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Antrag auf Gewährung einer Sachbeihilfe
Einzelantrag

Priority Programme 2171 “Dynamic Wetting of Flexible, Adaptive and Switchable Surfaces”

Reconfigurable surfaces with switchable wettability based on shape-changing polymers

Rekonfigurierbare Oberflächen mit schaltbarer und adaptiver Benetzbarkeit basierend auf formverändernden Polymeren

Neuantrag

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Project Description

1 State of the art and preliminary work

Surfaces with switchable/adaptive behavior [1-8] are of growing interest for microfluidic devices [9-11], sensors [12-15], functional coatings [16-19], logical devices [20] and for biotechnological applications [21-25]. To date, stimuli-responsive surface were designed mainly using self-assembled monolayers [19], polymer brushes [26] and oxides of transition metals [27]. Exposure to environmental stimuli (solvent, pH, temperature and light) of these materials changes composition in the topmost layer that affects their surface properties including adhesion, friction and wetting. It is known that wetting behavior is affected by two main factors: surface chemistry and surface topography. Although, change of chemistry and topography are often simultaneous, their contribution to wetting is different – usually either one or another factor dominates.

Design of switchable surfaces. *Surfaces with switching chemical composition.* Usually surfaces with switchable wetting behavior are designed using *chemical substances with switchable polarity.* These can either be low molecular weight substances, which form self-assembled monolayers (SAMs), or polymers, which form brush-like layers. Examples of chemical groups are carboxylic and amino groups, which can be either is charged or uncharged state depending on pH. Charged state provide good wetting behavior, uncharged state is less wetted [19, 28].

Due to their high-molecular weight polymers are usually not well miscible even low molecular weight solvents (entropy contribution to mixing Gibbs energy decreases with increasing molecular weight) and there are many polymers, which demonstrate switching of properties because mixing Gibbs energy changes its sign upon increase of decrease of temperature – low and upper critical solution behavior. This effect of *switching of miscibility of polymer chains with solvent* has also been used for design of polymer brushes with switching wetting properties. [29-31]

Internal reorganization in the topmost surface layers leading to minimization of interfacial tension is third possibility for design of surfaces with switchable wetting properties. For example, hydrophobic and hydrophilic groups tend to migrate to the surface when material contacts air and water, respectively. The most pronounced example of switchable surfaces based on internal reorganization are mixed polymer brushes [7, 17, 32]. In all these examples, chemical composition in the topmost surface layer was switched in order to achieve switching of wetting behavior.

It was found that proper combination of topography and switching of surface chemistry allows considerable enhancement of switching of wetting properties. For example, polymer brushes grafted on rough surfaces are able to switch between absolute wetting (0°) and absolute non-wetting (180°) [17]

Surfaces with switching topography. Design of surface with switching wetting behavior using switching topography is usually more challenging because number of materials, which undergo considerable reversible shape transformation at the conditions close to ambient is limited.

The easiest way to achieve reversible switching of surface topography is *mechanical deformation* of elastic materials (rubbers) with topographically structures surfaces. [33] The advantage of this approach is its simplicity. The approached requires manual deformation that does not allow achievement of local switching and autonomous switching. Moreover, size of the sample changes. A variant of mechanical deformation is pneumatic actuation, which was also used for actuation of surface features [34-35]. They require pressure source.

Shape-memory polymers [36-37] allow similar effect. The shape-memory polymer with structured surface is deformed (stretched or locally pressed) at elevated temperature and then cooled down below melting/glass transition temperature to keep “frozen” topography. Increase of temperature “unfreezes” polymer chains and initial surface topography is restored. Although, relaxation of topography occurs autonomously when proper temperature is achieved, manual deformation is necessary to form temporary topography.

Hydrogels allow considerable and fully reversible switching of topography [38]. On the other hand, hydrogels always remain hydrophilic and no switching of wetting behavior is observed. Switching of wetting properties of hydrogel can be observed when hydrogel is used for actuation of more

hydrophobic substances. For example, Sidorenko et al. developed *hydrogels with integrated rod-like particles* films [18]. These rod-like particles can either be attached to substrate where the film are deposited or be freely – moving. Depending on whether the rods were attached or not, the films demonstrated either classic switching behavior (exposure to water makes surface hydrophilic and drying makes it hydrophobic) or inverse one (exposure to water makes surface hydrophobic and drying makes it hydrophilic).

Magnetic field can be used to deform (bend and twist) surface topographic features which contain magnetic particles. [39-42]. Such magneto-sensitive surfaces can be fabricated either by curing of polymer precursor with magnetic particles in mold or by curing of magneto-fluid with polymer precursor in magnetic field. Although demonstrated results are very interesting and magnetic field allows considerable deformation of topographical features and switching of wetting properties, the published paper bring just a little ща understanding of mechanisms of switching and interplay between difference forces (magnetic field, elastic forces and surface tension).

Another kind of surfaces with switchable topography are formed by *stressed semicrystalline polymers*. These polymers demonstrate reversible transformation of pattern upon cyclical changes of temperature between room temperature and temperature slightly lower than melting point. [43] The shape variation are however relatively small.

Liquid crystalline elastomers **[44]** are also able to demonstrate switching of surface topography. Their synthesis is however complicated. Most of them have relatively large actuation temperature (above water boiling point) and number of systems which are able to change their topography. Therefore, commonly UV light is used for induction of topographical changes in liquid crystals with photosensitive groups [45].

Till now most research on surfaces with switchable wetting was focused on polymer brushes and self-assembled monolayers. Number of papers devoted to surfaces with switchable topography is very limited that is due to difficulty of their fabrication. Among all kinds of materials, which are able to demonstrate switching of shape, semicrystalline ones, hydrogels with inclusions of hydrophobic elements and surfaces with magnetic particles are most promising for design of surfaces with switchable topography and wetting. The number of works on these materials is however very small that does not allow making conclusions about their complex wetting behavior.

Effect of switching topography on wetting. There are plenty works where effect of topographical pattern on wetting properties was investigated. One of most earliest belong to Cassie, Baxter and Wenzel [46-47]. Models of Cassie, Baxter and Wenzel predict contact angles which correspond to thermodynamic equilibrium. In many cases, in particularly when materials, which builds surface is moderately hydrophobic, measured values of contact angle are out of equilibrium. Recently, Marmur and Extrand have proposed different models how to describe behavior on such surfaces [48-49]. In fact, out of equilibrium value of contact angle means that it is not a state function (depends on state and is independent of path how this state was achieved) but depends on path/way how liquid comes in the contact with surface [50]. *Thus, one can expect that behavior of a liquid droplet on surfaces during change of topography will be different from behavior of droplet on static surfaces with similar geometry.*

Summary of state or art. Surface with switchable topography are highly interesting because they must allow enhanced and yet complex (anisotropic) switching of wetting. Their development and understanding of their wetting during switching remains underdeveloped and poorly understood. The missing points are technologies for fabrication of such surfaces and understanding of wetting in transition states (non-equilibrium wetting)

Preliminary work

Our group has strong expertize and extensive preliminary work in switchable surfaces, shape-changing materials and 3D printing, which are needed for the realization of this project.

Switchable surfaces based on polymer brushes. Design and investigation of stimuli-responsive surfaces is one of the research expertise of the applicant (totally more than 20 papers were published on this topic). Stimuli-responsive polymer surfaces were prepared by “grafting to” of end-functionalized polymer and “grafting from” (surface initiated polymerization. The stimuli-responsive surfaces were applied as environmental sensors [4], for controlled protein and particle adsorption and for in vitro control of biomolecular motor systems for nanotechnological applications. As an example, we have developed method for fabrication of patterned component polyelectrolyte brush with switchable topography and wetting [9].

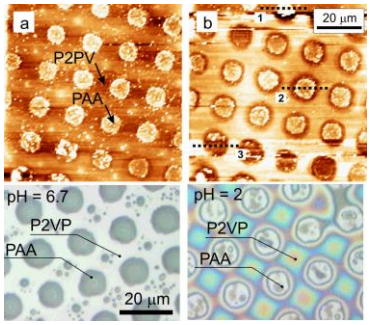

Figure 1. *Switching of wetting behavior of patterned polyelectrolyte brushes (PAA-polyacrylic acid, P2VP – poly(2 vinyl pyridine)* [LI1]

Shape-changing materials. One of the main activities of our group in present is the development of shape-changing polymers and understanding of mechanisms of their actuation. Our group works on hydrogel-based shape-changing polymers as well as semicrystalline ones. For example, we developed a number of approaches for design of self-folding films for bio-related applications using different stimuli-responsive polymers. We utilized poly-(*N*-isopropylacrylamide)-based copolymer with lower critical solution temperature (LCST) behavior, [24], similar copolymer with upper critical solution temperature (UCST) [26], hydrolizable polysuccinimide [27], gelatin [25] as well as hyaluronic acid and alginate [LI1-LI7]. We explored effect of the shape of the layer on the 3D shape of folded object (**Figure 2**) [51-5253].

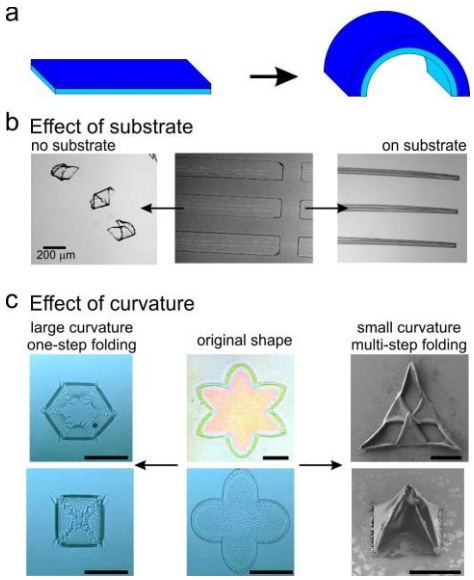

Figure 2. *Different scenarios of deformation of bilayer based on poly(N-isopropylacrylamide)-based hydrogel (a) depending on presence of substrate (b) and shape of the film (c). Scale bars are 200 μm.* [52-54] *Scale bar is 200 μm.*

Recently, we have started to work with reversible actuators based on semicrystalline polymers. For example, we discovered a new unexpected effect of reversible actuation of an ultrathin bilayer formed by not-stimuli-responsive hydrogel and semicrystalline polycaprolactone. [37] [LI8] In one approach, we have fabricated Janus-like acrylonitrile butadiene styrene (ABS)-polycaprolactone (PCL) and polylactide (PLA) - polycaprolactone (PCL) fibers by simultaneous extrusion of two polymers (**Figure 4a,b**). [LI9] [38] The fibers were not crosslinked i.e. polymers could flow and undergo plastic deformation above their melting point. We observed the reversible bending of the bilayer upon its heating above and cooling below the melting point of PCL. This result was absolutely unexpected since the polymers are not crosslinked and PCL was completely molten upon heating (maximal temperature was 100°C), and it must undergo plastic deformation i.e. it must flow. Multiple fibers can be assembled together in complex structures, which also demonstrate actuation behavior.

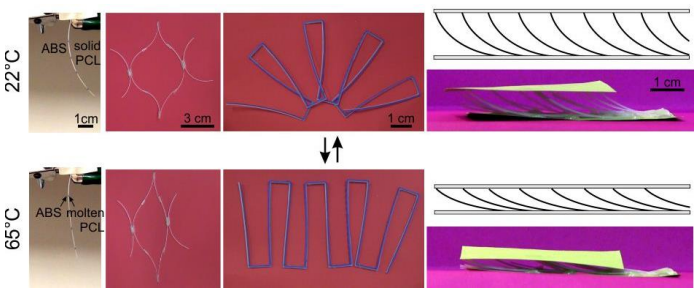

Figure 3. *Reversible actuation of Janus ABS-PCL fiber and structures based on them upon the change of temperature* [38]

Fabrication/3D printing. Our group has extensive experience in methods for fabrication using polymers such as photolithography (**Figure 1**, **Figure 2**), fiber spinning (**Figure 3**), and 3D printing (**Figure 4**). In particular, we have used open-source fused filament Prusa I3 3D printer as basis. Firmware of this printer (Marlin, written in C++) is in open access and can be modified on demand. Currently, we are equipped with 3 self-made 3D printers (**Figure 4**). One of them allows printing of one kind of hydrogel at room temperature in one printing run. Second one allows printing of 4 thermoplastics in one printing rut at temperature up to 300°C (**Figure 4**d). Third, one allows printing of 4 thermoplastics/hydrogels in one printing run at temperature up to 120°C. Second and thirds printers are equipped with high voltage power supply (30 kV, **Figure 4**e), which is controlled using Arduino. We utilized available 3D printers for printing of biomaterials and recently we developed new 4D biofabrication methods to print shape-changing biodegradable polysaccharides (alginate and hyaluronic acid-based hydrogels) [LI10] [55]

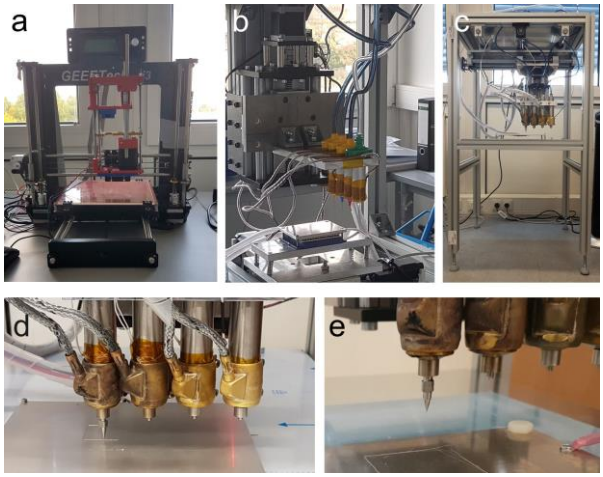

Figure 4 *Built 3D printers for printing of hydrogels and polymer melts with installed syringe pump (a) and pneumatic dispensers (b,c) with heating possibility up to 120°C (b) and up to 300°C (c). (d, e) - magnifications of 3D printer shown in (c); (d) – direct printing; (e) – melt electrospinning writing*

1.1 Project-related publications

1.1.1 Articles published by outlets with scientific quality assurance, book publications, and works accepted for publication but not yet published.

[LI1] Synytska, A; Stamm, M.; Diez, S.; **Ionov, L**.* Simple and fast method for the fabrication of switchable bicomponent micro-patterned polymer surfaces, ***Langmuir*** 2007, *23(9)*, 5205-5209. DOI: 10.1021/la063601y

[LI2] Stroganov, V.; Zakharchenko, S.; Sperling, E.; Meyer, A.K.; Schmidt, O.G; **Ionov, L***. Biodegradable self-folding polymer films with controlled thermo-triggered folding, ***Advanced Functional Materials*** 2014, 24(27), 4357–4363.

[LI3] Magdanz, V.; Stoychey, G.; **Ionov, L***.; Sanchez, S.*; Schmidt, O. Stimuli-Responsive Microjets with Reconfigurable Shape ***Angew. Chem. Int. Ed.*** 2014, 126(10), 2711. DOI: 10.1002/anie.201308610

[LI4] Jiang, S.; Liu, F.; Lerch, A.; **Ionov, L.***; Agarwal, S.* Unusual and superfast temperature triggered actuators *Advanced Materials* **2015**, 27 (33), 4865-4870.

[LI5] Apsite, I.; Stoychev, G.; Zhang, W.; Jehnichen, D.; Xie, J.; **Ionov, L.*** Porous stimuli-responsive self-folding electrospun mats for 4D biofabrication *Biomacromolecules*, **2017**, 18 (10), 3178–3184.

[LI6] Stoychev, G.; Reuther, C.; Diez, S.; **Ionov, L.*** Controlled retention and release of biomolecular transport systems using shape-changing polymer bilayers *Angewandte Chemie* **2016**, 55 (52), 16106–16109.

[LI7] Stroganov, V.; Pant, K.; Stoychev, G.; Janke, A.; Jehnichen, D.; Fery, A.; Handa, H**.; Ionov, L. *** 4D biofabrication: 3D cell patterning using shape-changing films *Advanced Functional Materials* **2018** DOI: 10.1002/adfm.201706248 accepted.

[LI8] Stroganov, V.; Al-Hussein, M.; Sommer, J.U.; Janke, A.; Zakharchenko, S.; **Ionov, L.*** Reversible thermosensitive biodegradable polymeric actuators based on confined crystallization, *Nano Letters* **2015**, 15 (3), 1786–1790.

[LI9] **Ionov, L. *;** Stoychev, G.; Jehnichen, G.; Sommer, J.U. Reversibly actuating solid Janus polymeric fibers *ACS Applied Materials & Interfaces* **2017**, 9 (5), 4873–4881.

[LI10] Kirillova, A.; Maxson, J.; Gomillion, C.T.; **Ionov, L.*** 4D Biofabrication Using Shape-Morphing Hydrogels *Advanced Materials* **2017,** 29, 1600811.

1.1.2 Other publications

none

1.1.3 Patents

1.1.3.1 Pending

none

1.1.3.2 Issued

none

2 Objectives and work programme

2.1 Anticipated total duration of the project

36 months, anticipated project starting date 1.10.2019

2.2 Objectives

The project aims to understand dynamics of switching of wetting properties of surfaces with switchable topography/softness based on phase-changing/shape-changing polymers. In spite of obvious simplicity, this is very complex task because properties of targeted switchable surfaces are characterized by three main components: (i) mechanical and actuation properties of material (G´, G´´, stoke-force dependence), (ii) surface tension γ_{sv} (hydrophilicity / hydrophobicity) and (iii) topography. Forth component is (iv) surface tensions of a testing liquid (γ_{lv}, γ_{ls}). The interplay between these four components defines how liquid interacts with switchable surfaces. **The main challenge of project is to separately elucidate effects of change of softness, topography and hydrophilicity/hydrophobicity on switching of wetting properties.**

Any surface with active topographically elements (switchable topography) can be adaptive or not adaptive depending on ratio between surface tension (generated by liquid droplet) and force generated upon actuation/deformation of topographic features. We can define purely adaptive surfaces and purely not-adaptive surfaces as follows:

- Adaptive surfaces are ones where surface tension forces are must stronger when elastic forces, needed to deform features to considerable extend. Even if features are able to change their shape and generate force in response to external stimuli, their movement and final shape upon contact with droplet will be determined by surface tension.
- Not-adaptive surfaces are ones where elastic forces, needed to deform materials to considerable extend, are must larger than surface tension i.e. droplet does not deform topographical features. Topography of such surfaces is not affected by water droplet.

Energy of mechanical deformation is bulk property and scales with volume, surface energy scales with surface area. Thus, mechanical properties must dominate for large features, while surface forces dominate for small features. In other words, any shape-changing material will demonstrate purely adaptive behavior when size of shape-changing elements is small, non-adaptive behavior will dominate for large sizes. The sizes at which transition between adaptive and non-adaptive behavior is observed depends on elastic properties (Young's modulus) of shape-changing polymers, which will be used for fabrication of switchable surfaces. Another very important factor, which affects mechanical behavior is that polymers are not purely elastic but viscoelastic. The balance between elasticity and plasticity depends on time scale and temperature (time-

temperature superposition). This effects are particularly strong around glass transition temperature, melting point as well as upon transition from rubbery and crystalline states to viscous flow. Considering these transitions is very important because they are used for design of actuating structures i.e. complex mechanical properties (G´, G´´) of shape-changing polymers change during their actuation. The same material can behave like rubber on one timescale and flow on another timescale (like Silly Putty).

Thus, ratio between surface tension and mechanical properties can be influenced in three ways.

- By varying the size of features we can gradually vary behavior of surfaces from purely adaptive to purely non-adaptive.
- By changing mechanical properties*:* Transition around Tg and Tm will also allow change of balance between surface tension and rigidity because elastic moduli change. Change of temperature around Tg and Tm will allow situ investigation of transition from adaptive to switchable behavior.
- By varying the time scale on which interaction between surface and liquid occurs – for example by changing the speed of sliding of water droplet, which depends on slope of sample.

By varying of temperature, size of features and conditions of experiment we should be able to efficiently control surface forces as well as mechanical properties and tune adaptive behavior of surfaces with switchable topography. In this project we will understand influence of ratio between surface forces and mechanical properties (by varying temperature and size of features) on ability of surfaces to switch their topography and wetting behavior upon external stimulation. **In first application period we will focus on investigation of effect two out of three factors – switching of mechanical properties of materials and switching of topography. Combination of effects of switching of topography, switching of mechanical properties and hydrophilicity and hydrophobicity will be studied in second funding period**.

2.3 Work programme incl. proposed research methods

Working plan consist of three main work packages. First we will develop generic methods for fabrication of surfaces with active topographic elements using polymers (WP1). Next we will fabricate topographically structured surface made of materials with tunable elastic modulus and understand their interaction with liquid droplets (WP2, **Figure 5a**). These surfaces will not have switchable functions. The idea is to understand transition from regime when mechanical properties dominate to regime when surface tension forces dominates. This information is very important for understanding of interactions between switchable surfaces and liquid droplets. Finally (WP3), we will introduce switching of topography by using two hydrophobic polymers with different properties or by magnetic particles (**Figure 5b**). The intrinsic wetting properties of materials will remain nearly unchanged (both materials are hydrophobic with nearly the same surface tension) that will allow investigation of effect of switching of topography on switching of wetting properties.

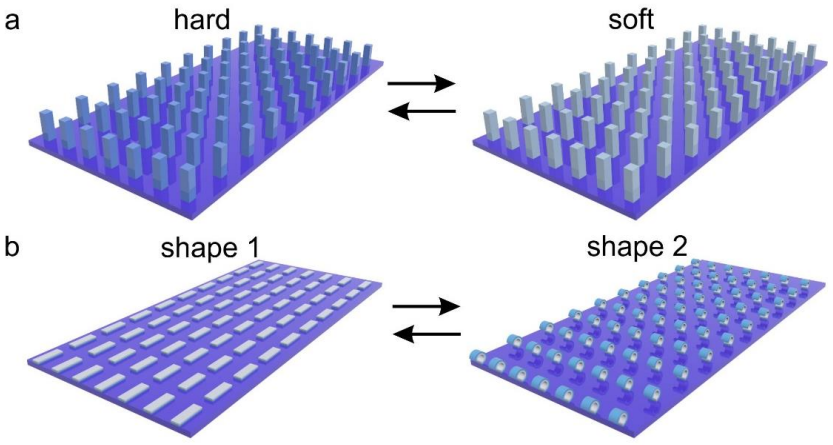

Figure 5. *Surfaces with adaptive and switchable wetting behavior based on stimuli-responsive polymers*

WP1. Development of approaches for fabrication of surfaces

Fabrication: First we will develop methods for fabrication of surfaces with adaptive/switchable topography. We will use all our previous experience in fabrication of actuating polymeric

structures and adapt available technologies for new purpose. Adaptive surfaces will be fabricated using one kind of polymer, surfaces with switchable topography have to consist of two polymers with different properties. Mono and bi-component topographically structured surfaces will be fabricated using different 3D printing technologies. We consider use of stereolithography, direct dispensing 3D printing of melts/solutions and melt electrospinning writing. Each of these methods use own advantages and disadvantages. *Direct dispensing* 3D printing of polymer melts allows printing of multiple materials (available 3D printer allows printing of 4 materials in one run) with 100 µm resolution. Resolution can be improved in two ways. First possibility is printing of *photocrosslinkable polymer precursors* with very low viscosity and its photocrosslinking. Second option is use of high voltage electric field between nozzle and substrate – *melt electrospinning writing*, which allows resolution down to 1 µm. Electric field deforms droplets of polymer solution/melt that leads to its elongation and formation of a thin fiber. The best results are achieved when polymer melts are used because they are cooled down below flow point must faster when solvent is evaporated from polymer solution that allows formation of single fiber and its very precise deposition. *Stereolithography* (laser scanning and DLP-based one) allows very good resolution (10 µm) but suitable for fabrication of monocomponent 3D structures. It assumes use of photocrosslinkable substances. Fabrication of multicompoment 3D structures is challenging because it requires exchange of photopolymer. We will explore fabrication of mono-component topographically structured surfaces with using stereolithography, direct dispensing and melt electrospinning writing. Bicomponent shape-changing topographically structured surfaces will be fabricated direct dispensing and melt electrospinning writing.

There is also a difference in limitation of different 3D printing methods from point of view of possible shape. Extrusion printing allows fabrication of pillars with high aspect ratio but with relatively low resolution. Melt electrospinning writing is based on formation of continuous fibers, which are deposited horizontally. Therefore, formation of vertical pillars with high aspect ratio is not possible. One can however produce long walls with high aspect ratio. Stereolithography allows fabrication of vertical structures with high aspect ratio and very high resolution from single material.

We expect that mechanical/structural properties of polymers obtained via melt extrusion, melt electrospinning writing, direct extrusion of solutions of polymer precursor with following crosslinking and stereolithography will be different. Direct dispensing printing of melts must result in formation of non-crosslinked non-oriented material with no internal stress, melt electrospinning writing has all features of fiber spinning and must result in formation of non-crosslinked stretched fibers with oriented polymer chains. Physical crosslinking will be provided by entanglements. Direct dispensing printing of polymer precursors with following crosslinking and stereolithography will result in non-oriented crosslinked materials. Crosslinked polymer above their melting point will behave like elastomer or thermoset depending on crosslinking density. Crosslinked polymers are expected to have lower degree of crystallinity than extruded one. Actuating properties of materials depend on degree of crystallinity and physical/chemical crosslinking. Therefore, actuating properties of materials obtained using different methods are expected to be different.

Polymers: We will use polymers with relatively low melting points (35 – 70°C) such as polycaprolactone, polycaprolactone-based polyurethanes and polyalkyl(meth)acrylates for fabrication of surfaces with switchable mechanical properties and topography. These polymers are stiff when crystalline and soft when molten. Moreover, crystallization/melting results in small change of volume (5-10%) that will be utilized for design of actuating elements. The exact value of melting point of polycaprolactone can be adjusted by varying its molecular weight and melting point of polyalkyl(meth)acrylate can be tubed by length of acrylate tail. We will use polyalkyl(meth)acrylates with C18-C22 alkane tail. Addition of benzophenone derivatives allows photocrosslinking of these polymers that will be used to tube mechanical properties.

Polymers for melt electrospinning writing and direct dispensing of polymer melts will be synthesized using atom transfer radical polymerization (polyalkyl(meth)acrylate) or by ring opening polymerization (polycaprolactone). These are standard polymerization techniques and expertize is available in the group. We will vary molecular weight of polymers in order to tailor their viscoelastic properties. Polycaprolactone-based polyurethanes will be synthesized using polycaprolactone diols, diisocyanates such as toluene diisocyanate and diols such as butanediol.

These polymers have two softening temperature. One is at ca 20-30°C and corresponds to melting of polycaprolactone fragments, another is at ca 120° and corresponds to breaking of hydrogen bonds between polyurethane fragments. By varying the ratio between of PCL and polyurethane fragments, we will be able to vary elastic modulus of polymers in rubbery state.

Photocrosslinkable polymer/polymer precursor for direct dispensing printing and stereolithography will be synthesized by using of macromonomers with one or two terminal (meth)acrylate groups. The macromonomers will be synthesized by reaction of (meth)acryloyl chloride or anhydride with oligomer with two terminal alcohol groups. Diol-oligomers will be either purchased (polycaprolactone diols with different molecular weights are available at Sigma Aldrich) or synthesized. diol terminated oligoalkyl(meth)acrylates will be synthesized using initiator and chain-transfer agent with OH groups (2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] and cysteine). Degree of photocrosslinking will be varied by varying light dosage and will allow control of elastic modulus of polymer.

Output: library of polymers with tailored viscoelastic properties and methods for microfabrication of structured surfaces using these polymers

WP2. Topographically structured surfaces with switchable softness

We will start with switchable surfaces with one degree of switching - switchable softness of topographical elements. These elements will not change their topography but only their softness/hardness. A substrate where these features are fabricated will be rigid (not bendable). Switching of softness of topographic features will be achieved by using crosslinked phase-transition polymers - semicrystalline polymers with relatively low melting point such as polycaprolactone (Tm = 65°C), polycalrolactone-based polyurethanes and polyalkyl(meth)acrylates (Tm depends on length of alkyl tail and is in the range from 10°C to 60°C). Chemically crosslinked polycaprolactone and polyalkyl(meth)acrylates demonstrate transition between rigid crystalline state (below melting point) and rubbery state (above melting point). Polycalrolactone-based polyurethanes are thermoplastic elastomers, which behave like rubber a low temperature, but can be molten at elevated temperature like plastic materials. Elastic moduli of polymer in crystalline state/glassy is typically several hundred megapascals. Elastic moduli in rubbery states determined by crosslinking density and is typically in order of hundreds of kilopascals and few megapascals. Thus, switching of elastic modulus between hundreds megapascals and hundreds kilopascals/few megapascals.

Polymer pattern will be printed on rigid substrates using one of methods described in WP1. Polycaprolactone and polyaklyl(meth)acrylates will be crosslinked using UV light. For this, benzophenone derivatives added to polymer will be used as photoinitiator. Photocrosslinkable polyalkyl(meth)acrylates will be synthesized by copolymerizing of alkyl(meth)acrylates and benzophenone acrylate. The degree of crosslinking will be controlled by irradiation time and amount of benzophenone/ benzophenone acrylate in the polymers in the range 0 mol % 10 mol %. The amount of benzophenone must be kept as small as possible in order not to influence crystallinity of polymers. Polyurethanes shall not be crosslinked as they are thermoplastic elastomers. The crosslinking density in the form of molecular weight of polymer chains between crosslinking/entanglement points (*Mc*) will be determined by measuring of elastic modulus (E) and $E = \frac{3\rho \mathrm{RT}}{M_c}\left(1 - \frac{2M_c}{M}\right)$, where ρ is the density of rubber; *R* – gas constant; *T*- temperature; *M* is molecular weight of polymer before crosslinking, *E* - elastic modulus obtained from DMA experiments [39]. Since melting/crystallization of polymers occurs in relatively broad temperature range, elastic moduli can be gradually and reversibly varied between two states (hundreds and few megapascals) by tuning temperature between crystallization and melting points. The mechanical properties of polymers and structured surfaces will be monitored by Dynamic Mechanical Analysis (DMA) and rheology. Dependence of loss and storage modulus on temperature and frequency will be used to assess viscoelastic properties of polymers and relaxation time.

We will use substrates with similar hydrophobicity as polymers (contact angle is between 70° and 110°). Usually it will be the same polymers deposited on solid metallic plate. Melt electrospinning writing requires use of conductive metal substrates, which are usually relatively hydrophilic. We

will modify metal surface with silanes (a variety of silanes with different hydrophobicity/hydrophilicity are commercially available) to adjust it to contact angle of polymers.

We will fabricate and explore wetting properties of two kinds structured surfaces (**Figure 6**): surfaces with pillars (able to bend in x and y directions) and walls (able to bend in one direction). Because of symmetry we do not expect anisotropy of wetting on pillars but wetting must be anisotropic on surface with walls. We will vary the following geometric parameters such as length (width) or pillars and walls, their height and distance between them. These structures will be fabricated using methods discussed in WP1. We expect that increase of height and decrease of thickness of features must make them more bendable and will make material more adaptive. Opposite change of thickness and height will make material more rigid and less sensitive to presence of liquid.

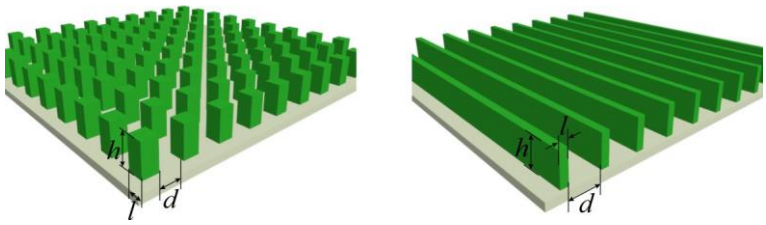

Figure 6. *Schematic of structured surfaces (pillars and walls), which will be prepared.*

We expect that behavior of droplet on hard and soft structures will be different. Increase of droplet volume (advancing contact angle) will first not change the area under droplet and contact angle will increase (point 2, **Figure 7a**). Contact angle will increase and, as soon as its passes over certain energetic level, the droplet will jump to next feature (point 3, **Figure 7a**). This will result in decrease of contact angle. In the case of soft pillars advancing droplet will bend pillar and energy of transition from state (1) to state (3) (**Figure 7a**) will be lower than in case when pillars are rigid. We will vary size of features, crosslinking density and surface tension of profiling liquids (organic liquids, water, salty solutions) in order to investigate interplay between surface tension and mechanical properties. We expect that cyclical changes in contact angle will be observed during measurements on surfaces with relatively large features (1/10 of the lateral dimension of droplet).

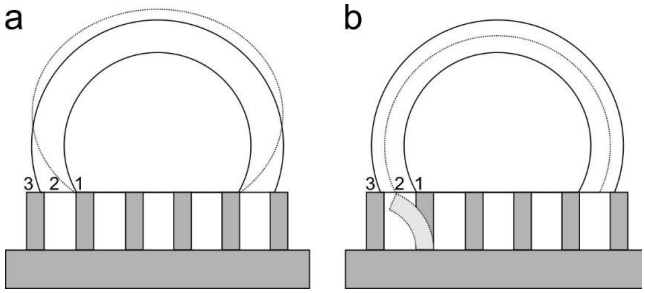

Figure 7. *Expected behavior of advancing droplet on surface with rigid (a) and soft (b) structural elements 1,2,3 – represent expected shape of droplet while size of water droplet increases.*

Collaboration: In this WP, I will collaborate with Dr. Karpitschka in order to understand switching of wetting dynamics on surfaces during change of mechanical properties. Together with Prof. J. Thiele we will investigate behavior of drop pairs on switchable elastic substrates. Collaborations with Dr. G. Auernhammer, Dr. K. Harth and Dr. R. Berger are important for detailed investigation of wetting. I will collaborate with Dr. S. Gurevich in the field of modelling of wetting of structured surface.

Output: investigation of effect of switching of softness of topographical features on switching of wetting.

WP3. Surfaces with actively switchable topography and rigidity

In third part of the project, we will add second degree of switching – switching of shape of topographical elements. There are two ways how switching of shape will be achieved. In first approach we will use topographic features formed by polymer bilayer consisting of one crosslinked semicrystalline polymer with low melting point and another passive hydrophobic polymer. Actuation occurs because of expansion/shrinking of first polymer due to its

melting/crystallization as it is described in our previous paper. Actuation is, thus, accompanied by softening/hardening of semicrystalline polymer. In the second approach, we will add magnetic iron particles (available commercially) to polymers to produce magneto-sensitive topographically structured surfaces. The difference between these two approaches is that in first case mechanical properties of materials and generated force are linked to each other. In the second approach, mechanical properties of materials and generated force are decoupled. This allows to independently tune mechanical properties (by varying temperature) and force acting on topographic features (by varying distance between magnet and sample). By tuning mechanical properties of materials (elastic modulus depend on temperature) we will be able to tune sensitivity of material to magnetic field. Effect of mechanical properties is investigated in WP2 that must allow elucidation of effect of shape transformation on switching of wetting behavior. In contrast to materials with switchable softness (WP2), these surfaces demonstrate active switching of topography i.e. contact line/area under the droplet and on the periphery of droplet change.

In our experiments we will use two kinds of actuating structures – pillars and walls (lamellas) as it is illustrated in **Figure 8** and used in WP2. In contrast to WP2, actuation offers additional degree of freedom – direction of movement. For example, infinite walls, which are attached to a substrate over whole their length, are able to bend longitudinally. On the other hand, walls with limited length, which are fixed on a substrate only in one point must be able to bend transversely. We will use this principle to design surfaces with different kinds of switchable patterns.

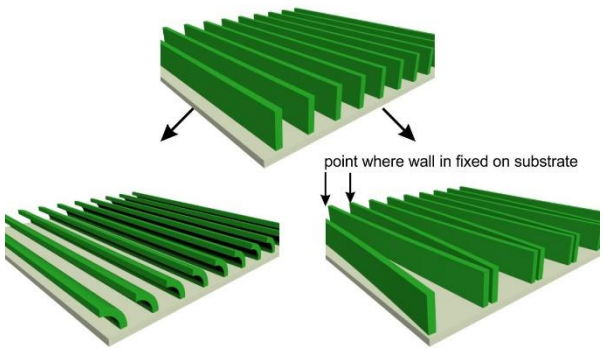

Figure 8. *Scheme of actuation of lamellas with different attachment to a substrate (left – attachment along full length, right – attachment in one point)*

Very important property of shape-changing materials is force-stroke behavior. This dependence is linear for fully elastic materials, whose deformation is described by Hooke's law. Since polymers are not fully elastic and do not really follow Hooke's law (for example, for rubbers shear stress (τ) - deformation (λ) curve is described as $\tau = G\left(\lambda - \frac{1}{\lambda^2}\right)$, G is shear modulus), the force-stroke curve is not linear (**Figure 9**) Force is maximal in the beginning of deformation; it decays while material actuates is null when stroke is maximal. Force-stroke behavior depends on elastic properties of materials (Young's modulus) and elastic energy stored in materials/force applied to material. We expect that actuating surface will affect wetting and liquid droplet will affect actuation behavior. Surface tension can act against force generated during actuation (stroke decreases) and along it (stroke increases). Thus, actuation i.e. amplitude of switching of topography can be reduced and enhanced. This, as expected will have effect on switching of wetting properties.

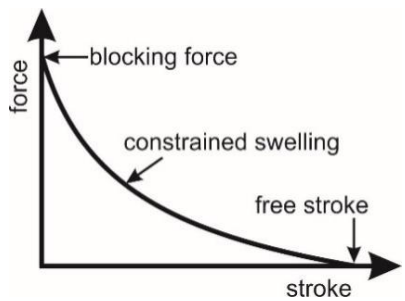

Figure 9. *Typical force-stroke curve of hydrogel actuator.*

In order to understand interactions between liquids and actuating surfaces we will perform set of wetting experiments. The investigation and interpretation of wetting properties of active surfaces is highly complex because it is expected that dynamic (kinetics) of change of properties can influence wetting properties. We distinguish four kinds of measurements, which can be performed on active surface depending whether is surface stimulated and whether droplet is externally affected by any force (advancing/receding/sliding droplet) (Table 1). These measurements must allow answering on following questions:

- How is reversible switching when droplet in on surface constantly and when measured without drop.
- Does droplet affect behavior of materials and how?
- Does switching of properties of surfaces affect droplet and how?

Table 1. Summary of wetting experiments, which will be performed.

		Droplet during measurements	
		No external force on droplet	**Force acts on droplet, moving (advancing / receding / sliding)**
Material during measurements	**No action on materials**	*Static wetting, static surface:* fix properties of surface and investigate static contact angle	*Dynamic wetting, static surface:* fix properties of surface and investigate advancing / receding / sliding droplets
	External action on material: materials properties change	*Dynamic surface, static wetting:* measure on deposited drop while surface properties change	*Dynamic surface, dynamic wetting:* investigate advancing / receding / sliding droplets while surface properties change

We will perform the following experiments to investigate switchable wetting:

- Macroscopic measurement of static and dynamic angle, optical tomography for asymmetric droplets on anisotropic surfaces.
- Microscopic investigation of contact between liquid and surface using CryoSEM, total internal reflection microscopy and confocal microscopy

These measurements will allow elucidation of correlation between topography, mechanics and surface tension properties of surfaces, microscopic wetting (contact line and contact surface) and macroscopic wetting (contact angle) (**Figure 10**).

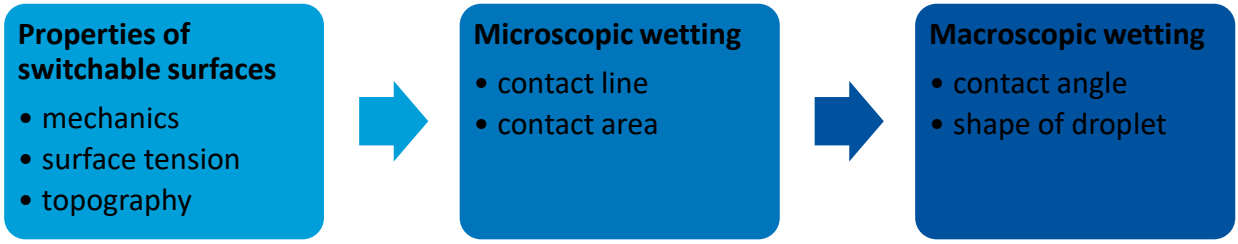

Figure 10. *Envisioned correlation between properties of switchable surfaces, wetting on micro and macro-scale wetting.*

Finally, possibilities to switch wetting properties locally will be investigated. We will utilize sensitivity of all kinds of use materials to temperature - either only mechanical properties of both mechanical properties and shape depend on temperature. The local heating of surfaces can be done using laser. Sensitivity of materials to light will be provided

Collaboration: Collaborations with Dr. G. Auernhammer, Dr. K. Harth and Dr. R. Berger are important for detailed investigation of wetting. I will collaborate with Dr. S. Gurevich to model wetting of structured surface.

Output: investigation of effect of switching of topography on switching of wetting.

Project outlook: In first application period we will investigate effects of switching of mechanical properties and topography. In second application period we plan to investigate effects of switching of hydrophilicity/hydrophobicity of shape-changing elements.

Educational goals: We plan to participate in summer schools organized in the frames of SPP. We plan to educate students in the field of shape-changing polymeric materials as well as in advanced fabrication techniques (3D printing). Moreover, we plan to prepare hands-on tutorials (funding for student assistants is requested) for graduate (MS and PhD students) explaining physics of polymers, which allows design and fabrication of surfaces with switchable topography and wetting.

Table 1. *Description of work packages and time schedule*

Work Package (WP)	1st year				2nd year				3rd year			
	I	II	III	IV	I	II	III	IV	I	II	III	IV
WP 1. Development of approaches for fabrication of surfaces												
WP2. Topographically structured surfaces with switchable softness												
WP3. Surfaces with actively switchable topography and rigidity												
Reports, publications												

2.4 Data handling

All data developed in this project will be stored on our institute's raid systems, which are connected to our own backup-systems. Raw simulation data (time series) will be back- on external storage media in order to keep them available for longer times. High level data and graphs from the simulations will be secured by the IT-system of the University of Bayreuth for at least 10 years.

2.5 Other information

Please use this section for any additional information you feel is relevant which has not been provided elsewhere.

none

2.6 Descriptions of proposed investigations involving experiments on humans, human materials or animals

none

2.7 Information on scientific and financial involvement of international cooperation partners

None

2.8 Information on scientific cooperation within SPP2171

Embedding of proposals into Priority Programme.

The Priority Programme embeds individual and cooperative projects with main research activities in the fields of (i) design of switchable/adaptive surfaces, (ii) development of methods for investigation of wetting and (iii) understanding of wetting on via correlation between experiment and modelling. Cooperation between projects from all three categories is essentially required for complete understanding of wetting on dynamic surfaces.

This proposal is located in the first category (design of switchable/adaptive surfaces). We will also perform contact angle measurements on these surfaces. In order to get full understanding of their complex wetting behavior in dynamic conditions, cooperation with scientist with expertise in

methods for investigation of wetting as well as in modelling of wetting is required. Therefore, the following cooperations are envisioned.

- Cooperation with Dr. S. Karpitschka (expertize in wetting on soft surfaces) is very important for understanding of wetting of surfaces with switchable rigidity. My group will provide flat substrates with switchable elastic modulus to perform model investigations of effect of softness of wetting (Karpitschka project). In my project, we will understand effect of mechanical properties of structured substrates on dynamics of spreading of droplets and effect of droplet on dynamics of change of shape of surface structures.
- Cooperation with Prof. J. Thiele (expertize in wetting of soft elastic surfaces) is important for understanding of cooperative behavior of multiple droplets on soft substrates. We plan to investigate behavior of drop pairs on switchable elastic substrates.
- Cooperation with Dr. M. Brinkman (expertizes in wetting on soft surfaces) is also very important for understanding of wetting of surfaces with switchable rigidity. My group will provide flat structured substrates with wall with switchable elastic modulus. Together, we will understand effect of mechanical properties of structured substrates on dynamics of spreading of droplets and effect of droplet on dynamics of change of shape of surface structures.
- Cooperation with Dr. G. Auernhammer (expertize in confocal microscopy) is required for characterization of 3D shapes of droplets. Together will investigate 3D shapes of droplets on structured surfaces.
- Cooperation with Dr. K. Harth (expertize in total reflection microscopy) is required for investigation of contact between liquid droplet and surface. We will observe contact area and contact line between liquid and dynamic structures. We will also observe how surface structures deform droplet and will be deformed by droplet.
- Cooperation with Dr. R. Berger (expertize in drop adhesion force instrument) is required for characterization of strength (surface tension) of interaction between surface and droplet using DAFI method. From these experiments we will estimate dynamics and character (elastic, viscoelastic) of deformation of surfaces structures and dynamics of switching of wetting. Thus, cooperation with these scientists will allow complete experimental characterization of a liquid drop from point of view of shape and strength of interactions.
- Cooperation with scientists, who are experts in modelling of liquid droplets on structured surfaces, is required for understanding and interpretation of experiment results of wetting on surfaces with switchable geometry (drop shape as well as adhesion between surface and droplet). Our group will cooperate with Dr. S. Gurevich and Dr. M. Brinkmann. We will work on developing of model describing dynamics of wetting on structures.

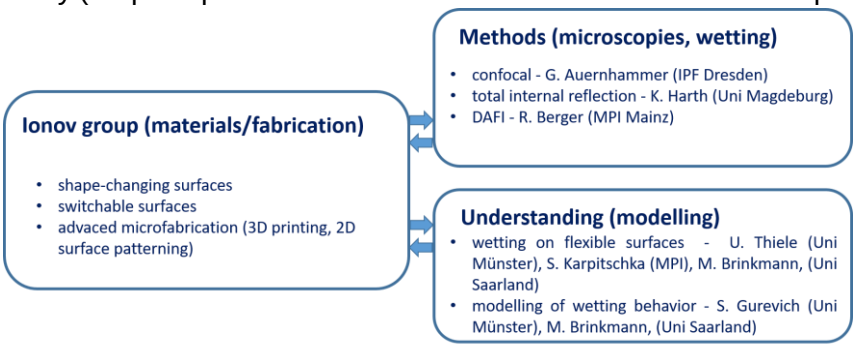

Figure 11. *Scheme of cooperation within SPP*

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4 Requested modules/funds

Explain each item for each applicant (stating last name, first name).

4.1 Basic Module

4.1.1 Funding for Staff

	Staff	Wage group	Position (month)	Standard sum
1	PhD (M.Sc., Chemistry)	TV-L E13	36 (75% position)	48.375 €/year
1	Student assistant (SHK)*			6.000 €/year
	Total			**54.375 €/year**

SHK (student assistant) students will prepare hand-on tutorials

Total Costs Personnel **163.125 €**

One PhD student with background in polymer materials and microfabrication (photolithography, 3D printing) is requested.

4.1.2 Direct Project Costs

4.1.2.1 Equipment up to €10,000, Software and Consumables

Description	Costs
Polymers, solvents and other chemicals	7.000 EUR/year
Parts for 3D printer	3.000 EUR/year
Total	**30.000 EUR**

4.1.2.2 Travel Expenses

	Conferences	Expenses
1	SPP workshop	800 EUR/year
1	International/national Conference (e.g. ACS National Meeting, MRS)	1000 EUR/year
1	Visits to other groups, summer school and SPP meetings*	800 EUR/year
	Total	**8.400 EUR**

* The following SPP meetings are planned
  * 1st and 2nd year: one SPP workshop (4 days)
  * 1st year: Advanced School (5 days)
  * 2nd year: PhD-candidate workshop (4 days)
  * 3rd year: international conference - (5 days)

4.1.2.3 **Visiting Researchers** (excluding Mercator Fellows)

none

4.1.2.4 Expenses for Laboratory Animals

none

4.1.2.5 Other Costs

none

4.1.2.6 Project-related publication expenses

Prof. Dr. Leonid Ionov
We plan to publish in open Source journals which require page charges 750 EUR/year

4.1.3 Instrumentation

4.1.3.1 Equipment exceeding Euro 10,000

Our lab is fully equipped with methods for rheological/mechanical characterization of polymers as well as microfabrication (direct dispensing and melt electrospinning writing). Prof. Ionov has extensive previous experience in wetting characterization of surfaces. This research topic is however not main topic of research now and the main research focuses now are shape-changing materials and additive fabrication. The contact angle measurements are, however, essential for realization of this project. There are no other research activities in the group, which require contact angle measurement, and it is needed only for realization of this project. Therefore, contact angle measurements cannot be funded from basic group funding and DFG funding is requested.

Contact angle measurements device (two syringes) with control of inclination 20.061 EUR

4.1.3.2 Major Instrumentation exceeding Euro 50,000

none

5 Project requirements

5.1 Employment status information

Prof. Dr. Ionov, Leonid, permanent position (W2)

5.2 First-time proposal data

None

5.3 Composition of the project group

Prof. Dr. Leonid Ionov - (permanent position): project realization and coordination. Prof. Ionov will be responsible for building of 3D printer
Mr. Juan Gomez (PhD student): area of expertize – 3D printing
Ms. Indra Apsite (PhD student): area of expertize – electrospinning

5.4 Cooperation with other researchers

5.4.1 Researchers with whom you have agreed to cooperate on this project

- Dr. Günter K. Auernhammer/Prof. Andreas Fery/Dr. Petra Uhlmann (Leibniz Institute of Polymer Research, Dresden) – confocal microscopy investigations of droplets
- Dr. Kirsten Harth (University of Twente) - total internal reflection microscopy.
- Dr. Rüdiger Berger/Prof. Hans-Jürgen Butt (Max Planck Institute for Polymer Research) - drop adhesion force instrument / DAFI
- Dr. Stefan Karpitschka (Max Planck Institute for Dynamics and Self-Organization) – wetting on flexible surfaces
- Dr. Svetlana Gurevich/Prof. Andreas Heuer (University of Münster) - modelling of wetting behavior
- Dr. Martin Brinkman (University of Saarland) – wetting/condensation of soft substrates
- Prof. Uwe Thiele (University of Münster) – wetting on soft surfaces

5.4.2 Researchers with whom you have collaborated scientifically within the past three years

Scheibel, Thomas (Uni. Bayreuth); Agarwal, Seema (Uni Bayreuth); Stamm, Manfred (IPF Dresden), Diez, Stefan (TU Dresden); Synytska, Alla (IPF Dresden); Dunlop, John (Uni. Salzburg); Volodkin, Dmitri (Nottingham Trent University); Handa, Hitesh (University of Georgia); Locklin, Jason (University of Georgia); Minko, Sergiy (University of Georgia), Gomillion, Cheryl (University of Georgia); Jehnichen, Dieter (IPF Dresden); Xie, Jin (University of Georgia); Stoychev, Georgi (University of North Carolina), Kirillova, Alina (Duke University), Wang, Xianqiao (University of Georgia); Choudhury, Soumyadip (Chemnitz University); Azizi, Mazen; Mechtcherine, Viktor (TU Dresden), Sommer, Jens-Uwe (IPF Dresden); Raguzin, Ivan (IPF Dresden); Dubey, Nidhi

5.5 Scientific equipment

University of Bayreuth possess all needed equipment. Part of it belongs to Bavarian Polymer Institute (BPI).

- Laboratory – ca 400 m^2
- SAXS/WAXS Ganesha for investigation of structure of polymers is available (Key-lab “Mesocscale Characterisation: Scattering Techniques”).
- Xplore Instr. BC, microcompounder with load 5 – 15 g for polymer compounding (BPI Key-lab “Small Scale Polymer Processing”).
- Leo1530 SEM (BPI Key-lab “Electron and Optical Microscopy”)
- DSC for thermal characterization of polymers is available.
- Rheometer Scientific, DMTA Mark IV for characterization of visco-elastic properties of polymer is available (BPI Key-lab “Small Scale Polymer Processing”). Similar one is planned to be purchased for this project from startup funding.
- Two home-made 3D printers with optional melt electrospinning and stereolithography 3D printer are available in the Ionov group.

5.6 Project-relevant cooperation with commercial enterprises

If applicable, please note the EU guidelines on state aid or contact your research institution in this regard.

none

5.7 Project-relevant participation in commercial enterprises

Information on connections between the project and the production branch of the enterprise

none

6 Additional information

Third-party funding for this project has not been applied for.