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Deposition of NonFouling Plasma Polymers to a Thermoplastic Silicone Elastomer for Microfluidic and Biomedical Applications

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ABSTRACT: Plasma polymerization is used for the modification and control of surface properties of a highly transparent, thermoplastic elastomeric silicone copolymer, GENIOMER® 80 (G80). PEG-like diglyme plasma polymer films were deposited with ether retentions varying between 20% and 70% as measured by X-ray photoelectron spectroscopy analysis which did not affect the transparency of the substrate. Films with ether retentions of greater than 70% inhibit protein binding (bovine serum albumin and fibrinogen) and cell proliferation. A short oxygen plasma pretreatment enhances the adhesion and stability of the film as shown by protein binding and cell adhesion experiments. The transparency of the material and the stability of the coating makes this material a versatile bulk material for technical (e.g., lab-on-a-chip) and biomedical (e.g., intraocular lens) applications. The G80/plasma polymer composite is stable against vigorous washing and storage over 5 months and, therefore, offers an attractive alternative to poly(dimethylsiloxane).
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INTRODUCTION

To date, poly(dimethylsiloxane) (PDMS) has been a material especially well adapted for the fabrication of microsystems and is used as a component for the fabrication of optical lenses for biomedical applications.[1,2] The flexibility of PDMS is suitable for the integration of actuators such as microvalves and micropumps into microfluidic systems.[1,3] In the case of biomedical lenses, flexibility is needed during surgery, for optimal accommodation in the eye and for wearing comfort. In both applications, PDMS-based materials have the disadvantage of poor control of surface properties.[1,3] Therefore, alternatives to PDMS have been investigated including polystyrene, polyethylene terephthalate, and fluoropolymers.[4,5]

GENIOMER® 80 (G80) is a relatively new potential candidate material that contains more than 90% siloxane. It is composed of silicone/urea copolymer with a silicone soft segment and organic hard segment. It is highly transparent due to its silicon nature and does neither contain any plasticizers nor reinforcing fillers. G80, as well as PDMS, is inert and rather biocompatible (at least for *in vitro* applications) and has similar mechanical properties to PDMS making it suitable for soft lithography fabrication. G80 can be processed as a thermoplastic which is an advantage over PDMS for large scale production. G80 is currently used for encapsulating photovoltaic cells[6] and as a filler in wood composites[7] but has not been used for biomedical or microfluidic applications to date.

One major disadvantage common to most polymers used for microfluidics and biomedical applications is their high affinity for cell attachment and low surface energy.[8] Silicone resins and polymers exhibit high affinity for proteins which then promote cell attachment and proliferation. Endowing surfaces with nonfouling properties is important in a diverse range of applications, such as, in the marine industry,[9] microfluidic channels,[10,11] dental implants,[12] and biomedical devices.[13] For microfluidic and biomedical applications, ultrathin nonfouling layers are required to maintain their mechanical and optical properties, while also inhibiting protein adsorption. Cell attachment is initiated by adsorption of proteins through static interactions, to which cells can attach and proliferate. Inhibiting the initial adsorption of proteins is, therefore, key to rendering a surface "nonfouling."[14]

The most widely used group of materials used for this purpose are molecules which contain functional ether groups. While there is now extensive data to show that these coatings show remarkable resistance to bio-fouling, the mechanisms for these properties are not fully understood.[15–18] Despite this, it is clear that the density of ether groups on the surface determines the

ability of the coating to resist protein adsorption,[19] and it has been shown there is a critical thickness of ~3–4 nm below which protein resistance decreases dramatically.[20]

There are a number of existing methods for depositing these molecules on surfaces, including direct chemical grafting,[21,22] UV-induced copolymerization,[23] physisorption,[17] and self-assembled monolayers.[24] These techniques are all wet-chemical methods and may necessitate some surface preparation and subsequent drying and processing. Substrate geometry may also adversely affect the coating properties. One alternate technique is plasma polymerization, where an electrically excited gas phase is used to graft volatile molecules (and fragments thereof) to the surface.[25] Radio frequency (RF) power is applied to a low pressure gas to initiate a plasma phase that consists of high energy electrons, ions and radical, and neutral species.[26] Due to the separation of charges that results at the substrate surface, ions are accelerated to the surface and arrive at high energy (>10 eV). These ions can then either deposit themselves[27] or create radical sites for neutral species to graft to.[28] Plasma polymerization has a number of advantages over more traditional wet-chemistry methods as the process is dry, virtually substrate independent,[29,30] no complex surface preparation is required, and can easily be used to form ultrathin (<10 nm) conformal layers, even on substrates with complex geometries.[31] It has even been shown recently that plasma can be ignited in 50 μm diameter microchannels, opening the possibility for surface modification of microfluidic devices.[32] In the context of deposition of ether containing plasma polymers, it has been shown that using low average power per molecule increases the retention of the ether group, and, therefore, the efficacy of the deposit.[33,34] Plasma polymers with up to 80% retention of the ether group have been reported.[35]

The current work focusses on modifying 2D surfaces of G80 by deposition of ether containing plasma polymers to render them nonfouling without affecting their optical and mechanical properties. These 2D model surfaces are used as a test platform for other geometries, such as, microfluidic channels or complex surfaces. Particular attention is paid to increasing the stability of the films and their efficacy in aqueous media.

EXPERIMENTAL

Abbreviations

FBS, foetal bovine serum; rhEGF, recombinant human epidermal growth factor; DMSO, dimethyl sulfoxide; PBS, phosphate buffered saline; BSA, bovine serum albumin; RF, radio frequency; DMEM, Dulbecco's Modified Eagle's Medium; F12 Ham's F12 supplemented medium, MQ, Milli-Q water; UV, ultra-violet.

Materials

Diethylene glycol dimethyl ether (diglyme) was purchased from Sigma-Aldrich. Prior to plasma deposition, dissolved gas was removed by repeatedly freezing with liquid nitrogen and then thawing under vacuum. The protein solutions were prepared immediately before use by dissolving BSA (purchased from Sigma) or Fibrinogen (purchased from Sigma F8630) into PBS solutions at a concentration of 10 wt % for BSA and 2.5 wt % for fibrinogen.

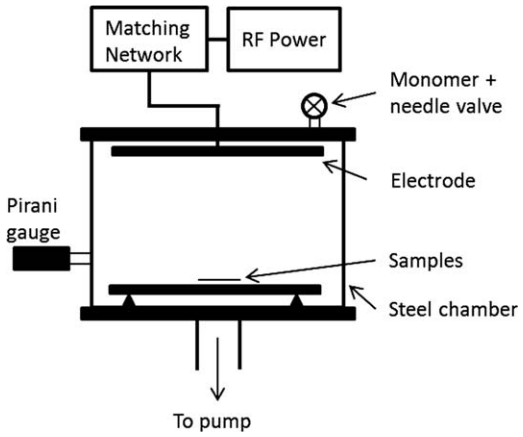

Figure 1. Schematic of the parallel-plate plasma chamber including RF power supply, matching network, and needle valve for introducing monomer.

Preparation of Geniomer® 80 Discs

Geniomer® 80 (Wacker, Germany) granules were dissolved in Tetrahydrofuran (THF) purchased from Sigma and poured into glass petri dishes to give a final thickness of the material of around 1 mm. The THF was allowed to evaporate overnight. The solidified substrate was then peeled out of the glass dish and cut into 1 cm diameter discs. The side originally in contact with the glass was then used as the substrate in all subsequent experiments.

Plasma Deposition

The plasma chamber consisted of a 0.25 m steel cylinder with internal diameter of 0.3 m (Figure 1). The chamber was evacuated using a rotary pump, with a liquid nitrogen trap fitted between the chamber and the pump. The chamber pressure was measured using a Pirani gauge, and the base pressure was $<10^{-1}$ Pa. Degassed diglyme monomer was introduced into the chamber via a needle valve. Samples were placed in the centre of the base plate of the chamber for deposition. RF power at 13.56 MHz was applied to an internal electrode of 0.28 m diameter via a Coaxial power supply (RFG050-13) with a matching network (AMN 150R). Samples were pretreated with an oxygen plasma at 2.0 Pa and 20 W for 30 s as this was shown to improve adhesion between the surface and the plasma polymer layer. Diglyme deposition experiments were conducted at between 0.5 and 2.0 Pa, which correspond to diglyme flow-rates of 1–3.5 sccm. The deposition time was either 90 min or 140 min. The samples were then removed from the chamber and placed in sterile petri dishes prior to subsequent testing.

X-Ray Photoelectron Spectroscopy

The chemical composition of the plasma polymer (pp) deposits were analyzed by X-ray photoelectron spectroscopy (XPS) using a SPECS SAGE XPS system with a Phoibos 150 hemispherical analyser at a take-off angle of 90°, and a 9 channel detector. The analysis area was circular with a diameter of 3 mm. All the results presented here corresponded to the use of the Mg $\kappa\alpha$ ($h\nu = 1253.6$ eV), operated at 10 kV and 10 mA (100 W). The

background pressure was 2.0×10^{-6} Pa. A pass energy of 100 eV and energy steps of 0.5 eV were used to obtain wide scan spectra, while 20 eV pass energy and energy steps of 0.1 eV were used for the high-resolution spectra of the C1s core line peaks. Spectra were analysed using CasaXPS (Neil Fairley, UK). A linear background was applied to all C1s spectra and synthetic C1s peaks were fitted to the C1s envelops following Beamson and Briggs.[36] The line shape used throughout was GL30 (30% Lorentzian, 70% Gaussian), and the full width half maximum of the C1s synthetic peaks remained constant at 1.5 eV. Spectra were charge corrected relative to the aliphatic carbon peak at 285 eV. Surface elemental stoichiometries were determined from peak-area ratios after being corrected with the experimentally determined sensitivity factors, and were reliable to ±10%.

Testing of Film Stability

To test the stability of the plasma polymer films, each sample was placed on the bottom of a 24 well microtiter plate, submerged in PBS and shaken at 80 rpm overnight. Then samples were washed several times in MQ, shaken in MQ at 80 rpm for another 2 h and air dried prior to further surface analysis testing. For long term aging, samples were placed in covered petri dishes and exposed to ambient air for up to 5 months. As a control, 1 cm diameter PDMS discs were subjected to the same plasma deposition and aging conditions as the G80 samples. PDMS discs were prepared in glass petri dishes using the Sylgard 184 silicone elastomer kit (Dow Corning), following the manufacturer's instructions. The PDMS was cured at 60°C overnight before plasma deposition.

Protein Binding Experiments

Samples were placed into 24-well culture plates, incubated in PBS for 1 h. Protein adsorption was started by replacing the PBS with the respective protein solution. The plate was incubated at 37°C for 16 h, rinsed gently in PBS and in MQ and then air dried overnight prior to surface analysis testing.

Cell Culture

Mouse 3T3 cells (ATCC) were maintained in DMEM supplemented with 10% FBS and 100U/mL/100μg/mL penicillin/streptomycin solution and maintained at 37°C. Discs coated for 140 or 90 min, respectively, with diglyme pp were placed in 24-well tissue culture plates (Sarstedt) and to remove any air trapped between the disc and the bottom of the well, the plate was briefly placed under vacuum. PBS solution was then added for 1 h. The PBS was removed and each well was seeded with 6×10^5 cells. The cells were allowed to incubate overnight and cell attachment was observed before a viability assay was applied. Images were captured under phase contrast using a Nikon TE2000U microscope.

Cell Viability Assay

A stock solution of resazurin in PBS (110 μg/mL) was prepared and applied as a 10% (v/v) solution in cell culture media to each of the wells. The cells were allowed to attach overnight before each well was gently washed with sterile PBS. The positive control was a tissue culture well with cells added and the negative control was a well with no cells. 200 μL of the resazurin solution was then added to each well and incubated for 2 h. The solution was then transferred to a 96 well plate to be read at 570 nm and 600 nm. As resazurin is nontoxic to the cells, fresh medium was reapplied to the 24 well plates. The assay was repeated with the same cells at 72 h after initial seeding to observe the effects of longer term culture. Cell viability was calculated by 570–600 λ of each sample. A one-way Analysis of Variance with a Tukey post test (GraphPad InStat) was performed on the resazurin, and a $P < 0.05$ was considered to be statistically significant.

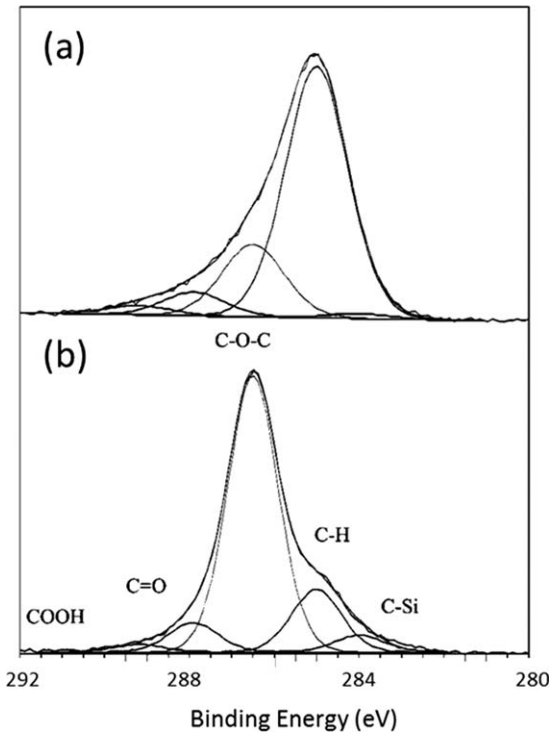

Figure 2. C1s coreline spectra of diglyme plasma deposits showing a change in retention of the ether group with power / flowrate. Conditions were 0.5 Pa/10 W (a) and 2.0 Pa/1 W (b).

RESULTS AND DISCUSSION

Surface Characterization

Following plasma deposition of diglyme surfaces, XPS was performed to determine the surface chemistry. Figure 2 shows the C1s coreline spectra for deposits at high power/flow rate [Figure 2(a)] and low power/flow rate [Figure 2(b)]. At high power/flow rate, the dominant peak was observed at 285 eV with a tail on the high binding energy side of the spectra. At low power/flow rate, however, the dominant peak occurred at 286.5 eV, with only a minor shoulder appearing at 285 eV.

Synthetic peaks were applied to the spectra following Beamson and Briggs.[36] The peak at 285 eV is assigned to aliphatic carbon (C—H, C—C) while the peak at 286.5 eV is assigned to the ether group (C—O—C). Minor peaks on the high energy binding side are also fitted at 288 (C═O) and 289.2 eV (COOH). A small peak on the low binding energy side is also observed at 284 eV which is assigned to C—Si, which may be due to a bond between the plasma deposit and the substrate, or the substrate itself. Importantly, the results demonstrate that decreasing the

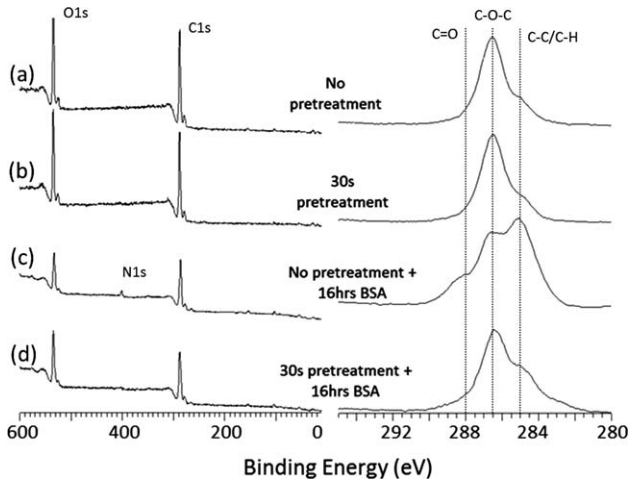

Figure 3. XP spectra of diglyme plasma deposits (a) on G80, (b) on G80 pretreated with oxygen plasma, (c) on G80 after immersion in BSA solution, and (d) on G80 pretreated with oxygen plasma after immersion in BSA solution.

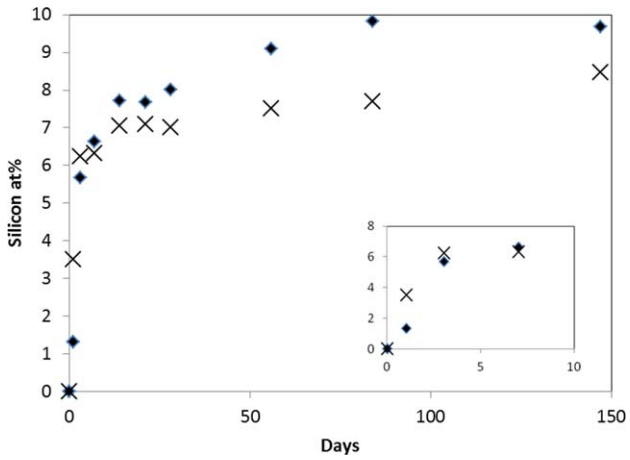

Figure 4. Atomic percentages of silicon detected on diglyme coated G80 (X) and PDMS (◆) after aging in air. Insert: data for the first 7 days. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

power/flow rate ratio increases retention of the ether group as reported previously.[37,38]

Plasma Polymer Film Stability

Plasma polymer film stability was achieved on G80 only after a pretreatment in oxygen plasma conducted at 1.0 Pa and 20 W for 30 s. As shown previously, exposure to plasma oxidation results in PDMS becoming hydrophilic due to the presence of silanol surface groups.[39] This helps to overcome some of the issues with PDMS for microfluidic applications, but does not render the surface nonfouling. It can be assumed that a similar process occurs on G80 surfaces as it is also a siloxane based polymer. Bombardment with high-energy ions from the plasma phase also results in formation of radical sites, which promotes adhesion in the early stages of plasma polymer deposition.[40] Figure 3 shows the XP spectra of diglyme films deposited on G80 with and without pretreatment. The spectra are almost identical after deposition, showing that the surface chemistry of the films is not altered by pretreatment. However, after contact with BSA solution for 16 h, the untreated films showed a significant decrease in ether content, shown by a decrease in the C1s peak at 286.5 eV. This was also accompanied by the appearance of a nitrogen peak due to adsorption of BSA to the surface. The sample which had been pretreated showed a smaller change in the ether content from 70% to 51%. While the ether content of the film decreased, interestingly no nitrogen peak was recorded, indicating that the surface was still resistant to protein adsorption. Minor silicon peaks were observed for both samples after contact with BSA solution. This may be due to a decrease in film thickness, or to diffusion of the silicon species from the G80 substrate through the film to the surface.[41]

A separate study regarding stability of the diglyme pp film in air demonstrated that this may be the case. On diglyme pp treated G80, silicon can be detected on the surface within 24 h when allowed to age in air (Figure 4). There is rapid diffusion of silicon to the surface during the first 7 days, after which, the surface stabilizes and the detected silicon remains relatively stable (approximately 7 at.%). A similar diffusion pattern is observed with PDMS, but unlike the G80, still has silicon continuing to diffuse to the surface after 80 days (approximately 8–9 at.%). This demonstrates that G80 allows greater long-term control of surface chemistry than PDMS.

Protein Adsorption

Samples of plasma deposited diglyme were prepared under various conditions on silicon wafer, resulting in surfaces with varying degrees of ether group retention. These samples were then placed in contact with BSA solutions overnight with gentle stirring. After being in contact with the BSA solution for 16 h, the samples were removed from the solution and gently rinsed with MQ. These samples were then analyzed by XPS, and the nitrogen to carbon ratio determined. The results in Figure 5 show a linear relationship between *N/C* ratio and retention of the ether group. Critically, the plot shows that for deposits with greater than ~70% ether retention, the surface is rendered essentially nonfouling (over this time period) in agreement with previous

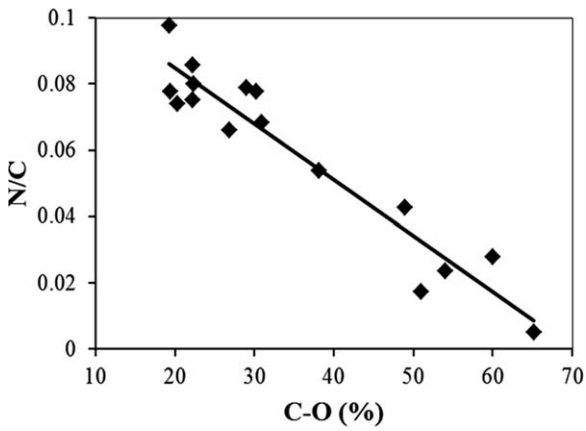

Figure 5. *N/C* ratio determined by XPS for plasma deposited diglyme after being in contact with BSA solution for 16 h.

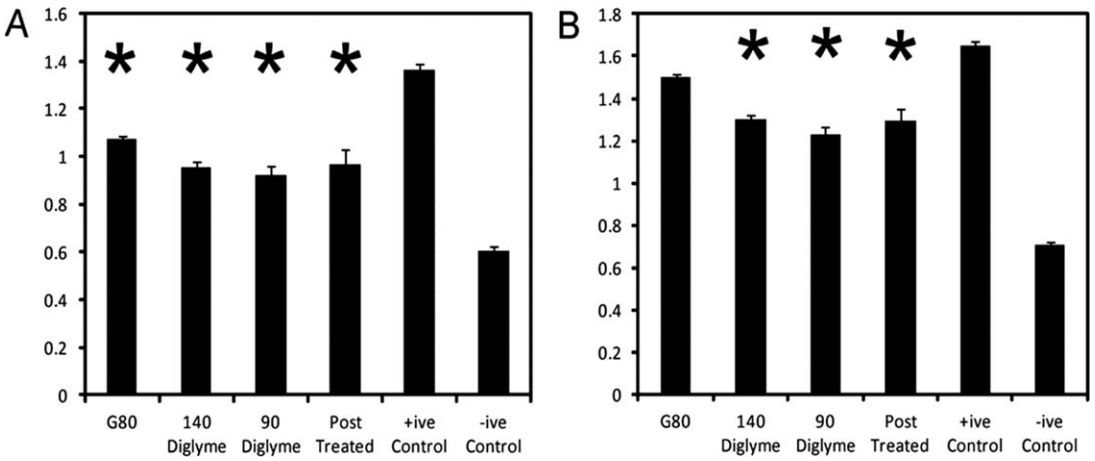

Figure 6. Viability results of 3T3 cells cultured over 24 h (A) and 72 h (B). *y* axis are absorbance units. * represents a statistically significant difference in comparison to the positive control. Error bars = SEM.

results.[42] This can be illustrated with recourse to the spectra in Figure 2. The low power/high flow rate deposit shown in Figure 2(b) had an ether content of 71%, and showed no nitrogen peak after being in contact with BSA ($N/C = 0$). In contrast, the high power/low flow rate deposit [Figure 2(a)] showed a significant nitrogen peak and an N/C ratio of 0.096, indicating adsorption of protein to the surface. The N/C ratio of the BSA was measured to be 0.17, showing that over half of the high power/low flow rate surface was covered with BSA. It was, therefore, determined that all following deposition experiments on G80 would be conducted at 2.0 Pa and 1 W as this produced surfaces with 70% ether content.

Cell Culture—3T3 Cells

The 3T3 cells did not attach well to any of the G80 surfaces in comparison to the positive control as shown in Figure 6. At 24 h, there was no statistical difference in the number of cells attached between any of the G80 surfaces, indicating good nonfouling properties of the material and the diglyme coating in the short term. However, it is clear from Figure 7 that the cells attached to the bare G80 surface exhibit cellular projections, indicating good attachment to the surface which enables proliferation over longer time periods. These cellular projections are not observed for cells attached to diglyme pp coated surfaces, indicating the attachment of the cells to the surface is weak. At 72 h, the long-term nonfouling properties of the diglyme pp becomes apparent, where only the diglyme pp-coated surfaces demonstrated low cell viability after a 3 day period in culture. Oxygen post-treatment on the diglyme pp surface did not effect 3T3 cell attachment, even over a 3-day culture period. This indicated that the post-treatment does not completely destroy the diglyme coating, but allowed for proteins not related to cell attachment to bind to the surface.

CONCLUSIONS

G80 can be dissolved in tetrahydrofuran and then simply cast into many geometries. Subsequent coating of the surface using diglyme plasma polymer has been demonstrated to render the surface nonfouling, resisting protein adsorption, and cell proliferation. The stability of the deposited plasma polymer was increased by pretreating the surface with a brief oxygen plasma. It was also shown that the deposited layer is more stable on G80 than on PDMS substrates over an extended period.

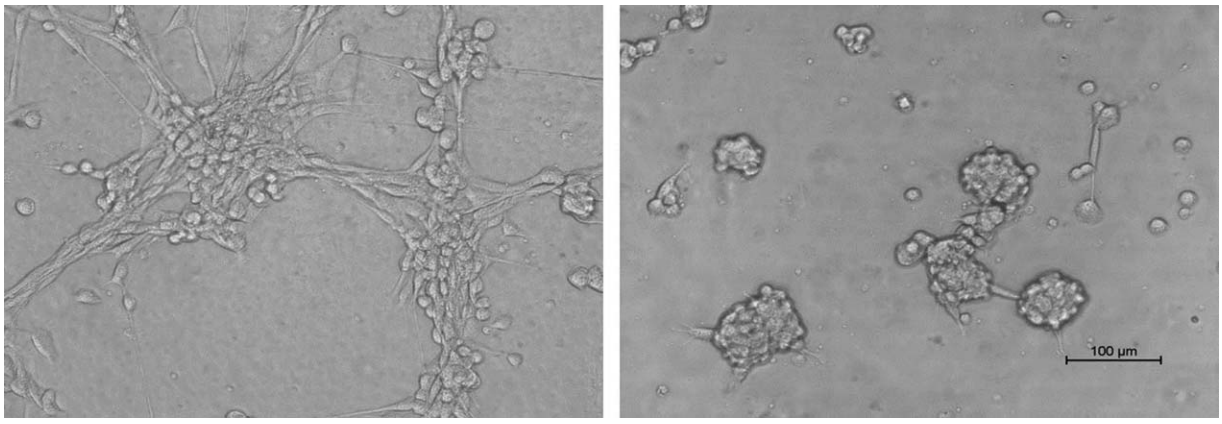

Figure 7. Microscopy image of cells on bare G80 (left image) and G80 with diglyme plasma deposit for 90 min (right image) 22 h after seeding. Wells were seeded with 6×10^5 3T3 cells.

Combined with its optical and mechanical properties, this makes G80 an excellent alternative material for biomedical and microfluidic applications.

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