FINAL PROJECT REPORT

Instrument: Tandem Forest Values
Project number: TFV2018-0065
Project title: Strongly adsorbed polymer layers for modification of cellulose surfaces towards new functional materials (STRONGAD)
Project duration: 1st January 2019 – 31st December 2020
Hired employees: Dr. Wenyang Xu
Principal Investigators (PIs): Prof. Eero Kontturi (Aalto University, Finland), Prof. Torbjörn Pettersson (KTH, Sweden)

1. Description of the research that has been carried out

Introduction

The aim of STRONGAD was to introduce the concept of solid-state adsorption as a tool for surface modification for ligno-cellulosic materials. Solid-state adsorption of so-called Guiselin layers proceeds in a straightforward manner: a polymer film deposited on an interface with another solid material is heated above its glass transition (T_g) or melting point (T_m), and subsequently the excess polymer is rinsed out with a good solvent, leaving behind an ultrathin (<10 nm) adsorbed polymer film.[1-5] Guiselin layers had been previously investigated solely within the realm of solid-state physics and as a result, STRONGAD initially took up the formidable challenge to instate Guiselin layers as tools in materials science with lignocellulosic substrates as the specific demonstrators. If successful, our research plan in 2018 duly noted, the use of Guiselin layers would provide a realistic alternative for surface modification of many a substrate – from nanopapers and pulp fibres to cellophane films – instead of covalent modification routes[6] which are often not scalable, environmentally hazardous, and/or economically unrealistic.

Several proof-of-concept type of findings were established in STRONGAD, including stability of Guiselin layers and their performance in hydrophobic modification of nanopaper surfaces.

Major deviations from the original research plan

We set out to establish the process of Guiselin layers for any types of lignocellulosic substrates. However, we soon found out that the stability of the layers was not reliable. This was all the more compromised when accounts on the irreproducible nature of Guiselin layers were published during the time of STRONGAD.[3] As a result, we had to start establishing the procedure with hard, totally planar inorganic (silicon) substrates instead of cellulose that was originally planned. We managed to corroborate both the stability and the reproducibility of Guiselin layers on silicon, after which we proceeded with the initial plan, first to examine Guiselin layers on cellulose model films and subsequently on genuine lignocellulosic substrates, such as cellulose nanopaper. Because of these early stage impediments in the project – coupled with the hindrances brought in by Covid-19 – the emphasis was set to WP1 (Model film studies) and WP2 (Basic studies of Guiselin layers on lignocellulosic substrates), whereas WP3 (Applications) was subsided. Because we wanted to have a reliable proof of concept from Guiselin layers by the end of STRONGAD, much attention was paid to the part in WP1 where Guiselin layers were deposited on cellulose model films. Furthermore, many of the polymers, that were envisaged to be used for Guiselin layer deposition, had to be omitted.

Another deviation from the original plan concerned the mobility of Dr. Xu who was supposed to spend the best part of 2020 in KTH, Stockholm. In early 2020, the visit was scheduled from April to December 2020, but because of the outbreak of Covid-19, the visit was postponed several times, and finally realised for a reduced period September – December 2020. The whole situation with Covid-19

slowed down the experimental work with laboratories at Aalto being totally closed for 3 months in spring 2020. This led to a decision to postpone publishing at the cost of executing the experimental plan to as great an extent as possible. In consequence, no scientific papers have been actually published from STRONGAD as of yet, but two papers have been submitted and a third one is under preparation.

Results obtained

Stability of the Guiselin layer

During our initial tests, we encountered dewetting-type of rupture patterns in some of the Guiselin layers that were made of polystyrene (PS) which is the most common polymer used for solid-state adsorption in literature.[2-3] Based on the trials, we set out to do a full-length study of the stability of Guiselin layers from PS grades of varying molecular weights (M_w) on single-crystal silicon wafers with a native oxide layer on top. Figure 1 exposes the core findings of the study as atomic force microscopy (AFM) images where lower M_w PS (< 100 kDa) underwent spinodal dewetting (Figure 1a and 1b) and PS with ~200 kDa M_w was subjected to heterogeneous dewetting (Figure 1c) during the Guiselin layer preparation. The only truly stable layer with full coverage resulted from high M_w PS (~500 kDa, Figure 1d).

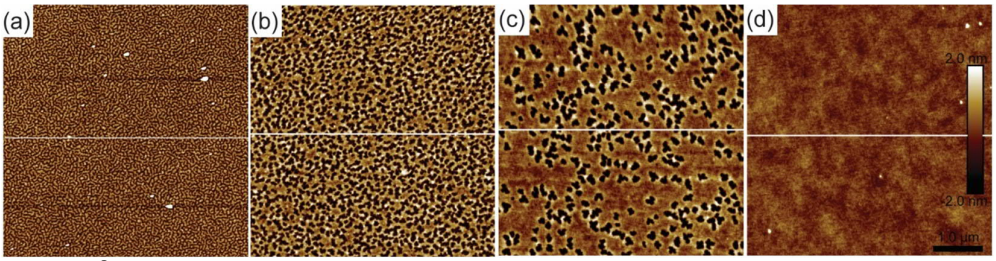

Figure 1. 5×5 µm^2 AFM height images of representative Guiselin layer films of PS of different average molecular weights: (a) 30kDa, (b) 35kDa (polydisperse with bimodal distribution), (c) 192kDa, and (d) 560kDa.

Table 1. Static, advancing θ_a and receding θ_r contact angles of water on the adsorbed PS with different molecular weight*

Thin films on silica	Static contact angle, θ_s/°	advancing / receding contact angles, θ_a/θ_r (°/°)	Simulated static contact angle[#], θ_{sim} /°	Contact angle hysteresis, θ_a - θ_r/°
PS 30 kDa	89	94/72	83	22
PS 35 kDa	91	95/76	86	19
PS 192 kDa	91	97/82	89	15
PS 560 kDa	91	96/82	89	14
PS560k_spin-coating[&]	92	96/82	89	14
PS560k Guiselin layer_post-annealing[£]	92	95/81	88	14

[*] Standard deviation of the contact angle measurement is ± 2%

[#] θ_{sim} is computed from $\cos\theta_{sim}=(\cos\theta_a+\cos\theta_r)/2$ according to Cassie-Baxter relation

[&] Spin coated film without posttreatments into a Guiselin layer

[£] Spin coated film, annealed for Guiselin layer formation but not treated with solvent to remove the excess film

However, it was noteworthy that the differences in surface coverage, visible in Figure 1, did not affect the transition of the interfacial energy into the hydrophobic regime after Guiselin layer deposition. Indeed, all Guiselin layers from PS managed to transform the silicon wafers with an initial contact angle with water at <5° into interfacial hydrophobic materials with water contact angles at ~90° (Table 1). This behaviour was ascribed to the Guiselin layer surfaces as being in Cassie state where the water droplet does not penetrate into the troughs of the disrupted film.

In addition, Guiselin layers on Si/SiO_x substrate were characterized with x-ray photoelectron spectroscopy (XPS), ellipsometry, and nanoscale infrared (IR) microscopy. The latter technique was able to show that the ruptured films had silica exposed at the bottom of the troughs. All in all, these results set an important precedent for characterising and understanding the Guiselin layer behaviour on cellulose surface which were subsequently placed under extensive scrutiny. The results of PS Guiselin layers on Si/SiO_x were compiled in an independent manuscript that has been submitted to publication.

Guiselin layer on cellulose model film

We utilized flat and smooth, ultrathin model films of cellulose to establish the existence of Guiselin layers on cellulose. We emphasize that nobody has managed to demonstrate previously that Guiselin layers can be deposited on any polymeric substrates as they have always been deposited on hard substrates, silicon wafers being the most prominent examples.[2-3] Amorphous cellulose substrates were prepared by spin coating a dissolving cellulose derivative, trimethylsilyl cellulose (TMSC) which was regenerated into cellulose by exposure to HCl vapour (TMSC-R).[7] The verification of a Guiselin layer of PS on cellulose (TMSC-R+PS) was gained by XPS (Figure 2).

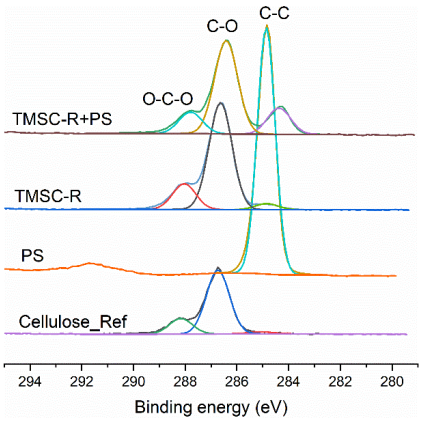

Figure 2. High resolution C 1s XPS data on references (cellulose and polystyrene), TMSC-R and TMSC-R after polymer solid-state adsorption (TMSC-R+PS).

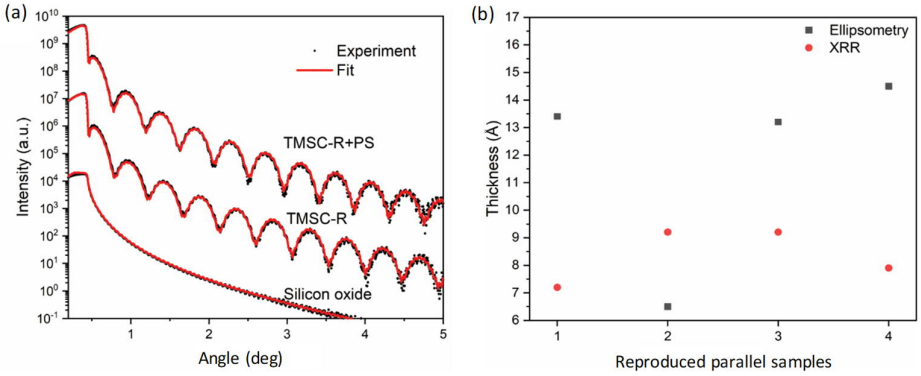

Figure 3. (a) X-ray reflectivity curves of SiOx layer, and regenerated cellulose film before (TMSC-R) and after (TMSC-R+PS) solid-state adsorption of PS. Black dots denote the experimental data; full lines are the model independent fitting results. (b) The thickness comparison using ellipsometry and XRR with the same samples.

It proved difficult, however, to gain information on the thickness of the Guiselin layer from PS on a cellulose film. We utilized both x-ray reflectivity (XRR) (Figure 3a) and ellipsometry which both suggested that the adlayer of PS on cellulose amounted to a thickness of roughly one nanometre (Figure 3b). AFM (not shown) did not reveal any morphological details of the Guiselin layers on cellulose, mainly because the roughness of the ultrathin cellulose film is relatively higher than that of

silicon wafers. Nevertheless, it was clear from the contact angle measurements that we had managed to hydrophobize the cellulose films by solid-state adsorption of Guiselin layers (Table 2). In addition to the presented data, we performed extensive surveys on the influence of annealing time and the number of washing steps on the integrity of Guiselin layers on cellulose. Moreover, ultrathin model films from diverse cellulosic components, such as cellulose nanocrystals (CNCs) and cellulose nanofibres (CNFs) were trialled as substrate for Guiselin layer deposition. Although the thickness of the films could not be measured due to the roughness of the nanocellulosic substrates, the hydrophobic nature brought in by the PS Guiselin layer was not compromised. These results encouraged us to move from ultrathin model films into the realm of genuine cellulose substrates.

Table 2. Roughness and contact angle (static, advancing (θ_a), and receding (θ_r)) of water on PS560k before and after Guiselin layer process, and on TMSC-R before and after polymer adsorption

Samples	Roughness (R_q)* /Å	Static contact angle /°	θ_a/°	θ_r /°
PS560_Spincoating	-	92.2±0.1	93.4±0.5	86.9±0.3
PS560_Guiselin	2.9	91.0±0.4	92.9±0.3	86.1±0.2
TMSC-R	3.6	28.0±0.5	41.3±1.4	28.0±2.0
TMSC-R+PS560 Guiselin	3.3	71.3±0.5	90.2±3.3	72.2±0.1

*Root mean square roughness (R_q) as obtained from AFM image

In addition to the aforementioned results on cellulose model films, sum frequency generation (SFG) studies were undertaken on amorphous cellulose (TMSC-R) films with a PS Guiselin layer. Figure 4 shows an SFG spectrum of such system. Because of the overlap between the dominant OH stretch (3000-3600 cm^{-1}) in cellulose and the aromatic C-C in PS (3000-3200 cm^{-1}), the film was treated in D_2O which exchanged the accessible OH groups in cellulose to OD groups, shifting the OD stretch below 2800 cm^{-1}. All aspects of the OH→OD exchange as well as the PS layer interaction with the cellulose film were not straightforward in the abundance of SFG spectra collected. Therefore, we chose to engage in a collaboration with a molecular simulation team which is modelling the SFG spectra in order to gain more in-depth information on the molecular premises of the system. The collaboration is still ongoing and the SFG results will be published later in a separate publication.

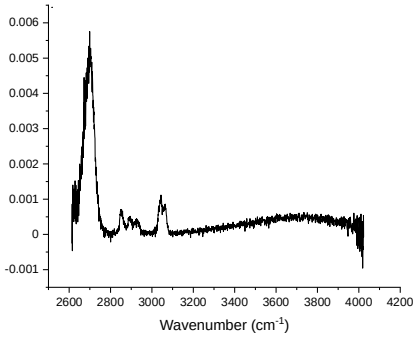

Figure 4. SFG spectrum of amorphous cellulose film (TMSC-R) with a PS Guiselin layer on top. The film has been imbibed in D_2O which has exchanged the protons in cellulose OH groups into OD groups.

Hydrophobization of cellulose nanopaper and paper by poly(lactic acid)

Cellulose nanopaper made of wood-based CNFs was used as a substrate for Guiselin layers from poly(lactic acid) (PLA). No conspicuous morphological changes have occurred due to the Guiselin layer (Figure 5c) when compared with the control reference (Figure 5a), but a slight smoothening of the features was detected with roughness analysis (R_q of 21.7 nm for Figure 5a in contrast to 15.1 nm for Figure 5c). The lack of contrast in the AFM phase image suggested a full coverage of PLA over the imaged area (Figure 5d).

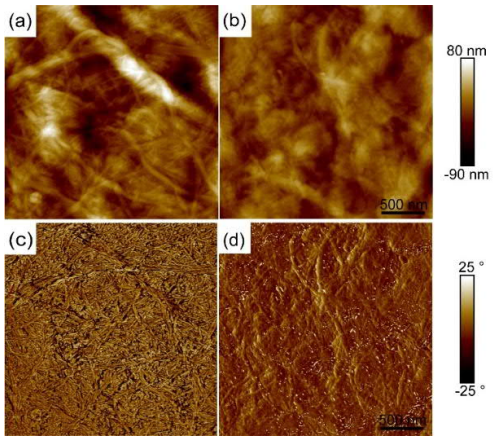

Figure 5. (a) AFM height image with roughness (Rq) of 21.7 nm and (c) AFM phase image of nanopaper control reference; (c) AFM height image with roughness (Rq) of 15.1 nm and (d) AFM phase image of Nanopaper+PLA Guiselin layer.

As shown by static contact angle measurements with water, successful hydrophobation by Guiselin layers of PLA was accomplished on multiple cellulose substrates: CNF nanopaper, Whatman 1 filter paper and cotton textile fabric (Table 3). We emphasise that dynamic contact angle measurements were not feasible with water because of the highly hygroscopic nature of the macroscopic cellulose substrates, that is, water droplets would just absorb onto the substrate during the prolonged measurement. It is curious that when model films and CNF nanopapers were used as the substrates, the Guiselin layers represented a typical water contact angle of pristine PLA films (75°-85°). By contrast, filter paper and textile fabric as substrates resulted in PLA Guiselin layers of significantly a more hydrophobic nature with contact angles well above 100°. This is due to the multiscale roughness of the fibre-based substrates. The results were backed up with XPS (not shown).

Table 3. Static water contact angles for various cellulosic substrates with a Guiselin layer deposited from PLA on top.

Samples with a PLA Guiselin layer	Static contact angle /°
TMSC-R model film	75±1
CNF nanopaper	83±4
Whatman 1 filter paper	115±5
Cotton textile fabric	137±5

Conclusions on the obtained results

Although STRONGAD was heavily biased on model film studies, we conclude that it was successful in establishing a proof-of-concept for utilising Guiselin layers in surface modification of lignocellulosic substrates. Commonplace with a fundamental approach, many unexpected difficulties were encountered, the major hindrances being the stability of the Guiselin layer and the challenges in measuring the precise thickness of the Guiselin layer when deposited on a cellulose model film. These challenges were successfully overcome, providing the PIs with new insight on surface analytics and solid-state behaviour of polymers. It is also evident that macroscopic substrates, such as cellulose nanopaper and normal paper can be modified with Guiselin layers. Two submitted publication that have been spawned by STRONGAD are strong indications of a new direction in surface modification. Even though STRONGAD was not implemented to the full extent of its initial project plan, the results provide a firm basis for the PIs to go to new directions and seek for additional funding with the concept.

References
1. Guiselin, O., Irreversible Adsorption of a Concentrated Polymer Solution. *Europhys. Lett.* **1992,** *17* (3), 225-230.
2. Napolitano, S., Irreversible adsorption of polymer melts and nanoconfinement effects. *Soft Matter* **2020,** *16* (23), 5348-5365.
3. Thees, M. F.; McGuire, J. A.; Roth, C. B., Review and reproducibility of forming adsorbed layers from solvent washing of melt annealed films. *Soft Matter* **2020,** *16* (23), 5366-5387.
4. Gin, P.; Jiang, N.; Liang, C.; Taniguchi, T.; Akgun, B.; Satija, S. K.; Endoh, M. K.; Koga, T., Revealed Architectures of Adsorbed Polymer Chains at Solid-Polymer Melt Interfaces. *Phys. Rev. Lett*. **2012,** *109* (26), 265501.
5. Simavilla, D. N.; Huang, W.; Vandestrick, P.; Ryckaert, J.-P.; Sferrazza, M.; Napolitano, S., Mechanisms of Polymer Adsorption onto Solid Substrates. *ACS Macro Letters* **2017,** *6* (9), 975-979.
6. Habibi, Y., Key advances in the chemical modification of nanocelluloses. *Chem. Soc. Rev.* **2014,** *43* (5), 1519-1542.
7. Kontturi, E.; Suchy, M.; Penttilä, P.; Jean, B.; Pirkkalainen, K.; Torkkeli, M.; Serimaa, R., Amorphous Characteristics of an Ultrathin Cellulose Film. *Biomacromolecules* **2011,** *12* (3), 770-777.

2. Scientific publications to emerge from STRONGAD

There are no accepted publications from STRONGAD results as of yet, but two publications have been submitted:

(i) Wenyang Xu,* Karl Mihhels, Nikolay Kotov, Sakari Lepikko, Robin H.A. Ras, C. Magnus Johnson, Torbjörn Pettersson,* and Eero Kontturi* *Solid-state polymer adsorption for surface modification: the role of molecular weight*

(ii) Wenyang Xu,* Oliver Werzer, Panagiotis Spiliopoulos, Karl Mihhels, Roland Resel, Etula Jarkko, Torbjön Pettersson,* and Eero Kontturi* *Modifying cellulose surfaces with nanocoating by solid state adsorption*

A third manuscript is under preparation as we are still working with molecular dynamics simulations to illuminate the complex features of the SFG spectra collected. The paper will be completed during summer and submitted and published later in 2021.

3. Description of how the grant has contributed to competence building that will facilitate and strengthen long term collaboration between Finland and Sweden

The grant has enabled specific collaboration with between the PIs. Although collaboration between KTH and Aalto has been commonplace in history, the two PIs had not been engaged in formal collaboration before despite mutual interests and having known each other for over a decade. The grant and the joint postdoc have enabled the PIs to discover the strengths that we have on the different sides on the Baltic sea, particularly with regards to the special equipment available on each side. Whenever either one is in need of a certain analytical tool, there is no barrier to contact KTH or Aalto and arrange measurement time and/or a small scale researcher exchange. This will be growing in importance in the future when taking into account the increasing academic stature and funding pool of Profs. Kontturi and Pettersson.

Both PIs have still roughly 25 years of academic career ahead of them and the STRONGAD collaboration has provided them with a joint and original topic that they can utilise in multiple projects in the years to come. A generic approach to surface modification has can certainly come in handy particularly in application-related projects with lignocellulosics. Solid-state adsorption may also play a larger role when the two PIs are seeking for joint funding, namely from the EU. In fact, Profs. Kontturi and Pettersson have already identified the Pathfinder call in Horizon Europe as a possible instrument for joint funding.

4. Description of research areas being started or strengthened at the departments in Finland and Sweden

STRONGAD was an important project from the point of view of surface analytics. As already described in the *Results* section, the analysis of a very thin (nm scale) adsorbed polymer film on an ultrathin cellulose film was a formidable challenge that could not be overcome by routine techniques in either Aalto or KTH. In consequence, we had to resort to analytical methods with which we had little or no prior experience: XRR, ellipsometry, SFG, and nano IR microscopy. They are all available at the campus of either Aalto or KTH but we had never thoroughly familiarized ourselves with the techniques or were aware of their full analytical potential. This is certainly an important practical asset in the future of both PIs whose research often revolves around surface analytics. Furthermore, the results from the SFG measurements have also initiated further research on computational modelling of interactions of molecules to amorphous cellulose a research field that have not been explores previously, and that we believe can explain some of the unexpected outcome from this project.

For KTH, a further practical advance was the hands-on experience to prepare and work with different types of cellulose model films.

On a broader context, STRONGAD was the first profound encounter for all participants – Profs. Kontturi and Pettersson as well as Dr. Xu – with solid-state polymer physics. Expanding the area from solvent-based approaches has widened their perspective and will certainly be beneficial in future projects – both in terms of new ideas and in technical implementation.

5. Description of how the grant has contributed to strengthening the forest sector in Finland and in Sweden.

A conceptually new way/technique of surface modification of cellulose was introduced in STRONGAD. Given that the results were largely of fundamental importance, the immediate benefits for the forest sector are not palpable at present. It is evident that in high volume products, such as paper and board, Guiselin layers with a batch-like solvent leaching step may not be ideal routes to surface modification. However, in new products sought after by the forest industry, the results in STRONGAD may find relevance; for example, when preparing (nano)composites for specific functional purposes, Guiselin layers can act as compatibilizers with the polymer matrix.

The departments both at Aalto and KTH have historically close contacts with the forest sector. The PIs are looking forward to incorporate the results, experience and knowledge gathered from STRONGAD to the discussions with the industrial partners. Dr. Xu has moved on to do his second postdoctoral stint in Åbo Akademi (Finland) which is another institute with closely-knit ties to the forest industry.

6. Description of communication with relevant stakeholders and end users.

All scientifically relevant results from STRONGAD will be disseminated in the form of scientific publications, ensuring that the scientific community will receive full exposure of the achievements. Moreover, we will disseminate the results in future scientific conferences – a medium which has been greatly suppressed during Covid-19.

STRONGAD proposal envisaged the use of an industrial steering group that was supposed to have regular meetings throughout the project. Due to the abrupt onset of Covid-19 at the beginning of STRONGAD, however, no physical meetings were feasible. Nevertheless, individual discussions were undertaken with all supporting partners: SciTech Services, Andritz Oyj, and BillerudKorsnäs AB. They have been kept up to date with the progress and outcome of STRONGAD.

As mentioned in the previous section, close ties to the forest industry for both Aalto and KTH will facilitate the future applications of the fundamental knowledge gained in STRONGAD.

7. Financial accounting

The table below reveals the budget expenditure in STRONGAD.

Budget:	Total (SEK)		Costs:	Aalto (SEK)	KTH (SEK)	Total (SEK)
Direct salaries	875 843		Direct salaries	847 349,01		847 349,01
Personal side costs	437 921		Personal side costs	393 878,53		393 878,53
Overhead	1 024 736		Overhead	925 989,25		925 989,25
Travel	311 186		Travel	146 706,45		146 706,45
Material	103 729		Material	238 730,91		238 730,91
External services	41 491		External services	52 578,46		52 578,46
Other costs	62 237		Other costs	9 723,49	285 714,00	295 437,49
Workshop	142 857		Workshop		142 857,00	142 857,00
Total	**3 000 000**		**Total**	**2 614 956,09**	**428 571,00**	**3 043 527,09**
TFV	**2 000 000**		**TFV**	**1 714 286,00**	**285 714,00**	**2 000 000,00**