE-DMA$^{29}$.

Figure 10. Reference curve for PFDA:PFPE-DMA 9, constructed using the ratio between the peak integral of peak at 725 cm$^{-1}$ and 1451 cm$^{-1}$ characteristic for CF$_3$ and OCH$_2$ groups, respectively (left) and reference curve for PFDA:PFPE-DMA 20, constructed using the ratio between the peak integrals at 725 cm$^{-1}$ and 1451 cm$^{-1}$ characteristic for CF$_3$ and OCH$_2$ groups, respectively (right).
The peak integral of the PFDA characteristic peak (CF\textsubscript{3}), the acrylate peak (C=\text{C}) and the internal reference peak (OCH\textsubscript{2}) as a function of the position in the vertical (thickness) direction of the coating for a system of PFDA:PFPE-DMA 9 - 47:53 are shown in Figure 11.

![Figure 11](image)

**Figure 11.** Peak integral variation through the thickness of the coating for a sample of PFDA:PFPE-DMA 9 - 47:53. The top of the coating is at 0 μm. The vertical red lines indicate the boundaries between the glass and the polymer.

As can be observed the CF\textsubscript{3} peak shows well defined boundary for the coating, however due to the probing volume the transition from the glass cell to the polymer was not sharp. The instrument has a probing volume of about 2 - 3 μm\textsuperscript{3}. Therefore, the data close to the boundaries was affected for both surroundings. In order to avoid misinterpretation because of this effect, it was defined that only data with value of the peak integral greater than the half of the maximum peak integral for each peak, within the coating region, will be considered.

The peak integral of the acrylate peak is shown in this case to illustrate complete conversion throughout the coating. At first glance seems to be a change in the peak integral for the CF\textsubscript{3}, and the opposite change can be observed also in the peak integral of the internal reference and even in the COC peak. This could be an indication of a gradient of concentration through the coating. However, it is known the laser intensity decreases with focus depth, so basically with the thickness of the coating. Therefore, to avoid this effect with focus depth the ratio of the CF\textsubscript{3} peak integral and the internal reference peak integral were calculated (Figure 12).
Figure 12. Variation of the ratio of the peak integrals between the CF₃ peak and the internal reference peak through the thickness of the coating for a sample of PFDA:PFPE-DMA 9 - 47:53.

Figure 12 shows that indeed there is a change in the concentration of the PFDA through the coating. By using the corresponding calibration curve to define the volume fraction of PFDA in the coating, the corresponding ratios calculated were transformed to volume fraction values (Figure 13).

Additional measurements using T328 were done. However, the results were not satisfactory and the ratio of the peak integral between the CF₃ peak and the internal reference peak remained constant through the thickness of the coating (see, Appendix section A3). This indicates that the light gradient from 100% to 19% in transmittance reached using T328 at its maximum soluble concentration in a cell with thickness of 30μm was not a sufficient light gradient to create a concentration gradient. Therefore, the photo-absorber T328 was discarded as an alternative and Octabenzone was used as photo-absorber during this study.

Figure 13. PFDA volume fraction profile for a polymer coating using a sample of PFDA:PFPE-DMA 9 - 47:53 with an induced light gradient (•) and without a light gradient (○).
It is worth to highlight that the PFDA volume fraction profile of the sample without a light gradient (green circles) can be considered as the starting point for the sample with a light gradient (blue squares). As was expected PFDA is the monomer that diffuses faster towards light source and a higher PFDA concentration at the top of the coating was achieved (0.526). Moreover, a PFDA volume fraction difference from top to bottom of almost 0.15 was obtained.

Following the same procedure measurements using different monomer mixture ratios were done. Figure 14 correspond to the results of photo-enforced stratification obtained for different monomer mixture ratios of PFDA:PFPE-DMA 9.

From the results in Figure 13 and Figure 14 it is possible to conclude that a photo-enforced concentration gradient was achieved for all monomer mixtures of PFDA:PFPE-DMA 9. The best results are obtained for the PFDA:PFPE-DMA 9 – 73:27 sample, where a difference of PFDA volume fraction higher than 0.2 between top (0.786) and bottom (0.565) was reached.
Figure 14. Photo enforced stratification results of the coating for a sample of PFDA:PFPE-DMA 9 - 26:74 (left) and PFDA:PFPE-DMA 9 – 73:27 (right). **a.** Peak integral variation through the thickness of the coating **b.** PFDA volume fraction profile. The top of the coating is at 0 μm. The vertical red lines indicate the boundaries between the glass and the polymer.

As the other cross-linker, PFPE-DMA 20, has a higher molecular weight and a longer chain, it was worth to evaluate if a higher concentration gradient can be accomplished because a higher difference in mobility in comparison with PFDA. Therefore, measurement using different monomer mixture ratios of PFDA:PFPE-DMA 20 were also performed. **Figure 15** corresponds to samples with different monomer mixture ratios of PFDA:PFPE-DMA 20.
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Figure 15. Photo enforced stratification results of the coating for a sample of PFDA:PFPE-DMA 20 – 27:73 (left), PFDA:PFPE-DMA 20 – 50:50 (center), and PFDA:PFPE-DMA 20 – 79:21 (right).

a. Peak integral variation through the thickness of the coating b. PFDA volume fraction profile.

The top of the coating is at 0 μm. The vertical red lines indicate the boundaries between the glass and the polymer.

The results in Figure 15 clearly show that a photo-enforced stratification was achieved for all monomer mixtures of PFDA:PFPE-DMA 20. However, in this case the best results were obtained for the sample of PFDA:PFPE-DMA 20 – 50:50 with a PFDA volume fraction difference higher of 0.3 from top to bottom. This supports the reason about how important the difference in mobility is in the diffusion and counter diffusion process to create a concentration gradient. Because the PFPE-DMA 20 has a longer molecule chain, the difference in mobility with PFDA is higher and thus a higher concentration gradient is enhanced.

Although the results for the sample PFDA:PFPE-DMA 20 – 79:21 show a difference of PFDA volume fraction of 0.13 from top to bottom, the difference between the PFDA volume fraction between top and bottom was less than the obtained with similar sample using the cross-linker PFPE-DMA 9. This could be due to the molecular size of the PFPE-DMA 20 is higher than the PFDA. Therefore, the solution becomes more viscous and this affects the mobility of the molecules within the mixture. Thus, the diffusion and counter diffusion of the molecules within the coating becomes more difficult diminishing the concentration gradient.
The previous results demonstrated clearly that the volume fraction for the monomers on top and bottom are different and that a concentration gradient has been reached using a photo-enforced stratification. A summary of the results is shown in Table 2.

<table>
<thead>
<tr>
<th></th>
<th>PFDA:PFPE-DMA 9</th>
<th>PFDA:PFPE-DMA 20</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFDA Vol. Fract. Starting</td>
<td>0.257</td>
<td>0.472</td>
</tr>
<tr>
<td>PFDA Vol. Fract. Top</td>
<td>0.316</td>
<td>0.526</td>
</tr>
<tr>
<td>PFDA Vol. Fract. Bottom</td>
<td>0.198</td>
<td>0.38</td>
</tr>
<tr>
<td>Delta Top-Bottom</td>
<td>0.118</td>
<td>0.146</td>
</tr>
</tbody>
</table>

Table 2. PFDA volume fraction after photo-enforced stratification for different monomer mixture ratios of PFDA:PFPE-DMA 9 and PFDA:PFPE-DMA 20.

Table 2 shows that the best results for photo-enforced stratification were obtained using the sample PFDA:PFPE-DMA 20 - 50:50 with a PFDA volume fraction difference higher than 0.3 from top to bottom, ranging from 0.638 to 0.332. In addition, the best results for the mixture PFDA:PFPE-DMA 9 were obtained with the sample PFDA:PFPE-DMA 9 – 73:27 with a PFDA volume fraction difference higher to 0.2 from top to bottom. By using the calibration curves, the profile of PFDA volume fraction within the coating was determined. These results for the samples PFDA:PFPE-DMA 9 – 73:27 and PFDA:PFPE-DMA 20 - 50:50 are shown in Figure 16. Additional results are presented in Appendix section A4.
Figure 16. Profile of PFDA volume fraction for a sample of PFDA:PFPE-DMA 9 – 73:27 with a maximum of 0.786 on top (T), minimum of 0.565 at bottom (B) and a starting point (S) of 0.730 (Left), and profile of PFDA volume for a sample of PFDA:PFPE-DMA 20 – 50:50 with a maximum of 0.638 on top (T), minimum of 0.332 at bottom (B) and a starting point (S) of 0.498 (Right).

Figure 16 shows the profile of PFDA volume fraction within the coating for a sample of PFDA:PFPE-DMA 9 – 73:27 and a sample of PFDA:PFPE-DMA 20 - 50:50. For PFDA:PFPE-DMA 9 – 73:27 a maximum PFDA volume fraction of 0.786 at top (T) and a minimum of 0.565 at bottom (B) were determined. For a sample of PFDA:PFPE-DMA 20 - 50:50, a PFDA volume fraction of 0.638 on top (T), and a minimum of 0.332 at bottom (B) were determined.

As the purpose of this study is to demonstrate the possibility of increase the damage resistance of fluoropolymers, therefore the storage and loss modulus of PFDA was measured. The storage and loss modulus for different volume fraction of PFDA with PFPE-DMA 9 and 20 can be observed in Figure 17. It can be seen that the lowest modulus corresponds for the mixture PFDA:PFPE-DMA 20 – 50:50 and higher modulus were achieved for PFDA:PFPE-DMA 9 – 5:95 and PFDA:PFPE-DMA 9 – 95:5. The U curve shape originates from the semi-crystalline structure of the PFDA after polymerization. Therefore, increasing the volume fraction of PFDA from 50% in the mixture makes the polymer more semi-crystalline, and therefore has an increase in storage modulus as was reported by Yao et al.37. A concentration gradient throughout the coating will lead to different storage modulus in top and bottom of the coating. Therefore, according with the necessary application it can be selected between a coating with a harder top layer and a softer bottom or vice versa.
Analyzing the storage and loss modulus graphs it is easy to see that the higher slope is located in volume fractions of the PFDA around 75% especially in combination with PFPE-DMA 9. Thus, the most potential candidate to achieve the aim of this work should be a sample with a volume fraction of PFDA around 75% with PFPE-DMA 9 because slight differences in composition will result in large differences in modulus.

The results for a sample of PFDA:PFPE-DMA 9 – 73:27 were analyzed in Figure 18. It can be seen that indeed the stratified sample allows to have different values for the storage and loss modulus through the coating.

The substantial difference in volume fraction between the bottom and the top of the coating allowed to observe and important change in the mechanical properties in Figure 18, from a lowest value about 37MPa and reaching a bit more than 159MPa
for the storage modulus. This means a difference of more than four times the storage modulus from the bottom to the top of the coating.

The mixture PFDA:PFPE-DMA 20 was analyzed as well to compare the results of the mechanical properties. The results for a sample of PFDA:PFPE-DMA 20 – 79:21 are shown in Figure 19.

**Figure 19.** Photo-enforced stratification results: Storage and Loss modulus for a sample of PFDA:PFPE-DMA 20 – 79:21 with an indication of the range covered by the stratified coating produced.

From Figure 19 it can be seen that for a sample of PFDA:PFPE-DMA 20 – 79:21 a storage modulus difference from top (159MPa) to bottom (75MPa) higher than 80MPa was achieved.

In order to give a complete overview of the topic with this study, additional samples with different monomer mixture ratios for PFDA:PFPE-DMA 9 and 20 were evaluated as well. A summary of the results is shown in Table 3. The detailed results are presented in Appendix section A5.
Table 3 shows that a difference from top to bottom for all the monomer mixture ratios was obtained. The highest increase of the mechanical properties was reached using the sample PFDA:PFPE-DMA 9 - 73:27, with storage modulus values ranging from 37 MPa at the bottom to 160 MPa at the top. This represents a 4-fold increase in storage modulus for the top of the coating. Using the sample PFDA:PFPE-DMA 20 – 79:21 highly satisfactory results were also achieved. A difference of 84 MPa between the storage modulus of the top and the bottom was obtained.

In addition, from Table 3 it is worth to highlight the results for the sample PFDA:PFPE-DMA 20 – 50:50. A maximum PFDA volume fraction of 0.638 at top (T) and a minimum of 0.332 at bottom (B) were determined. This is a substantial difference in volume fraction between the bottom and the top of the coating. At the same time, this significant difference allowed to observe and important change in the mechanical properties with a 4-fold increase in storage modulus for the top of the coating.
Conclusions

The purpose of this project was to demonstrate an alternative production technique that allows an increment of the damage resistance in fluorinated polymers. The large range of different moduli for monomer mixtures opened the possibility to tune the modulus at the top and bottom of the coating by using a gradient of light to induce a gradient of concentration. To achieve the desired concentration gradient, a UV light gradient was induced by the use of a photo-absorber.

Analysis of the extinction coefficient of different photo-absorbers were done to get an indication of the best photo-absorbers. Moreover, the solubility of the photo-absorbers with monomers was also performed. This allowed us to discard some photo-absorbers and highlight others. In the particular case of the photo-absorber T328 for example, despite the high values for extinction coefficient, the solubility constraints made that the gradient of light was lower than Octabenzone which has a lower extinction coefficient.

Using the maximum amount soluble of the photo-absorber Octabenzone, a sufficient light gradient able to induce a photo-enforced stratification was obtained. The photo-enforced stratification was proven using Raman spectroscopy and concentration gradients were observed for several samples. This concentration gradients were related with the mechanical properties in terms of storage and loss modulus.

Photo-enforced stratification has been achieved for all monomer mixtures with both cross-linkers. Using the sample PFDA:PFPE-DMA 20 - 50:50 a difference of PFDA volume fraction higher than 0.3 from top to bottom of the coating was achieved. Additionally, using the sample PFDA:PFPE-DMA 9 – 73:27 a difference of PFDA volume fraction higher than 0.2 from top to bottom of the coating was obtained.

In accordance with the photo-enforced stratification results, all monomer mixture ratios with both monomers show differences for storage and loss modulus.
from top to bottom of the coating. The significant difference in PFDA volume fraction achieved allowed to observe and important change in the mechanical properties. Using the sample PFDA:PFPE-DMA 9 - 73:27 a difference from top to bottom of the coating for storage modulus higher than 120MPa was achieved. This represents a 4-fold increase in storage modulus for the top of the coating, reaching 160 MPa. Moreover, using the sample PFDA:PFPE-DMA 20 – 79:21 a storage modulus ranging from 159 MPa to 75 MPa was obtained.

This results elucidate the generation of a sufficient gradient of light able to induce a photo-enforced stratification within a fluorinated polymer coating, which in turn allows to tune the mechanical properties for top and bottom of the coating in order to increase the damage resistance of the coating.
Outlook and recommendations

Additional alternatives to increase the light gradient looking for a higher concentration can be evaluated. Alternatives such as the increase of the path length, meaning the thickness of the coating, can be reviewed. However, it is worth to mention that additional aspects must be taken into account. For example, for the mentioned option, if the diffusion path is too big diffusion problems could diminish the desired concentration gradient. In addition, the fact that Octabenzone is also used as a photo-initiator is another parameter to study. This means that Octabenzone can be degraded during the reaction changing the light gradient over time.

Another point for future research can be related with a higher increase of the damage resistance properties. Therefore, similar studies using another monomer with a higher modulus to increase the damage resistance properties need further study. In general, monomers with a shorter chain (such as Methyl methacrylate) could be taking as a possible candidates. However, additional factors like compatibility of the system and possible future problems like delamination must also be considered.
References


Vertical photo-enforced stratification for more damage resistant antifouling coatings


Appendix

A1. Raman spectra PFPE-DMA 20

S1. Raman spectra of the polymerized monomer PFPE-DMA 20.
A2. Amount of time available and kinetic

A set up for the polymerization in situ on the Raman microscope was used. The results for conversion as function of dose for three different amounts of the photo-initiator in the system (PFDA:PFPE-DMA – 25:75) are shown in S2. Conversion was calculated following the progressive decrease on intensity for the characteristic peak at 1638 cm⁻¹, corresponding to C=C (Figure 4). Dose was calculated using Equation 3.

\[ D = I \times t \]

Equation 3. Dose (D) calculated in mJ/cm² as function of intensity (I) in mW/cm² and time (t) in seconds.

The intensity was also varied using two LED lamps with the selected wavelengths, 365nm and 310nm. However, in both cases the intensity is kept constant at 0.58mW/cm² and 0.20 mW/cm², respectively, and time was the variable as is shown in S2.

S2. Conversion versus dose of the system (PFDA-MD700-25): a. Using a 365nm LED lamp, with different weight percentage of the photo-initiator D1173, with constant intensity at 0.58 mW/cm². b. Using a 310nm LED lamp, with 1 wt% of photo-initiator D1173. The lines are depicted just to guide the reader.

From S2 (a) it can be seen the dramatic effect that the photo-initiator has on the kinetic of the system. Using the LED lamp of wavelength 365nm and with an intensity of 0.58 mW/cm², adding 1.18 wt% of photo-initiator to the system only 150s (87 mJ/cm²) were required to reach a 98.6% conversion. In the same way from S2 (b)
it can be seen that using the LED lamp of wavelength 310nm and with an intensity of 0.20 $mW/cm^2$, adding 1wt% of D1173 in to the system at the same 150s (30 $mJ/cm^2$) a conversion of 99% was reached. Even though it was a fast polymerization, from the study of Kommeren et.al. it was known that this amount of time is enough for the diffusion of monomers$^{26}$. Despite, the fact that Kommeren et al.$^{26}$ used a different photo-absorber, it was assumed the current polymerization times available are sufficient for diffusion and counter diffusion of the monomers.
A3. Results using the photo-absorber T328

Additional analysis about the effectivity of the light gradient generated using T328 were done. The peak integral of the PFDA characteristic peak (CF$_3$), the acrylate peak (C=C) and the internal reference peak (OCH$_2$) as a function of the thickness of the coating (increases going down from top through the coating to the bottom) for a system of PFDA:PFPE-DMA 9 - 57:43 + 1wt% D1173 + 0.011M T328 polymerized using the LED lamp of 365nm with intensity of 0.58 mW/cm$^2$ are shown in S3.

S3. Peak integral variation through the thickness of the coating for a sample of PFDA:PFPE-DMA 9 - 57:43 + 1wt% D1173 polymerized using the LED lamp of 365nm with intensity of 0.58 mW/cm$^2$. The thickness increases going through the coating from top to bottom. The peak integral of the acrylate peak is shown in this case to illustrate the grade of polymerization obtained. The values are around 0 and almost constant as was expected, indicating a complete polymerization in the whole coating. On the other hand, although there is an apparently change in the peak integral for the CF$_3$, this same change can be observed also in the peak integral of the internal reference and even in the COC peak. This is because the slight variation is due to a normal variation of the laser intensity of the microscope typical in these measurements in the perpendicular direction. Therefore, this results show that there was not a significant change in the peak integral of the CF$_3$ peak through the thickness, which indicates the concentration of PFDA has little, if any, change through the coating and therefore can be considered as constant in the whole coating. However, to avoid misinterpretations and to clarify doubts generated by the intrinsic variation of the laser intensity of the equipment, the
ratio of the peak integrals for the CF$_3$ peak and the internal reference peak was calculated (S4).

![Graph showing variation of ratio of peak integrals through thickness.](image)

**S4.** Variation of the ratio of the peak integrals between the CF$_3$ peak and the internal reference peak through the thickness of the coating. The blue line corresponds to a trend line.

The results for the ratio clearly show that indeed there was not a significant change, if any, on the concentration of the PFDA through the coating. Additionally, the trend line (blue line) has a corresponding slope of -2.46015*10$^{-4}$ and a standard error of 8.96504*10$^{-4}$, indicating no variation. Moreover, using the corresponding calibration curve to define the volume fraction of PFDA in the coating, a maximum volume fraction equal to 0.59 and a minimum of 0.55 were determined, supporting the previous results.

Since available diffusion amount of time was within the desired range it can be concluded that for the system analyzed in this study a gradient from 100% to 19% in transmittance reached using T328 at its maximum soluble concentration in a cell with thickness of 30μm was not a sufficient light gradient to create a concentration gradient and thus a higher gradient of light is necessary.
A4. Vertical photo-enforced stratification results


S5. Profile of PFDA volume fraction for a sample of PFDA:PFPE-DMA 9 - 47:53 with a maximum of 0.526 on top (T), minimum of 0.380 at bottom (B) and a starting point (S) of 0.472 (Left), and profile of PFDA volume fraction for a sample PFDA:PFPE-DMA 9 – 26:74 with a maximum of 0.316 on top (T), minimum of 0.198 at bottom (B) and a starting point (S) of 0.257 (Right).

From S5 it can be seen that for a sample of PFDA:PFPE-DMA 9 - 47:53 the PFDA maximum volume fraction corresponds to 0.526 at top (T) and the PFDA minimum volume fraction to 0.380 at bottom (B). For a sample PFDA:PFPE-DMA 9 – 26:74 a maximum PFDA volume fraction of 0.316 on top (T), and a minimum of 0.198 at bottom (B) were obtained.

Additional experiments for samples with different monomer mixture ratios of PFDA:PFPE-DMA 20 were performed. The result are shown below.
Photo-enforced stratification results: Profile of PFDA volume fraction for a sample of PFDA:PFPE-DMA 20 – 27:73 with a maximum of 0.313 on top (T), minimum of 0.219 at bottom (B) and a starting point (S) of 0.266 (Left), and profile of PFDA volume fraction for a sample of PFDA:PFPE-DMA 20 – 79:21 with a maximum of 0.856 on top (T), minimum of 0.725 at bottom (B) and a starting point (S) of 0.791 (Right).
A5. Mechanical properties

The results of storage and loss modulus after photo-enforced stratification for a sample of PFDA:PFPE-DMA 9 – 47:53 are depicted in the S7. Therefore, the maximum difference was about 15MPa and 2MPa for the storage and loss modulus, respectively.


The results of storage and loss modulus after photo-enforced stratification for a sample of PFDA:PFPE-DMA 9 – 26:74 are depicted in the S8.


This sample showed particular results because the increase in volume fraction of PFDA means a decrease in the storage modulus. Therefore, if the purpose was the same that with the other samples evaluated, this one should be used on the opposite direction. However, it could be also that other applications require a material with a softer top layer and a harder at the bottom.
Additional experiments for samples with different monomer mixture ratios of PFDA:PFPE-DMA 20 were performed. The result are shown below.

From the results for a sample of PFDA:PFPE-DMA 20 – 27:73 (S9), it can be seen that despite the variation in volume fraction of PFDA the storage modulus remained almost constant within this coating. This could be an interesting very soft material offering almost constant mechanical properties but with a gradient in concentration along the thickness.

![Graph S9](image1.png)

_S9. Photo-enforced stratification results: Storage and Loss modulus for a sample of PFDA:PFPE-DMA 20 – 27:73 with an indication of the range covered by the stratified coating produced._

The results for a sample of PFDA:PFPE-DMA 20 – 50:50 are shown in S10. A PFDA volume fraction difference of more than 0.3 from top to bottom was achieved. A maximum value of 0.638 at top (T) and a minimum of 0.332 at bottom (B) were determined. This is a substantial difference in volume fraction between the bottom and the top of the coating. At the same time, this significant difference allowed to observe and important change in the mechanical properties with a 4-fold increase in storage modulus for the top of the coating.
S10. Storage and Loss modulus for a sample of PFDA:PFPE-DMA 20 – 50:50 with an indication of the range covered by the stratified coating produced.