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Screening platform for identification of suitable monomer mixtures able to form thin-film coatings on polyurethanes by UV initiated free radical polymerization

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Abstract

Screening platforms have become a valuable tool for exploring large libraries of surface chemistries helping the discovery of new materials for especially biological applications. Methods applied in these platforms, however, are mainly based on inert bulk synthesis at picoliter scale, resulting in non-covalently attached molecules on stiff glass substrates. This is a poor representation of a potential final product from an industrial perspective. To overcome this, we have developed a screening platform capable of conducting UV-initiated free radical polymerization (FRP) directly onto a flexible polyurethane under ambient conditions. The platform allows for the study of solvent and monomer effects under industrially relevant conditions and was used to graft a series of homo and copolymer systems (2,2,2-trifluoroethyl methacrylate (TrFEMA), N-isopropyl acrylamide (NIPAAm), diethylene glycol methyl ether methacrylate-co-poly(ethylene glycol) methyl ether methacrylate, (MDEGMA-co-MPEGMA) and acrylic acid (AA)), which was confirmed by both water contact angle (WCA) and x-ray photoelectron

spectroscopy (XPS) analysis. The versatility of the system was further demonstrated through investigation of terpolymer systems, and direct evaluation of their antifouling properties using a fluorescein labeled bovine serum albumin (BSA).

Keywords: Screening; Surface initiated polymerization; Water contact angle; XPS; UV-grafting; Free radical grafting

Introduction

A determining factor for a material's potential application is its surface physical and chemical properties and being able to tailor these properties allows for a significant expansion of the range of application. Polymers are often used as inexpensive bulk materials with good mechanical properties, but do not necessarily comprise the desired surface properties. Especially, when used in biological environments, where there are specific requirements to surface chemistry and topology in order for the material to be compatible with the surroundings or promote certain interactions¹⁻⁴. The complexity of these systems makes discovery of novel materials a tedious and time-consuming process that requires testing of hundreds if not thousands of different formulations to find suitable candidates even through a rational design approach. To accelerate development and to illuminate non-intuitive structure-property relationships, use of screening platforms have become a popular method of choice either for determination of interactions with cells and proteins^{5,6}, enzymes⁷ or for determination of surface properties of polymers⁸⁻¹⁰. Large chemical libraries can be obtained through systematic and combinatorial mixing of compounds. For polymer grafting, such platforms are often based on automated picoliter scale synthesis conducted on glass slides under inert atmosphere¹⁰⁻¹⁴. The small scale allows for hundreds of samples to be placed on a single glass slide with minimum use of material. The small volume, however, imposes the

limitation that polymerizations are run under bulk conditions without the use of solvents. Such methods are therefore restricted to investigate monomer ratios and not effects of polymerization conditions such as concentrations and solvents. The inert conditions used during polymerization are also difficult to obtain at an industrial scale and therefore, to better simulate the final product, polymerizations should be conducted under ambient atmosphere. In addition, glass as a substrate cannot directly be compared to surface modification of polymer substrates, and such systems will therefore only be model systems. This is especially important when working with cell scaffolds where the flexibility of the matrix and substrate is very important for e.g. cell proliferation^{15,16}.

The aim of this work was therefore to develop a screening platform along with a suitable method able to conduct surface modifications under normal atmosphere directly onto a flexible polymer substrate for combinatorial investigations of both homo and copolymer systems. To further enable testing of solvents and monomer concentrations on a flexible substrate the design had to comprise chemical and heat resistant parts and with reaction vessel dimensions of at least microliter volume. The platform thereby presents the opportunity to screen polymer surface modifications and conditions through the use of an industrially relevant process.

Experimental

Materials

All chemicals and solvents were of analytical grade and were used without further purification as obtained from commercial suppliers, unless stated otherwise. Inhibitors were removed from the monomers prior to use by passing them through a short plug flow column of basic alumina.

Characterization

Water contact angle measurements were conducted on a Dataphysics Contact Angle System OCA 20. Static contact angles were measured on a droplet of 4 μl Millipore water. X-ray photoelectron

spectroscopy (XPS) was performed on a Thermo Fisher Scientific K Alpha (East Grinstead, UK) using monochromatized aluminum KR radiation in a 400 μm spot on the sample. Survey and high-resolution spectra were acquired and analyzed using the manufacturer's Avantage software package. Fluorescence intensity measurements and UV-vis spectroscopy was carried out on a POLARstar Omega from BMG Labtech, where fluorescence measurements were conducted using an excitation filter at 485 nm and an emission filter at 520 nm scanning across the surface in a matrix scan of 10x10. Differential scanning calorimetry (DSC) was performed on a DSCQ1000 from TA Instruments. The thermal analyses were performed at a heating and cooling rate of 10 K/min. The melting temperatures (T_m) are reported as the peak temperatures of the endothermic melting peaks. Glass transition temperatures (T_g) were measured at the inflection point.

One way analysis of variance (ANOVA) was done in Minitab 18 using the Tukey method with a 95% confidence interval in order to calculate statistically significant differences between a set of obtained values.

Preparation of the screening platform

The screening platform consists of two individual metal plates; a top plate (a) and a bottom plate (c) (see Figure 1). The top plate was made from aluminum with dimensions 127.7 x 85.5 x 7.0 mm and contains 96 wells with a diameter of 6.1 mm and 12 holes for screws with a diameter of 3.3 mm. On the bottom side of the top plate, metal rings around each well was milled in a height of 0.5 mm. Furthermore, the top plate was coated with an Accofal 2G54 Teflon coating from ACCOAT a/s. The bottom plate was made from stainless steel with dimensions of 127.7 x 85.5 x 3.0 mm.

Preparation and pretreatment of setup

A PU plate was cut into suitable dimensions and washed with first ethanol and then acetone and left to dry for a few minutes. The PU substrate was then placed between the top and bottom plate and fixed with screws. The setup was heated at 155 °C for 15 min and the screws were tightened before increasing the temperature to 160 °C for another 60 min. The screws were tightened once more and the setup was left to cool to room temperature.

Embedding of photo initiator

To each well 80 µl of a 0.5 M stock solution of Irgacure 2959 in THF/MeOH (1:4, v:v) was added. The solution was left to evaporate overnight in the dark, resulting in solvent casting of the photo initiator in the polymer surface.

General procedure for polymer grafting

A stock solution of 3.0 M acrylic acid in H₂O/MeOH (1:1, v:v) was made and 0-55 µl of this solution were added in to their respective wells. The solution was diluted with H₂O/MeOH (1:1, v:v) to give a total volume of 80 µl. The plate was left under orbital shaking for 5 min at 200 rpm at 25 °C in a Hettich Benelux Cooling Thermomixer MKR 13. Thereafter the plate was exposed to UV-light ($\lambda=365$ nm, 10 mW/cm²) for 30 min. at 25 °C under continued shaking at 200 rpm. Thereafter, the reaction mixture was removed, and wells were washed excessively with solvent (H₂O/MeOH (1:1, v:v)). In addition, all wells were refilled with pristine solvent mixture and left shaking at 200 rpm at RT for 15 min. The rinsing procedure was repeated with H₂O, where after the wells were filled with H₂O and shaken at 200 rpm at RT for 15 min to remove any residual solvents. The top plate was removed and replaced with an aluminum frame, which was fixed with screws and covered with aluminum foil. The setup was left to dry in vacuum oven at RT overnight. All samples were conducted in triplicates. Different solvents were used for specific monomers as

follows: AA : H₂O/MeOH (1:1, v:v), NIPAAm : H₂O/MeOH (1:1, v:v), MDEGMA-co-MPEGMA 500 : H₂O/MeOH (1:1, v:v), TrFEMA-co-MAA-co-MPEGMA 500 : EtOH.

Anti-fouling test

A surface was exposed to a solution of 0.04 mg/ml fluorescein labeled BSA in PBS buffer and left for 2 h at RT. The plate was covered with aluminum foil to reduce evaporation and to prevent the solution from drying out. The sample was then washed excessively with PBS buffer and dried in air. The fluorescence intensity was measured using an excitation wavelength of 485 nm and emission wavelength of 520 nm.

Results and Discussion

To enable testing of different polymerization conditions, an inert holder that would allow parallelization of experiments in separate vessels, was required. As an additional restraint, the intended platform was required to be able to handle a broad range of solvents as well as to be suitable for semicrystalline plastics such as polyurethanes with melting points above 150°C. The design of the platform was based on a standard 96 well microtiter plate and was divided into three separate parts as can be seen in Figure 1.

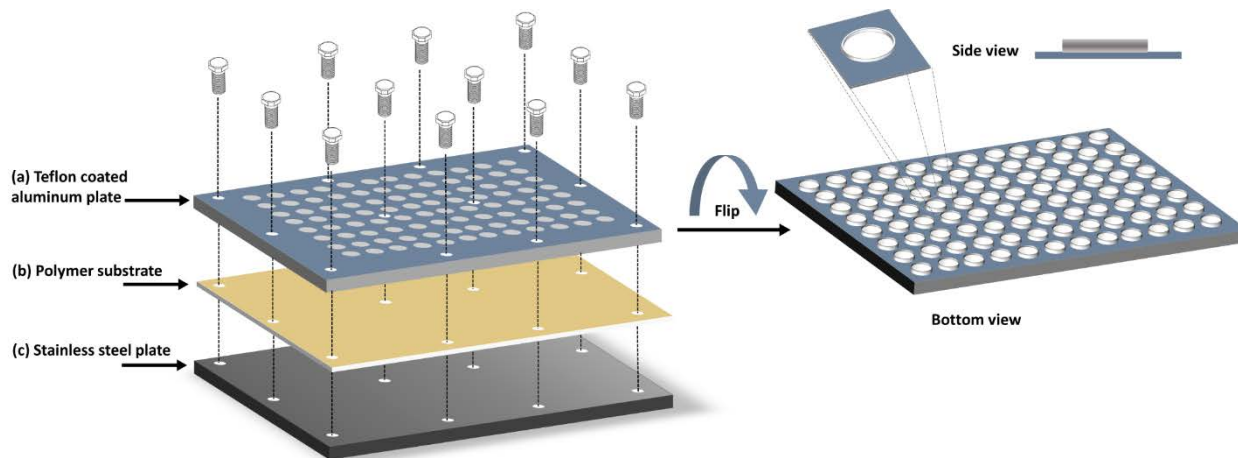


Figure 1. Schematic representation of screening platform (left) and bottom view showing milled edges around the wells (right), where a is the well plate, b is the polymer substrate and c is a supporting stainless steel plate.

The top plate (a) were made from aluminum and comprises 96 wells with an inner diameter of 6.1 mm and a height of 7.0 mm giving a well volume of approximately 200 μ l. The well size in this platform permits microliter scale experiments, opening the possibility to investigate the influence of solvents as well as monomer concentrations. A Teflon coating was applied to plate (a) to provide a non-stick surface, allowing it to be detached after polymerization without compromising the grafted surface and to access the samples for analysis. The coating also makes for an easy-to-clean surface, permitting it to be re-used after each experiment. When assembling the setup, the polymer substrate (b) was placed in-between plate (a) and the steel support (c) and held together by screws. Having the polymer as a separate part makes switching between substrates a simple process within one platform, making it possible to test the same conditions on various materials. The only requirement being, that the substrate can be made into a film or sheet. To prevent leakage and potential mixing of contents a tight seal between polymer and plate (a) was secured with a thin metal rim around each well on the bottom side of plate (a) (see Figure 1, right). During the thermal treatment, the setup is heated to 160 $^{\circ}$ C, just below the melting point of the polymer, which in this case is a PU ($T_m = 166$ $^{\circ}$ C). This softens the substrate and in combination with pressure from the screws, allows the metal rims to submerge into the polymer film, effectively sealing off each chamber. The high temperature treatment additionally also straightened out any unevenness in the film resulting from processing ensured a good adhesion of the polymer film to the stainless steel support. Such unevenness in film thickness commonly result from release of internal stress after processing, which it is critical to remove to ensure an efficient sealing across the entire surface.

Therefore, the heat treatment was important with respect to both sealing the system and to obtain a flat homogeneous surface.

Activation of and Grafting onto Polyurethane

Most polymer surfaces are inert by nature and require activation through implementation of functional groups or initiating species to facilitate modification by polymerization. This can be done through a stepwise activation and subsequent polymerization as is commonly done by use of controlled radical methods such as surface initiated atom transfer radical polymerization¹⁷⁻¹⁹, which provides high control for modification of surfaces²⁰⁻²². Such processes typically requires inert conditions, which is not always possible in an industrial setting. In this case, we have evaluated the use of direct grafting using photo initiators under ambient conditions using the screening platform. Such systems have been applied for modification of polymer surfaces^{23,24}. Some monomers are more tolerant to oxygen during polymerization, and identification of such systems would be of significant industrial interest for coating applications of thin surface coatings. Therefore, the polymer surface was activated for polymerization by embedding a photoinitiator, Irgacure 2959, into the polymer surface by solution casting, as shown in Figure 2.

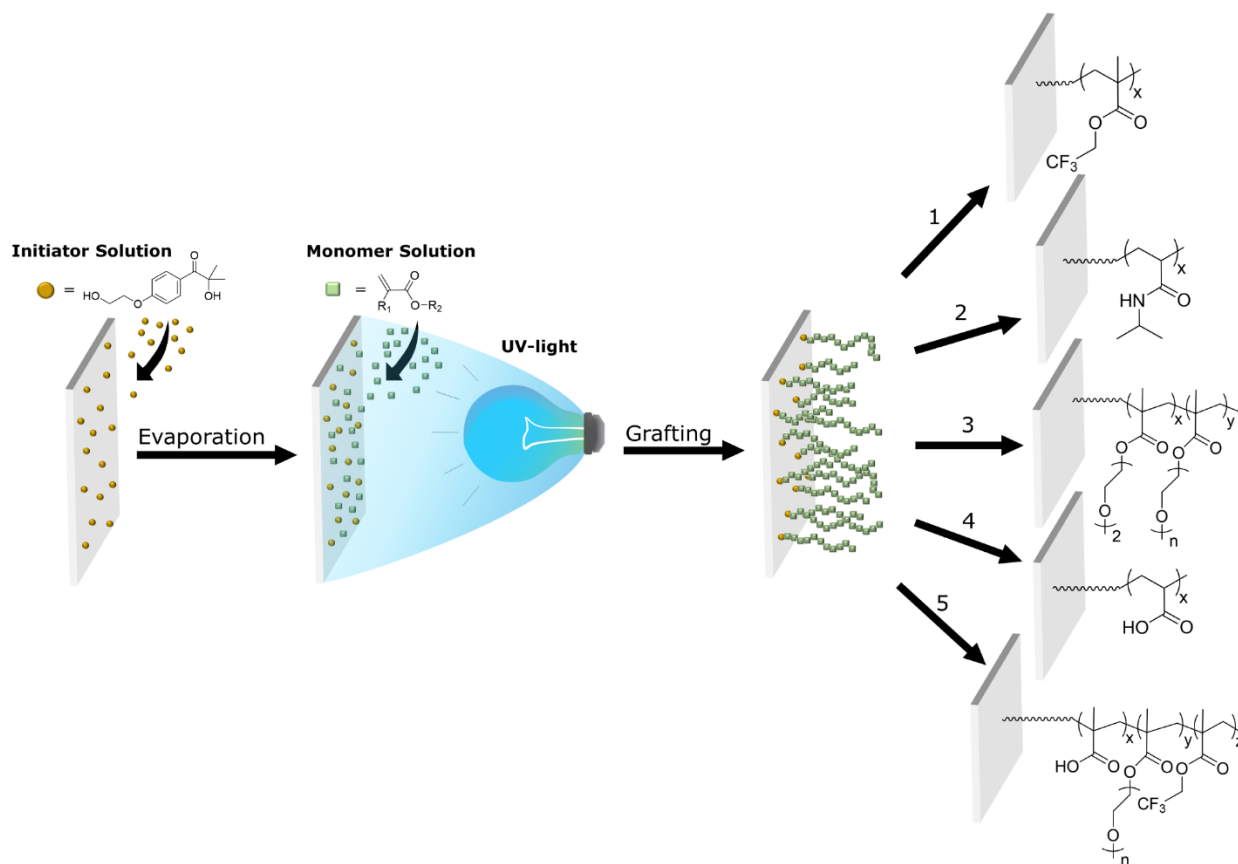


Figure 2. Schematic representation of embedding of photo initiator into polymer substrate followed by grafting of monomer through UV-activation. The illustrated surface modifications are 1) 2,2,2-trifluoroethyl methacrylate (TrFEMA), 2) N-isopropyl acrylamide (NIPAAm), 3) Diethylene glycol methyl ether methacrylate-co-poly(ethylene glycol) methyl ether methacrylate, Mn=500 (MDEGMA-co-MPEGMA 500), 4) Acrylic acid (AA), 5) MAA-co-MPEGMA 500-co-TrFEMA.

The initiator was dissolved in a mixture of THF/MeOH (1:4, v:v), where THF serves the purpose of slightly dissolving the PU substrate, while MeOH swells it. Due to this combination of solvents, solution casting of the photoinitiator solution onto the PU surface, results in embedment of the photo initiator into the outer layers of the surface. Subsequently, it can be functionalized through photoinitiated free radical polymerization with various monomer solutions. By exposing the entire

system to UV-light, grafting of monomers from and into the polymer surface takes place, resulting in formation of thin layers of surface grafted polymers as illustrated in Figure 2. Through this method, the formation of radicals are mainly occurring in close proximity to the surface of the substrate. This therefore limits the formation of non-grafted homopolymer compared to having the initiator added as a reagent in solution. This was also confirmed by analysis of the polymerization solutions after grafting, which contained no detectable amounts of free polymer (by SEC and NMR). After completed surface grafting, the detachable top plate (a) can be removed, enabling the surface to be analyzed by various classical analytical tools for surface analysis, such as WCA measurements, XPS as well as fluorescence intensity spectroscopy and UV-Vis spectroscopy. Since the top-plate is only mechanically bonded, it is possible to disassemble the structure without risking polluting the surface with polymer fragments originating from adhesives or other types of sealants as is commonly used in other applications.

To investigate the possibilities of grafting commonly used acrylic and methacrylic monomers onto surfaces under ambient conditions, a range of different monomers were attempted grafted to the PU surface using UV initiated free radical polymerization. Initially, acrylic acid (AA) was grafted to the PU using a series of AA feed concentrations in an attempt to create a hydrophilic surface by introduction of carboxylic acid functionalities. Investigations of the effect of feed concentration with respect to hydrophilicity and elemental surface composition were done through WCA and XPS analysis, which can be seen in Figure 3 A and D, respectively. The WCAs obtained for the grafted surfaces ranged between 89-40°, which is substantially lower than that of the pristine polyurethane surface (104°). The lowest WCA of 40° was observed at 1.31 M, reflecting a clear shift from a hydrophobic to a hydrophilic surface, and at the same time illustrating the importance of testing of different concentrations of monomers for surface grafting reactions. The grafting was

further confirmed by XPS (Figure 3 D), showing higher oxygen content and no nitrogen atoms in the surface, corresponding to the structure of a surface grafted layer of poly(AA). This was further corroborated by FT-IR measurements of the grafted polymers (SI-Figure 2). The presence of surface grafted AA was confirmed by a broad OH stretch for all samples ($2300\text{-}3600\text{ cm}^{-1}$), as well as a characteristic change to the carbonyl stretch resulting from the carbonyl in AA (1700 cm^{-1}). In addition, also the effect of increasing the AA concentration in the feed, was reflected in an increasing strength of the bands assigned to the PAA. In addition, WCA measurements (Figure 3 A), show a trend of decreasing contact angle with increasing monomer concentration, suggesting a higher degree of polymerization at higher monomer concentrations (as expected). ANOVA analysis revealed significant differences not only between the pristine and modified surface but also between individual monomer concentrations, which distribute into three separate groups. Concentrations from 0.19 to 0.56 M group together in category A along with the pristine surface, showing that these concentrations only led to a minor change in surface hydrophilicity. Experiments conducted at concentrations of 0.75 M to 0.91 M, showed some impact on the WCA and were grouped together in the intermediate category BC. At high concentrations of 1.31, 1.69 and 2.06 M a clear impact of grafting was observed by significantly reduced contact angles, and these group together in group E, CDE and DE respectively.

Coatings containing poly(ethylene glycol) (PEG) have been of great interest in the field of biomedical devices both due to their ability to create low friction surfaces but also their biocompatibility and being FDA approved²⁵. Through parallelization in the screening platform, copolymers of diethylene glycol methylether methacrylate (MDEGMA) and poly(ethylene glycol) methylether methacrylate (MPEGMA 500) were therefore prepared at various feed ratios of the two monomers. The relation between feed composition and WCA was investigated along with

XPS analysis as shown in Figure 3 B and E, respectively. A decrease in WCA was observed as MDEGMA was replaced with increasing amounts of MPEGMA ($M_n=500$ g/mol) throughout the series. This was expected due to the longer PEG side chain in MPEGMA, resulting in a more hydrophilic monomer. However, only a minor decrease in contact angle from 104° for the pristine surface to 101° at 100 mol% MDEGMA was seen, which reduced to 66° for the 6.25/93.75 mol% MDEGMA/MPEGMA copolymer. In general, one would expect a much lower contact angle for these hydrophilic monomers. Similarly, the XPS data (See Figure 3 E) only showed a minor increase in oxygen, while the nitrogen peak from the PU substrate was still visible. In combination, this indicates that only a very thin coating of the hydrophilic monomers was formed on the PU. This was also corroborated in the FT-IR data (SI-Figure 4), where no significant differences were observed, though the similarity in composition of the monomers and the PU substrate makes small differences difficult to confirm. The statistical analysis of the WCAs, showing that no significant difference can be found between the pristine and modified surfaces, which all belongs within group A with the exception of 6.25 mol% MDEGMA, even though a general trend of decreasing WCA was observed across the series. Grafting under ambient conditions can therefore only be concluded to result in a very thin layer of poly(PEGMA) or poly(MDEGMA), though this is sufficient to change the immediate surface chemistry (WCA measurements).

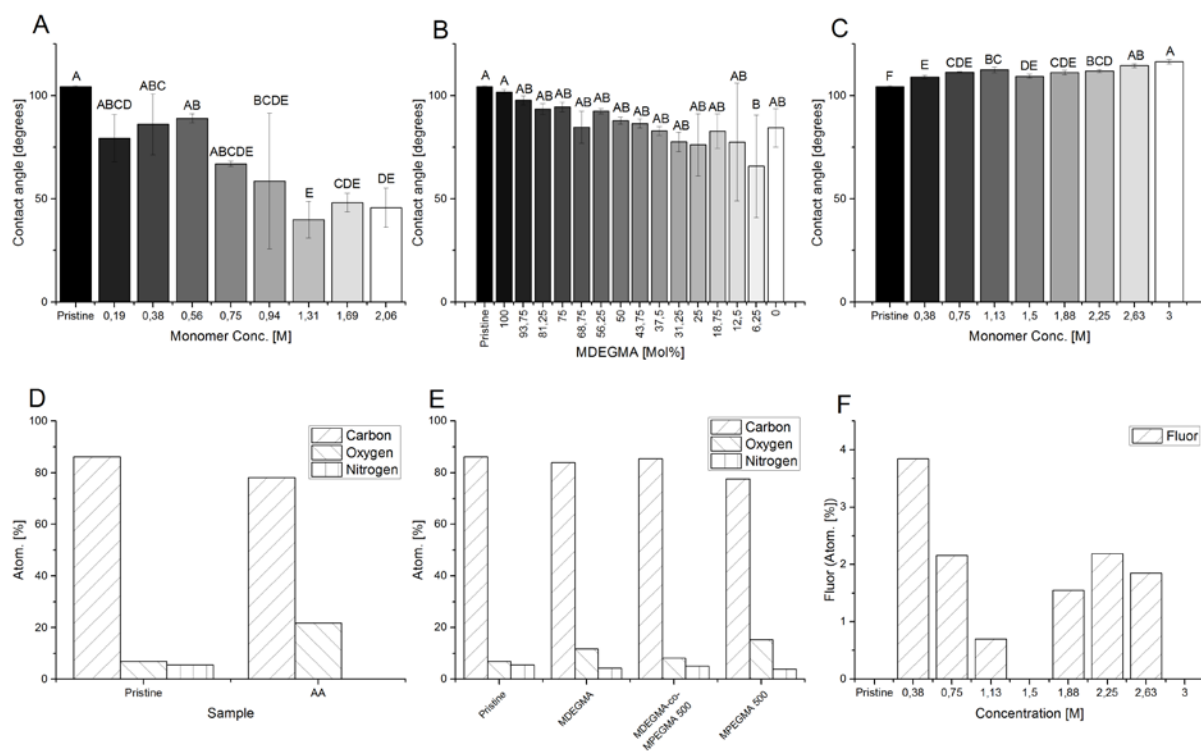


Figure 3. WCA and XPS data of PU surface modified with AA (A and D), MDEGMA-co-MPEGMA 500 (B and E) and TrFEMA (C and F) respectively.

Conversely, hydrophobic surfaces can be prepared through grafting of fluoride containing monomers. As an example of a fluorinated monomer, 2,2,2-trifluoroethyl methacrylate (TrFEMA) was grafted at various monomer feed concentrations to create a low energy surface. The WCA and the atomic fluor composition of the surface were measured and the results can be seen in Figure 3 C and F, respectively. The contact angle increased with increasing monomer concentration from 109° at 0.38 M to 116° at 3 M. The pristine surface was assigned by ANOVA analysis to group F, which does not appear at any of the data points obtained, indicating that all modified surfaces were significantly different from the pristine surface. Even at low concentration of 0.38 M, the contact angle was significantly different to that of the pristine surface. The trend shown for the WCA measurements, indicates an increasing hydrophobicity of the surface, which would be expected to

correlate with an increasing fluorine content. However, XPS analyses of the surfaces showed that this was not the case (Figure 3 F). Fluorine is seen for most of the samples, though the concentration does not appear to follow a trend. Optical microscopy images of the samples (Figure 4) reveal that this is due to an uneven coverage of polymer on the surface. The grafting conducted on the surface was incomplete and formed aggregates, which are seen as black dots in Figure 4.

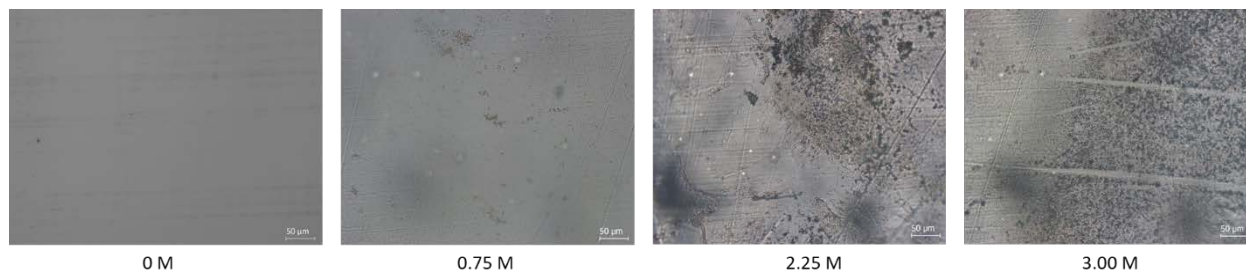


Figure 4. Microscopy images of TrFEMA modified PU at monomer feed concentrations of 0, 0.75, 2.25 and 3.00 M.

The aggregates increase in size and become more dominant with increasing monomer concentration, explaining the increase in WCAs. Analyzing the surfaces by FT-IR only showed insignificant changes in the spectra with increasing concentration, reflecting the incomplete reaction of the monomer. In conclusion, the fluorine monomer cannot be grafted in a homogeneous layer under ambient conditions even though the polymerization does result in a minor increase in the WCA.

A similarly often used monomer is N-isopropylacrylamide (NIPAAm), which, in addition to changing hydrophilicity upon thermal stimuli in solution, have been shown to have great potential for controlled drug delivery systems and nanofiltration membranes^{26,27}. The polymer in solution has a lower critical solution temperature (LCST) of 31-33°C, resulting in hydrophobic properties above this point and hydrophilic properties below. The transition is caused by a rearrangement of the polymer chains starting as a linear conformation at low temperature, where amide groups are able to form hydrogen bonds to water. Increasing the temperature creates inter and intramolecular

hydrogen bonds, forcing the polymer into a coiled structure, leaving only the hydrophobic backbone exposed. Grafting of the monomer was similarly conducted in a series of monomer feed concentrations with subsequent WCA and XPS analysis as presented in Figure 5 A and B respectively. To show that the thermoresponsive properties can be transferred to the polymer surface, the WCA of the NIPAAm modified PU was also measured both above and below the LCST (see Figure 5 C).

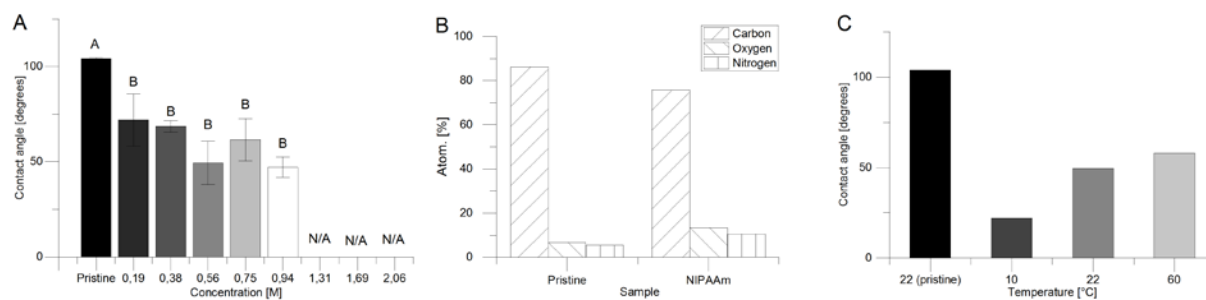


Figure 5. WCA of NIPAAm modified PU at various monomer feed concentration (A), XPS data (B) and WCA at various temperatures (C).

NIPAAm concentrations were varied within the range of 0 - 2.06 M in the feed and from this experiment, an important limitation concerning monomer concentration was observed. When the NIPAAm concentration was increased above 1 M, cross-linking occurred, resulting in large gel formations on the surface (see SI-Figure 1). The gels did not adhere well to the substrate and had poor mechanical stability. This demonstrates that the monomer concentration is an important parameter to consider and has great influence for the outcome of the polymer coating. Due to this cross-linking at high monomer concentrations, the XPS analysis was therefore carried out at 0.56 M, below the gel point. From Figure 5 B, the ratio between oxygen and carbon (O/C) and nitrogen and carbon (N/C) can be calculated to 0.15 and 0.12 respectively. This corresponds to that of NIPAAm, which have an O/C and N/C ratio of 0.14. This was also corroborated by FT-IR (SI-

Figure 5), where a clear NH stretch (3300 cm^{-1}) was seen for all concentrations below the gelation point. The thermoresponsive properties were observed by WCA measurements for one of the surfaces (NIPAAm, 0.56 M). At high temperature (60°C), the modified surface showed a WCA of 59° , which was reduced to only 22° at 10°C (Figure 5 C). This clearly show that the surface is thermoresponsive, though the transition appear at lower temperatures, compared to the typically observed LCST for NIPAAm. LCSTs have been seen to vary according to molecular weight and structure of the polymer, and it is hypothesized that this may be the reason for the observed deviation.

Overall, it can be concluded that some monomers (AA, NIPAAm) effectively can be grafted in homopolymerization to the PU surface under ambient conditions, while others are less efficient (PEGMA, MDEGMA and TrFEMA).

Anti-fouling Amphiphilic Surface

Screening platforms are ideal for creating large libraries of complex systems in combination with parallelized analysis. To illustrate the possibility to do combinatorial studies, three monomers were tested a surface coating, methacrylic acid (MAA), 2,2,2-trifluoroethyl methacrylate (TrFEMA) and MPEGMA 500. The selection was based on the fact that polymer coatings comprising both hydrophobic and hydrophilic segments have proven to be effective in preventing fouling from e.g. marine life²⁸⁻³⁰. The intention of this study was therefore to investigate the optimal formulation to prevent fouling against a fluorescein labeled bovine serum albumin protein (BSA). For each monomer, stock solutions of 1 M concentration in EtOH were made and the ratio of monomers were systematically varied throughout three sets of terpolymer systems named A, B and C (see Figure 6 A, B and C). The sets all contained different base levels of MPEGMA 500 at 12.5, 25.0 and 37.5 mol% for A, B and C respectively. Tuning the hydrophobicity was done by

adding MAA and TrFEMA in various ratios to give nine formulations for each set, providing a total of 27 formulations. The obtained WCA and fluor content from XPS of each formulation for A, B and C can be viewed in Figure 6, D-F and G-I respectively.

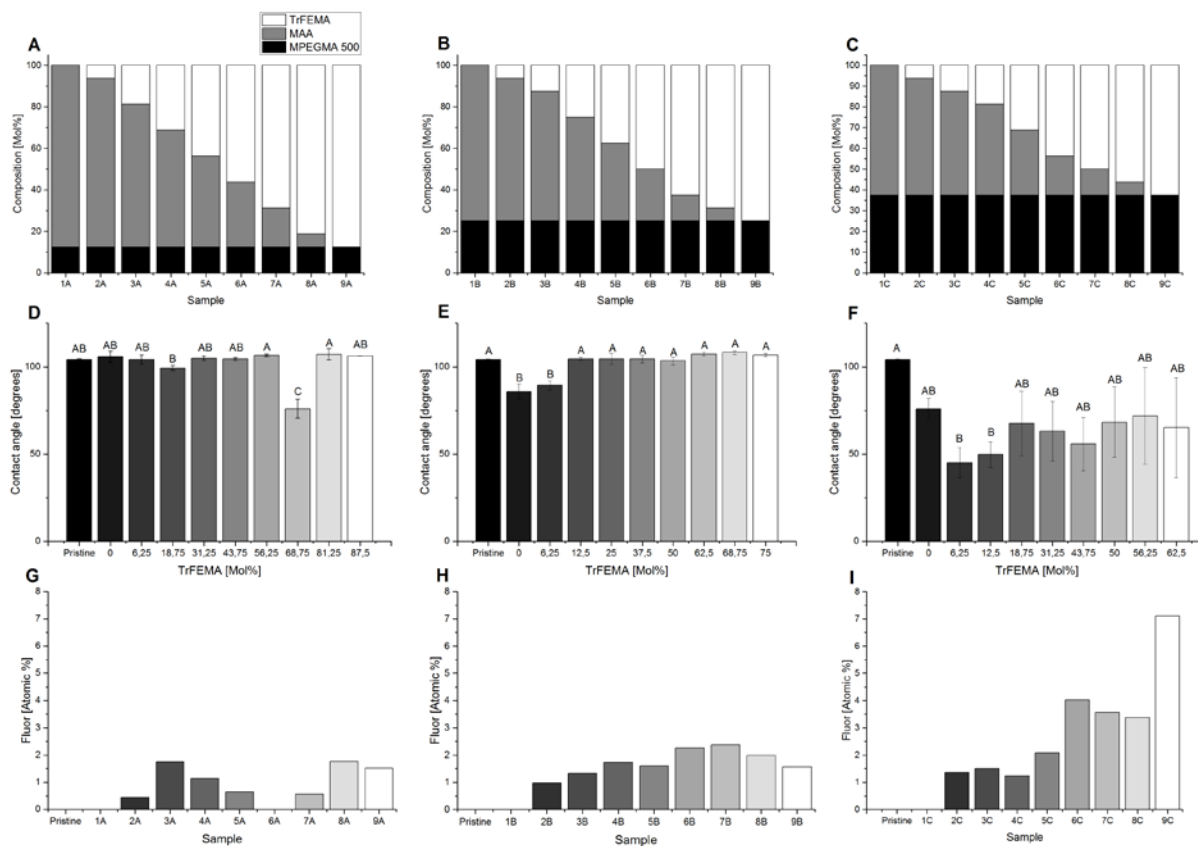


Figure 6. Composition of terpolymer set A, B and C, black: MPEGMA 500, grey: MAA and white: TrFEMA (A, B and C) and their respective WCA (D, E and F) and XPS data on fluor content (G, H, I).

The outcome of the WCA of terpolymer set A and B was heavily influenced by the presence of hydrophobic TrFEMA, even at small feed concentrations (see Figure 6 D and E). The contact angle of the samples barely deviated from that of the pristine surface, which was also seen from the ANOVA analysis. This was an unexpected result, considering that both MAA and MPEGMA 500 are both hydrophilic and present in high concentrations and a lower contact angle should be

observed. A minor exception to this was the samples at 0 and 6.25 mol% TrFEMA in Figure 6, E, which obtained a WCA of 85 and 90° respectively. The ANOVA analysis shows that the contact angles are significantly different to that of the pristine surface, but quickly rises to above 100° at 12.5 mol% TrFEMA (see Figure 6 E).

For terpolymer C, however, the higher MPEGMA 500 content of 37.5 mol% was enough to counteract the hydrophobic effects of TrFEMA, resulting in a substantial drop in WCA (see Figure 6 F). The high content of MPEGMA 500 additionally increased the observed hysteresis of the systems illustrating the amphiphilicity of the surface. Therefore, no significant difference between the modified and the pristine surface was found from the ANOVA analysis, with the exception at 6.25 and 12.5 mol% TrFEMA (see Figure 6 F).

Figure 6 G, H and I, illustrates the level of fluor in each sample for terpolymer set A, B and C, respectively. A linear trend with a steady increase in fluor with respect to increasing mol% of TrFEMA was expected for all terpolymer systems, but only terpolymer C showed this trend clearly. In Figure 6 G, the fluor content is very low and the grafting appears to be sporadic, whereas for Figure 6 H, a trend was initially seen but with the last two samples slightly decreasing. Terpolymer set C obtained a gradual increase in fluor with a maximum of 7.1 atom%. This is attributed to TrFEMA copolymerizing better with MPEGMA 500 than MAA. Between the three sets of surfaces, a higher content of fluor is therefore seen for higher contents of MPEGMA 500. To test the anti-fouling properties, the modified surfaces were exposed to a 0.04 mg/ml fluorescein labeled BSA protein phosphate-buffer saline (PBS) solution. The mean value of the resulting intensity for terpolymer set A, B and C can be seen in Figure 7 A, B and C respectively.

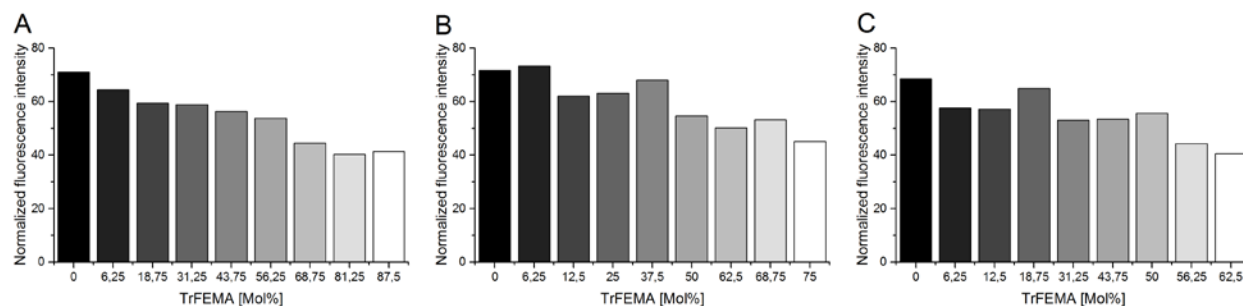


Figure 7. Fluorescence intensity of adsorbed fluorescein labeled BSA of terpolymer set A, B and C (A, B and C respectively) after 2 h. exposure to a 0.04 mg/ml PBS solution.

Comparing the analytical data and the obtained anti-fouling study showed that copolymers purely of MPEGMA 500 and TrFEMA gave in general the best fouling resistance for all terpolymer systems. The lower the feed concentration of MAA was, the better the fouling resistance became. An intuitive explanation would be that MAA was able to create either hydrogen bonds or electrostatic interaction with the protein through carboxylic acid groups (COO^-/COOH). Thereby, even small contents of MAA would create binding sites for the protein to adhere.

Conclusion

A new screening platform capable of modifying a thermoplastic polyurethane via UV-initiated FRP under ambient conditions was developed. The setup comprises 96 reaction wells and was demonstrated with a series of acrylate and methacrylate monomers using both WCA, FT-IR and XPS data to validate the outcome of the polymerizations. The system allowed for investigations of the influence of feed concentration in relation to surface wettability. Through ANOVA, a clear correlation between WCA and feed concentration/composition were found for AA, MDEGMA-co-MPEGMA 500 and TrFEMA. However, XPS showed that grafting of MDEGMA-co-MPEGMA 500 and TrFEMA was found to be inefficient, leading to aggregates on the surface in the case of TrFEMA. Additionally, for NIPAAm systems, it was found that concentrations above

0.94 M resulted in crosslinking and proved to be an important factor for optimal grafting for this type of monomer, underlining the importance of screening polymerization conditions. Finally, a combinatorial screening of amphiphilic terpolymer systems comprising TrFEMA-co-MAA-co-MPEGMA 500 was conducted, illustrating how combining monomers can beneficially improve the outcome of the polymerizations under ambient conditions. For the terpolymers, compositions containing MAA had higher protein adhesion compared to those consisting only of TrFEMA-co-MPEGMA 500. This was attributed to hydrogen bonding/ionic interactions through the carboxylic moiety of the MAA.

The platform can be adapted to fit different polymer substrates and is resistant to both heat and chemicals and represents a new and useful tool in the discovery of novel surface modifications for polymeric materials in an industrially relevant setting.

Acknowledgement

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Supporting Information: Picture of gelled NIPAAm polymerization (Figure S1), FT-IR spectra of grafted surfaces (Figure S2-S6).

Table of Contents graphic:

