Topical Review

Plasma surface engineering for manmade soft materials: A review

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Abstract

Manmade soft materials are important in a wide range of technological applications and play a key role in the development of future technologies, mainly at the interface of synthetic and biological components. They include gels and hydrogels, elastomers, structural and packaging materials, micro and nanoparticles as well as biological materials. Soft materials can be distinguished from liquids owing to their defined shape and from hard materials by the deformability of their shape.

This review article provides an overview of recent progress on the plasma engineering and processing of softer materials, especially in the area of synthesis, surface modification, etching, and deposition. The article aims to demonstrate the extensive range of plasma surface engineering as used to form, modify, and coat soft materials focusing on material properties and potential applications. In general, the plasma provides highly energetic, non-equilibrium conditions at material surfaces requiring to adjust the conditions for plasma-surface interaction to account for the specifics of soft matter, which holds independent of the used plasma source. Plasma-induced crosslinking and polymerization of liquids is discussed to transform them into gel-like materials as well as to modify the surface region of viscous liquids. A major field covers the plasma surface engineering of manmade soft materials with the help of gaseous reactive species yielding ablation, nanostructuring, functionalization, crosslinking, stiffening, and/or deposition to obtain demanded surface properties or adhesion to dissimilar materials. Finally, plasma engineering of rigid materials is considered to induce surface softening for the enhanced contact with tissues, to allow interaction in aqueous media, and to support bonding to soft matter. The potential and future perspectives of plasma engineering will be discussed in this review to contribute to a higher knowledge of plasma interaction with sensitive materials such as soft matter.

1. Introduction

Soft matter is referred to materials that can easily be deformed by thermal fluctuations and external forces due to their low shear modulus relative to their bulk modulus. This implies that it is a material with only a small number of strong crosslinks between molecular chains or particles as depicted in figure 1 – typically in the order of 1 among 100 atoms [1]. Microscopically, it thus appears rather as a liquid, whereas it is a solid at the macroscopic level, i.e. macroscopic flow is prevented.
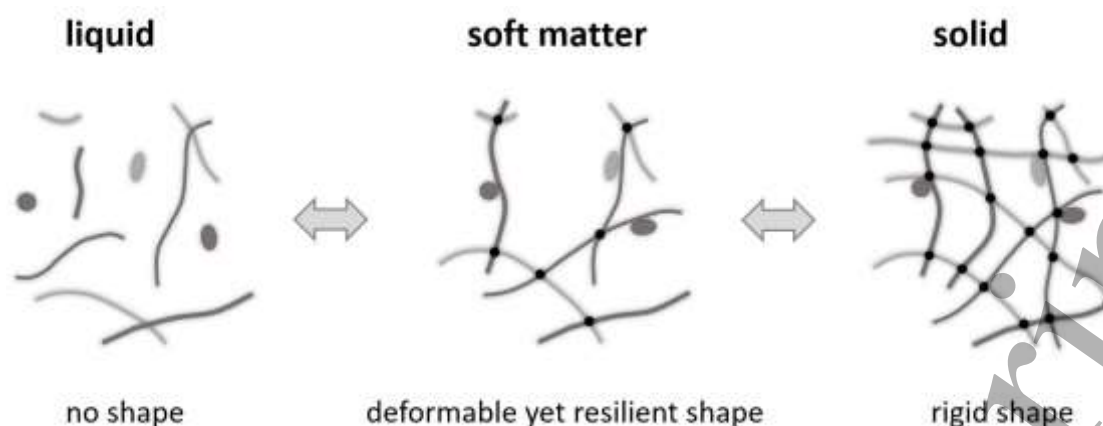
Figure 1. Soft matter can be understood as the transition state between a liquid and a solid by introduction of a limited number of interconnections (black dots) between its molecules giving the material an easily deformable, soft shape.

Soft materials have stable yet flexible characteristics, in a way in between liquids and solids, since they do not flow like water and are not hard like stone. An in-depth discussion of the characteristics and distinction of soft materials can, for example, be found in [2,3]. Soft matter is well known from living matter such as cells and tissues [4]. Cell assemblies are elastic, especially at short time scales: when deformed, they recover their initial shape. Since cells are alive, they can change their shape over time by consuming energy, thus showing also viscous properties. We will focus, however, on inanimate, that is, manmade soft matter, which is deformable yet having a resilient shape.

As depicted in figure 2, plasma surface engineering enables the crosslinking of (suitable) liquids to transform them into soft materials. Surface stiffening of soft materials can be used to make them more resilient, also allowing the deposition of thin films on such soft matter. Induced chain scission by plasma interaction, on the contrary, might transform a solid material surface into a softer, deformable state.
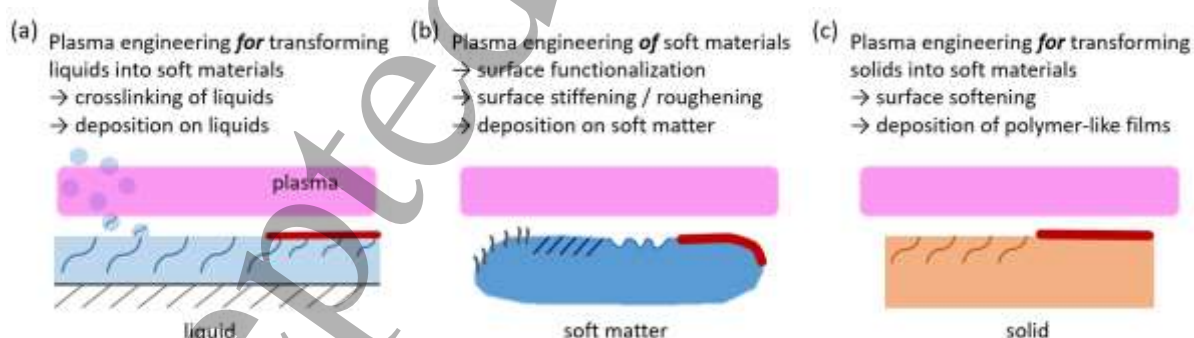
Figure 2. Scope of plasma surface engineering: (a) to transform viscous liquids into soft materials through plasma-liquid surface interaction, (b) to modify and coat soft materials, and (c) to transform solid surfaces into softer surfaces by softening and deposition.

Material classes belonging to soft matter range from gels, colloids, and liquid crystals over biomaterials to polymers, in particular those with low glass transition temperature, T_g, or high surface-to-volume ratio. T_g denotes the temperature (range) where the amorphous regions of a polymer change from a rigid glassy material

to a soft (not melted) material in the rubbery state showing increased molecular mobility. Rubber elastomers with T_g below room temperature thus appear soft and flexible, while their crosslinking prevents free flow of the molecular chains distinguishing them from viscous liquids – characteristic for soft matter. Most of all, the shape of a rubber can be set by its degree of crosslinking. Accordingly, the first processing of soft materials in human history is considered to be the production of rubber shoes by indigenous people of the Amazon basin about 2500 years ago [1]. The sap from the Hevea tree (a liquid of independent, flexible polymer chains) was put around the foot and dried in air. Oxidation results in the formation of some bridges between the chains producing a tension-resistant soft material known as latex rubber. This rubbery protective and waterproof "sneaker" made rough treks through the dense rainforest less damaging to the feet. UV light from the sun or heat near a fire might have helped the photo-oxidative crosslinking process – evincing early surface engineering for manmade soft materials with demanded properties. The involved photo-oxidation and crosslinking processes are nowadays fairly well understood, which might proceed in a similar way also in a plasma environment [5,6]. While this UV aging affects the entire material, plasma enables controlled surface engineering. Plasma interaction deposits energy yielding hardening of soft materials, densification of porous material, radical formation, and crosslinking or destruction by forming low molecular weight or volatile species. This review will focus on plasma surface engineering to produce or modify manmade soft materials based on activation, crosslinking, and also deposition processes.

2. Plasma Surface Engineering – General Overview

Weakly ionized plasmas as used for plasma surface engineering are distinguished by 'hot' electrons with energies in the range of eV and 'cold' heavy gas particles remaining close to room temperature. The highly mobile electrons pick up energy during collisions from electric (or electromagnetic) fields and readily leave the plasma creating a sheath and a potential gap between materials' surfaces and the quasi-neutral plasma. The latter results in the acceleration of positively charged particles from the plasma that deposit a kinetic energy at the surface, again in the order of eV, yet with limited flux. These highly non-equilibrium conditions enable the breakage of any kind of chemical bonds, while allowing for the treatment of temperature-sensitive materials. An excellent overview of the plasma-chemical and physical processes can be found by Michelmore et al. [7]. Many excellent reviews and books have been published in recent years beside still valuable elderly review articles to discuss several aspects of plasma surface treatment and coating of polymers [8-13]. Different plasma sources and equipment have been developed and improved over years including capacitively and inductively coupled plasmas (CCP and ICP), microwave (MW), arc and magnetron discharges as well as combinations running with continuous or modulated (pulsed) power from low pressure (LP) to atmospheric pressure (AP). For the latter special configurations have been investigated such as dielectric barrier discharges and various plasma jet configurations [14]. The importance of plasma diagnostics has critically been reviewed by Thiry *et al.* [15]. Therefore, merely a brief overview of plasma-surface interaction will be provided that is relevant for manmade soft materials.

The plasma creates electrons, ions, excited and dissociated particles as well as UV radiation, which can all interact with material surfaces. Most of all, positive ions that are accelerated across the plasma sheath collide with neutral particles depending on the ratio of sheath thickness to ion mean free path length. These elastic or charge exchange collisions result in the transfer of momentum to neutrals, which increases with pressure. For

example, at a pressure of 1 Pa, the flux of accelerated neutrals with energies >0.1 eV already exceeds the ion flux in an Ar plasma, while at 20 Pa, it is about 30 times higher [16]. The deposited kinetic energy by all species incident on a material surface provide the energy for surface diffusion and bond breaking at low temperature, i.e., highly energetic, non-equilibrium conditions. As an estimate for the averaged deposited energy (in [eV per surface atom/molecule] or [eV nm^{-3}]) the incident energy flux can be related to the affected near-surface volume [10]. The affected volume and the related interaction depth, however, are often not well defined. Note that for manmade soft materials and polymers, the near-surface density can be lower than the bulk density due to reduced chain entanglement and an increased number of chain ends. Thus bond scission, formation of radicals, diffusion, and crosslinking is enabled but also secondary processes such as electron or photon emission and heat dissipation near the surface depending on the energy flux and interaction depth. Khelifa et al. considered, in particular, the role of near-surface free radicals [17]. The plasma-induced activation of organic materials using an inert gas creates free radicals by interaction with plasma particles, ions, electrons, and energetic UV radiation. The deposited energy enables excitation and cleavage of homolytic C–C, C–H, and C–O bonds leaving free electrons at the fragments. Such reactions can induce crosslinking in soft materials, but also formation of low molecular weight oxidized materials (also named LMWOM) yielding degradation and ablation, since free radicals tend to react with oxygen-containing groups [18]. By avoiding oxidation the maintained free radicals can be used for an intended surface functionalization step [19]. The radical density is enhanced by plasma power, which increases particle flux and energy as well as UV intensities, approaching saturation at higher powers, probably due to radical recombination [20,21].

Most of all, accelerated ions can deposit a high energy in a thin surface layer of around 1 nm exceeding the threshold for chemical and/or physical etching [10]. UV radiation incident at the material surface with comparable energy flux to ions in a plasma, on the contrary, deposit their energy over a larger volume, tens of nm deep [22]. Accordingly, only minor etching effects by UV radiation are observed [10]. The effect of energetic UV radiation on soft materials, however, should be considered especially for extended plasma treatment times [23]. It is, for example, well known that Si–C and C–H bond rupture occurs in polymethylsiloxane resins when they are exposed to UV radiation. While at lower energies (higher wavelengths) Si–CH$_2$–Si linkages are formed, higher energy absorption at lower UV radiation wavelengths results in oxidation and formation of Si–CH$_2$–CH$_2$–Si linkages [24]. Those linkages, however, are absent in the deposition of polydimethylsiloxane (PDMS)-like plasma polymers, which led to the conclusion that UV radiation can be neglected during the growth of thin plasma polymer films [25]. The reason for this might be the steadily modified surface region due to film growth. resulting in crosslinking and densification, allowing, for example, the deposition of hard coatings [26]. To treat soft materials and to enable the deposition of rather soft plasma polymer films with retained functional groups, on the contrary, the energy flux from the plasma needs to be limited, while gas phase processes gain importance [27,28]. To this end, the control of plasma-surface interaction by plasma conditions (power input, pressure) and plasma exposure of the soft substrates (biased, floating, or remote) is crucial.

Plasma polymerization denotes the process that converts starting molecules via plasma activation into a deposit, the plasma polymer film (PPF). The starting molecules are often a gas, the monomer, as in Plasma Enhanced Chemical Vapor Deposition (PECVD), but can also be a solid, liquid, or aerosol that is polymerized by the plasma interaction. For PECVD processes, the plasma activation is microscopically governed by the electron energy distribution function (corresponding to electron density and temperature) and the residence time of the

monomer in the active plasma zone. Macroscopically, these quantities can be related to the energy available per monomer molecule in the plasma (specific energy input, SEI) depending on power per monomer flow rate, W/F [29]. This energy in the order of eV defines the plasma-chemical reaction pathway via activation, dissociation, and ionization reactions depending on the corresponding threshold energies. Accordingly, plasma polymers show highly branched and crosslinked structures different to conventional polymers [30]. Hence, both plasma chemistry (by the selection of the starting molecules and their energy uptake) and plasma physics (by the role of ions during plasma-surface interaction) are key parameters for the engineering of manmade soft materials and deposition of functional films [12,13].

Note that neutrals can also become directed by electric fields in a plasma, as discussed above. In an asymmetric CCP with pure hexamethyldisiloxane (HMDSO) as monomer at 20 Pa, for example, we found that the flux of film-forming species, which amounts to roughly one seventh of the overall neutral flux to the driven electrode, is about 15 times higher than the ion flux, yielding an about 100 times higher neutral flux in total [29]. From this estimation it becomes apparent that a substantial part of the neutrals that initially travel by diffusion can get directed towards the electrode, about 30% at 20 Pa, gaining kinetic energies of >0.1 eV (>500 m s^{-1}) [16]. With many collisions such as at atmospheric pressure, momentum is transferred to all neutrals, which gain an overall directed velocity of about 1 m s^{-1} in an air corona discharge resulting in the so-called ionic wind [31]. Furthermore, ion-neutral synergies have well been recognized, for example, enhancing etching rates when both ions and neutrals interact at the surface [32]. Thus, non-equilibrium conditions are present in plasma surface engineering at various energy levels providing a versatile and unique surface modification tool.

3. Plasma Engineering *for* Transforming Liquids into Soft Materials

This section mainly considers the crosslinking of viscous liquids to form hydrogels as well as the deposition on hydrogels by plasma engineering (figure 3). Engineered hydrogels are a key material, e.g., for various biomedical applications [33,34]. In addition, plasma-induced polymerization of other suitable liquids and deposition on such liquids is touched on briefly. While these are emerging fields, knowledge gaps still exist regarding the interaction depth of the various plasma species with viscous liquids yielding crosslinking.
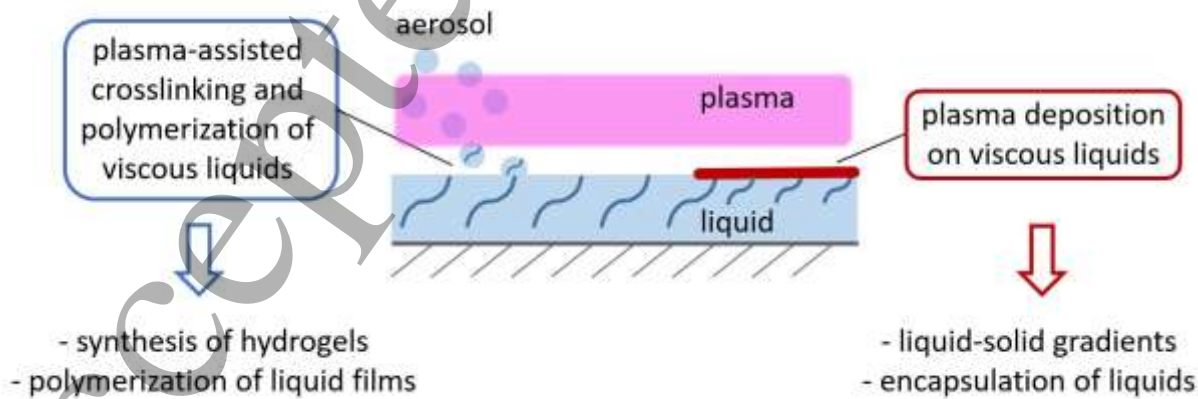
Figure 3. Plasma engineering for transforming viscous liquids into soft materials through plasma-liquid surface interaction resulting in crosslinking and polymerization or by deposition on viscous liquids.

3.1 Plasma-assisted synthesis of hydrogels

Hydrogels are three dimensionally crosslinked polymeric networks which can retain a huge amount of water due to their soft and porous hydrophilic structure but do not dissolve in water [35]. They represent synthetic polymers with good biocompatibility and transparency, and are responsive by different stimuli (radiation, heat, pressure, chemicals, pH, ionic strength, etc.). Biocompatibility is defined by strongly bonded water molecules, where the intermediate water in the hydrated polymer matrix is considered to play a predominant role [36-38]. The similarities to biological tissue makes hydrogels an interesting material for a wide range of applications, especially in the biotechnical, medical and pharmaceutical field [39,40]. Examples are drug delivery systems, membranes for biosensors or contact lenses [39,41-47]. Furthermore, hydrogel-based sensors and actuators make use of the materials capability to change its volume in response to a change in environmental conditions [48,49]. Hydrogels are usually synthesized using chemical methods by heating an aqueous solution of monomers, crosslinking agent, and initiator. As it was demonstrated by Malik *et al.*, the polymerization of vinyl molecules in aqueous solutions can also be initiated by a plasma [50]. A pulsed corona discharge was utilized to create reactive oxygen species (ROS) in water such as hydroxyl radicals, $OH^{\bullet}$, which initiate the linear polymerization of acrylamide, $CH_2=CHCNH_2$, inducing gelling in the solution within minutes. Adding acrylic acid (AAc), $CH_2=CHCOOH$, and a crosslinking agent in the solution allowed to produce highly water-absorbing poly(acrylamide-co-acrylic acid) hydrogels. The plasma synthesis route was found to be comparable to the conventional chemical method. Such copolymers find numerous applications as detergent additives, water treatment chemicals, and superabsorbents. Likewise, glow discharge electrolysis plasma (GDEP) was used to synthesize hydrogels from polyvinylpyrrolidone (PVP)/AAc mixtures in aqueous solutions [51]. The co-polymerization is mainly initiated by $OH^{\bullet}$ through the energy absorbed by water molecules from the plasma. The synthesized PVP-based hydrogel can be used as adsorbent for the removal of heavy-metal ions from wastewater. Furthermore, the mechanical properties of self-standing hydrogels that can be photo-crosslinked *in situ* by introduction of methacrylate functional end groups in the polymer chains can be improved after pre-crosslinking induced by an AP plasma [52]. A new platform for several applications related to plasma medicine might thus be set up based on polymer solutions with hydrogel forming ability.

To produce strongly water absorbing hydrogels it is beneficial to use water-soluble polymers and to crosslink them [35]. One such example is polyethylene glycol (PEG) which is used in many biomedical, pharmaceutical and industrial applications due to its excellent biocompatibility [53-55]. PEG with molecular weights below 1 kDa appears as a transparent and viscous liquid. By processing PEG liquids with a low pressure Ar/O_2 plasma (CCP RF at 10 Pa) we could recently show that crosslinking and solidification of the liquid can be achieved resulting in stable hydrophilic and water absorbing surfaces [56]. Compared to other methods such as dipping or spraying, this approach aimed at the plasma treatment from the top of the PEG liquid, while the actual functional PEG side was built underneath the liquids solidified surface regarding the penetration depth of the plasma crosslinking effect. Afterwards, the lower PEG side was made accessible by adding a stabilizing silicone backing, turning the sample around and washing the unbound PEG liquid off. In this way, a solid-liquid gradient ranging over ~200 nm could be obtained, whereby the attached uppermost PEG layer was shielded from the strongly crosslinking plasma conditions [57]. The loss of the PEG molecules' hydrophilic and water-absorbing properties through excessive fragmentation could thus be prevented [58,59].

Another method for the fabrication of hydrogels via plasma treatment has been reported by Satapathy et al. based on an argon microplasma to produce a gelatin-graphene oxide nanocomposite hydrogel serving as scaffold for orthopedic tissue engineering [40]. The plasma treatment allowed the free radical initiated molecular interaction

between the liquid polymer gelatin and graphene oxide resulting in crosslinking and polymerization to produce a biocompatible hydrogel, while the primary structure of the gelatin could be maintained (figure 4). Compared to other crosslinking methods the capability of the plasma process to precisely control the degree of crosslinking improved cell proliferation, growth and viability. Furthermore, applying plasma processes avoids the usage of toxic and non-biocompatible chemical initiators or crosslinking agents commonly applied in wet-chemical processes [40,60,61].
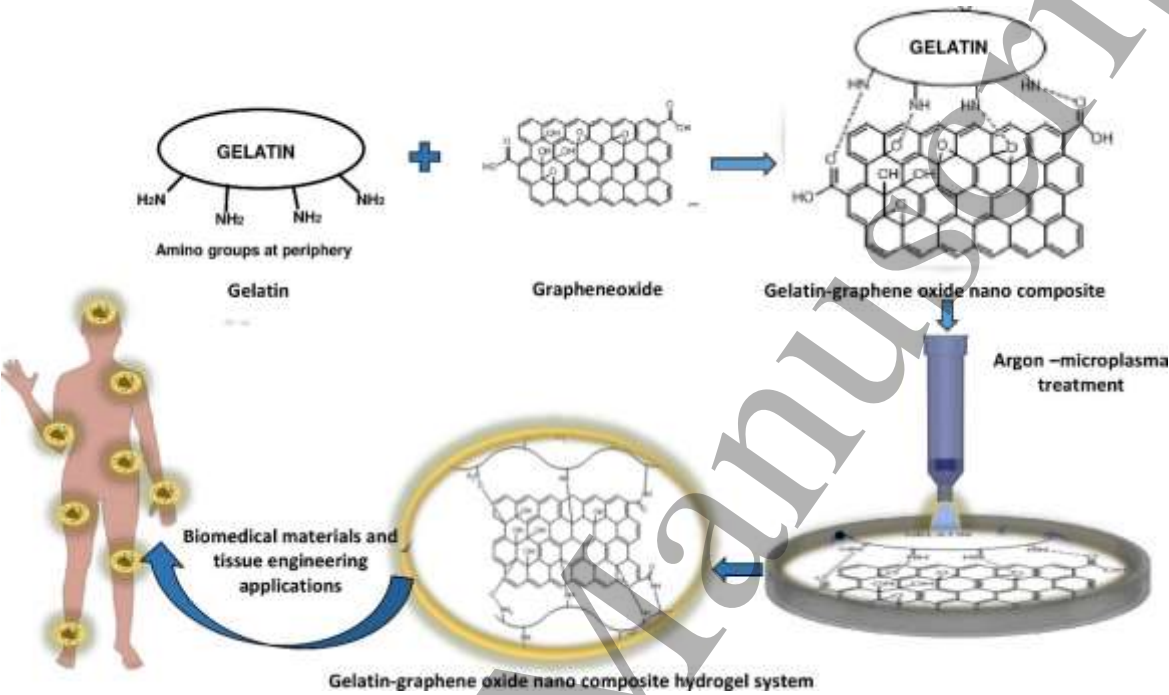
Figure 4: Schematic presentation of Ar microplasma-mediated gel-GO nanocomposite hydrogel synthesis and its biomedical applications. Reprinted from [40]. © 2017 Satapathy et al.

Besides the internal crosslinking of the molecular chains building the hydrogel, immobilization and stable attachment of hydrogel-like coatings to a specific surface is crucial for many of the above mentioned applications. Substrate materials can simply be dipped in a hydrogel solution and crosslinked by subsequent plasma treatment. Polyvinylidene fluoride (PVDF) microporous membranes with surface-immobilized PEG were prepared by argon plasma-induced grafting (RF CCP at 100 Pa) to induce anti-fouling properties [62]. Plasma processes are also capable of performing both liquid application of hydrogels and immobilization on a surface in one step, whereas other methods require more complex, time consuming multi-step processes [55]. Dow Corning Plasma Solutions (DCPS) introduced a method named atmospheric pressure plasma liquid deposition (APPLD), where precursors are introduced directly as a liquid aerosol into a non-equilibrium AP plasma as depicted in figure 5 [63]. "Soft-polymerized" ethyleneglycol methacrylate and polyacrylic acid coatings were deposited on polyester fabrics by guiding the fabric continuously between multiple electrodes used for He-based plasma activation and plasma liquid deposition. The method further allows to entrap active substances such as anti-microbial species, e.g. quaternary ammonium salts, by dissolving them in the liquid precursor.
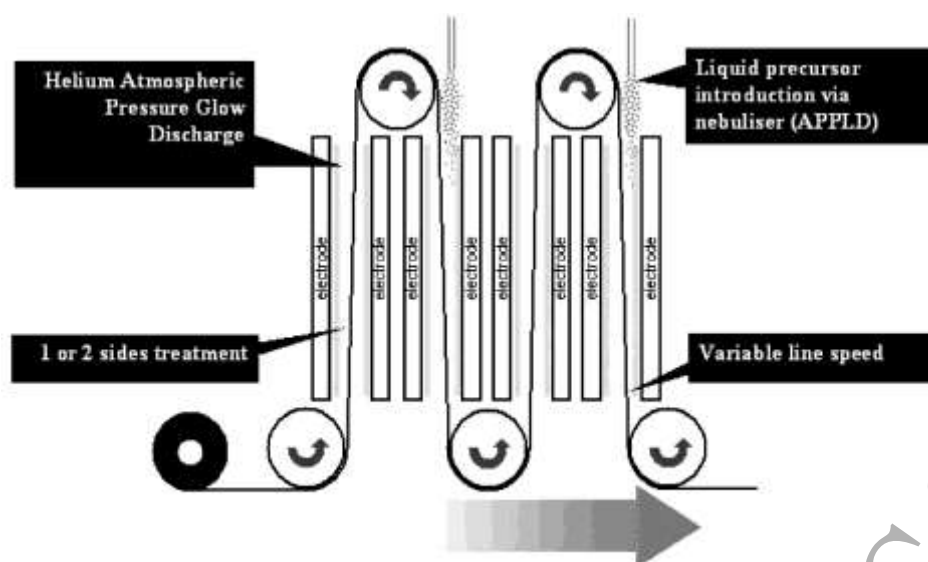
Figure 5: Schematic representation of the APPLD pilot line showing plasma activation and liquid aerosol introduction in a continuous process. Reproduced with permission from [63]. © 2006 John Wiley & Sons, Ltd.

A similar APPLD process was used by Nisol et al. to deposit hydrogel-like coatings from tetraethyleneglycol dimethyl ether (tetraglyme) as liquid precursor injected in the remote discharge and treated for 10 min in an Ar plasma retaining a high PEG character of the deposit [64]. Furthermore, aerosol-assisted plasma deposition from PEG aqueous solutions can be supported by plasma polymerization of ethylene in a DBD working with He [65]. The latter formed a matrix entrapping the PEG domains on a polycarbonate substrate responsible for scarce endothelial cell adhesion and growth using a suitable concentration of PEG in the atomizer solution (10% w/v). Another approach based on plasma immersion ion implantation has been explored by indirectly using plasma for the immobilization of acrylamide and silk hydrogels on solid polymeric substrates [61,66]. As described by the authors, ions produced in a plasma and accelerated towards a polymeric substrate cause bond dissociation and formation of radicals in the near-surface area, which promote polymerization of hydrogels and their bonding to the solid surface. Walia et al. used this effect to prepare polymeric substrate materials containing mobile radicals by applying a nitrogen plasma [61]. When exposing as-treated substrates to a monomer solution, polymerization reactions occurred leading to a crosslinking of the monomer molecules among each other as well as a covalent attachment to the substrate. Thus, long-term stable solid-hydrogel hybrid structures were produced exhibiting excellent adhesion between hydrogel and substrate.

3.2 Plasma-induced polymerization of viscous liquids

Similar to hydrogels, any kind of polymerizable liquids can be applied to a surface as thin film and crosslinked by a subsequent plasma treatment as depicted in figure 6. As an example, polystyrene (PS) used as insulating material in pulsed power devices was coated with a liquid film of a mixture of methyl-methacrylate (MMA) and dodecafluoroheptyl-methacrylate (DFHMA; mass ratio 19:1; 5 μm thickness) followed by Ar plasma treatment at medium pressure (~2000 Pa) [67]. The liquid mixture polymerized by plasma activation on the PS substrate enhancing its volume resulting in a distinctly increased surface charge dissipation rate.
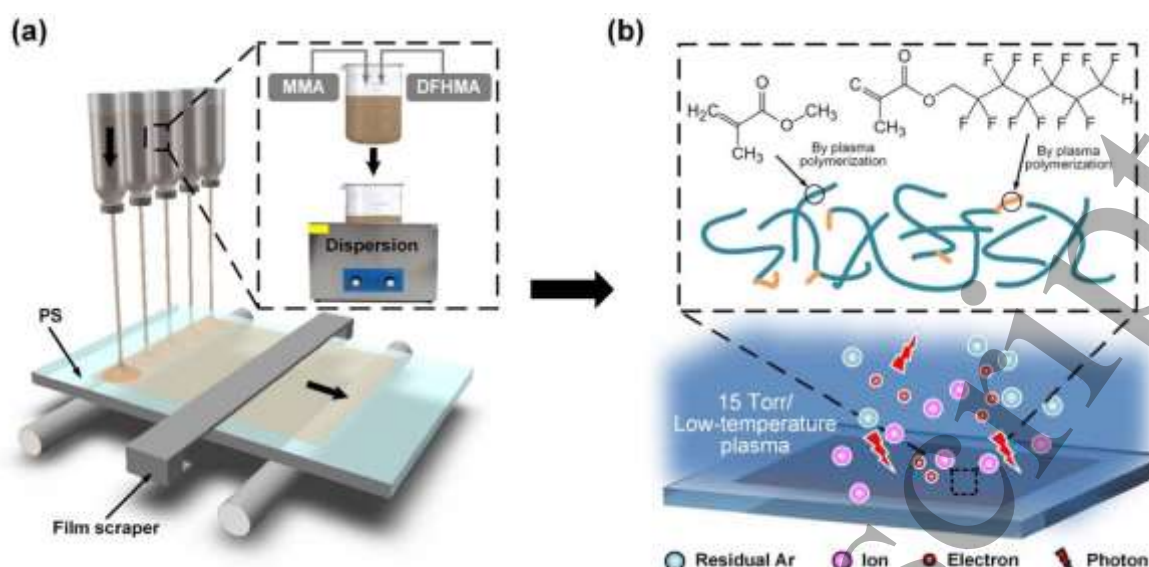
Figure 6: Schematic diagram of a system for liquid application (a) and subsequent plasma-induced polymerization (b). Reproduced from [67]. © 2020 IOP Publishing Ltd

Likewise, a thin liquid layer of an allyl ether-substituted six-membered cyclic carbonate (A6CC) was spin-coated on a substrate and transferred to an AP plasma with air to study plasma-induced free radical polymerization [68]. The plasma deposition of functional thin films with pendent cyclic carbonates was enabled, for instance, to exploit their high reactivity toward primary amines for sensing and biotechnological applications. Moreover, a wide range of aerosols, that is liquids (or even solid particles) suspended in a gaseous medium, can be supplied to an AP plasma for deposition at various substrate surfaces. An excellent review on recent advancements in the use of aerosol-assisted AP plasma deposition was given by Palumbo et al. [69].

3.3 Plasma film deposition on viscous liquids

Plasma surface engineering can also be used to partly crosslink a low vapor pressure liquid monomer – such as PEG, as discussed above – leading to the formation of a hydrogel, which is at the same time covered with a thin film when polymerizing gases are introduced. In this way, hydrocarbon coatings were deposited on liquid PEG held in petri dishes [56,57]. In a first process step Ar plasma was used to partly crosslink the uppermost layer of the liquid PEG. Subsequently, an ethylene, C_2H_4, plasma was applied leading to a 200 nm thick film covalently bond to the crosslinked PEG layer. Since the process was applied from the top, the PEG underneath the uppermost solidified layer remained liquid and the process thus resulted in the formation of a solid-to-liquid gradient with an observed penetration depth of about 200 nm [57]. The deposited a-C:H film properties were adapted to PEG by starting the deposition at enhanced pressure (20 Pa), that is with lowered energy flux incident on the viscous liquid surface, and reducing the pressure during film growth to 10 Pa. Hence, a gradient in crosslinking was applied, since the energy flux was enhanced with maintained gas phase conditions [70]. The as-deposited PPF covering the liquid PEG was sufficiently stable to support a 3 mm thick layer of liquid polydimethylsiloxane (PDMS), which served as a stabilizing backing for the sample after being cured. Thus, the samples could be lifted off the petri dish and turned upside down for further analysis of the surface functionalized with PEG. Figure 7a shows the FTIR spectra of two reference samples, cured PDMS and liquid PEG, and a spectrum of a PEG sample treated with Ar plasma and coated by C_2H_4 plasma. A subsequent second

Ar plasma treatment was applied to the sample to improve the adhesion between the a-C:H coating and the silicone backing. The spectrum of the plasma-treated PEG sample can be distinguished from the PDMS background by the characteristic PEG signals (O–H streching vibration between 3650 cm^{-1} and 3100 cm^{-1} and the asymmetric C-H stretching vibration of CH_2 at 2862 cm^{-1}. Their appearance verifies the presence of covalently bonded PEG on the samples surface. The C=O and C=C stretching vibrations at 1724 cm^{-1} and 1639 cm^{-1}, respectively, can be associated with a partial crosslinking of the PEG molecules and with oxidative degradation due to exposure to oxygen and light after the process [58,71-74].

The effect of PEG attachment to the surface becomes obvious when looking at the apparent contact angles displayed in figure 7b. The values were measured on three reference samples (cured silicone (PDMS): 115.9° +/- 1.2°, the plasma-polymerized hydrocarbon film (a-C:H): 72.7° +/- 1.6°) and liquid PEG: 20.0° +/- 1.2°) as well as on the plasma-coated PEG sample, which did immediately absorb the water droplet resulting in a not measurable WCA. Long-term measurements revealed that the WCAs slightly increase over time, which might be an effect of migrating PDMS oligomers. In any case, the hydrophilic character of the sample's surfaces can be maintained even over long time periods and after rinsing the samples several times with deionized water, which indicates that the otherwise water-soluble PEG is covalently attached to the surface.
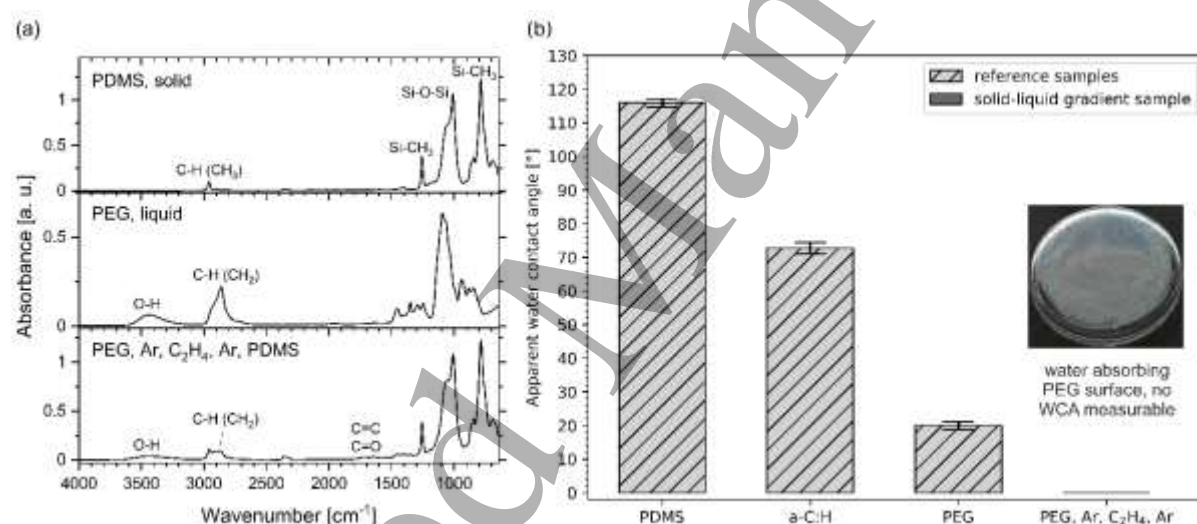

Figure 7: (a) FTIR spectra of cured polydimethylsiloxane (PDMS), liquid polyethylene glycol (PEG) and the plasma-coated PEG sample with PDMS backing. (b) Apparent water contact angles measured on reference samples (cured silicone (PDMS), plasma-polymerized hydrocarbon film (a-C:H), liquid PEG) and on the plasma-coated PEG sample. The photograph shows the water absorbing PEG surface with the silicone backing underneath.

In another approach, different kinds of liquid substrate materials such as silicone oils, liquid PDMS, glycerin, liquid paraffin, ionic liquids, and vegetable oils have been used to synthesize metal films and metal nanoparticles and to investigate film growth including hydrocarbons on such liquids as summarized in [56]. The various methods to grow films on liquids are discussed for diverse applications such as the encapsulation of liquids for the production of optical microdevices, drug delivery systems, microfluidics, biocompatible membranes, and sensor materials. As an example, thin gold films were sputter-deposited (30 nm, 1 Pa) on tapered optical fibers surrounded by a low refractive index nematic liquid crystal to investigate the influence on light propagation

inside the taper structure for potential sensor applications [75]. Moreover, oriented carbon nanostructures (OCNs) with dominant graphitic characteristics have been synthesized by plasma-assisted (Ar/H$_2$ RF ICP, ~55 Pa) structure reformation of resorcinol-formaldehyde polymer gels [76]. Defect-rich OCN structures exhibited excellent gas sensing properties to ethanol at room temperature. As a final example, an AP plasma jet can be used to form high value organic nitrogen-containing chemicals by exposing liquid toluene to a flow of plasma-activated N$_2$ [77].

4. Plasma Engineering of Soft Matter – Surface Modification

This section considers specific features of the plasma surface modification dealing with manmade soft materials (figure 8). At first, some principles of plasma treatment of polymers are discussed relevant, e.g., for the photolithographic patterning of organic materials [10]. Plasma engineering of rubbers and PDMS is discussed in more detail regarding stiffening, surface functionalization, and coating. Furthermore, the plasma deposition of thin films on hydrogels has emerged as an important industrial topic. In addition, fibers and biomaterials are briefly revised. While these fields make use of established plasma processes, challenges remain in the precise control of both gas phase and surface processes with respect to the provided energy and created reactive species. The plasma treatment of polymer powders and its related applications has been extensively discussed in a review by Arpagaus et al. [78], while plasma synthesis for nanoparticles was covered by Jang et al. [79]. Those topics will not be discussed further here. Likewise, the plasma interaction with bioorganisms and food has been addressed by recent review articles [80-82].
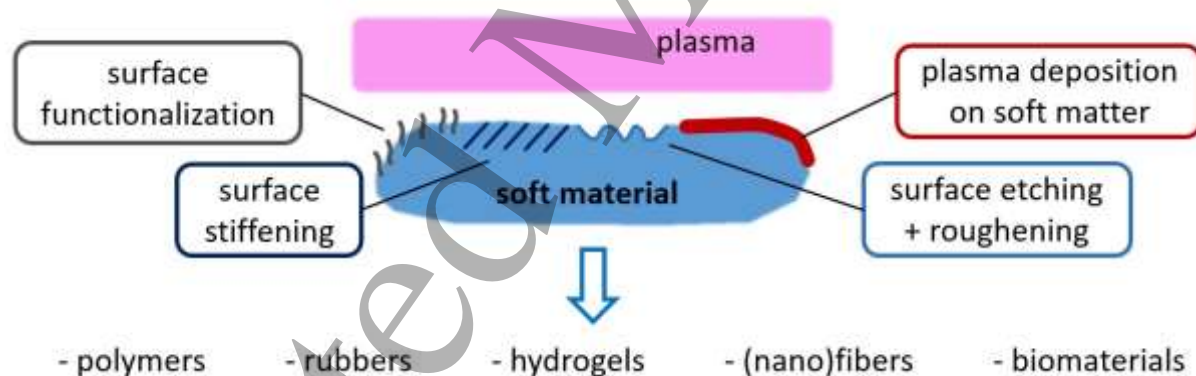

Figure 8. Plasma engineering of various soft materials for the controlled surface modification by surface functionalization, surface stiffening, surface etching and roughening, and plasma film deposition.

4.1 Plasma surface engineering of polymers

Many organic polymers might be assigned to the class of soft matter. There are different features that such polymers have in common: the carbon backbone, C-H bonds, oxygen functionalities like O=C-O and C-O as well as phenyl groups, a cyclic group of atoms with the formula C$_6$H$_5$ [83]. Many elastomers are among such organic compounds, whereas silicone rubbers are an example of a non-organic polymer containing silicon together with carbon, hydrogen, and oxygen such as (CH$_3$)$_2$-Si-O units. The latter are generally non-reactive, stable, and resistant to extreme environments and temperatures while still maintaining their useful properties. The "soft matter character" of polymers might be distinguished by their glass transition temperature, T_g. Above

T_g, segmental and chain motion is enabled, whereby the polymer viscosity can be strongly decreased to a so-called liquid state at elevated temperatures. As the long chain molecules in polymers are less entangled due to enrichment of shorter chains and chain ends close to their surface, polymers show a reduced T_g close to free surfaces [84]. This effect might especially be important for polymer nanofibers thus representing a special class of soft matter. However, T_g can also be increased close to an interface via hydrogen-bonding interactions between the polymer and hydroxyl groups present at the bonding partner [85]. Similarly, T_g was found to be increased for thin (<100 nm) polymer films, spin-coated on Si wafers and annealed, which also lowered the etch rate of the poly methyl-methacrylate (PMMA) films in a plasma [86]. Plasma surface engineering of polymers should thus consider varying T_g and related film inhomogeneities of thin supported polymer films [87].

On top of this, plasma polymer treatment is a complex interplay of ion energies, ion flux, synergies with radical fluxes, and UV radiation with the polymer properties, where the deposited energy, i.e. the energy flux per affected near-surface volume should only be considered as a guiding principle. Bond dissociation by ions is reported for the C-CH$_3$ bond at ion energies of ~4 eV, for the O-C=O bond at ~5 eV and for the C=O bond at 8 eV [83,88]. By controlling the process pressure and power input, ion energies can be decreased to values below 6 eV thus avoiding severe degradation of the respective bonds [88], whereas increased ion energies (and fluxes) yield enhanced etch rates. Strong plasma interaction can further result in an increase of surface temperature that can distinctly increase etch rates when reaching temperatures exceeding T_g of the treated polymer [89]. On the contrary, a 1-2 nm thick stiff overlayer can be induced at the polymer surface due to ion modification resulting in increased surface roughening (depending on polymer structure and deposited energy) and reduced etch rates with plasma exposure time, while new surface functionalities are introduced [10,90,91]. The etch rates also depend on chemical structure of the polymer such as oxygen content as well as crystalline/amorphous regions with preferred etching of the amorphous parts [92]. Furthermore, as demonstrated in figure 9, etch rates can drastically be increased by ion-radical synergies as seen by comparing Ar, O$_2$, and Ar/O$_2$ plasmas [93,94]. Physical etching as in Ar rather results in stiffening of a polymer surface. The produced crosslinked layer can continue to increase in thickness for prolonged plasma exposure times involving UV radiation, known as CASING (crosslinking by activated species of inert gases) [95,96]. The combined action of Ar ions and atomic O, on the contrary, causes oxidative ablation and surface roughening. Besides such O radicals, OH radicals are considered to be the most important reactive oxygen species (ROS) in polymer surface treatment using plasma [97]. The role of plasma chemistry finally becomes dominant for plasma treatment of polymers using AP plasmas [98]. Here, the presence of water in a polymer might also be considered that significantly impacts its properties, as water acts as a plasticizer, lowering the polymer's T_g and increasing its mobility. Hence, given that most polymers are hygroscopic, the impact of water represents a critical parameter, which requires further studies [99].
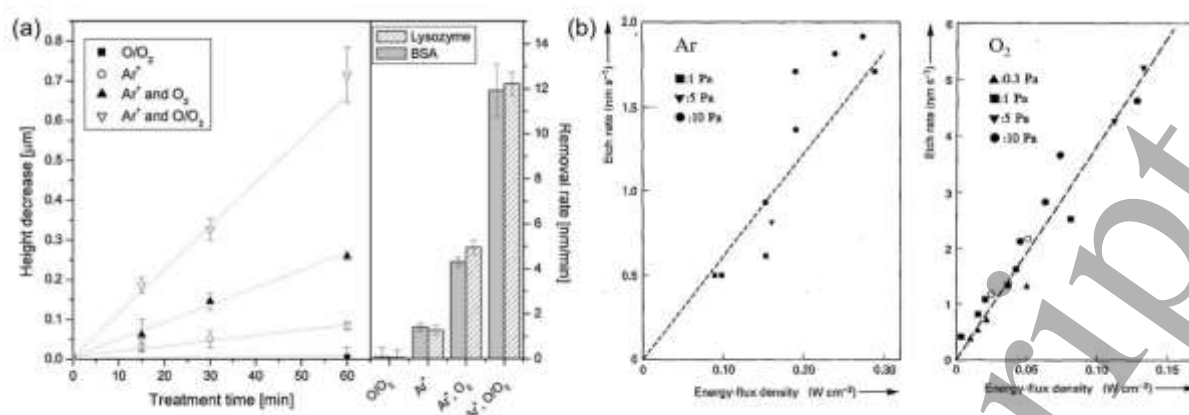
Figure 9: Synergistic effects of ions and radicals in plasma etching of organic material using Ar and O_2. a) Increasing etch rates of proteins by combining Ar ions (100 eV) and O/O_2 using a beam source with controlled fluxes. Reproduced with permission from [93]. © 2009 John Wiley & Sons, Ltd. b) Comparison of Ar and O_2 plasma etching of a novolac-based photoresist using a reactive ion etcher. The slope indicates different deposited energies as relevant for physical and chemical etching. Reprinted with permission from [94]. © 1994 AIP Publishing

4.2 Plasma surface engineering of rubbers

Rubbers or elastomers represent a special class of amorphous polymers owing to their low T_g being in a soft or rubbery state at ambient temperatures. Another characteristic of rubbers beside deformability is their tackiness. The sticky surfaces of rubbers result in stick-slip motion when rubbing against other material, which is unwanted for wipers on the windscreen or syringe plungers moving in the cylinder. Therefore, oil and fat are commonly added to improve the surface lubricity of elastomers. When oil and fat run dry, however, drawbacks such as gradual increase in the friction coefficient arise. For instance, car windshield wipers become noisy within 6 months of use [100]. Plasma engineering has thus been explored to remove the tackiness of rubber materials in order to reduce the coefficient of friction relevant e.g. for syringes, valves, and wipers that show high deformability and related friction forces.

For rubbers, mainly plasma-modified layers or plasma polymer layers are considered, since inorganic coatings show a mechanical mismatch requiring transition layers of the first kind. For example, thin fluorocarbon plasma polymers deposited on ethylene propylene diene terpolymer (EPDM) substrates reduce stickiness and enhance abrasion resistance, however, providing limited protection, while thicker films tend to fragment under wear [5]. In order to provide a wear-resistant protective layer with good sliding properties on the surface of a wiper blade rubber, at first, an organic soft SiOCH plasma polymer layer (~10 nm) was deposited followed by a gradual change in plasma gas composition (increasing addition of a hydrocarbon gas) and bias voltage (to induce increasing ion bombardment) resulting in an about 1 μm thick hydrophobic coating with increasing crosslinking towards its surface [101]. Note that the gradually adjusted deposition process to adapt the different mechanical properties of substrate and coating via an extended interface needs to be as smooth as possible, for example, the change in electrical discharge conditions such as excitation voltage, ion current, and bias voltage should not show abrupt transitions to avoid peaks in internal stress formation [102]. It should further be considered that rather mild plasma conditions, that is, low power and non-oxidative conditions, enable the formation of a lower interface roughness (≤3 nm) supporting the deposition of soft SiOCH layers [103]. Deposition of SiOx films, on the contrary, show a larger interface roughness of around 10 nm. Changes in gas composition (such as addition

of oxygen) and power input during the plasma deposition process can well be handled, whereas changes in pressure needs advanced process control. Likewise, a so-called "flexible DLC" thin film has been developed to improve surface properties of rubber seal rings as used for zoom lens systems of 35 mm compact cameras. Following H_2 plasma cleaning, a CH_4 plasma (low-pressure RF with amplitude modulation) was applied to deposit a-C:H films with adjusted, i.e. reduced, hardness [100].

Similar to the discussed plasma surface modification methods, plasma engineering is used to improve adhesion of rubbers to different bonding partners. Using inert gas plasmas a complex interplay with the rubber material can be observed yielding, for example, increased peel strength of a styrene–butadiene–styrene (SBS) elastomer with a polyurethane adhesive already after short plasma treatment of 5-15 s [104]. Extended plasma treatment times first result in lowered adhesion followed by a re-increase in peel strength for times around 10 min. Three main effects were discussed to be responsible for this behavior, namely, formation of free radicals, crosslinking, and plasma etching of the SBS surface, which might act differently on adhesion due to subsequent oxidation reactions in air. Again, the interface formation is crucial for adhesion. While a thin interface (of a few nm) promotes interfacial slippage reducing adhesion, a wider interface (>10 nm) allows larger energy dissipation and enhanced adhesion when viscoelastic properties are adjusted [2]. Air-fed atmospheric pressure plasma jets can already strongly enhance adhesion by cleaning, activation and roughening of rubber surfaces also supporting chain interpenetration with soft adhesives as e.g. frequently used in automotive industry [105]. Yet also low cost, low pressure air-fed plasma treatments are relevant, e.g., for the activation of crump rubber to enhance adhesion in crump rubber modified binders for asphalt used for roads [106].

Polydimethylsiloxane (PDMS) is a widespread substrate used for microfluidic devices due to low-cost fabrication and simple micro-patterning [107]. The hydrophobic material, however, requires an improved wettability when used in the form of microchannels for aqueous analytes to spread and flow smoothly through the device to enable lap-on-a-chip systems requiring molecular separations, cell culture in microchannels and biomolecular detection via immunoassays. An early work aiming for the controlled functionalization of a silicone rubber was performed by Hsiue et al. [108]. Ar plasma treatment for 1 min (RF CCP with moderate power input at 26 Pa) was applied to the silicone to induce free surface radicals followed by exposure to an oxygen gas flow for 20 min. Graft polymerization with poly(2-hydroxyethyl methacrylate) [poly(HEMA)] was conducted immediately afterwards to enhance cell adhesion [108]. Numerous work followed including plasma activation (e.g. Ar or O_2 plasma), plasma grafting (e.g. AAc after plasma activation) and, in particular, plasma polymer deposition of hydrophilic thin films as partly summarized in [14,109,110]. Maintaining wettability of PDMS, however, remains still a challenge considering its low T_g of around -120°C, which also affects adhesion. The migration of uncured PDMS oligomers from the bulk to the surface and the rearrangement of highly mobile polymer chains turning Si-OH bonds toward the bulk are supported at room temperature yielding hydrophobic recovery [110]. Hence, not only surface modifications but also modifications of the bulk PDMS are investigated, e.g., by extracting oligomers or mixing with further polymers.

Furthermore, PDMS as a bioinert synthetic polymer is commonly used as biomaterial, e.g. as a cell culture substrate, with tunable elastic properties. Oxidation by plasma treatment induces surface functionalization but also a surface stiffening effect. This effect can approximately be described by a two-layer material model composed of a thin, stiff plasma-oxidized layer (of >100 nm and elastic modulus in the MPa range) superimposed on a thick layer of bulk polymer (with an elastic modulus of around 10 kPa) [111]. The outermost silica-like layer as formed on PDMS by oxygen plasma can even show an elastic modulus exceeding 1 GPa for

extended plasma exposure, finally leading to the occurrence of surface microcracks [112]. The stiffening effect should thus be considered for cell-biomaterial interactions, since the mechanical properties of the cell substrate is believed to have implications for cultured cell behavior. PDMS materials can indeed be provided with a wide range of stiffness (modulus ranging from 4 to 70 kPa) by varying the ratio of silicone elastomer to crosslinking (curing) agent. The crosslinker, however, also affects surface properties such as interfacial adhesion force and hydrophobicity due to a reduction in free polymer chains and shorter chain ends near the surface resulting in lower tackiness, which was found to predominantly affect bacterial adhesion over mechanical properties [113]. To this end, PDMS substrates with varying stiffness have all been coated by a 2 nm thick PDMS-like plasma polymer. Differences in surface properties (tackiness, wettability) were leveled out, while the mechanical properties were retained by minimizing the stiffening effect. Hence, possible mechanosensing of bacteria has to be limited to a nanoscale region near the surface – at least on soft materials. Note that protein adsorption was found to be rather unaffected by mechanical properties of the surface [114]. Finally, the plasma coating of PDMS should consider the formation of an adjusted vertical mechanical gradient at low plasma intensities to match the largely different moduli of substrate and coating [115]. Interestingly, the hydrophobic recovery of oxygen plasma-treated PDMS was observed to be suppressed after printing of a polyacrylamide hydrogel, which is an important finding to fabricate soft stretchable devices [116].

4.3 Plasma surface engineering of hydrogels

Plasma can also be used to modify the surface structure of hydrogels. One example for the usefulness of such a process is the treatment of silicone hydrogel contact lenses leading to specific changes in surface morphology which can improve the material's wettability and thus inhibit protein attachment [117]. Plasma exposure can also cause wrinkled patterns on the surface of hydrogels by exposing them to oxidizing plasmas [56,118]. Plasma treatment used to functionalize hydrogel surfaces also opens up a wide range of possible applications [119]. By implementing oxygen-rich functional groups, the surface chemistry of the hydrogel can be altered enhancing hydrophilicity [120]. Surface functionalization can further lead to an improved cell adhesion without affecting the mechanical properties of the bulk material. One example is the functionalization of poly(vinyl alcohol)-based hydrogels using RF, microwave and reactive ion plasmas, respectively [121-123].

Furthermore, plasma polymer deposition in the context of hydrogels has several advantages compared to other methods allowing a precise control of the hydrogel properties, e.g., to adjust wettability and permeation properties. Accordingly, plasma coating on contact lenses is a well-established method, whereby H. (Kogi) Yasuda provided pioneering work [124-126]. Among different applied PPFs, about 20 nm thick moderately hydrophilic coatings using a gaseous mixture of CH_4 with air (ion vapor deposition at ~7 Pa) were found to withstand swelling upon hydration providing biocompatibility and barrier characteristics without significantly reducing oxygen and ion permeability of the hydrogel lens (figure 10). To allow for suitable flexibility, barrier and permeation properties, the deposited energy during film growth becomes the key factor. Ultimately, the green plasma process was shown to be economically favorable compared to wet-chemical coatings.

Thissen et al. investigated the effect of allylamine, $CH_2=CH-CH_2-NH_2$, plasma-polymerized films on ready-made silicone hydrogel contact lenses (RF plasma at 20 Pa) demonstrating that biocompatibility could be improved by reducing biofouling [127]. Similarly, Rout and Girard-Lauriault deposited flexible plasma-polymerized hydrocarbon films (low-pressure RF CCP) containing oxygen- and nitrogen-rich functional groups on the surface of hydrogels used for the fabrication of contact lenses [119]. The surface properties could be well

adjusted by uniform PPFs using low-energy plasma conditions (low power at 80 Pa), i.e. with moderate ion bombardment energies due to collisions, while lower working pressure (10 Pa) resulted in fractures and nonuniformity of stronger crosslinked films. High flexibility of adequate PPFs is thus required showing good water barrier properties despite their high hydrophilicity and a good stability in aqueous environments. Likewise, atmospheric pressure plasmas can be used to deposit functional thin films on hydrogels. Hydrogels comprising polyvinyl alcohol (PVA) and sodium alginate were subjected to a parallel plate-DBD and coated using the monomer HMDSO with three different carrier gases (Ar, He and N_2) [128]. The plasma treatment rendered the hydrogels stiffer and tougher allowing the prolongation of drug release (5-fluorouracil) in an oral controlled delivery system for improved patient compliances.
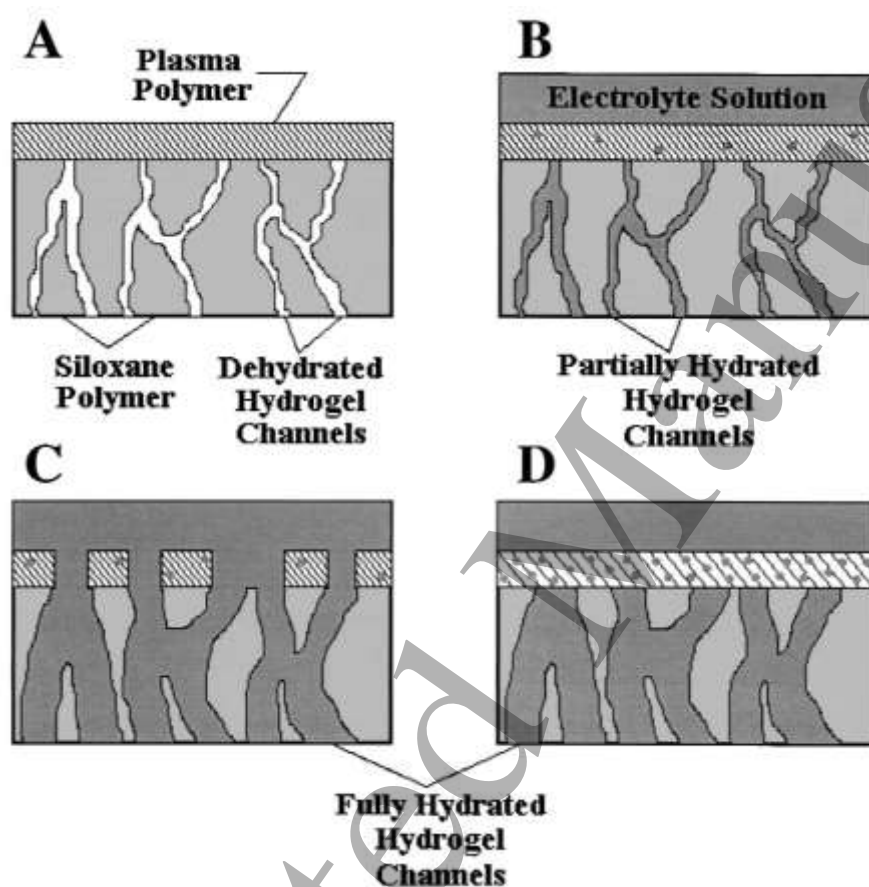

Figure 10: Schematic representation of the required plasma polymer film integrity and barrier properties when deposited on a swellable siloxane-based hydrogel. (A) before hydrogel hydration; (B) after hydration with a crosslinked PPF restricting full hydration and salt intrusion; (C) fractured, nonuniform plasma polymer on a fully hydrated hydrogel; and (D) demanded PPF characteristics allowing suitable flexibility, barrier and permeation properties. Reproduced with permission from [125]. © 2001 John Wiley & Sons, Ltd.

4.4 Plasma surface engineering of fibers and biomaterials

The plasma etching of fibers is of high interest, for example, for medical sutures [129]. Monofilaments of polypropylene (PP), polyethylene terephthalate (PET), polydioxanone (PDO), and modified glycolic acid were etched in an oxygen plasma (CCP at 10 Pa) with different etching times, while limiting heating of the sutures to around 40°C. The observed nanostructures on the suture threads by oxygen etching partly enhanced bacterial repellence. Similarly, functional particles embedded in fibers during fiber production can be exposed to the

surface by plasma etching. To examine the uniformity of plasma etching around a fiber, we placed a PET monofilament (Ø 32 μm; density 1.38 g cm^{-3}, tensile strength 0.55 GPa) directly at the RF-driven electrode and at floating conditions 15 mm above the electrode using Ar/O$_2$ plasma in a symmetric CCP reactor (Ø 30 cm, electrode gap 5 cm) with 50 W and 10 Pa (figure 11). Plasma exposure time of 2 min caused distinct etching effects for the fiber surfaces exposed to the active plasma showing nanostructures made of crystalline lamellae, while shadowing effects reduced the etching rate at the side and almost fully avoided etching on the lower side touching the electrode, which clearly indicates the importance of ion energy and flux for plasma etching. For the conditions at floating potential, a longer plasma exposure of 10 min was selected to roughly match the etch rate at the upper side of the monofilament. Etching occurred all around the fiber with enhanced etching effect indicated by partly collapsed nanostructures at the lower side facing the plasma-sheath boundary, where the electron energy is enhanced. Careful selection of process conditions is thus required when uniform etch effects are demanded.
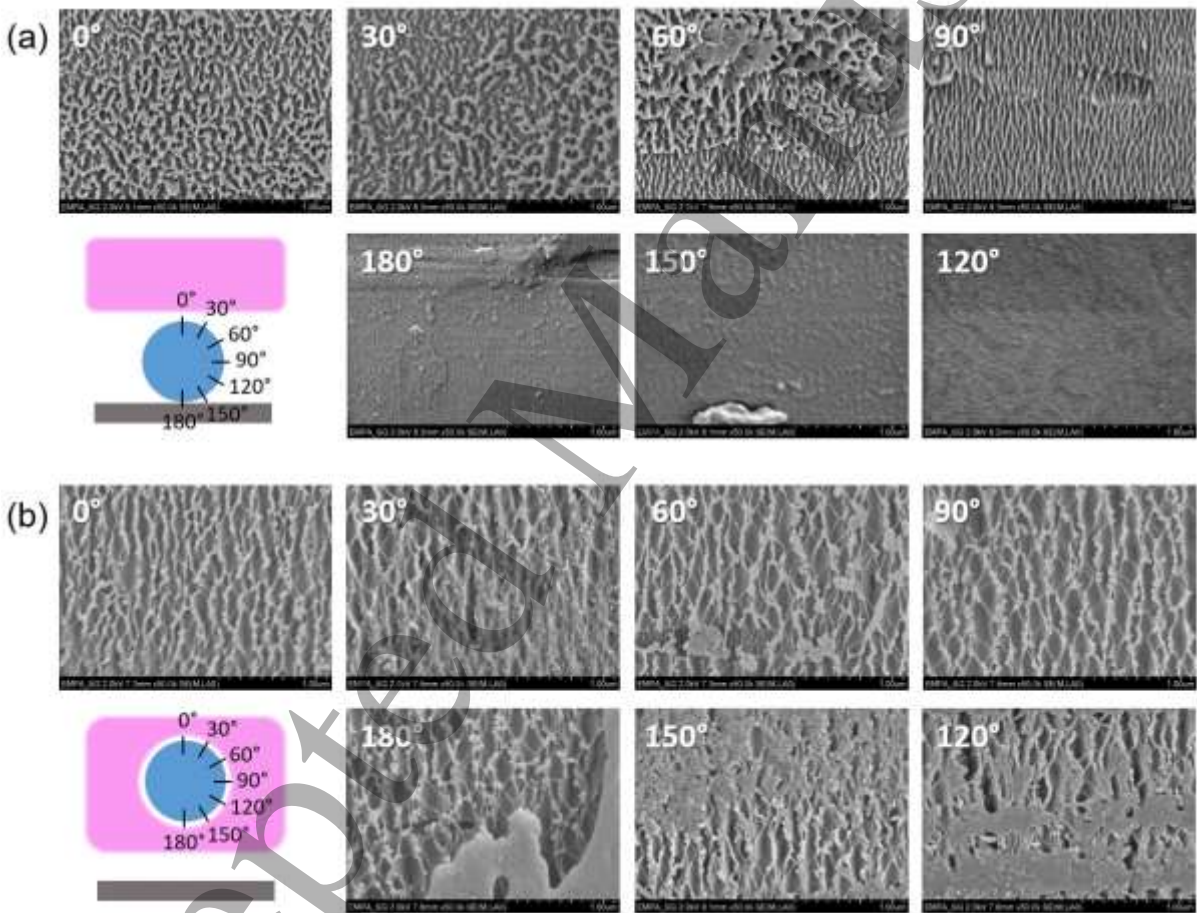
Figure 11: Plasma etching effect around a PET monofilament fiber (Ø 32 μm) using Ar/O$_2$ (RF CCP at 10 Pa) analyzed by scanning electron microscopy (50'000x). (a) Fiber was placed directly at the RF electrode (2 min plasma exposure), (b) fiber was mounted 15 mm above the electrode at floating conditions in the plasma (10 min plasma exposure to adjust the etch rate at 0° position).

Plasma treatment (10 min with air at 3 Pa) has also been performed with elastane monofilaments (Ø 50 μm) as used in clothing industry as it is stronger and more durable as rubber [130]. Elastane is a highly stretchable elastomeric fiber consisting of rigid and flexible segments in the polymer chain. The rigid highly crystalline

polyurethane segments were found to be less affected by the O_2/N_2 plasma as indicated by more intense x-ray diffraction pattern. Preferable plasma etching of the flexible segments can thus be inferred yielding a more elastic fiber by surface softening. Plasma deposition, on the contrary, can be used to enhance wettability of fibers by depositing ultrathin C:H:O PPFs. If such coatings are deposited uniformly on monofilaments that are twisted afterwards to obtain a yarn, the water transport by the hydrophilized yarns can be investigated in detail important for medical textiles, moisture management in functional clothing, or production of fiber reinforced materials [131]. Furthermore, metallization of fibers by plasma technology allows for electrically conductive fibers as used for surface bioelectric dry electrodes as well as for antibacterial textiles [132-134].

Plasma surface engineering is of particular interest for the functionalization of soft biomaterials including biodegradable polymers [135,136]. Generally, polymers require surface modifications to enhance biocompatibility and to attain further surface functionalities [137]. For example, polycaprolactone (PCL) patches were etched by O_2 plasma to obtain nanotopographical features to fabricate hierarchical multiscale scaffolds [138]. Furthermore, polylactic acid (PLA) films can be evaporated and crosslinked by plasma treatment during deposition, thus adjusting their biodegradability for controlled drug release [139]. Electrospun nanofibers are frequently used as substrate material to immobilize biomolecules due to their large surface area to volume ratio and interconnectivity [140]. Moreover, their mechanical properties are attractive to design biomaterials [141,142]. Plasma engineering provides an important tool to further modify the surface properties of nanofibers as recently reviewed by Dufay et al. [143]. Adjusted plasma conditions based on balanced etching/deposition conditions enable surface functionalization with carboxylic groups fixed within nm-thick PPFs in a CO_2/C_2H_4 plasma (RF CCP at 10 Pa) [144]. Those highly porous substrates were found to maintain their improved wetting properties over many years (>10 yrs as recently checked by our group). Likewise, good penetration depth of functional PPFs into nanofibrous and porous scaffolds was observed for the plasma polymerization of cyclopropylamine (RF CCP at 50 Pa) due to surface diffusion of reactive species having different sticking probabilities [145]. Atmospheric pressure plasmas can be used in a similar way to deposit nitrogen-containing PPFs into 3D scaffolds made of PCL with good penetration depth [146]. Similarly, sponges made of cellulose fibers can be functionalized by plasma surface engineering for biomedical applications [147] as well as cellulose-based products for paper industry [148]. For this purpose, also plasma deposition at atmospheric pressure is gaining increasing interest for industrial applications. However, significant differences in the nano/microstructure of PPFs should be considered when deposited on nanofibers either at LP or AP conditions. The latter shows a pronounced tendency to form particulate structures that might support water repellency using hydrophobic HMDSO-derived coatings deposited on PVA electrospun nanofibrous mats [149]. Likewise, hydrophobization of cellulose and PET film surfaces was performed by an APP jet treatment using silicone-based precursors yielding extremely water- and oil-repellent surfaces [150]. APP jet coatings are thus considered as a next generation technology to produce high performance textiles [151].

In order to functionalize porous polymer structures and to enhance wettability, plasma immersion ion implantation is another important technology. Polymer bone scaffolds have been treated in a pulsed DBD at low pressure showing evidence that ion implantation reached all locations in the scaffold, even for pore sizes as small as 1 mm [152]. Finally, plasma sputtering can be used to deposit metal particles or films on nanofibrous membranes for photocatalytic and antibacterial properties, which is difficult to achieve using other techniques [153].

5. Plasma Engineering for Transforming Solids into Soft Materials

In this section, the potential of surface softening of solid substrates is discussed based on plasma etching of polymers yielding roughening and nanostructuring. Moreover, the broad field of deposition of soft, polymer-like plasma films on rigid substrates is touched on briefly. As depicted in figure 12, both approaches aim for adapted surface properties with respect to stiffness, elasticity, flexibility, and adaptiveness important for the bonding of dissimilar materials and for the interface and integration between synthetic components such as prostheses and humans as well as for soft robot manipulations [154,155]. This section thus aims at minimizing issues due to mechanical mismatch between soft and rigid materials at the nanoscale as well as improving the contact to biological media and tissue also considering water interaction, leaving ample room for novel findings.
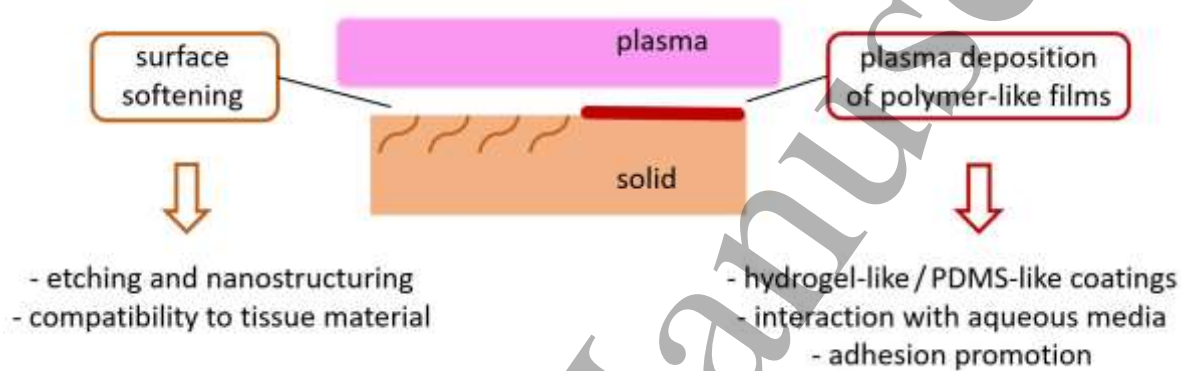

Figure 12. Plasma engineering for transforming solids into soft materials through plasma-induced surface softening or by deposition of softer plasma polymer films on rigid substrate materials.

5.1 Plasma engineering for surface softening

Many high-performance polymer materials as used, e.g. for implants, have a rigid surface yielding high friction coefficients and incompatibility with tissue material, thus requiring softer surfaces [156]. As discussed above, the interaction with inert gas plasmas mainly results in stiffening of soft materials due to the formation of a crosslinked near-surface layer accompanied by physical etching processes and UV radiation. Adding reactive gases such as O_2 to a plasma, on the contrary, largely enhances etching rates involving ion-assisted chemical reactions [93]. This plasma-chemical etching of polymers induces chain scission and ablation of weaker polymer segments such as amorphous sections (see also figure 11). Plasma-based nanostructuring of polymers can thus be induced [157]. The group of Gogolides *et al.* performed an important study on the mechanical properties of plasma-etched PMMA plates using a low-pressure (0.75 Pa) ICP with oxygen [158]. Increasing plasma etching duration resulted in pronounced nanostructuring of the polymer surface accompanied by a reduction in hardness and reduced modulus. Plasticity of the surface, however, was found to increase, readily yielding deformation and wear. The soft surface structure, however, can partly be stabilized by water immersion and drying due to coalescence of nanofilaments forming "microhills" [159]. Extended plastic deformation of the softened surface can also be avoided by subsequent plasma coating protecting the nanotextured structures. Likewise, Zhang *et al.* used an O_2 plasma (ICP, 40 Pa) as a surface roughening method for an acrylic resin denture base material to improve bonding with a soft liner [160]. The induced surface softening helps to match the mechanical properties of the rigid polymer and the soft matter. The acrylic-based and auto-cured soft liner is applied as shock absorber

between the prosthetic device replacing missing teeth and the tissue of the oral cavity. Powell and co-workers investigated the nanotopographic control of cytoskeletal organization using O_2 plasma etching (reactive ion etching at ~0.2 Pa) to generate a nanofibrillar polyethylene terephthalate (PET) surface [161]. Nanostructures with ~200 nm long clustered fibrils stable in culture medium (mouse 3T3-L1 preadipocytes) were obtained by limiting heat transfer during plasma etching following a "thermal bonding" procedure as described in [162]. In the absence of intracellular stress fibers characteristic of cell growth on "normal" planar surfaces was observed on the plasma-etched surface (figure 13). Adhesion and mobility of cells might thus be altered in a predictable manner at flexible nanofibrillar surfaces with sufficient peak height by maintaining chemical composition, thus pointing out the effect of surface topography. In addition, cells might be directly sensitive to material stiffness and strain [163]. A recent study demonstrated that the stiffness of a pillar array made of PDMS also affected cytoskeleton organization, where pillar heights larger than diameter and distance resulted in lowered stiffness [164]. Within a window of proper matrix rigidity, actin organized into a system with circular fiber symmetry on soft pillars, while it aligned into stress fibers only at stiffer pillars.
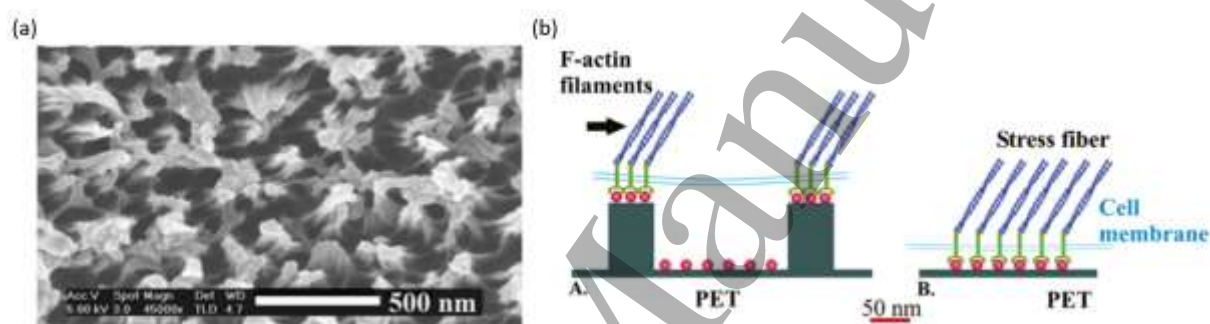
Figure 13: (a) SEM image of a nanofibrillar PET surface after etching for 30 min in oxygen plasma with "thermal bonding" followed by soaking in media at 37 °C for 24 h. (b) Model for integrin-ligand binding on nanofibrillar vs smooth surfaces. While, on nanofibrillar surfaces, surface-adsorbed ligands are present both on the fibrils and in the valleys, cells are believed to bind only at tips of the fibrils, where F-actin filaments can be formed without forming clusters enabling stress fibers. Adapted with permission from [161]. © 2006 American Chemical Society

5.2 Deposition of polymer-like, soft plasma coatings

Plasma polymers are distinguished from their conventional polymer counterparts by an increased crosslink density due to activation in the gas phase and plasma-surface interaction. Polymer-like films formed by plasma polymerization of methylmethacrylate (ppMMA) were compared to conventional PMMA films cured with a crosslinking agent as used as hydrogel [165]. The observed swelling in nitrobenzene as examined by neutron reflectometry was found to be limited to 7.5% for ppMMA, whereas >36% was observed for PMMA indicating increased crosslink density for the plasma-deposited polymer-like coating. The stiffness range that can be achieved for soft PPFs might thus be smaller as for conventional polymer films, however, the plasma polymers can be deposited with uniform crosslink density ranging from nanometer up to micrometer thickness. Cured hydrogel films, on the contrary, typically show variations in the crosslink density due to preferential segregation of the crosslinking agent normal to the substrate surface.

Plasma polymerization has been proven to serve as a tool for producing hydrogel thin films attached to a surface [60,166]. By using a capacitively coupled reactor N-isopropylacrylamide hydrogel films were deposited onto silicon wafers. Film properties like crosslink density, stability, and swelling properties in aqueous environments and adhesion could be precisely controlled by adjusting the plasma parameters. Investigating plasma polymerization (pulsed RF plasma at 10 Pa) from 2-hydroxymethyl methacrylate (HEMA) monomer, the Young's modulus of the obtained hydrogel-like coatings could be tuned from 1 MPa up to 4.5 MPa by identifying regimes with equal chemical composition controlled by the energy input in the plasma, W/F [167]. Surface stiffness can thus be adjusted by maintaining other surface properties. Polyethylene oxide (PEO)-like functional coatings can be deposited showing either cell-repulsive or cell-adhesive properties depending on their crosslinking degree [168]. A good overview of the numerous activities in the field of low-pressure plasma generation of hydrogel-like coatings can be found in [169]. Moreover, also atmospheric pressure plasma methods are becoming increasingly available to deposit hydrogel-like films as antifouling surfaces and to control cell-surface interactions, e.g., as interface to enhance surgical implants [64,170,171]. In particular, 2-methyl-2-oxazoline or 2-ethyl-2-oxazoline, heterocyclic chemical compounds containing one atom each of oxygen and nitrogen, can be plasma-polymerized in a nitrogen DBD or in a pulsed low-pressure plasma, which are difficult to synthesize by conventional methods [14]. Such oxazoline precursor-derived plasma polymer coatings comprise unique properties such as the partly retention of intact oxazoline rings on the surface, which opens new opportunities in bio-sensing and medical diagnostics [172].

The importance of fragmentation in the gas phase depending on energy input, W/F, as well as of the plasma-induced crosslinking at the surface controlled by the deposited energy for polymer-like soft coatings can be investigated by changing power input and pressure. For example, controlled degradability of ester-rich PPFs can be adjusted as shown in figure 14 yielding higher ester content and less crosslinking at lower W/F and reduced ion bombardment using ethyl lactate or dimethyl carbonate in a low-pressure plasma [173-175].
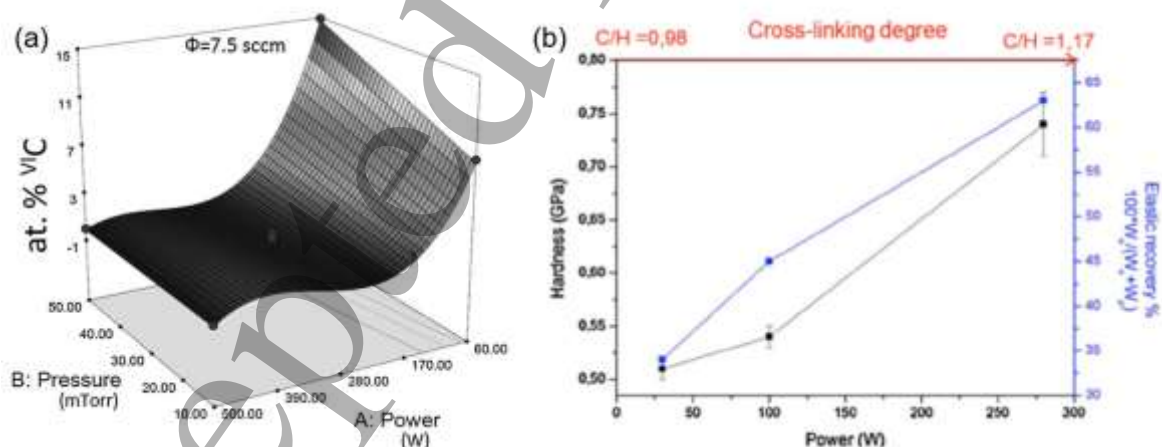
Figure 14: Plasma polymerization of polymer-like, ester-rich films using ethyl lactate in an RF-driven plasma reactor, (a) amount of carboxylic/ester groups (at% ^{VI}C) depending on pressure and power input, (b) mechanical properties depending on power input at fixed pressure of 10 mTorr and monomer flow rate of 5 sccm. Reproduced with permission from [173,174]. © 2001 John Wiley & Sons, Ltd.

Likewise, PDMS-like PPFs can be deposited at mild plasma conditions from HMDSO by controlling fragmentation and film growth conditions. To this end, we used a large asymmetric CCP reactor to

systematically investigate the deposition of hydrophobic PPFs using HMDSO diluted in Ar [29,176]. Most of all, at a specific energy input (SEI) around the threshold energy required to activate the plasma-chemical reaction pathway (~14 eV), reactive $(CH_3)_2$-Si-O species are formed in the plasma resulting in the deposition of hydrophobic, soft PDMS-like films. At increased SEI, enhanced fragmentation takes place in the plasma yielding SiOCH films with reduced hydrocarbon and increased oxygen content (due to post-plasma oxidation at trapped radicals). In addition, densification and crosslinking can be enhanced at the surface further reducing hydrophobicity. Selection of appropriate parameters is thus required to apply rather mild plasma conditions for the deposition of soft coatings, also enabling the defined treatment of highly sensitive materials. In agreement with these findings, Rangel et al. could show that the density and mechanical properties of HMDSO-derived PPFs deposited at floating conditions (RF CCP at 16 Pa, highly diluted in Ar) clearly scale with power input, that is, SEI by using a fixed monomer flow rate, due to increasing abstraction of methyl groups in the gas phase [177]. Soft PDMS-like films with a hardness of 0.4 GPa were observed at low power, while hardness increased up to 6 GPa for strong monomer fragmentation.

As already discussed above, PDMS-like PPFs were deposited on silicone substrates with different ratios of elastomer to curing agent allowing largely varying stiffness. The deposited 2 nm thick film only slightly increased the mechanical properties of the silicone substrates at maximum to 3.6 MPa for the lowest ratio of elastomer to curing agent of 5:1 [113], staying well in the range of e.g. dental elastomers used for soft lining materials [178]. The polymer-like HMDSO plasma films themselves show higher Young's moduli in the range of 1-5 GPa depending on its crosslinking degree. Optimization towards PDMS-like films, however, allows high elastic recovery up to 95% after indentation measurements [179]. Such highly methyl-terminated coatings are used for their hydrophobic properties (water contact angle of 103-105°) that can be applied to various substrate materials showing excellent adhesion and permanence [91]. Remarkably, the interaction of HMDSO PPFs with water still holds a few surprises. Immersed in water over hours and days, they show a reduced water contact angle after removal and drying, pointing to the formation of hydrophilic surface spots [176]. The amorphous branched plasma-deposited film structure contains strained Si–O–Si bonding groups favoring the formation of near-neighbor pairs of silanol (Si–OH) groups [180]. Such polar surface spots promote attachment of water molecules and subsequent intrusion forming nanochannels by further localized hydrolysis reactions and water attachment [181,182]. Such water-filled finger-like channels reach a depth of about 10 nm in the PPF when immersed in water over several hours as revealed by neutron reflectometry (figure 15). Accordingly, the detected amount of water by SEIRAS increased over the first hours of immersion. Water molecules confined to these sub-nm pores within the hydrophobic PPF can arrange as 1D water wires [183]. The involved single-file water molecules show reduced hydrogen bonding compared to bulk water leading to an orientational and dipolar ordering [184]. This ferroelectric alignment of the water molecules within the HMDSO PPFs that is built up over a few hours upon water immersion results in the formation of long-range dipolar fields [185]. Based on SEIRAS results, this water interaction induces reordering of water at the hydrophobic film surface with less water molecules oriented perpendicular to the surface as seen by the relative decrease in the IR bending band around 1635 cm^{-1} specific for perpendicularly oriented OH water [182]. As it is known, water molecules are slightly more parallel oriented on extended smooth hydrophobic surfaces due to a lack of hydrogen bonds in the direction towards the surface [186]. The further orientation of water parallel to the surface due to the emergence of a long-range dipolar field might thus be interpreted as enhanced hydrophobicity. Hence, PDMS-like films immersed in water change their surface (wetting) properties over time which, for example, affects protein adsorption [185].

Note that this effect might be less present at nanostructured surfaces due to more random water orientation [186]. Furthermore, water permeabilities have been found to be strongly enhanced through hydrophobic nanochannels raising interest in energy-efficient nanoscale filtration [187]. Likewise, gas purification might become attractive by high H_2 permeance and H_2/N_2 selectivity [188]. On the contrary, corrosion protection requires sufficiently thick HMDSO-based plasma coatings to block water penetration within relevant time scales. Consequently, 150 nm films were reported to provide excellent corrosion barrier properties against strong alkaline solutions deposited on chemically non-resistant SiOx barrier coatings [189]. In general, the interest in desirable wetting surfaces by surface wettability alteration has gained growing interest in recent years [190].
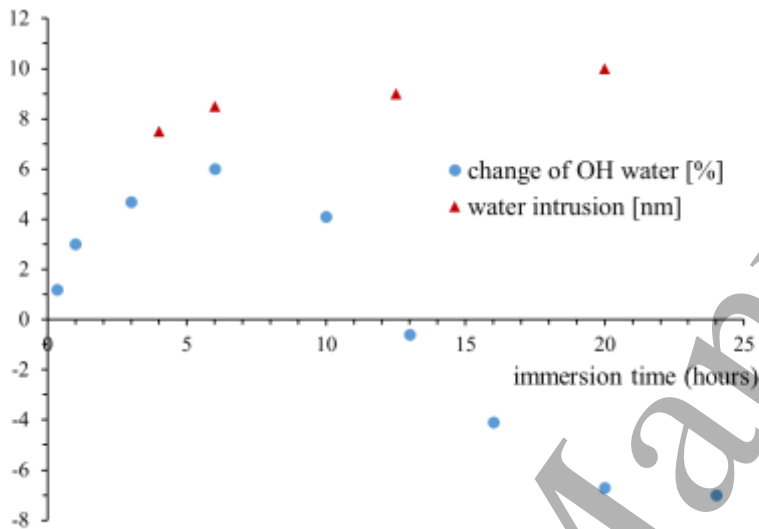
Figure 15: Water penetration depth in PDMS-like PPFs detected over time of immersion in ultrapure water. Minimum swelling and a water uptake of 2-5 vol% has been identified by neutron reflectometry (with D_2O). The relative change in IR band at 1635 cm^{-1} OH bending modes) according to perpendicularly oriented OH water using SEIRAS denotes at first an increase likely due to the water molecules penetrating the PPF by a reaction-diffusion mechanism, while at longer time scales (approaching saturation) a reordering of water molecules at the hydrophobic film surface can be deduced with less water molecules oriented perpendicular to the surface.

The retention of polar (as for hydrogel-like films) and nonpolar (as for PDMS-like films) functional groups in the energetic plasma environment has been a topic of research since decades, e.g. using pulsed plasmas to lower the average energy input, albeit with some limitations [191]. Using monomers that also tend to self-polymerize such as acrylic acid, rather soft, gel-like films with high functional group density can be deposited at low SEI [192]. Such films, however, show a low stability in humid environments, and an increased SEI might be required for different applications to stabilize the C:H:O PPFs by crosslinking at the expense of functional group density [193]. While SEI governs the fragmentation in the gas phase, stability and functional group density is further affected by ion bombardment at the surface as has been shown for various PPFs [28,176,194]. Different strategies to obtain stable and functional PPFs have thus been explored including formation of a vertical gradient structure in the PPF during plasma deposition and chemical post-plasma treatments [195]. Recently, protonation of the starting molecules in the gas phase has been identified as an interesting approach to avoid strong fragmentation of monomers bearing functional groups at moderate SEI [196]. The examination of the fragmentation pathways of ethanol, C_2H_5OH, acetic acid, CH_3COOH, and glucose, $C_6H_{12}O_6$, in a plasma by ICP-

MS revealed that protonated molecules are indeed more stable in the gas phase than the free molecules [197]. Protonated molecules can thus also be detected by mass spectrometry, that is, at a significant distance from the plasma. The H$^+$-loaded molecular ions are accelerated in the plasma towards the substrate, where soft landing of protonated molecules retains their functionality [196]. This way, plasma polymer coatings were deposited from ethyl α-bromoisobutyrate that retained α-bromoisobutyryl functional groups able to graft a dense layer of hydroxyethyl methacrylate (HEMA) polymer brushes to allow for a soft material surface [198]. Operating at reduced power levels to support soft landing was also found to be suitable to enhance the selective retention of terpinen-4-ol monomeric units in PPFs to maintain their associated biologically relevant functionalities [199]. The bonding of rubber elastomers on a metal substrate can be increased by plasma polymer films with adapted properties. Mainly, C$_2$H$_2$-derived polymer-like coatings (RF plasma at 133 Pa, mixed with Ar, N$_2$, or O$_2$) have been studied that promote adhesion between steel and the rubber compound due to diffusion of sulfur from the rubber forming iron sulfide [200]. While thickness and crosslinking degree of the hydrocarbon PPF needs to be adjusted, another important aspect in metal-elastomer bonding is the thermodynamic adhesion, that is, the surface energy of the adhesive joint should be closer to the elastomer one, which has been verified for aluminum–polyacrylonitrile butadiene rubber (NBR) assemblies [201]. Furthermore, the retention of unsaturated carbon in the plasma polymer film is of essential importance for crosslinking with the rubber. From this, it has been inferred that S-containing C:H PPFs such as derived e.g. from thiophene (RF plasma at 27 Pa, mixed with Ar) are even advantageous when deposited as ultrathin layers (around 5 nm thick) on steel [202]. Recently, a glass transition temperature could be identified for propanethiol-based PPFs that correlates with their mechanical properties [203], which might be considered for bonding as well as for the deposition of soft coatings. For adhesion promotion in polymer composites, plasma polymer films containing functional groups are essential for covalent bonding to substrate and matrix. Additional introduction of aliphatic spacers could further flexibilize the interface between plasma polymer-covered substrate and the bonding partner to maximize adhesion in composites and laminates [204]. Furthermore, a smooth transition of chemical and mechanical properties at the interface of polymeric substrate and plasma coating can be achieved by generating gradients during film growth improving stability and adhesion [205].

6. Future perspectives

Manmade soft materials play a key role in the development of future technologies for a better, more sustainable world. Be it in the interface and integration between synthetic components and humans, in personalized medicine and diagnostics or the sustainable processing and recycling of objects around us – soft materials will be there [206]. Deformable and responsive materials constituted by polymers, gels, micro and nanoparticles, and integrated with biological systems including proteins, cells and bacteria offer tremendous potential for new research and innovative applications. In this context plasma surface engineering offers a powerful and versatile tool allowing: i) polymerization and crosslinking of viscous liquids to synthesize hydrogels, ii) surface modification of soft materials, also supporting the bonding between different soft materials or dissimilar materials, and iii) softening of rigid surfaces to enhance their interaction with tissues and aqueous media. Hydrogels as an important class of soft matter are hydrophilic, three-dimensional networks that are able to absorb large quantities of water or biological fluids, and thus have the potential to be used as prime candidates

for biosensors, drug delivery vectors, and carriers or matrices for cells in tissue engineering [33]. Despite their advantages of increased biocompatibility, tunable biodegradability, properly mechanical strength, porous structure, etc., the feasibility of applying hydrogels is still limited due to their low mechanical strength and fragile nature. Thus, novel hydrogels with stronger and more stable properties as well as adapted mechanical characteristics depending on the application field are still needed, opening up a wide range of options for plasma engineering. For example, hydrogel-like PPFs derived from oxazoline precursors gained increasing interest due to their highly functional, antibiofouling, and biocompatible properties making these coatings good candidates for surface modification of implantable medical devices, tissue engineering constricts, cell and drug delivery vehicles, and many others [172]. Novel methods such as plasma-assisted evaporation of polymers and hydrogels are at hand allowing the use of longer chain starting material to be plasma-polymerized into thin films. Likewise, extremely tough double network hydrogels, made of one rigid and brittle combined with one flexible and stretchable network, attracted interest opening up numerous potential applications mainly in the medical field [207,208]. This concept might also be taken up for plasma engineering. A related field that was recently addressed considers cold AP plasma-treated, improved hydrogels with high capacity to deliver plasma-induced reactive oxygen and nitrogen species (RONS) locally to tumors via an implantable delivery system, which represents a viable alternative to plasma generation of RONS in liquids and biological media [209].

Another increasingly used, engineered soft material allowing highly porous fibrous structures with adjusted mechanical properties matching body tissue properties is provided by electrospun nanofibers. Low bioactivity and biocompatibility, however, requires surface modification. Hence, plasma engineering is a versatile tool not only to enhance surface properties but also to adjust mechanical properties by crosslinking or porosity by etching, creating great opportunities for biomaterials and filtration [143].

Open questions about cell response to substrate rigidity as well as to other material and surface properties might be addressed by means of plasma engineering considering soft plasma polymer films with highly defined and controllable surface properties [113], for example, by altering crosslinking and degree of surface functionalization yet maintaining other material properties. For this purpose as well as for the plasma treatment of soft materials in general, more attention should be given to the deposited energy during plasma surface engineering as introduced in the general overview.

Finally, the interaction of manmade soft materials with water is of great importance yielding different ways of water penetration such as swelling, attachment of water molecules, hydrolysis reactions, and single-file water in nanochannels, inducing various effects on the interaction of soft materials in a chemical or biological environment, since surface-biomolecule interaction largely depends on the amount of intermediate water [210]. Such effects represent an opportunity to further tune surface properties by plasma engineering considering the relevant environment. Hence plasma engineering can be used in numerous ways to enhance soft matter applications, also enabling unique functionalization while being an environmental friendly technology, thus offering great opportunities for future applications.

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