Ministry of Environment and Food of Denmark
Environmental Protection Agency

Substitution of Organic Solvents in Production of new Adhesion Technology as an Alternative to Hazardous Gluing Processes

A project supported by Kemi i Kredsløb

MUDP report

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Contents

1. Preface

The project “Substitution of Organic Solvents in Production of new Adhesion Technology as an Alternative to Hazardous Gluing Processes” was funded by the Danish Environmental Protection Agency’s partnership ‘Kemi i Kredsløb’. It was carried out in the period from June 2018 to November 2019.

This report describes the motivation for the project, the results obtained during the project period, and a health and environmental assessment of RadiSurf’s nanoprimer process and the components involved. The aim of the project was to eliminate the use of hazardous chemicals in the nanoprimer process and thereby overall improve the nanoprimer technology. Furthermore, a second objective of the project was to demonstrate the use of the nanoprimer technology as an alternative to e.g. epoxy glues.

The project was carried out in a collaboration between RadiSurf Aps, Danish Technological Institute (DTI), and DHI group (DHI). Brüel & Kjær Sound & Vibration Measurement A/S (B&K) provided parts and tested the use of the nanoprimer technology as an alternative to an epoxy gluing in an existing product.

The project management was undertaken by Mie Lillethorup (RadiSurf), with significant contributions from Mikkel Kongsfelt, Michael Kristensen, Christina W. D. Nielsen, Bjørn Schytz Bruun, and Espen Hvidsten Dahl from RadiSurf, Simon Frølich, Emil Tveden Bjerglund, and Lars Haahr Jepsen from DTI, Dorte Rasmussen from DHI, and Anders Thyssen from B&K. Maria Thestrup Jensen has followed and approved the project on behalf of the Danish Environmental Protection Agency (EPA).

2. Summary and Conclusion

In this project RadiSurf's nanoprimer product, which facilitates bonding between dissimilar materials such as metal and plastic, was improved from a health and environmental perspective. Overall, the process to apply the nanoprimers on e.g. metal or glass surfaces was optimized, and problematic chemicals were eliminated. Besides, the replacement of epoxy glue with a nanoprimer to assemble two titanium parts was tested.

Main results and conclusions

The process to apply the nanoprimers was transformed from a 3-step to 2-step process in this project. The first 2 steps to activate and bind initiators for the polymerization to the surface involved the problematic solvents acetonitrile, methanol, and dichloromethane in the original process. These two steps were reduced to one step, which in the case of conducting substrates is done in an aqueous solution, and in the case of oxide-surface materials is done as a vapor deposition without any solvents. The second step to create the polymer brush nanoprimers involved copper-halogen salts (e.g. $CuCl_2$ or $CuBr_2$) as catalyst in the original process and the polymerization was carried out with acetonitrile as solvent. Besides, complete oxygen-free, inert condition was required. During the project this was radically transformed, and the outcome is a polymerization step, which today is done with a CuO catalyst in very low quantity, water/isopropanol as solvent, and oxygen tolerance. Beside from the elimination of hazardous components in the process, the current 2-step process to apply nanoprimers is also simpler and faster. Hence, overall this project has significantly improved RadiSurf's business opportunities in terms of a sustainable process which can be implemented at customer's facilities.

With a more stable and oxygen tolerant nanoprimer process, initial tests of a nanoprimer kit was also done in the framework of this project. A health and environmental assessment of all process steps were evaluated by DHI, and DTI tested the kit with the first version of a technical datasheet both with very valuable feedback for RadiSurf. Test and continued development of the kit continues post project, with a clear goal of selling and shipping nanoprimer agents to customers globally in 2020.

Finally, to improve the health and worker safety we tested the use of the nanoprimer technology as an alternative to traditional and somewhat problematic adhesives like epoxy glue. Specifically, a glass filled epoxy adhesive used to assemble two titanium parts in vibrational sensors at B&K was replaced with a polycarbonate sheet bonded to nanoprimed titanium parts. The results were satisfactory in terms of adhesion, but no electrical isolation was seen between the two sensor parts as needed. Further test to also obtain electrical isolation continues after the end of this project.

3. Sammendrag og Konklusion

RadiSurfs nanoprimer produkt, der skaber binding mellem forskelligartede materialer så som metal og plast blev i dette projekt forbedret i forhold til et sundheds- og miljømæssigt perspektiv. Helt overordnet blev processen til at påføre nanoprimerne på fx metal- og glasoverflader optimeret and problematiske kemikalier i processen blev elimineret. Derudover blev en epoxy limning til at sample to titanium dele forsøgt erstattet med RadiSurfs nanoprimere.

Hovedresultater og konklusioner

Processen til at påføre RadiSurfs nanoprimere blev i dette projekt transformeret fra en 3-trins til en 2-trins proces. De første to trin i den originale nanoprimer proces, der omfatter aktivering af overfladen og binding af initiatorer til polymeriseringen, involverede de problematiske solventer acetonitril, metanol og dichlormethan. Disse to trin blev reduceret til et trin, som i tilfælde af ledende materialer nu bliver gjort i en vandig opløsning og i tilfælde af materialer med oxidoverflader bliver gjort som en gasfasedeponering helt uden brug af solvent. Det andet trin til at lave polymer brush nanoprimere involverede kobbersalte (fx $CuCl_2$ eller $CuBr_2$) som katalysator i den originale proces og polymerisering blev udført med acetonitril som solvent. Desuden var fuldstændige inerte, oxygenfrie betingelser påkrævet. Gennem dette projekt blev polymeriseringen radikalt ændret, og den bliver i dag udført med meget lav koncentration af en CuO katalysator, med vand/isopropanol som solvent og oxygentolerance. Udover elimineringen af skadelige komponenter i processen, er den nuværende 2-trins proces til at påføre nanoprimerne også meget enklere og hurtigere at udføre. Projektet har i høj grad forbedret RadiSurfs forretningsmuligheder og mulighederne for fremtidig implementering af processen hos kunder.

Med en mere stabil og oxygentolerant nanoprimerproces blev de første test af et nanoprimer kit også udført indenfor rammerne af dette projekt. En sundheds- og miljømæssig evaluering af de enkelte procestrin blev lavet af DHI, og DTI testede processen med den første version af et teknisk datablad. Begge dele resulterede i værdifuld feedback for RadiSurf. Test og fortsat udvikling af et nanoprimer kit fortsætter efter dette projekt med et klart mål om at kunne forsende og sælge nanoprimer-opløsninger til kunder globalt i 2020.

For at forbedre arbejdssikkerheden og -miljøet testede vi også at bruge nanoprimerteknologien som et alternativ til traditionelle og skadelige adhæsiver som fx epoxy. Dette blev gjort i samarbejde med B&K hvor en epoxy-limning af to titanium dele i en vibrationssensor blev erstattet med en polykarbonat skive bundet til titaniumdelene gennem nanoprimere. Resultaterne var umiddelbart positive i forhold til vedhæftningsstyrke, men delene var ikke elektrisk isolerede med løsningen, som det ellers var påkrævet. Test i forhold til at sikre elektrisk isolation fortsætter efter dette projekt.

4. Introduction

4.1 Motivation and RadiSurf in a context

In a wide range of industries and sectors, the development of new materials and production methods are of crucial importance. In particular new hybrid materials, which combines metals and polymer materials to create e.g. lightweight components, are of immense interest. The task to combine the dissimilar materials is inherently challenging due to differences in physical and chemical properties of metal and polymer. Joining techniques usually rely on welding or brazing methods, which are demanding and almost exclusively applicable to joining similar materials (e.g. metal-to-metal or plastic-to-plastic). Mechanical attachments (fasteners, rivets, inserts, screws, or clips) are the traditional joining methods, but they present critical disadvantages regarding aesthetic appearance, thickness of the components, load distribution, risk of corrosion, and hygienic issues. Hence, industries are moving towards adhesives (glues) as replacements. However, most adhesive types on the market are standardized, off-the-shelf solutions not tailored to specific combinations of materials, and consequently this leads to suboptimal performance. In addition, adhesive's application procedures are in general difficult to integrate in established manufacturing lines, and they set high requirements to workers safety, due to toxic components involved. Besides, industries like medico and food/beverage are highly regulated in terms of choice of adhesive to prevent leaching of harmful chemicals in the final products.

RadiSurf was founded in 2015 as a spin-off from Aarhus University. RadiSurf addresses the drawbacks of traditional adhesive through an innovative, customized joining technology based on polymer brushes.[1] The solution replaces state-of-the-art adhesives. An ultrathin (30-100 nm) polymer brush coating on the metal is used as a nanoadhesive layer. The polymer brushes entangle with the polymeric networks of the plastic to firmly join polymer-based components with metals, carbon fiber, glass, and ceramics surfaces (patented).[2] The development of a simple, fast, and user-friendly industrial process to synthesize the polymer brushes on surfaces was started at RadiSurf 2-3 years ago (patent filed).[3]

Polymer brushes have been known since 1950's and extensively researched. Despite countless efforts, the process of making polymer brushes has so far not reached industrial scalability and attractive cost-efficiency. Besides, the process to synthesize polymer brushes traditionally uses unwanted substances, like dichloromethane and copper salts.

RadiSurf has developed a simple, scalable, and flexible process for polymer brush synthesis that industries may integrate into any manufacturing line (manual or automated). The core technology has a huge and diverse potential that targets applications where state-of-the-art solutions do not bond dissimilar materials satisfactorily or their application process is difficult. However, the original process has been dependent on the use of hazardous chemicals, which has been an obstacle for implementation of this technology. Efforts to exclude hazardous chemicals from the nanoprimer process, a main purpose of this project, are therefore a requisite to enable the successful scaling and implementation of RadiSurf's technology as a business and expand it to new sectors.

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[1] Polymer brushes are polymer chains chemically bound at one end to the surface of a given substrate. Due to the proximity of the polymer chains, they adopt a stretches confirmation resulting in so-called "polymer brushes".

[2] "Joining of polymer and surface-modified solid part" is already granted in Europe (EP2920230B1), approved in US (US20150316061A1 - soon to be granted) and pending in China (CN104937013A).

[3] "Compositions for Forming Polymer Brushes", Nielsen, S. U., Kongsfelt, M. S. (2018). WO2019196999.

4.2 Objectives of the project

The main objective of this project is to improve the nanoprimer process technology into an environmentally friendly, water/alcohol-based method eliminating the use of hazardous chemicals. This development will make RadiSurf's nanoprimer technology more attractive as an alternative to existing solvent based toxic adhesive solutions, such as cyanoacrylates and epoxies, and a necessary step to scale up and expand the use of the nanoprimer technology. This furthermore answers an important request from RadiSurf's existing and potential customers, to comply with health and environmental regulations.

The second objective of the project is to substitute epoxy adhesives in customer cases and demonstrate the use of the nanoprimer technology as an alternative to e.g. epoxy glue. In this context, we aim to develop a 2-component chemical kit, which can be readily implemented directly at the customer. The safety of using and implementing the chemical kit is of high importance, and it will be reviewed during this project.

4.3 Improving RadiSurf's nanoprimer technology

RadiSurf is a pioneer in the exploitation and application of polymer brushes as a joining technology of dissimilar materials. Polymer brushes are small polymer chains tethered (chemically) to a surface (e.g. metal, glass, ceramic, carbon). They have the capacity to entangle and integrate the polymeric network of a plastic component deposited on the surface coated with the polymer brushes, thus facilitating an extremely strong adhesion. The resultant interface is at nanometer scale (ultrathin and ultra-tight), chemically clean and invisible to our eyes, eliminating completely the need of a "glue" or any mechanical system to keep the two components attached (Figure 1).

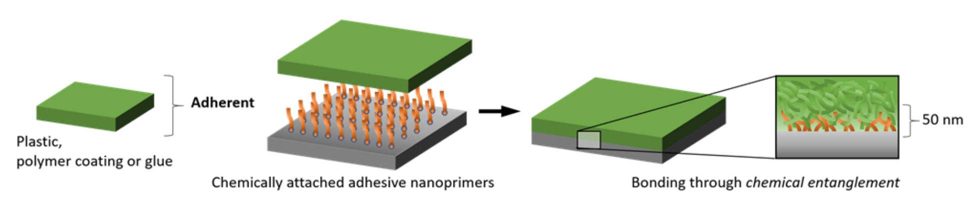

FIGURE 1. The nanoprimer adhesion technology.

The process to synthesize polymer brushes on metal/glass/carbon/ceramic surfaces is traditionally a 3-step process. Step 1 and 2 activates of the base material (metal, glass, carbon, or ceramic surfaces) with a thin layer of reactive initiator molecules, whereas step 3 is the polymerization of monomers into polymer chains, forming the polymer brushes (Figure 2). In RadiSurf's original nanoprimer process, these process steps involve problematic chemicals (e.g. acetonitrile in step 1, dichloromethane in step 2, and dimethylformamide and copper-halogen salts in step 3).

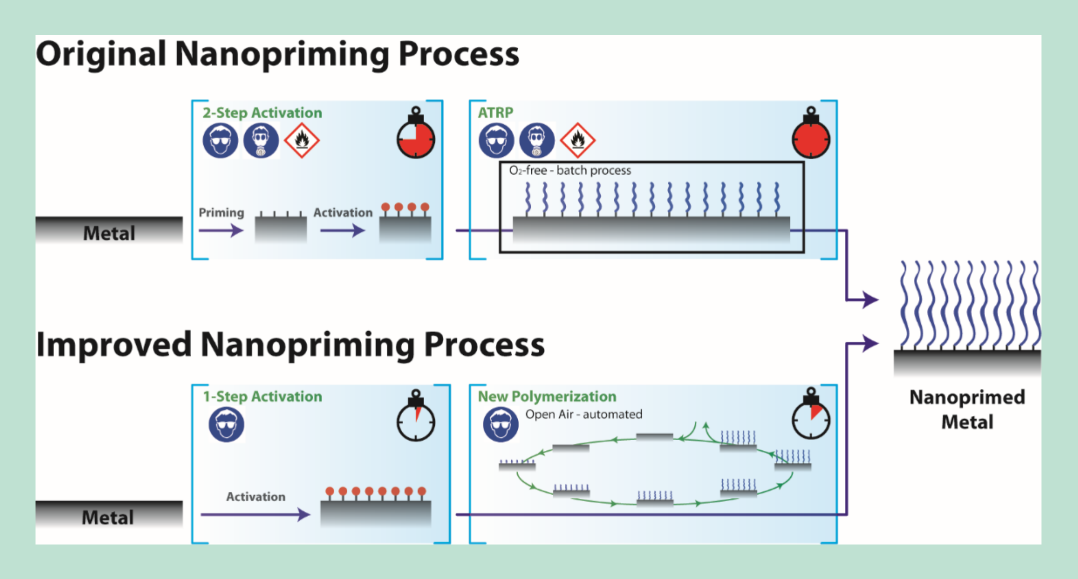

FIGURE 2. Process steps to create polymer brush nanoprimers. The original nanoprimer process is illustrated in the top, and new improved process in the bottom.

Throughout this project the focus has been to exchange the 2-step activation (step 1 and 2) with a 1-step activation process, which (1) reduces the process and handling time and (2) eliminates the use of acetonitrile and dichloromethane. Besides, we have developed a revolutionary polymerization process, which can be scaled up for industrial processes without strict requirements for control of the atmosphere. The new polymerization process contains two customized aqueous/alcohol-based solutions: the activation agent and polymer agent. The process used controls the formation of polymer brushes of pre-determined lengths (5-200 nm) and varied densities within minutes (5-60 min). The polymer brushes are carefully designed a priori to efficiently interact and mix with the polymeric part desired to bond. Importantly, the new polymerization process excludes the use of dimethylformamide and copper-halogen salts.

The process development of RadiSurf's nanoprimer technology since RadiSurf was founded, is illustrated in Figure 3 which, besides a significant reduction in process time and exclusion of problematic chemicals, also is characterized by a more tolerant and worker-friendly process. The original nanoprimer process had strict requirements to control of the atmosphere surrounding the polymerization solution. Small traces of oxygen quenched the surface polymerization to grow polymer brushes, which even in the hands of trained personal, resulted in a high process failure rate. All surface polymerizations were carried out in tightly sealed vessels and all solutions needed tedious and time-consuming processing to remove all oxygen prior to the polymerization. This significantly restricted geometries and sizes of customer-products, which could be successfully coated with nanoprimers.

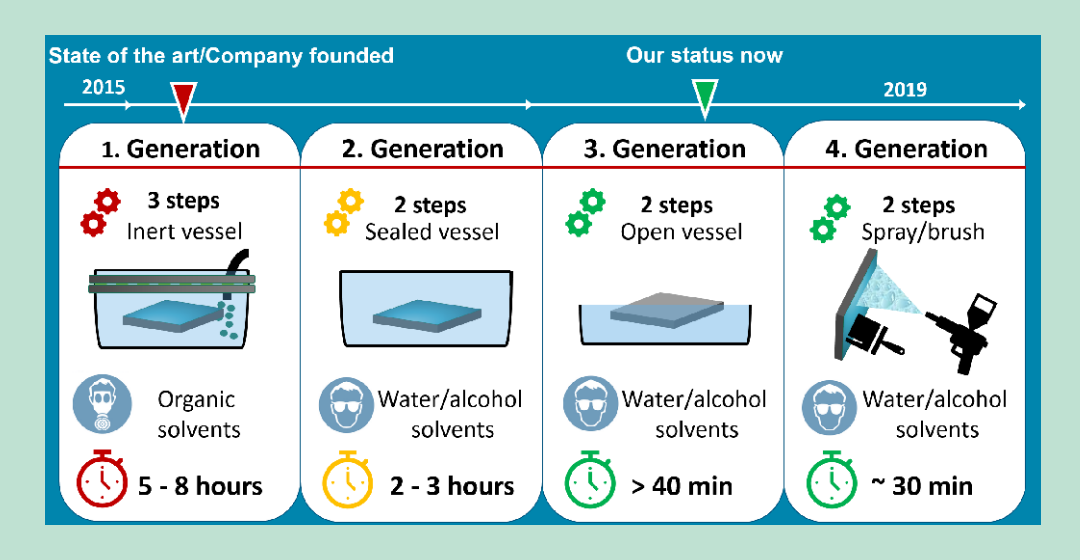

FIGURE 3. Nanoprimer process development since RadiSurf was founded, going from a highly oxygen sensitive surface polymerization to a process working in open or partly open vessels.

When starting the present project, we had proof-of-concept for our most advanced nanoprimer processes to work in open atmosphere in water/alcohol solvents, while others (our nanoprimer for adhesion to poly(methyl methacrylate) (PMMA) and polycarbonate (PC)) were trailing behind as 1st or 2nd generation. Hence, we have worked towards developing the PMMA and PC nanoprimer process to 3rd generation – using benign solvents and proceeding ideally with no control of atmosphere with low failure rate. At the same time, we have been looking into worker-friendly nanoprimer processes, which can be applied in open atmosphere (4th generation).

4.4 Chemicals of concern in original nanoprimer process

Chemicals of concern in the original nanoprimer process involve acetonitrile (MeCN), methanol (MeOH), dichloromethane (DCM), dimethylformamide (DMF), and copper-halogen salts (e.g. $CuCl_2$ or $CuBr_2$).

The first step of the 2-step substrate activation for the original nanoprimer process (illustrated in Figure 2), was done in two different ways depending on the substrate. For conducting metal substrates, like stainless steel, an electrochemical aryl diazonium process was used, whereas a solution-based organosilane process was used for substrates displaying an oxide surface, e.g. aluminum, titanium, and glass (Figure 4). The second step of the substrate activation was a second dip process.

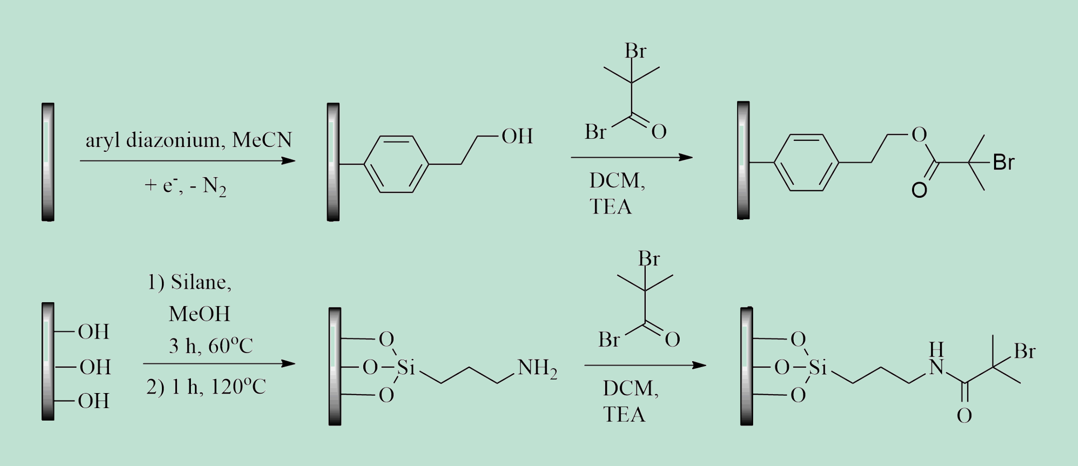

FIGURE 4. Top: Electrochemical grafting of 4-(2-hydroxyethyl)benzenediazonium tetrafluoroborate (HEBD) followed by reaction with α-bromoisobutyryl bromide (BIBB) on conduction substrates. Bottom: Dip-coating of 3-aminopropyltrimethoxysilane followed by reaction with α-bromoisobutyryl bromide (BIBB) on oxide surface, e.g. aluminum, titanium, and glass.

As seen in Figure 4, either MeCN or MeOH were used in step 1, whereas the second step involved DCM. MeCN, MeOH, and DCM are not on the candidate list under the REACH Regulation, including substances of very high concern which may have serious effects on human health or the environment. However, MeCN is cancerogenic, harmful if swallowed or in contact with skin, and toxic to aquatic life with long lasting effects.[4] MeOH is toxic and suspected of causing cancer.[5] DCM is suspected of causing cancer[6] and another problematic element is that DCM is a greenhouse gas not regulated by the Montreal Protocol.[7]

In the original nanoprimer process, the second process step to create polymer brushes, the important surface polymerization, was based on the atom transfer radical polymerization (ATRP) process, which uses copper-halogen salts (e.g. $CuCl_2$ or $CuBr_2$) as catalyst. $CuCl_2$ and $CuBr_2$ are very toxic to aquatic life with long lasting effects,[8,9] and hence alternative catalysts were desired. Besides, the polymerization was carried out with MeCN as solvent.

Finally, to create a nanoprimer for adhesion to materials like rubber or PUR, a post-treatment of the polymer brushes was done to immobilize functional groups for specific adhesion. Here DMF was in general used as solvent to ensure good solvation of the polymer brush chains and diffusion of reactive species into the polymer brush structure. DMF is currently on the candidate list due to its reproductive toxicity, and it may damage fertility or the unborn child.[10] Besides, DMF is readily absorbed through the skin, and can cause liver damage.[11] Hence, a substitution of this solvent or complete elimination of the need for a post-treatment was needed.

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[4] https://echa.europa.eu/da/substance-information/-/substanceinfo/100.000.760

[5] https://echa.europa.eu/da/substance-information/-/substanceinfo/100.000.599

[6] https://echa.europa.eu/da/substance-information/-/substanceinfo/100.000.763

[7] Nat Commun. 2017; 8: 15962. doi: 10.1038/ncomms15962

[8] https://echa.europa.eu/da/substance-information/-/substanceinfo/100.028.373

[9] https://echa.europa.eu/da/substance-information/-/substanceinfo/100.029.243

[10] https://echa.europa.eu/da/substance-information/-/substanceinfo/100.000.617

[11] https://www.cdc.gov/niosh/docs/90-105/default.html

5. Methodology

5.1 Strategies to implement a health and an environmentally friendly nanoprimer processes

5.1.1 The original nanoprimer process

The original nanoprimer process (illustrated in Figure 2) consists of 2 parts. The first part is 2 steps, where the surface is activated in step 1a and initiators for the surface polymerization in bound to the substrate in step 1b. As mentioned earlier, the surface activation (step 1a) was done in two different ways depending on the substrate. The second part (step 2) is the surface polymerization to immobilize the polymer brush nanoprimers. The chemical components, their concentrations, and the process condition for the original nanoprimer process is given in Table 1:

TABLE 1. Processing conditions for the original nanoprimer process.

Conducting substrates	**Metal-oxide surfaces**
Step 1a – Surface activation	
• MeCN as solvent • 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte • Room temperature • 0.002 mM aryldiazonium salt • 5-10 min electrochemical deposition	Deposition: • MeOH as solvent • 20 mM organosilane • 60 °C • 3 h dip coating processing time Annealing (post-processing): • 120 °C in oven • 1 h
Step 1b – Immobilization of initiators for the surface polymerization	
• DCM as solvent • 0.05 M triethylamine as base/catalyst • 0.5 M α-bromoisobutyryl bromide • Room temperature • 1 h dip coating processing time	
Step 2 – Surface polymerization	
• MeCN as solvent • CuCl and $Cu(II)Cl_2$ as catalysts • 3 M methyl methacrylate • 6 mM *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine as ligand • 1 h pre-processing to remove oxygen followed by 3 h polymerization • Strictly inert atmosphere control (no oxygen) • 60 °C	

5.1.2 Alternatives to step 1 – Immobilization of initiators for polymerization

For part 1 in the nanoprimer process, we sought for a 1-step solution, where initiators for the surface polymerization were immobilized directly. Hence, new candidates were molecules possessing two functionalities: 1) a group which can bind to the surface (surface activation) and 2) a group acting as initiator for the surface polymerization, X. Such candidates are illustrated in Figure 5.

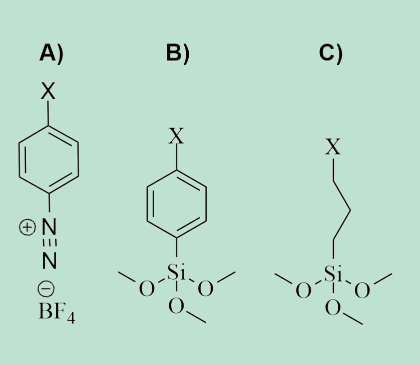

FIGURE 5. Chemical structure of initiators, which can be immobilized on a surface in 1 step. A) X-benzenediazonium salt (XBD), B) X-phenyltrimethoxysilane (XPhTMS), and C) X-propyltrimethoxysilane (XPTMS). Where “X” is the functional initiator group.

As seen from Figure 5a, for conducting substrates an aryl diazonium salt possessing an initiator functionality was identified. For metal-oxide surfaces, two candidates were identified both having a trimethoxysilane group in one end of the molecule and an initiator functionality in the other end of the molecule (Figure 5b and c). Besides, it is well known from literature, that many organosilane compounds are excellent candidates to be surface immobilized through a solvent-free vapor deposition process,[12,13] and hence this possibility was pursued in the project.

5.1.3 Alternatives to step 2 – The surface polymerization

The surface polymerization to create polymer brushes (step 2 in Figure 2) is the crucial step in the nanoprimer formation, and hence the step of highest priority in this project. At the same time, this step has been particularly challenging to scale, and therefore polymer brushes today still remain an academic discipline. Our focus has been to develop a process using benign solvents and catalyst, working preferable at room temperature and faster processing times, and allowing no or low atmosphere control. This disrupts the polymer brush synthesis and allows to fully transfer the polymer brushes to an industrial implementable process. In this project the single electron transfer living radical polymerization (SET-LRP) has been the starting point. SET-LRP has, in literature, within the last 5 years proven to be a reliable, controlled polymerization technique less oxygen sensitive that ATRP and based on aqueous/alcohol solvent systems.[14] This polymerization uses Cu(0) as an electron donor catalyst. The Cu(0) can be generated in situ by the disproportionation of Cu(I) to Cu(0) and Cu(II) in the presence of an appropriate ligand and solvent system or generated from a solid Cu source. Interestingly, SET-LRP has also been useful as a surface-initiated polymerization to create polymer brushes either generating Cu(0)

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[12] Sugimura, H., Hozumi, A., Kameyama, T., & Takai, O. (2002). Organosilane self-assembled monolayers formed at the vapour/solid interface. Surface and Interface Analysis, 34(1), 550–554.

[13] Zhang, F., Sautter, K., Larsen, A. M., Findley, D. A., Davis, R. C., Samha, H., & Linford, M. R. (2010). Chemical vapor deposition of three aminosilanes on silicon dioxide: Surface characterization, stability, effects of silane concentration, and cyanine dye adsorption. Langmuir, 26(18), 14648–14654.

[14] Lligadas, G., Grama, S., & Percec, V. (2017). Single-Electron Transfer Living Radical Polymerization Platform to Practice, Develop, and Invent. Biomacromolecules, 18, 2981–3008.

through the disproportionation reaction,[15] having Cu(0) as solid powder,[16] or using a Cu plate as the source of the Cu catalyst.[17]

In this project, our first approach was to develop a SET-LRP system appropriate to make PMMA brushes using a Cu-wire as the Cu(0) source generated in situ. From there we moved on and transformed the PMMA SET-LRP procedure into our newly developed polymerization method, Radi-LRP,[18] where solutions for Cu-catalyst are made ex situ, and used and activated only during the polymerization step. For the SET-LRP procedure and in particular our Radi-LRP procedure numerous screenings were conducted varying process conditions, such as solvent system, monomer concentration, ligand, activation type, temperature, and polymerization time.

Besides, DHI contributed with an environmental and health assessment of used and potential ligands and oxygen scavengers for the polymer brush process (section 7.1).

5.2 Surface characterization methods

5.2.1 Development of in-house water contact angle (WCA) equipment

An in-house setup to make water contact angle (WCA) measurements was made in the framework of this project. A sketch of the setup and a photo after making it is shown in Figure 6. All parts including a fixture for a digital camera, a stage with adjustable height for placing the substrate, a fixture for a micro syringe, and a fixture for lamps/back light exposure were 3D printed.

FIGURE 6. Sketch and photo of water contact angle equipment.

WCA measurements were measured by placing 2 µL deionized water on the substrate surface, and immediately capturing a photo.

A script was made to extract the WCA from a digital photo. Two examples are shown in Figure 7, where the angle between the water drop and the substrate is indicated with red lines. The left example is a stainless steel samples with PMMA brushes (WCA = 76 °), and the right photo is a glass substrate with polystyrene (PS) brushes (WCA = 86 °).

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[15] Turan, E., & Cayakara, T. (2010). Kinetic Analysis of Surface-Initiated SET-LRP of Poly(N-isopropylacrylamide). Journal of Polymer Science Part A: Polymer Chemistry, 48, 5842–5847.

[16] Ding, S., Floyd, A., & Walters, K. B. (2009). Comparison of Surface Confined ATRP and SET-LRP Syntheses for a Series of Amino (Meth)acrylate Polymer Brushes on Silicon Substrates. Journal of Polymer Science Part A: Polymer Chemistry, 47, 6552–6560.

[17] Zhang, T., Du, Y., Müller, F., Amin, I., & Jordan, R. (2015). Surface-initiated Cu(0) mediated controlled radical polymerization (SI-CuCRP) using a copper plate. Polymer Chemistry, 6, 2726–2733.

[18] Nielsen, S. U., Kongsfelt, M. S. (2018). Compositions for Forming Polymer Brushes. WO2019196999.

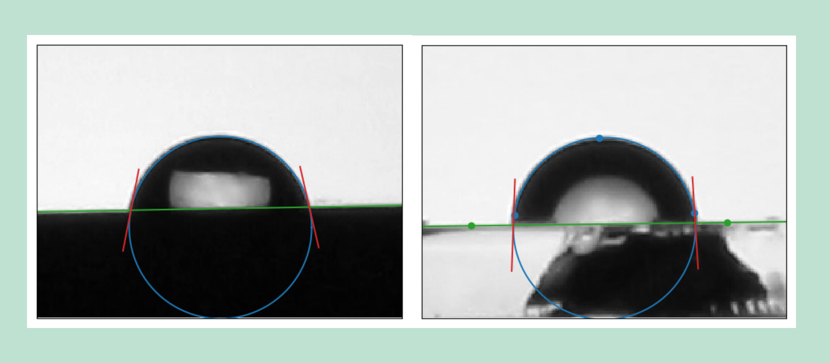

FIGURE 7. Examples of captures of water contact angle, after processing the photo with software developed in this project. Left: Stainless steel sample with PMMA brushes, WCA = 76 °; Right: Glass samples with PS brushes, WCA = 86 °

5.2.2 Ellipsometry

Dry-film thicknesses were measured using a rotating analyzer ellipsometer (Dre,Germany). Polished SS substrates were measured at 75° angle of incidence. The ellipsometric parameters of the bare (Δs, ψs) and polymer modified (Δp, ψp) substrates were measured in air at ambient temperature, where Δ is the phase shift and $\tan(\psi)$ is the amplitude ratio upon reflection. The complex refractive index of the bare substrate was calculated from the measured Δ s and ψs values. A three-layer optical model consisting of a substrate with a complex refractive index, the polymer layer with a refractive index (fixed at a constant value: real = 1.55; imaginary = 0) and thickness and the surrounding medium (air) was used to calculate the overall reflection coefficients for in-plane (Rp) and out-of-plane (Rs) polarized lights. The real and the imaginary parts of the refractive index of the bare substrate were obtained by measuring the clean substrates prior to modification.

5.2.3 X-ray photoelectron spectroscopy

A Kratos Axis Ultra-DLD spectrometer (Kratos Analytical Ltd., UK) operated using a monochromatic Al Kα X-Ray source at a power of 150 W was used. For the surface analysis an area of 300 × 700 μm^2 was employed. Survey spectra were acquired by accumulating two sweeps in the 0–1350 eV range at a pass energy of 160 eV. High-resolution spectra of the element of interest were acquired at a pass energy of 20 eV. The pressure in the main chamber during the analysis was in the 10^{-9} Torr range. The generated XPS data were processed using the computer software CasaXPS v2.3.19 (Casa software Ltd., UK). Atomic surface concentrations were determined from survey spectra following Shirley background subtraction. Binding energies of the components in the spectra were determined by calibrating against the C-H/C-C peak in the C1s spectra at 285.0 eV. For the surface analysis, two spots were measured on each substrate.

5.2.4 Qualitative adhesion assessment

After PMMA brush screenings, a quick assessment of the quality of nanoprimer, and hence the quality of the PMMA brushes, was done by adhering the nanoprimed substrates to a Plexiglas® (PMMA) sheet. The assembly was done by solvent welding, where 1 drop of dichloromethane or acetone was placed on the Plexiglas® along an edge, and a nanoprimed 1x1 cm stainless steel or aluminum samples was placed on the drop with half of the samples overlapping with the sheet, applying a gentle pressure for 10 s, before the assembly was left to dry until the next day. A qualitative adhesion score was given (1-5), after breaking off samples from the Plexiglas® sheet. 1 corresponds to no adhesion, 2 weak adhesion, 3 good adhesion, 4 good adhesion with plexiglass residues seen on the samples, and 5 cohesive failure.

Examples of Plexiglas® assembled with nanoprimed stainless steel substrate after a screening of the nanoprimer procedure are shown in Figure 8 along with photos of the qualitative test of both stainless steel and aluminum.

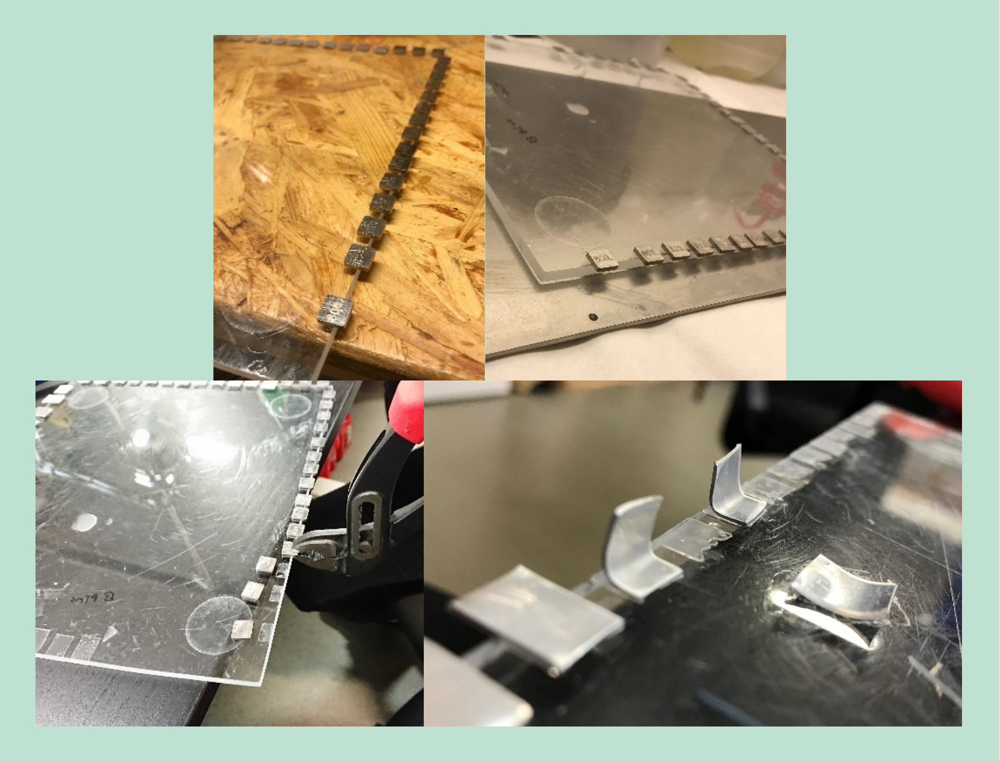

FIGURE 8. Assembly of Plexiglas® and nanoprimed test substrates (stainless steel and aluminum) before and during qualitative adhesion tests.

5.3 Analysis and quantification of catalyst solutions

The Cu-catalyst solutions used for the Radi-LRP procedure were analyzed as a part of this project. The nature of the catalyst was analyzed by dynamic light scattering (DLS), whereas the concentration of the catalyst was measured by atomic absorption spectroscopy and used to correlate absorption values measured by ultraviolet-visible spectroscopy (UV-vis) to concentration values.

5.3.1 Atomic absorption spectroscopy

Atomic absorption spectroscopy was carried out on a PerkinElmer PE300. The quantification was performed against traceable external standards of iron. The methodology used was based on the standard method DS 259: 2003: "*Determination of metals in water, sludge and sediments – General guidelines for determination by atomic absorption spectrophotometry in flame*". Before analysis, the sample was diluted 50 times and treated with nitric acid. All measurements are the average of duplicates.

5.3.2 Dynamic light scattering

Dynamic light scattering was carried out on a Zetasizer Nano series Nano ZS, where particles in the range 1-6000 nm are measured. The instrument's performance is checked by a validation where a standard dispersion of polystyrene particles is measured. Depending on the concentration of the sample, the sample was either analyzed directly or diluted with water before being transferred to the cuvette.

5.3.3 Ultraviolet-visible spectroscopy

UV-vis measurements were done on an LLG-uniSPEC 2 spectrophotometer. 3 spectral scans were recorded using deionized water as background in the range 450-1100 nm, and the spectra were averaged.

6. Results and Discussion

6.1 Part 1 – Immobilization of initiators for the polymerization

To immobilize initiators for the polymerization on various substrate materials, we sought for 1-step deposition processes, which eliminated the use of problematic and hazardous solvents. For conducting substrates, the electrochemical grafting of aryl diazonium salts can be carried out in aqueous solutions, however it should be verified, that the water does not react with the chemical functionalities of interest (the initiator functionality). For glass and metal oxide substrates, it is well known from literature, that many organosilane compounds are excellent candidates to be surface immobilized through a vapor deposition process, which completely eliminates the use of solvent and also a labor-intense cleaning step.[19,20]

6.1.1 Conducting substrates

Electrochemical grafting of X-benzenediazonium salt (**XBD**) on conducting substrates were tested in a 2 mM solution of **XBD** in 0.1 M phosphate buffered saline (PBS). At reductive potentials, the aryl diazonium salt is reduced at the electrode surface to the corresponding aryl radical, which readily reacts and forms strong, covalent bonds between the aryl compound and the surface of the conducting substrate. After electrolysis for 5 min at a reductive potential, the current had diminished to ~0 A, indicating completely blocking of the conducting surface, which is a strong indication of the formation of an isolating organic film. Table 2 shows the atomic distribution of the various elements present at the surface after electrografting **XBD** on a glassy carbon substrate. In particular the presence of N and Cl confirms the successful grafting of the diazonium salt (it is noted that some of the Cl-content also may originate from NaCl in the PBS buffer). The presence of Na and P suggest that ions from the PBS buffer are not sufficiently cleaned off after electrografting. However, these are expected to be removed with water rinse. The Cl-part of the diazonium salt is associated with the initiator for the following polymerization step, and they are therefore of crucial importance here.

TABLE 2. Atomic percentages measured by XPS of glassy carbon substrate electrochemically grafted with XBD.

O 1s %	C 1s %	N 1s %	Cl 2p %	Na 1s %	P 2p %	Si 2p %
14.3 ± 1.9	75.8 ± 3.7	2.9 ± 0.7	3.0 ± 0.7	1.7 ± 1.0	1.2 ± 0.6	1.2 ± 0.1

XBD-functionalized stainless steel substrates were used to grow PMMA polymer brushes (using the procedure developed in the project and described in section 6.2.2), which further demonstrated the successful 1-step immobilization of initiators on conducting substrates. Furthermore, the adhesion properties of stainless steel modified with **XBD**-PMMA were tested. As reference, stainless steel functionalized with the 2-step initiator was used (electrografting of 4-(2-hydroxyethyl)benzenediazonium tetrafluoroborate followed by reaction with α-bromoisobutyryl bromide (**HEBD+BIBB**)). Stainless steel rods treated with **XBD** and **HEBD+BIBB** were modified with PMMA brushes and overmolded with PMMA as illustrated in Figure 9.

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[19] Sugimura, H., Hozumi, A., Kameyama, T., & Takai, O. (2002). Organosilane self-assembled monolayers formed at the vapour/solid interface. Surface and Interface Analysis, 34(1), 550–554.

[20] Zhang, F., Sautter, K., Larsen, A. M., Findley, D. A., Davis, R. C., Samha, H., & Linford, M. R. (2010). Chemical vapor deposition of three aminosilanes on silicon dioxide: Surface characterization, stability, effects of silane concentration, and cyanine dye adsorption. Langmuir, 26(18), 14648–14654.

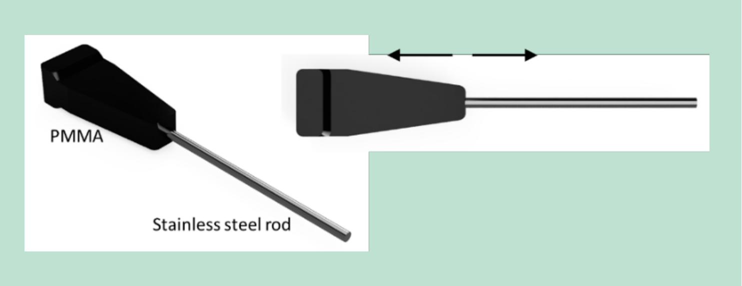

FIGURE 9. Illustration of pull-out specimens used to test the adhesion between stainless steel and PMMA. To test the adhesion, the PMMA and stainless steel were pulled apart.

Figure 10 shows the results of pull-out test, where it is seen that the **XBD** initiator performs as well as the 2-step **HEBD-BIBB** initiator in terms of adhesion to PMMA. Hence, the **XBD** initiator can be used as a 1-step initiator for Radi-LRP without compromising on the adhesion strength.

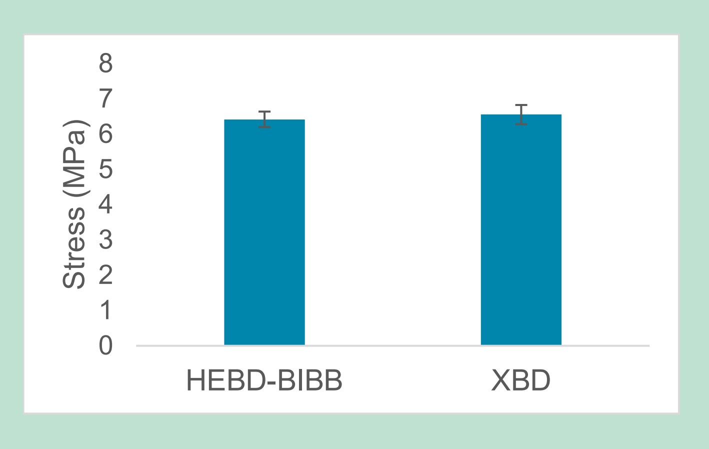

FIGURE 10. Comparing the effect of different initiator layers on stainless steel in the adhesion to PMMA. HEBD-BIBB is a 2-step diazonium-based initiator, and BD is a 1-step diazonium based initiator.

6.1.2 Metal oxide substrates

6.1.2.1 Vapor deposition of X-phenyltrimethoxysilane

For glass substrates and metal oxide surfaces, the solvent-free vapor deposition of X-phenyltrimethoxysilane (**XPhTMS**) was tested. The deposition was tested at various temperatures (25 – 100 °C) and deposition times (15 min – 24 h) at ambient pressure in a closed container. XPS analysis in general revealed successful deposition at various temperatures and times, but it was observed that slightly elevated temperature (45 °C) improved the stability of the layer for the following surface initiated polymerization. Across various substrate materials, vapor deposition of XPhTMS at 45 °C for 2.5 h was chosen as standard conditions moving forward, and Table 3 shows the atomic distribution of the surface elements measured by XPS on **XPhTMS** modified stainless steel, aluminum, and titanium. In all cases the presence of Cl confirms the successful immobilization of **XPhTMS**. The deposition time (and temperature) may be reduced, but the process has to be optimized for the individual substrate materials, which is beyond the scope of this project.

TABLE 3. Atomic percentages measured by XPS of stainless steel (SS), aluminum (Alu), and titanium (Ti) substrates after vapor deposition of XPhTMS.

	O 1s %	C 1s %	N 1s %	Cl 2p %	Na 1s %	Ca 2p %	Si 2p %	Fe 2p %	Al 2p %	S 2p %	Ti 2p %
SS	22.9	71.4	0.5	0.7	0.3	1.4	2.0	0.7	-	-	-
Alu	30.4	44.4	0.6	0.7	-	0.7	12.5	-	10.0	0.8	-
Ti	32.5	51.9	1.0	0.4	-	1.6	1.0	-	0.9	-	8.3

6.1.2.2 Vapor deposition of X-propyltrimethoxysilane

For glass substrates and metal oxide surfaces X-propyltrimethoxysilane (**XPTMS**) is an alternative candidate to XPhTMS, where the compound possesses two functionalities: 1) a group which can bind to the surface (trimethoxysilyl-group) and 2) a group acting as initiator for the surface polymerization (the X-end). The vapor deposition of **XPTMS** was tested at room temperature and 45 °C for 1-3 h at aluminum and glass substrates. By measuring the WCA after the deposition (Figure 11), it is clearly seen that an increase is seen in WCA going from blank (vapor deposition time = 0 h) to deposited substrates, which is a clear indication of deposition of **XPTMS**. It is also seen that 45 °C deposition temperature is more effective than room temperature. Similar to the conditions used for **XPhTMS**, we chose to use vapor deposition of **XPTMS** at 45 °C for 2.5 h as standard conditions across various substrates, which after various polymerization gave high quality polymer brush films. Again, the deposition time (and temperature) may be reduced, but the process must be optimized for the individual substrate materials, which is beyond the scope of this project.

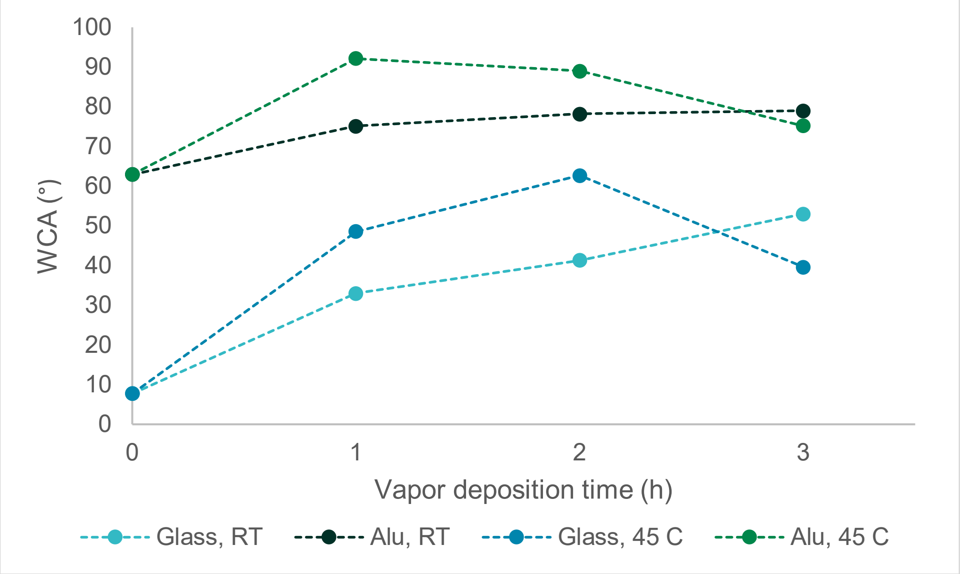

FIGURE 11. The water contact angle (WCA) measured after vapor deposition of XPTMS at room temperature (RT) and 45 °C for 1-3 h at glass and aluminum (Alu) substrates.

6.2 Part 2 – The surface polymerization

With developed and optimized procedures to immobilize initiators for the polymerization both on conducting substrates and on materials with oxide surfaces, the attention was drawn to the surface polymerization to grow polymer brush nanoprimers in an efficient manner using benign solvents and chemicals.

6.2.1 Testing SET-LRP of PMMA

Moving from a tedious, highly oxygen sensitive, and time consuming ATRP procedure with high failure rate and using problematic solvents and Cu-salts (Table 1), we initially sought for a SET-LRP procedure to create PMMA brushes. The Haddleton group recently described universal condition to polymerize acrylates, methacrylates, and styrene in solution by the SET-LRP procedure.[21] To polymerize MMA, the following conditions were used: [MMA]:[Initiator]:[PMDETA]:[$CuBr_2$]= [50]:[1]:[0.36]:[0.05] in 1:1 (v/v) monomer to solvent (*i*PrOH) ratio at 40 °C in the presence of a Cu(0) wire (PMDETA is a ligand). We transformed this procedure into a surface-initiated version, where the initiator was instead immobilized on the surface of aluminum substrates and the concentration of deactivator, $CuBr_2$, were varied along with the MMA/*i*PrOH ratio. For this screening both stainless steel samples treated with the **XPTMS** and **XPhTMS** initiator was used. The screening condition are outlined in Table 4. Two different ligands, L1 and L2, were used. The specific ligands used is proprietary information.

TABLE 4. Parameters used in Cu-wire SET-LRP screening to grow PMMA brushes on XPTMS- and XPhTMS modified stainless steel substrates.

Entry	MMA/*i*PrOH (v/v)	[MMA]/[Ligand]/[$CuBr_2$]	Ligand	Temp (C°)	Polymerization time (h)	Adhesion score (1-5)	
						XPTMS	XPhTMS
1-1	1:1	[50]:[0.36]:[0.05]	L1	60	2	4	3
1-2	1:1	[50]:[0.36]:[0.025]	L1	60	2	1	1
1-3	1:1	[50]:[0.36]:[0.013]	L1	60	2	1	1
1-4	5:3	[50]:[0.36]:[0.05]	L1	60	2	1	1
1-5	3:1	[50]:[0.36]:[0.05]	L1	60	2	1	1
1-6	1:1	[50]:[0.36]:[0.05]	L2	60	2	4.5	3
1-7	1:1	[50]:[0.36]:[0.013]	L2	60	2	3.5	3
1-8	1:1	[50]:[0.36]:[0]	L2	60	2	5	3

The quality of the nanoprimer was assessed by qualitative adhesion score (1-5; see section 5.2.4). Interestingly, only entry 1-8, XPTMS in Table 4 gave adhesion score corresponding to full cohesive failure, and hence gave a clear indication of the best quality of the nanoprimer. Entry 1-8 is the only entry with no addition of the cobber salt, $CuBr_2$, which was added to improve the control of the surface polymerization. We propose, that the $CuBr_2$ in this case deactivates the polymerization to a too large extent and prevent successful polymerization in 2 h reaction time. This screening provided a good indication, that PMMA brushes can be achieved by the SET-LRP process using a solid Cu(0) catalyst. However, the concentration of Cu(0) is poorly controlled in this process, and hence the aim was to transform the process to our Radi-LRP process.

6.2.2 Development and screening of Radi-LRP of PMMA

In the SET-LRP system described above, a Cu-wire functions as the Cu(0) source. Cu(0) is generated in situ during the course of the polymerization, and hence its concentration is poorly controlled. Therefore, the aim here was to transform the PMMA SET-LRP procedure into our

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[21] Whitfield, R., Anastasaki, A., Nikolaou, V., Jones, G. R., Engelis, N. G., Discekici, E. H., Fleischmann, C., Willenbacher, J., Hawker, C. J., & Haddleton, D. M. (2017). Universal Conditions for the Controlled Polymerization of Acrylates, Methacrylates, and Styrene via Cu(0)-RDRP. Journal of the American Chemical Society, 139, 1003–1010.

newly developed polymerization method, Radi-LRP,[22] where solutions of Cu-catalyst are made ex situ and used and activated only during the polymerization step. The preparation of the catalyst solution is described in Section 6.3.1.

More than 300 screenings were conducted here to find a viable procedure to reproducibly grow PMMA brushes. An example of such a screening is seen in Figure 12, where 12 polymerization conditions are tested simultaneously in test tubes with initiator immobilized substrates immersed in each solution.

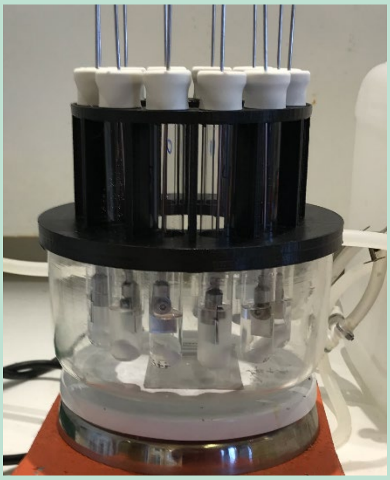

FIGURE 12. Photo of a Radi-LRP screening, where 12 different polymerization conditions are tested in parallel.

In general, the inactive Radi-LRP polymerization solution contained monomer, solvent (a mixture of water and MeOH, *i*PrOH, or DMSO), and catalyst/ligand. To control the processing condition, most screenings were conducted in inert atmosphere, where the solution was purged with argon gas before starting the polymerization. The polymerization solution was activated by the addition of the catalyst activator.

Table 5 shows the tested Radi-LRP components and the concentration range tested during the screenings, whereas Table 6 shows the process conditions tested.

TABLE 5. Concentration range of different components used in the screening of Radi-LRP of PMMA

Component	Concentration range	Role of component
MeOH	37-45 v/v%	Solvent
*i*PrOH	3.7-78 v/v%	Solvent
DMSO	24-50 v/v%	Solvent
H_2O	0.50-70 v/v%	Solvent
MMA	0.51-74 v/v%	Monomer
Ac1	YY-YY mg/mL	Catalyst activator
Ac2	YY-YY v/v%	Catalyst activator
CuO/L1 [a]	XX-XX mg/L	Catalyst/ligand
CuO/L2 [a]	XX-XX mg/L	Catalyst/ligand
CuO/L3 [a]	XX-XX mg/L	Catalyst/ligand

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[22] Nielsen, S. U., Kongsfelt, M. S. (2018). Compositions for Forming Polymer Brushes. WO2019196999.

[a] The concentrations are referring to the concentration of CuO. For the CuO/L3 complex, the concentration is deduced from UV-vis measurements and the correlation shown in Figure 15, and for CuO/L1 and CuO/L2 complexes similar measurements and correlation were used to estimate the catalyst concentration.

TABLE 6. Parameters and the range tested in the screening of Radi-LRP of PMMA

Parameter	Condition range
Temperature	20-60 °C
Time	10-180 min
Atmosphere	Inert (Ar-purged) or ambient

The results of each screening were assessed by measuring WCA and doing qualitative adhesion tests on a Plexiglas® plate (Section 5.2.4). Promising procedures were always tested in triplicate to ensure the reproducibility.

The best procedure and the procure currently used to grow PMMA brushes is presented in Table 7. As in Table 5 the concentration used of each component is proprietary information along with activator and ligand names, here hidden to protect RadiSurf's business. It is noted that the concentration of monomer is only 7 v/v% (0.7 M) compared to 32 v/v% (3 M) in the original ATPR based process (Table 1), an important factor in the health and environmental risk assessment (Section 7).

TABLE 7. Components involved in Radi-LRP of PMMA and processing conditions.

Component	Concentration	Role of component
*i*PrOH	-- v/v%	Solvent
H_2O	-- v/v%	Solvent
MMA	7 v/v%	Monomer
Ac1	-- mg/mL	Catalyst activator
CuO/L3 [a]	-- mg/L	Catalyst/ligand
Parameter	**Condition**	
Temperature	Room temperature, 20- 25 °C	
Time	1 h	
Atmosphere	Argon and ambient atmosphere	

Using the conditions outlined in Table 7, the polymer brush nanoprimer thickness was measured by ellipsometry after polymerization times from 15-60 min (Figure 13). The test was done on both XPhTMS- and XPTMS-functionalized stainless steel substrates. Already after 30 min, the polymer brush thickness has reached its maximum of 25-33 nm, and the polymerization has terminated as seen from similar thicknesses after 60 min of polymerization.

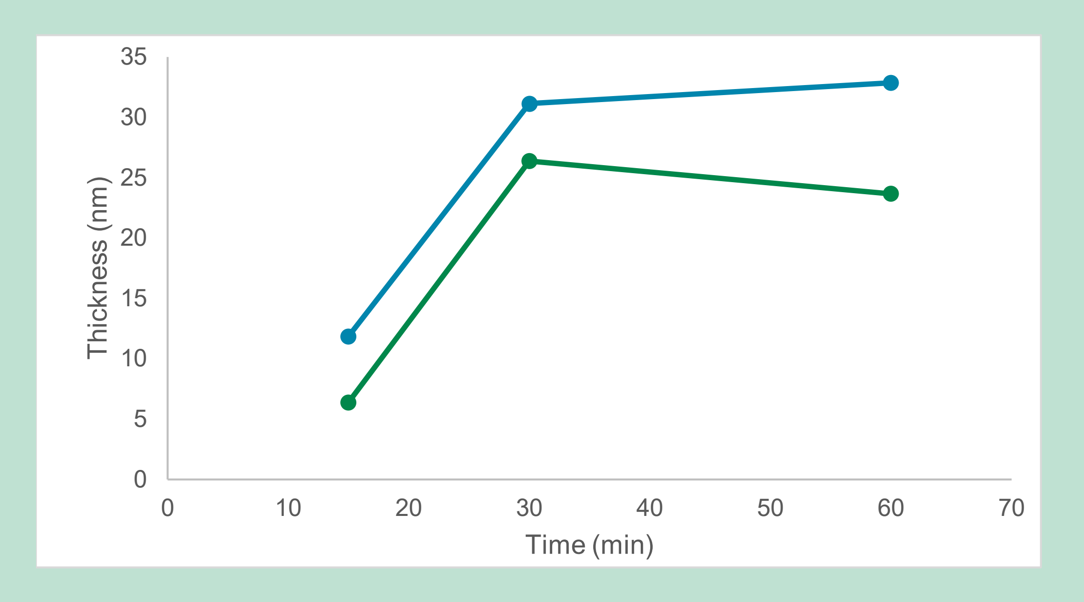


FIGURE 13. Thickness of polymer brush nanoprimer measured by ellipsometry as a function of polymerization time based on two different initiators. Green: XPhTMS initiator, Blue: XPTMS initiator.

The results presented in Figure 13 are based on polymerizations done under inert conditions. Interestingly, the same polymerization done under ambient atmosphere without any argon purging only resulted in a slight reduction in polymer film thickness (33 nm vs. 26 nm for XPTMS substrates polymerized for 60 min under argon and ambient atmosphere, respectively). Recent results have additionally shown the ratio between the concentration of catalyst/ligand and catalyst activator can be finetuned to diminish the degree of polymerization (hence obtain thicker polymer brush films) and also control the polymerization under ambient atmosphere.

6.2.3 HSPiP analysis to identify alternative solvent systems

In the project, the Hansen solubility parameters were used in order to predict alternative solvent systems for the polymerizations. The ‘Hansen-tool’ is one of the tools described on Kemi i Kredsløb’s webpage. The Hansen solubility parameters can describe most solvents and binders in terms of three parameters: The dispersion force D (sometimes called induced-dipole forces, London Forces, London Dispersion forces, or van der Waals forces), the dipolar intermolecular force P and the hydrogen bonding force H. The parameters are then used on the basis that “like dissolves like”. Mixing two solvents results in a mixed solvent with Hansen parameters in between the two solvents. Meaning that two solvents, when used separately, cannot dissolve a binder, but can dissolve the same binder when mixed in the right proportion.

As it would be prohibitively time-consuming to find the optimal combinations of solvents manually, this feature has been programmed in the HSPiP software making the process of determining optimal solvent mixtures considerably easier.

In this project, the methodology was used with two purposes:

- To identify alternatives to the water/isopropanol mixture used today
- Find a solvent system, with as high a water content as possible, that can readily dissolve methyl methacrylate

Using this approach, the solubility parameters of a water/isopropanol mixture were calculated. Based on these results the software was used to identify solvent systems with similar properties, that are based on water and a secondary solvent. The results suggested that FAME (fatty acid methyl ester) and n-Amyl Acetate are potential alternatives to isopropanol.

Further, a series of solvent systems were identified based on the solubility parameters of methyl methacrylate and with water as one of the solvents in the mixture. Several ‘conventional’ organic solvents such as hexane and toluene could be used together with water. However, their environmental and health profile is comparable to or worse than isopropanol. As an alternative also propylene carbonate and ethylene carbonate were identified that could potentially be used as alternative solvents for the polymerizations.

The output of a HSPiP analysis should always be critically evaluated. FAME is insoluble in water, and hence it is most likely that water, MMA and FAME are not miscible. Ethylene carbonate is a solid and therefore not relevant here. The most interesting candidate identified by the HSPiP analysis is propylene carbonate. Unfortunately, this solvent was not tested in the framework of this project. However, as a polar aprotic solvent it is a solvent of high interest to test, due to its low vapor pressure. This is particularly relevant for spray- and paint-on application of the Radi-LRP system, where evaporation of solvent is a major issue. The vapor pressure of propylene carbonate is 0.13 mmHg at 20 °C compared to 22, 17, and 29 mmHg for *i*PrOH, water, and MMA respectively.

6.3 Development of a ready-to-use chemical kit

An important aspect of the development of the Radi-LRP process described in the previous sections is to implement the procedure directly at our customers. RadiSurf aims at only having a polymer brush coating service for smaller customer’s with low production volumes, while the process should be directly implemented at the larger customer’s production line. By eliminating or substituting the use of problematic, hazardous chemicals in the nanoprimer process, it may be directly implemented in production lines without safety risks or strict worker safety requirements. The direct implementation of the nanoprimer process, is an important part of RadiSurf’s business model, where RadiSurf can sell the nanoprimer chemical kits and the license to use the process. We expect that an increasing number of consultancy services pilot projects will gradually translate to an increase in number of clients using our product and therefore sales of license package deals including ready-mixed chemical kits, license deals, service and operational support, leading a steady and sustainable growth of the company. Hence, ready-mixed nanoprimer kits based on the Radi-LRP process are crucial for RadiSurf. Initial test on such kits were tested in the framework of this project.

6.3.1 Preparation of catalyst for Radi-LRP

The catalyst for the newly developed Radi-LRP procedure to grow polymer brushes is based on Cu(0), similar to the SET-LRP process. However, in contrast to SET-LRP, where the catalyst is formed in situ during the polymerization, Radi-LRP utilizes a catalyst which can be formed in solution prior to the polymerization and can be stored and used on-demand. This is possible, because the catalyst is formed and stored in its domant, inactive, and stable state (CuO). Upon use in a polymerization, CuO is activated by removing oxygen and transforming the catalyst to its active state, Cu(0).

The catalyst was in this project prepared using two different methods, where the Cu-catalyst are formed from a solid Cu source in the presence of water and ligand (e.g. L1, L2, or L3). In method 1, a large variation in Cu concentration was seen from batch to batch, whereas method 2 to produce the Cu-catalyst solution was allowed easy and consistent production of larger volumes of catalyst solution.

The catalyst solution was always diluted to control the Cu concentration in the final polymerization solution.

6.3.2 Analysis and quantification of catalyst

It was of high importance to determine and control the Cu concentration of catalyst solution described in the previous section, both for the Radi-LRP screening program described in section

6.2.2 as well as for the production of catalyst solutions to be provided as a part of the chemical kit to make polymer brush surface coatings (section 6.3.3).
Using the L3 ligand, catalyst solutions with different Cu concentrations was produced using both method 1 and method 2. UV-vis absorption spectra were similar of catalyst solutions produced using both methods. An example of a spectrum from a catalyst solution produced via method 2 is displayed in Figure 14, where an absorption peak is centered at ~850 nm with a shoulder at ~700 nm. These peaks are both associated with the ligand-coordinated Cu catalyst. With an in-house UV-vis spectrophotometer at RadiSurf, it was of interest to use the absorption measured by UV-vis to determine the Cu concentration of catalyst solutions.

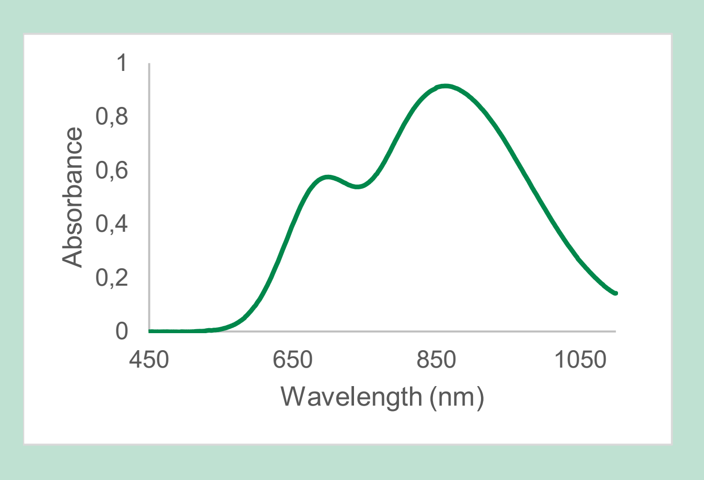


FIGURE 14. UV-vis absorption spectrum of catalyst solution produced using method 2 and the L3 ligand.

The Cu concentration of several catalyst solutions produced using both methods was measured using atomic absorption spectroscopy (AAS). As seen from Figure 15, a linear correlation is seen between the Cu concentration measured by AAS and the absorbance at 850 nm measured by UV-vis spectroscopy for both catalyst production methods. Using this correlation, the Cu concentration of L3 catalyst solutions, can always be obtained from the absorption at 850 nm measured using UV-vis spectroscopy. Besides, the convergence of the Cu concentration/absorbance correlation between the two catalyst production methods, is a good indication, that both catalyst production methods can be used indistinguishable. This was confirmed also, after obtaining similar polymer brush coatings using catalyst solution derived from the two methods.

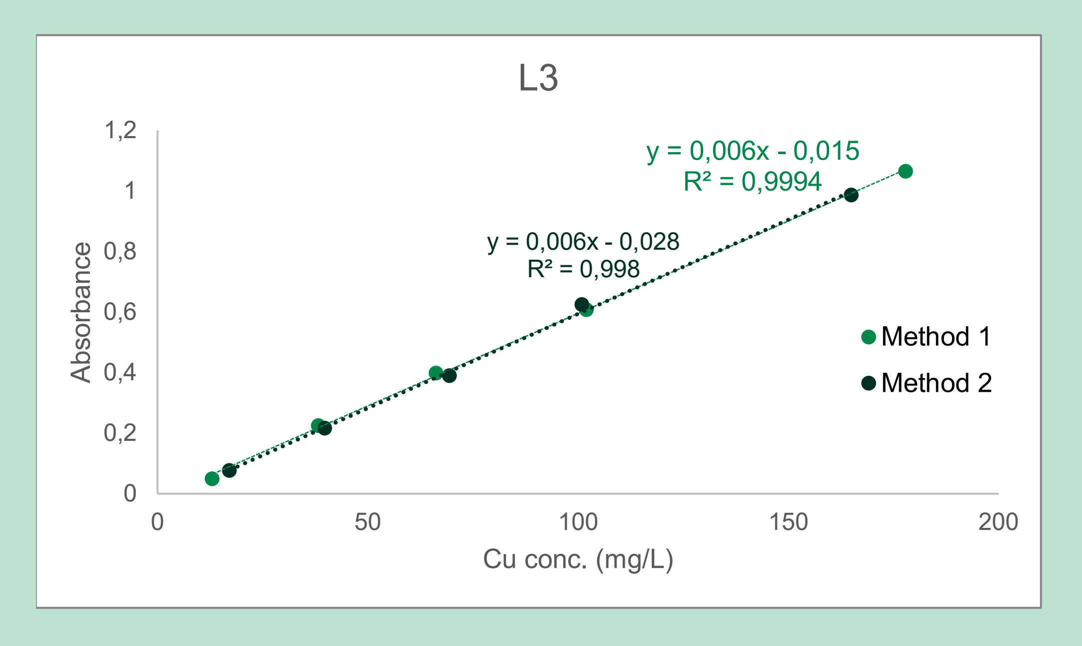


FIGURE 15. Correlation between the Cu concentration measured by AAS and the absorbance of the catalyst solution at ~850 nm measured by UV-vis spectroscopy. Catalyst solutions were produced using Method 1 (green) or Method 2 (teal).

Catalyst solutions produced using the two methods were also analyzed by dynamic light scattering (DLS), to get information of the size of Cu-ions and particles. Interestingly, the DLS method indicated that only Cu-ions and/or particles smaller than 1 nm was present in the catalyst solutions. No larger particles were detected, and it was therefore concluded that the catalyst mainly is in the form of Cu-ions coordinated to ligand.

6.3.3 Test of chemical kit

The process to make polymer brushes is in general an academic discipline only conducted in university research laboratories mainly due to the strict requirements to control of atmosphere. With the development of an oxygen-tolerant process to make polymer brush coatings, and the aim of a process to be implemented and handled by technicians at customer facilities, this project already at an early stage tested the Radi-LRP process outside RadiSurf's laboratories and in the hands of a chemist unfamiliar with polymer brush processes.

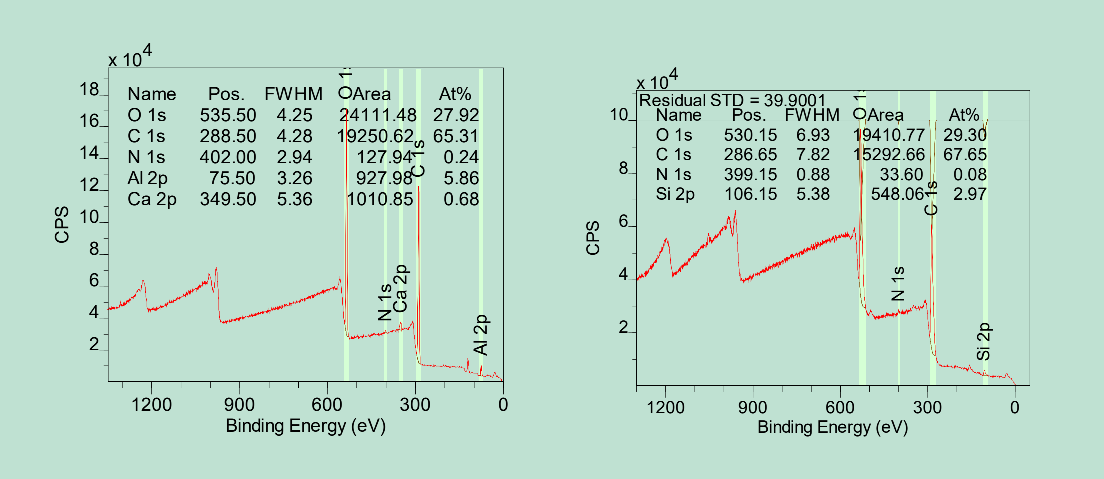
The screening program described in section 6.2.2 and the general development of the Radi-LRP procedure has in this project been focused on the nanoprimer for PMMA and PC. However, RadiSurf's most mature nanoprimer was already at the beginning of this project demonstrated in proof-of-concept to work in open atmosphere in water/alcohol solvents. Therefore, that nanoprimer process was the one being tested by a chemist at DTI.

RadiSurf prepared a technical datasheet (TDS, Appendix 1) and chemical solutions for the process. The chemical solutions provided were (1) **XPhTMS** in small vials for one-time use, denoted "RadiPrime™ 101 Activator" in TDS, (2) a combined solution of monomer, ethanol, water, and catalyst solution, denoted "RadiPrime™ 101 A" in TDS, and (3) solid Ac1, denoted "RadiPrime™ 101 B" in TDS. Besides, aluminum (1050 alloy) and glass substrates (1x1 cm) were provided to the polymer brush coating test.

Aluminum and glass substrates were treated according to the Processing section in Appendix 1.1 by DTI, and the substrates were subsequently analyzed by RadiSurf. WCA analysis gave WCA of 58 ° on both nanoprimed aluminum and glass, compared to 65 ° and 10 ° on the blank substrates, respectively. These values are within the range we see for this specific nanoprimer. A visual inspection of the aluminum sample (Figure 16) also indicates the formation of a polymer film on the surface, by the change in shade/tint of the sample.

FIGURE 16. Photo of (left) blank and (right) nanoprimed aluminum samples.

Besides, the nanoprimed aluminum and glass substrates were analyzed by XPS. Figure 17 shows survey spectra with the obtained atomic concentrations. The aluminum samples mainly contains carbon and oxygen on the surface with a C/O ratio of 65:28, very close to an expected ratio of 70:30. However, 6 Atom% aluminum is also seen, which indicates that the polymer brush film is very thin <10 nm, since XPS is very surface sensitive and only detects elements in the upper 10 nm of the surface. For the nanoprimed glass sample, the C/O ratio (68:29) is also close to the expected, and the Si content is low, indicating the successful nanopriming of the glass surface, though the polymer brush film in this case also is very thin (<10 nm).



Name	Pos.	FWHM	Area	At%
O 1s	535.50	4.25	24111.48	27.92
C 1s	288.50	4.28	19250.62	65.31
N 1s	402.00	2.94	127.94	0.24
Al 2p	75.50	3.26	927.98	5.86
Ca 2p	349.50	5.36	1010.85	0.68

Residual STD = 39.9001

Name	Pos.	FWHM	Area	At%
O 1s	530.15	6.93	19410.77	29.30
C 1s	286.65	7.82	15292.66	67.65
N 1s	399.15	0.88	33.60	0.08
Si 2p	106.15	5.38	548.06	2.97

FIGURE 17. XPS spectra of nanoprimed (left) aluminum and (right) glass substrates.

From the test of the nanoprimer chemical kit, it was observed, that the polymer brush formation was successful even out of the hands of chemist trained in doing polymer brush surface coatings. However, the polymer films seemed thinner than what is normally obtained in the laboratories at RadiSurf. Valuable feedback on the TDS from DTI both in terms of understanding, handling and safety was provided by DTI, used for generating the next version of a chemical kit for external use.

A risk assessment of the nanoprimer process was carried out by DHI. This is described in section 7.2.

6.4 Mechanical test of nanoprimers produced by Radi-LRP used for PMMA and PC adhesion

The performance in terms of adhesion to PMMA and PC of the nanoprimers applied using the newly developed Radi-LRP procedure was evaluated, by applying the nanoprimer on stainless steel and aluminum (1050 alloy) lap shear samples (50x10x2 mm). Two lap shear samples were assembled by heat pressing a sheet of PMMA or PC in-between the lap shear samples with 10x10 mm overlap as illustrated in Figure 18.

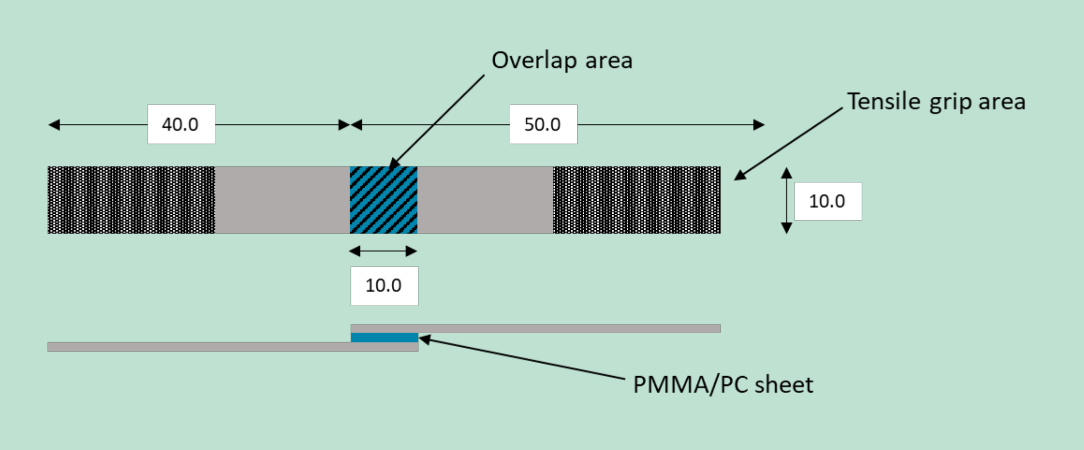


FIGURE 18. Illustration of lap shear specimen assembled with PMMA or PC sheet.

Heat pressing was done for 10 min with a 10 kg load at 170 °C using a 75 µm PMMA sheet or at 235 °C using a 125 µm PC sheet. After heat pressing the samples were cooled overnight before lap shear test.

The result of lap shear testing is shown in Figure 19, where it is seen that the lap shear adhesive strength is 35 ± 5 MPa for PMMA on stainless steel, 22 ± 3 MPa for PMMA on aluminum, 29 ± 3 MPa for PC on stainless steel.

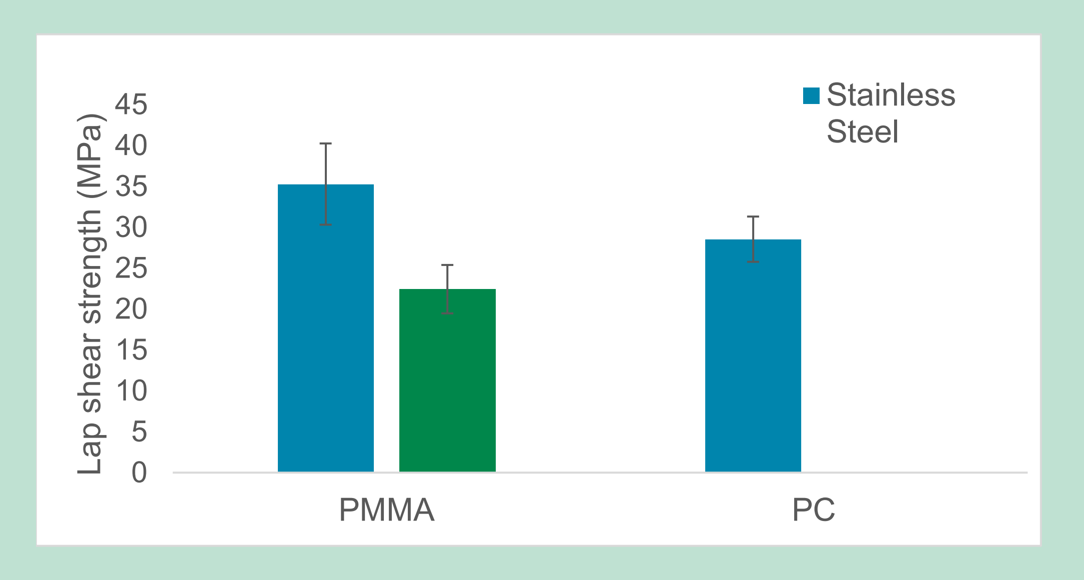


FIGURE 19. Lap shear adhesive strength for adhesion between nanoprimed stainless steel and PMMA and PC and between nanoprimed aluminum and PMMA.

Photos of the pulled lap shear samples are shown in Figure 20 in the case of stainless steel and and in Figure 21 in the case of aluminum. On the stainless steel samples, cohesive fracture is seen in all cases with PMMA and PC residues remaining on the samples. Cohesive fracture combined with the high lap shear strength proves the high performance of nanoprimers applied using the newly developed Radi-LRP procedure.

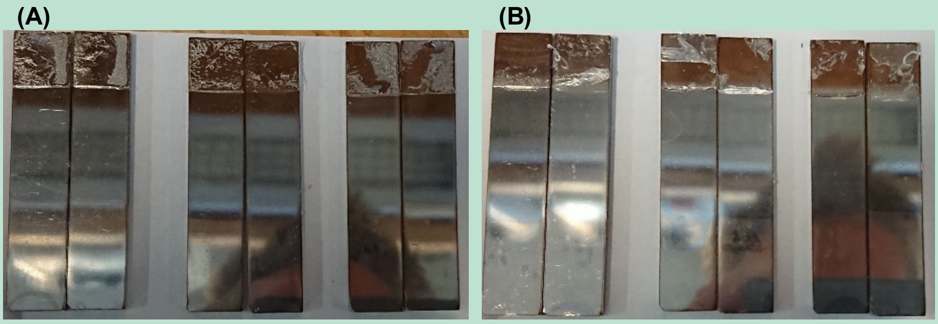


FIGURE 20. Photos of lap shear samples after lap shear testing. Stainless steel heat pressed with (A) PMMA sheet and (B) PC sheet.

In the case aluminum it is interestingly seen that the aluminum is bending during the lap shear test. It is important to note that the weakest point was not in the adhesion to the PMMA sheet. When applying load in single lab shear joints, the stress is not symmetric. Due to the high tensile strength of the PMMA, the aluminum act as a hinge, resulting plastic deformation and yielding of the aluminum (see Figure 21 and Figure 22). In the changed geometry, the epoxy will eventually fail due to the increased peel stress. Therefore, the reported lab shear strength is not only related to the adhesion strength. In future tests, we recommend to either change (reduce) the lab shear samples overlap or instead do butt end or pull-out test, to get better estimates of the adhesive strength.

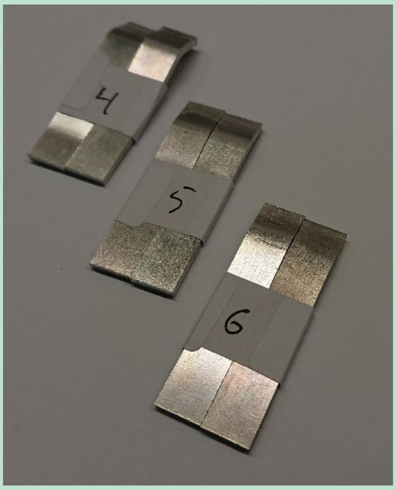


FIGURE 21. Photos of lap shear samples after lap shear testing. Aluminum heat pressed with PMMA. Note that the sample has bended during lap shear testing.

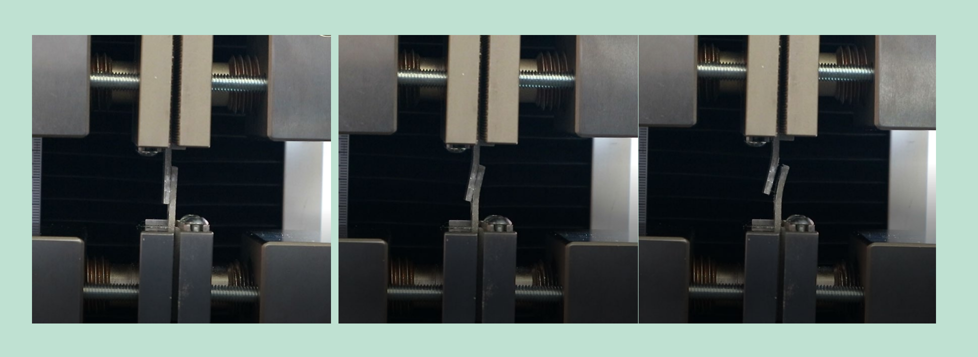


FIGURE 22. Photos captured during lap shear testing of aluminum/PMMA.

6.5 Customer Case: Replacement of epoxy-adhesive with thermoplastic sheet - Implementation and test at Brüel & Kjær

Brüel & Kjær Sound & Vibration Measurement A/S (B&K) currently uses a glass filled epoxy adhesive (Loctite Hysol from Henkel) to assemble two titanium sensor parts as illustrated in Figure 23. The epoxy is a glass-filled epoxy, where the glass beads of the adhesive is utilized to control the distance (~100 µm) between the two titanium parts, and at the same time ensure no electrical contact (short circuit). The sensor is a vibrational sensor, and the stiffness of the epoxy is therefore of high importance for the dynamical properties of the sensor. Due to health and worker safety concerns, B&K is interested in finding a replacement for the epoxy adhesive. Besides, when using the epoxy adhesive, B&K has experienced that they need to sandblast the parts immediately before gluing, which results in some logistic challenges.

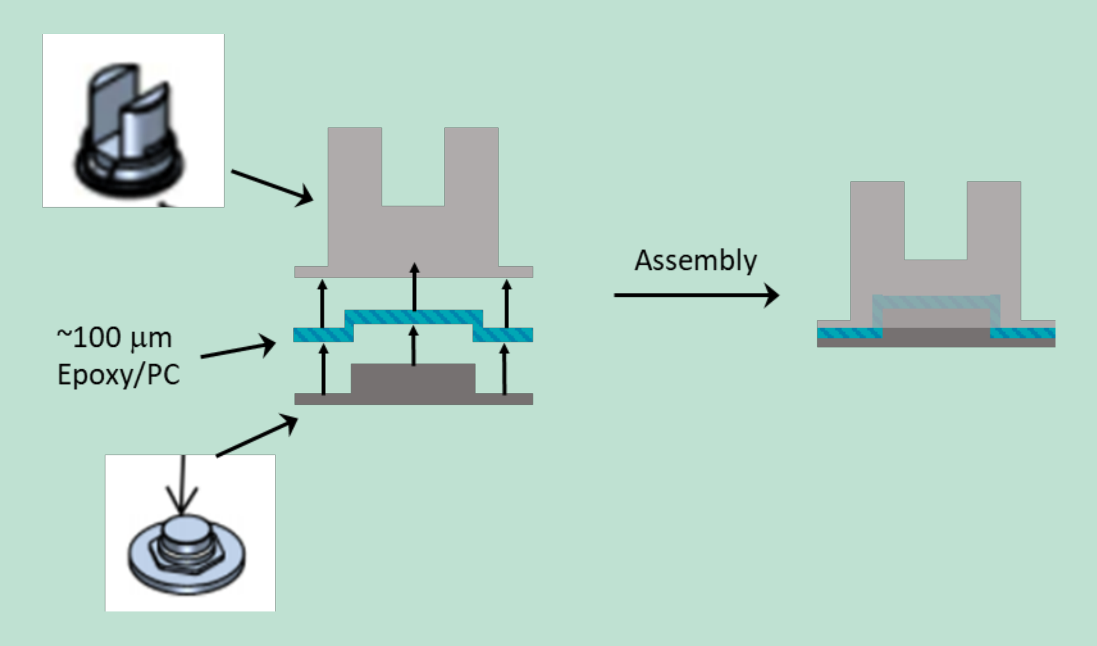


FIGURE 23. The vibrational sensor consists of two titanium parts normally assembled using a glass-filled epoxy adhesive.

6.5.1 Evaluation of PC sheet

In this project we proposed to replace the epoxy adhesive with a thin sheet of PC and utilize nanoprimers for PC to achieve adhesion between PC and titanium. PC was chosen due to its high thermal resistance combined with a high impact and tensile strength. PC sheets of 125 µm and 175 µm were initially tested herein.

B&K tested the dynamic properties of the sheets, by evaluating how a PC sheet in-between an accelerometer and a shaker table affected the frequency spectrum (Figure 24). The frequency response is an important quality control for the vibrational sensor, to ensure that the PC sheet is stiff enough and does not absorb vibrations.

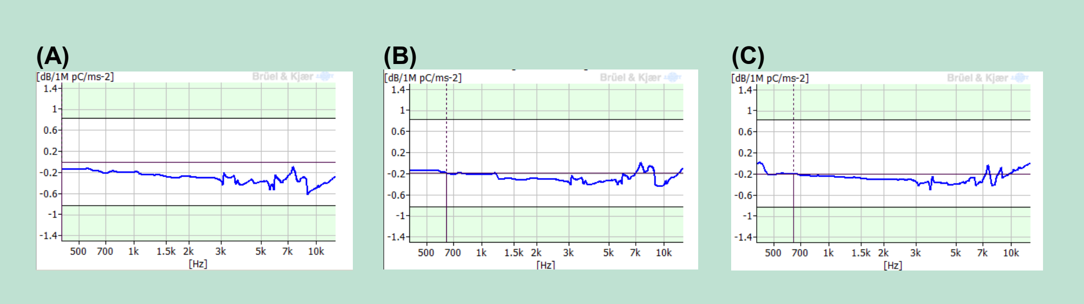


FIGURE 24. The frequency spectrum from an accelerometer on a shaker table with (A) nothing in-between (reference), (B) 125 µm PC sheet in-between, and 175 µm PC sheet in-between.

From Figure 24 it is seen that the frequency response is more or less unaffected by the 125 and 175 µm PC sheet. In particularly at higher frequencies (500 Hz to 12.8kHz – the frequency window shown in Figure 24), the curve would have deflected, if the PC sheet was too soft and had started to absorb the vibrations. Hence, it was concluded that the dynamical properties of the PC sheets fulfilled the requirements to potentially replace the epoxy adhesive.

6.5.2 Test of sensors assembled with PC sheet

The surface of the titanium parts illustrated in Figure 23 were nanoprimed using the procedure described in Table 7. The two sensor parts were assembled with a PC sheet in-between (Figure 25) using heat pressing conditions similar to the ones used in the lap shear tests discussed in Section 6.4. The heating elements were first heated to 235 °C. A piece of PC film was placed at the heated bottom titanium part (“hat”) and the top part was carefully placed on the film. The top part was softly pressed down on the film, to prevent the film from breaking. Afterwards the two parts were pressed with a load of 10 kg for 5 min. After cooling down, excess PC film was cut away with a knife.

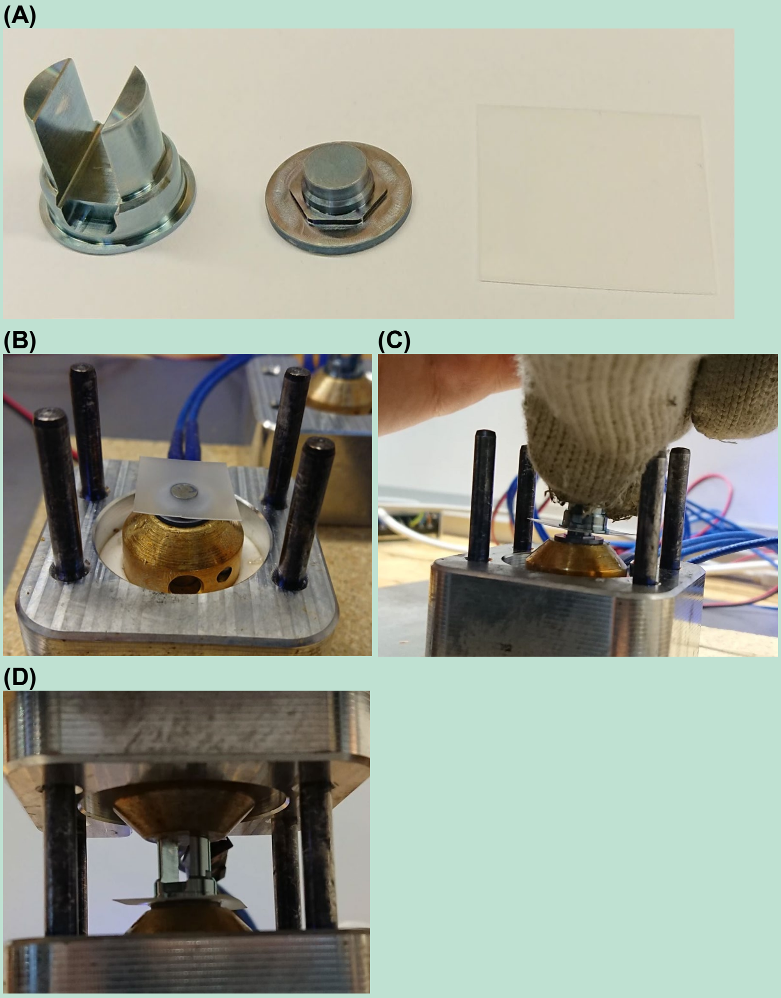


FIGURE 25. Assembly of two nanoprimed titanium sensor parts with PC sheet. (A) The two titanium parts and the PC sheet, (B) Heated bottom sensor part with PC sheet on top, (C) Top sensor part is carefully assembled with bottom part/PC sheet, and (D) 10 kg load of pressure applied.

Sensor parts assembled with 125 and 175 µm PC sheets were tested at B&K. The resonance frequency was 42.1 kHz and 43.1 kHz for parts assembled with 125 µm and 175 µm PC sheets, respectively, which is similar considering the uncertainty of the measurement. It is therefore concluded that the stiffness of the two PC sheets is similar. The adhesion was tested by twisting the parts apart. The parts assembled with 125 µm PC fell apart at 1 Nm, whereas the parts assembled with 175 µm PC was withstanding up to 2.2 Nm force, which is above the 2 Nm threshold value for B&K's application. Finally, the electrical isolation between the two sensor parts separated by the PC sheet was measured. Both in case of parts assembled with 125 µm and 175 µm PC sheets, no electrical isolation was seen between the two sensor parts.
Based on these results, it was concluded that the PC sheet was breaking during the heat pressing step. This also explains the poorer adhesion found for the thinner PC sheet, where we hypothesize that holes are easier formed in the thinner sheet during heat pressing, resulting in an overall smaller PC-titanium interphase. Next step of this project is to test different heat pressing conditions, but also include 100 µm glass beads in the PC sheet, to ensure a fixed distance between the sensor parts and at the same time avoid shorting the sensor parts. These tests are already work-in-progress with B&K.

7. Health and Environmental Impacts

7.1 Environmental and human health assessment of alternative ligands and polymerization activators

The chemical composition used in the polymer brush formation in general includes (1) monomer, (2) solvents, and (3) ligand/catalyst. Besides, the Radi-LRP version to create polymer brushes also contains an oxygen scavenger. In the process to develop a viable Radi-LRP process to create polymer brushes for PMMA and PC adhesion, it was from the beginning important to use benign solvents. The monomer can never be avoided, but its concentration can be minimized. For the ligand and the oxygen scavenger, RadiSurf made a list of ligands and oxygen scavengers either being used in current nanoprimer processes or candidates which could serve as substitutions. DHI made an environmental and human health assessment of all candidates listed by RadiSurf. The full assessment report is found in Appendix 2.1.

7.1.1 Environmental and human health assessment of ligands

Of the reviewed ligands (all nitrogen containing ligands, summarized in Table 8), none of the substances are immediately problematic for the environment and health. They have no classifications and the substances are not included in public available databases, the REACH candidate list,[23] the Substitute It Now List (SIN-List),[24] EUs list of endocrine disrupters,[25] and EU list of allergenic substances.[26] Furthermore, the substances are not considered to be PBT (Persistent, Bioaccumulative and Toxic).

Biodegradability data of L2 and L3 was partly based on quantitative structure–activity relationship (QSAR). Their chemical structures are similar to L1, and the calculations also showed consistency with biodegradability results obtained during laboratory studies of L1. Toxicity of L3 and L2 indicate a higher toxicity towards algae and a lower toxicity towards fish compared to L1. However, the toxicity to algae and daphnia generally lies within 1-100 mg/L for the three substances.

Data for L4, L5, and L6 are based on QSAR data. Only L5 is predicted to be biodegradable. L4 is expected to have the highest toxicity with EC50 for algae and daphnia at 7 mg/L and 29 mg/L respectively. None of these three substances are expected to bioaccumulate (Log Kow <3).

The main conclusions for the 6 reviewed ligands are summarized in Table 8, while data of the full analysis is provided in Table 10, Appendix 2. In general, L1, L2, and L3 are the three ligands of highest interest to RadiSurf. Based on the environmental and health assessment none of these are of immediately problematic, and therefore these were continuously being tested throughout this project.

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[23] https://echa.europa.eu/da/candidate-list-table

[24] https://chemsec.org/sin-list/

[25] https://ec.europa.eu/environment/chemicals/endocrine/strategy/substances_en.htm#priority_list

[26] https://ec.europa.eu/health/scientific_committees/opinions_layman/perfume-allergies/en/l-3/1-introduction.htm

TABLE 8. Main conclusions derived from environmental and human health assessment of ligands for the Radi-LRP process.

Substance	Comment
L1	Not immediately problematic for environment and health. No classification. Biodegradable. Overall low toxicity.
L2	Not immediately problematic for environment and health. No classification. Biodegradable (calculation). Overall low toxicity.
L3	Not immediately problematic for environment and health. No classification. Biodegradable (calculation). Overall low toxicity.
L4	Not immediately problematic for environment and health. No classification. Not biodegradable (calculation). Highest toxicity (EC50 for algae and daphnia 7 mg/L and 29 mg/L).
L5	Not immediately problematic for environment and health. No classification. Inherently biodegradable (calculation). Overall low toxicity.
L6	Not immediately problematic for environment and health. No classification. Not biodegradable (calculation). Overall low toxicity.

7.1.2 Environmental and human health assessment of oxygen scavengers

The reviewed oxygen scavengers (Ac1-7) are listed in Table 9. Of the reviewed substances, Ac1 and Ac3 are readily biodegradable, not expected to bioaccumulate, and they have no classifications.

Ac 2 is an inorganic substance and therefore not biodegradable. It has a high toxicity to algae, crustaceans, and fish with E(L)C50 values <1mg/L, and has a NOEC value for algae of 0.006 mg/L. Ac2 has no classification addressing human health and the environment, but the substance is presumed to have carcinogenic potential for humans based on animal experiments. It is recommended to substitute.

Ac7 has a harmonized classification addressing both the environment (H412) and human health (H341). It is not readily biodegradable and has a relatively high toxicity, and hence substitution is recommended.

Ac4 and Ac6 have low toxicity (E(LC)50 >> 100 mg/L), they have no classification addressing human health and the environment, and they are not included in any of the reviewed lists.

The main conclusions for the 7 reviewed oxygen scavengers are summarized in Table 9, while data of the full analysis is provided in Table 11, Appendix 2. In general, Ac1 and Ac2 were the two oxygen scavengers of highest interest to RadiSurf. Based on the environmental and health assessment, tests to substitute Ac2 with Ac1 were continuously being conducted throughout this project and Ac2 is no longer used in the standard operational procedures at RadiSurf. Besides, based the assessment we also never considered using Ac7 as a substitute, and it has also been removed from our list of potential oxygen scavengers moving forward.

TABLE 9. Main conclusions derived from environmental and human health assessment of oxygen scavengers for the Radi-LRP process.

Substance	Comment
Ac1	Not immediately problematic for environment and health. No classification. Biodegradable. Low toxicity.
Ac2	High toxicity. Presumed to be carcinogenic to humans. Substitution recommended.
Ac3	Not immediately problematic for environment and health. No classification. Biodegradable. Low toxicity.
Ac4	Not immediately problematic for environment and health. No classification. Overall low toxicity.
Ac5	Not immediately problematic for environment and health. No classification. Low toxicity.
Ac6	Not immediately problematic for environment and health. No classification. Low toxicity.
Ac7	High toxicity. Not biodegradable. Harmonized classification. Substitution recommended.

7.1.3 Handling of waste

Regarding the handling of waste generated from the nanoprimer process, there is no problem for the aquatic environment since all substances are disposed of as chemical waste. It is noted that, if waste were to be disposed via wastewater, a threshold would be given in the discharge permit to the emissions of the substances, which are not readily biodegradable and which have a toxicity between 1-100 mg/L.

Specific attention should be paid to Ac2 and Ac7, which must be disposed under controlled conditions. Besides, due to classifications, these would not be allowed to be released via waste water.

7.2 Health and environmental evaluation of nanoprimer process steps

The first generation of the Radi-LRP chemical kit was tested externally by DTI (section 6.3.3), while a health and environmental evaluation of the kit was done by DHI. The evaluation report is in found in Appendix 2.2. Similar to the test described in section 6.3.3, the analysis done herein is also based on the most mature Radi-LRP system. It is important to note that the main components of the chemical kit analyzed here and the component for Radi-LRP for PMMA/PC adhesion, are either identical or similar, and therefore most of the analysis can be directly translated to other Radi-LRP systems. The main difference will be the specific monomer and ligand used. This will specifically be addressed in the following.

7.2.1 Risk assessment of Radi-LRP chemical kit

A risk assessment of the process steps involved in the application of the Radi-LRP chemical kit was carried out by DHI. The two-step Radi-LRP process to create polymer brush surface coatings were split into activity steps, each describing the uses of chemical substances (Table 1, Appendix 2.2. The activities were characterized by assigning a process category (PROC), which is a part of a descriptor system developed by ECHA[27] to have a common description of uses across industries and countries. The description of uses is an important safety assessment for a new process, like RadiSurf's Radi-LRP chemical kit.

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[27] https://echa.europa.eu/documents/10162/13632/information_requirements_r12_en.pdf

Table 1 in Appendix 2.2 has fragmented the Radi-LRP process into specific activities and assigned a PROC (a complete descriptor list for PROCs are given in Table R.12-11 in ref 24) and risk management measures (RMM) to each activity.
Besides, chemical substances of each component of the chemical kit were evaluated in Table 2 in Appendix 2.2. An ABC-evaluation of the substances based on the hazard of the substances, divides the substances into 3 categories. A-substances are the most hazardous, while C-substances are the least. A-substances can in general cause very severe health effects (carcinogenic, mutagenic, or toxic to reproduction properties) or be environmental hazardous (no biodegradability, acute ecotoxicity, or bioaccumulation). The ABC-evaluation is in general used to assess if generate waste can be disposed via waste water. Also, the DNEL and PNEC levels are given. These are both related to the level at which no effects are expected, where DNEL (derived no effect level) is associated with human exposure limits and PNEC (predicted no effect concentration) is used for the environment/ecosystem.
Finally, the predicted exposure levels of the specific substances in the chemical kit, related to inhalation and dermal exposure, are given in Table 3 and 4, respectively, in Appendix 2.2. These values are derived based the PROCs given in Table 1, Appendix 2.2. From the predicted exposure levels, risk characterization ratios (RCRs) are calculated as exposure level/(DNEL: for human exposure, PNEC for environmental exposure).

The calculated RCR values based on inhalation measures given in Table 3, Appendix 2.2, find that glycidyl methacrylate (monomer) is the most critical substance. However, the RCR value is below 1 in all activities, and therefore the use is considered safe, if the work is done in agreement with the provided specifications (TDS). For the RCR values related to dermal exposure, glycidyl methacrylate is also the most critical substance. Here activity 6, 7, and 9 (steps involving mixing or pouring of chemical solutions) result in RCR values above 1, the therefore better measures to avoid dermal exposure should be taken. This could involve changing the specific handling or using better gloves. In the safety datasheet of GMA, it is recommended to use nature latex/chloroprene gloves of at least 0.6 mm of layer thickness for splash contact, which would be the case here. The break through time GMA in contact with this glove material is 49 min, which is beyond the working time here. Alternatively, butyl rubber gloves (0.3 mm) is also an option with break through time of 480 min. The risk assessment done here was based on a concentration of GMA of 15-20 v/v%. RadiSurf has since the evaluation optimized on the Radi-LRP procedure and has been able to decrease the concentration of GMA in the procedure to 4 v/v%, with an expectation that this could be reduced even further. Noteworthy, the RCR value related to dermal exposure for activity 9 is now close to 1 (1.07), while the value has decreased from 6.45 to 2.15 for activity 6 and 7. Hence, by using the new procedure and also using more protective gloves, the risk of handling the Radi-LRP can be eliminated. This is important information in regard to RadiSurf's preparation of material and safety data sheets.
It is also worth to note that the monomer used to create polymer brushes for PMMA and PC adhesion, does not have toxic and health hazards pictograms like glycidyl methacrylate evaluated here. A full health hazard and risk assessment should be done for this chemical also, but it is expected that RCR values in all cases will be below 1.

Finally, because the process involves A-chemicals, all chemicals should be collected and handled as chemical waste.

7.3 Measures taken by RadiSurf based on risk assessment

Based on the environmental and human health assessment of alternative ligands and polymerization activators done by DHI in this project, RadiSurf now only uses L1, L2, and L3 as ligands both in their standard operational procedures and in the continued development of new nanoprimer systems. For the oxygen scavenger, Ac2 has been completely eliminated in all processes and only Ac1 is used. Besides, the assessment has shed light on viable oxygen scavengers and ligands in considering the importance of the environment and the human health and also identified candidates which should not even be considered for RadiSurf's processes.

The health and environmental evaluation of the process steps involved in the nanoprimer application, has for RadiSurf identified critical steps in the process, regarding which process steps pose the largest risk to the worker and which chemicals are of highest concern in the same process. It was known from the beginning that the component of highest concern was the monomer. From the process evaluated by DHI in Section 7.2, RadiSurf has already halved the concentration of monomer from 13.6 v/v% to currently 4 v/v%, and we are convinced that it can be reduced more with further optimization. The lower concentration of monomer already decreased the RCR value for dermal exposure to 2.15. This combined with the use of latex/chloroprene or butyl rubber gloves will result in safe handling of the Radi-LRP solution. For the nanoprimer for PMMA and PC, the monomer concentration has been reduced from 32 v/v% to 7 v/v% during the development in this project, and we are also working towards reducing this concentration further. Besides, the monomer used for the nanoprimer for PMMA and PC does not have toxic and health hazards pictograms and hence is safer to work with.

8. Future Perspectives

8.1 Conclusions and commercial potential of the project outcomes

For any chemical technology to be broadly implemented into industry today, not only the commercial and feature benefits, but also the societal and environmental impact needs to be clearly beneficial. For RadiSurf as a startup company, to present and suggest a new technology for broad industrial implementation, it is detrimental to be able to verify and prove a strong commitment to supplying not only a new technology, but also a technology that follows the highest standards of health and safety and presents a minimal environmental risks. This is a clear priority and requirement from our customers.

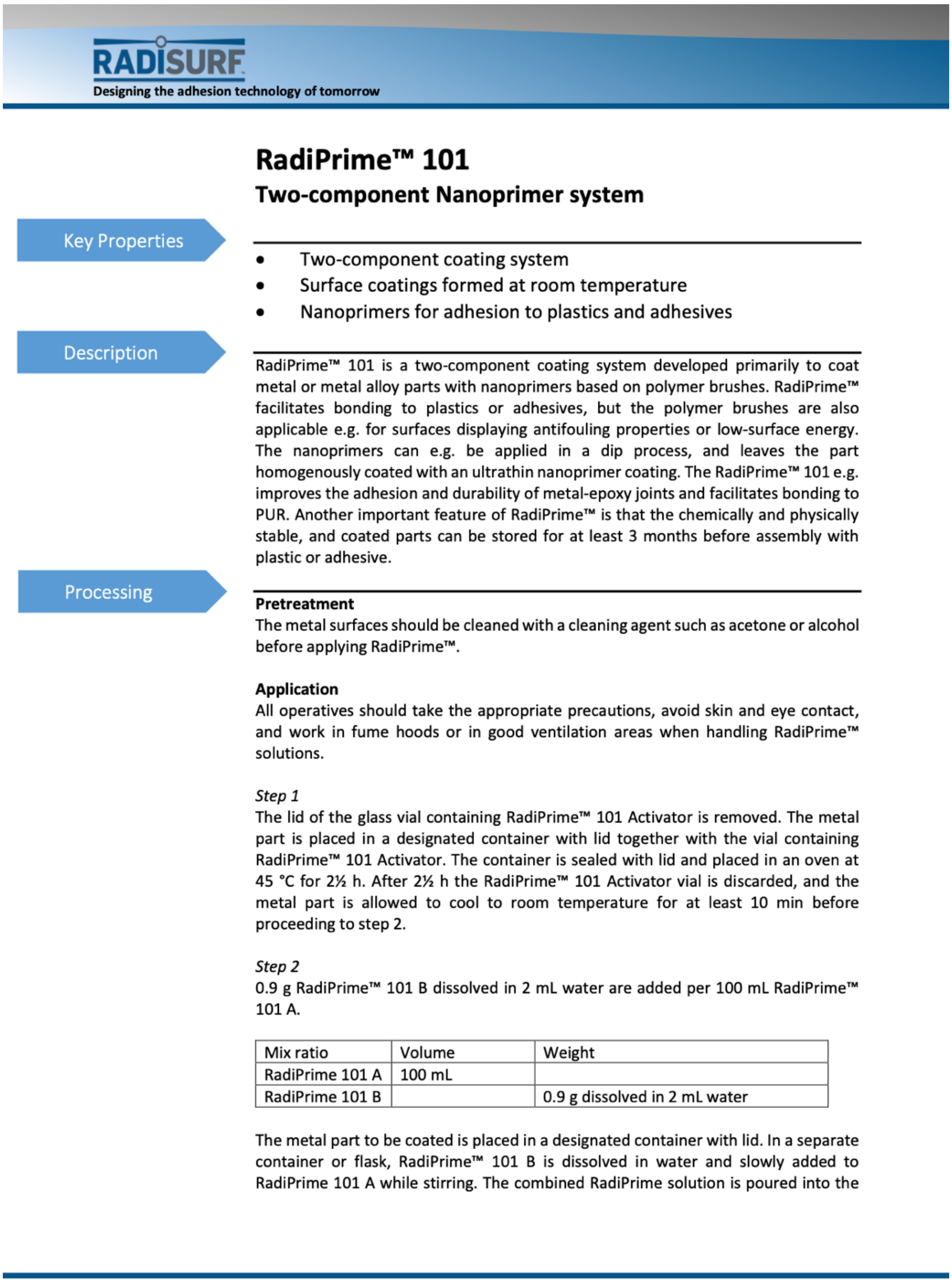
As a spin-off company from Aarhus University, RadiSurf's nanoprimer technology was originally developed towards a scientific standard for its features and unique chemistry. In this project we have shown how these high product standards are preserved while transforming the chemical processes into processes with high environmental and health and safety standards. We have shown how a strong focus on replacing hazardous chemicals is applicable not only to traditional products, but also in completely new unique developments at the highest scientific level.

These new developments will be paramount for the future of RadiSurf as a company. With these results, RadiSurf's alternative adhesion technology is now set for the last stage towards high volume implementation and will be able to approach some of the largest industries in the worlds, such as the automotive industry. We will be able to supply and deliver our chemicals directly to customers across the world following the highest chemical safety standards. RadiSurf already has test customers in 17 countries across multiples industries. Hence, the potential for exports of this technology is very large.

We expect to grow the company with high volume sales across Europe already in 2021, creating more than 20 new jobs with basis in Denmark in the coming 5 years. RadiSurf will continue its commitment to decreasing the environmental impact of advanced material's industries across the world using advanced surface chemistry.

Appendix 1. Documents for test of chemical kit

Appendix 1.1 Technical datasheet for test of chemical kit



RADISURF
Designing the adhesion technology of tomorrow

RadiPrime™ 101

Two-component Nanoprimer system

Key Properties

- Two-component coating system
- Surface coatings formed at room temperature
- Nanoprimers for adhesion to plastics and adhesives

Description

RadiPrime™ 101 is a two-component coating system developed primarily to coat metal or metal alloy parts with nanoprimers based on polymer brushes. RadiPrime™ facilitates bonding to plastics or adhesives, but the polymer brushes are also applicable e.g. for surfaces displaying antifouling properties or low-surface energy. The nanoprimers can e.g. be applied in a dip process, and leaves the part homogenously coated with an ultrathin nanoprimer coating. The RadiPrime™ 101 e.g. improves the adhesion and durability of metal-epoxy joints and facilitates bonding to PUR. Another important feature of RadiPrime™ is that the chemically and physically stable, and coated parts can be stored for at least 3 months before assembly with plastic or adhesive.

Processing

Pretreatment
The metal surfaces should be cleaned with a cleaning agent such as acetone or alcohol before applying RadiPrime™.

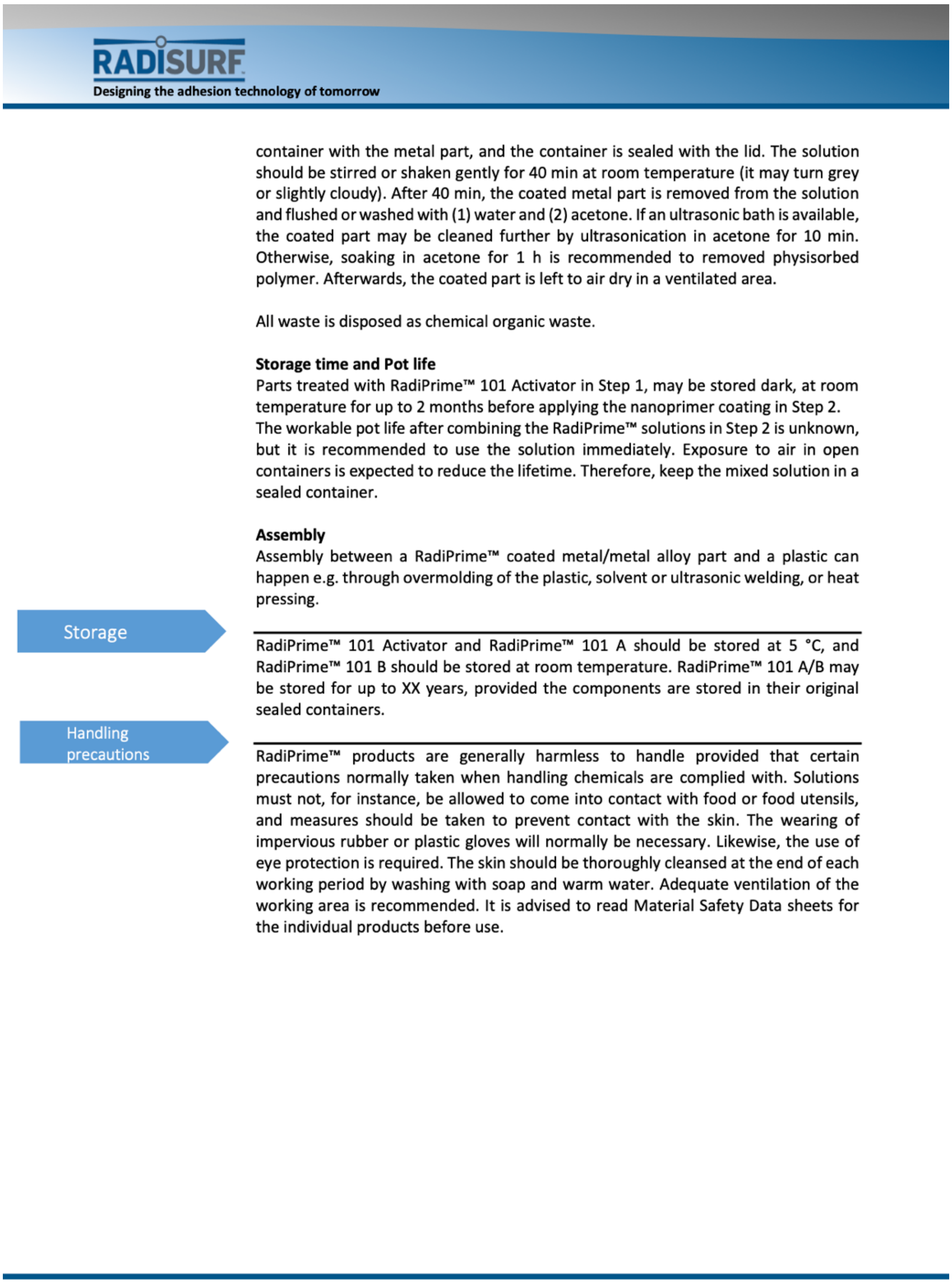
Application
All operatives should take the appropriate precautions, avoid skin and eye contact, and work in fume hoods or in good ventilation areas when handling RadiPrime™ solutions.

Step 1
The lid of the glass vial containing RadiPrime™ 101 Activator is removed. The metal part is placed in a designated container with lid together with the vial containing RadiPrime™ 101 Activator. The container is sealed with lid and placed in an oven at 45 °C for 2½ h. After 2½ h the RadiPrime™ 101 Activator vial is discarded, and the metal part is allowed to cool to room temperature for at least 10 min before proceeding to step 2.

Step 2
0.9 g RadiPrime™ 101 B dissolved in 2 mL water are added per 100 mL RadiPrime™ 101 A.

Mix ratio	Volume	Weight
RadiPrime 101 A	100 mL	
RadiPrime 101 B		0.9 g dissolved in 2 mL water

The metal part to be coated is placed in a designated container with lid. In a separate container or flask, RadiPrime™ 101 B is dissolved in water and slowly added to RadiPrime 101 A while stirring. The combined RadiPrime solution is poured into the



container with the metal part, and the container is sealed with the lid. The solution should be stirred or shaken gently for 40 min at room temperature (it may turn grey or slightly cloudy). After 40 min, the coated metal part is removed from the solution and flushed or washed with (1) water and (2) acetone. If an ultrasonic bath is available, the coated part may be cleaned further by ultrasonication in acetone for 10 min. Otherwise, soaking in acetone for 1 h is recommended to removed physisorbed polymer. Afterwards, the coated part is left to air dry in a ventilated area.

All waste is disposed as chemical organic waste.

Storage time and Pot life

Parts treated with RadiPrime™ 101 Activator in Step 1, may be stored dark, at room temperature for up to 2 months before applying the nanoprimer coating in Step 2.
The workable pot life after combining the RadiPrime™ solutions in Step 2 is unknown, but it is recommended to use the solution immediately. Exposure to air in open containers is expected to reduce the lifetime. Therefore, keep the mixed solution in a sealed container.

Assembly

Assembly between a RadiPrime™ coated metal/metal alloy part and a plastic can happen e.g. through overmolding of the plastic, solvent or ultrasonic welding, or heat pressing.

Storage

RadiPrime™ 101 Activator and RadiPrime™ 101 A should be stored at 5 °C, and RadiPrime™ 101 B should be stored at room temperature. RadiPrime™ 101 A/B may be stored for up to XX years, provided the components are stored in their original sealed containers.

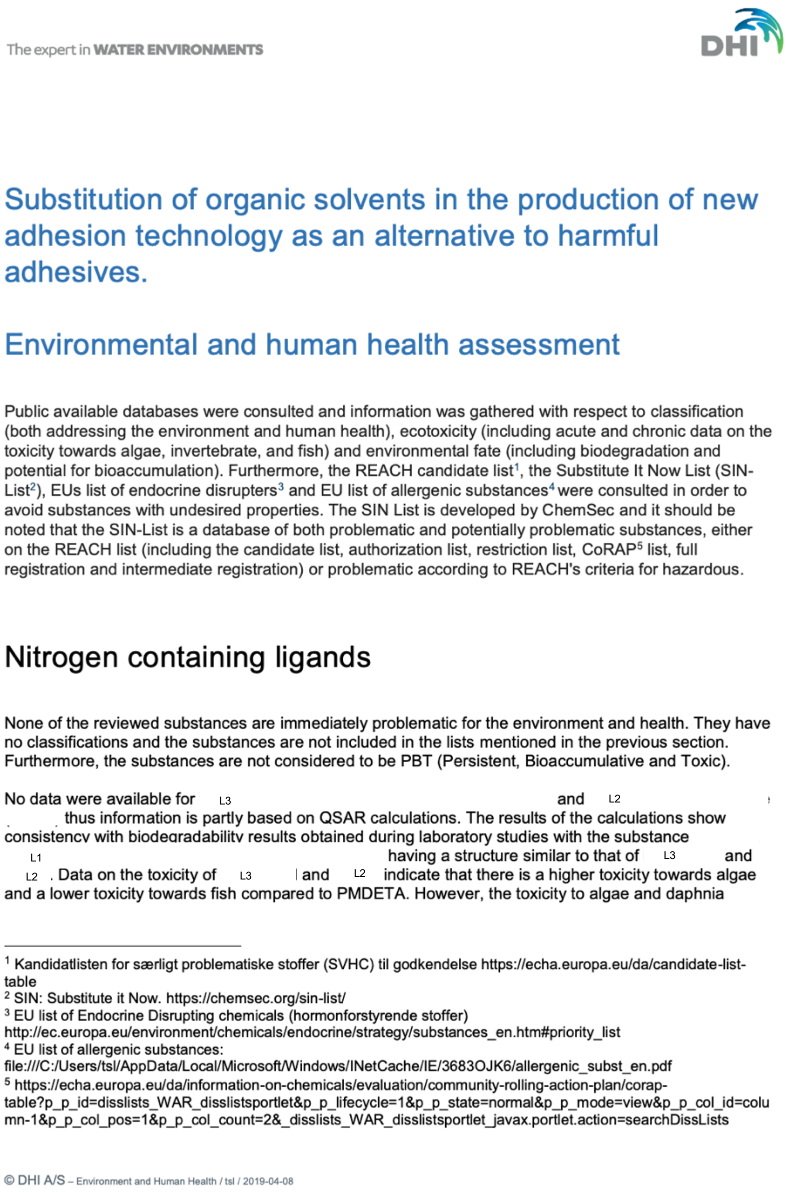
Handling precautions

RadiPrime™ products are generally harmless to handle provided that certain precautions normally taken when handling chemicals are complied with. Solutions must not, for instance, be allowed to come into contact with food or food utensils, and measures should be taken to prevent contact with the skin. The wearing of impervious rubber or plastic gloves will normally be necessary. Likewise, the use of eye protection is required. The skin should be thoroughly cleansed at the end of each working period by washing with soap and warm water. Adequate ventilation of the working area is recommended. It is advised to read Material Safety Data sheets for the individual products before use.

Appendix 2. Health and environmental evaluation by DHI

Note that names of substances are proprietary information and have been left out of this report.

Appendix 2.1 Environmental and human health assessment of alternative substances



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Substitution of organic solvents in the production of new adhesion technology as an alternative to harmful adhesives.

Environmental and human health assessment

Public available databases were consulted and information was gathered with respect to classification (both addressing the environment and human health), ecotoxicity (including acute and chronic data on the toxicity towards algae, invertebrate, and fish) and environmental fate (including biodegradation and potential for bioaccumulation). Furthermore, the REACH candidate list[1], the Substitute It Now List (SIN-List[2]), EUs list of endocrine disrupters[3] and EU list of allergenic substances[4] were consulted in order to avoid substances with undesired properties. The SIN List is developed by ChemSec and it should be noted that the SIN-List is a database of both problematic and potentially problematic substances, either on the REACH list (including the candidate list, authorization list, restriction list, CoRAP[5] list, full registration and intermediate registration) or problematic according to REACH's criteria for hazardous.

Nitrogen containing ligands

None of the reviewed substances are immediately problematic for the environment and health. They have no classifications and the substances are not included in the lists mentioned in the previous section. Furthermore, the substances are not considered to be PBT (Persistent, Bioaccumulative and Toxic).

No data were available for L3 and L2 thus information is partly based on QSAR calculations. The results of the calculations show consistency with biodegradability results obtained during laboratory studies with the substance L1 having a structure similar to that of L3 and L2. Data on the toxicity of L3 and L2 indicate that there is a higher toxicity towards algae and a lower toxicity towards fish compared to PMDETA. However, the toxicity to algae and daphnia

---

[1] Kandidatlisten for særligt problematiske stoffer (SVHC) til godkendelse https://echa.europa.eu/da/candidate-list-table

[2] SIN: Substitute it Now. https://chemsec.org/sin-list/

[3] EU list of Endocrine Disrupting chemicals (hormonforstyrende stoffer) http://ec.europa.eu/environment/chemicals/endocrine/strategy/substances_en.htm#priority_list

[4] EU list of allergenic substances: file:///C:/Users/tsl/AppData/Local/Microsoft/Windows/INetCache/IE/3683OJK6/allergenic_subst_en.pdf

[5] https://echa.europa.eu/da/information-on-chemicals/evaluation/community-rolling-action-plan/corap-table?p_p_id=disslists_WAR_disslistsportlet&p_p_lifecycle=1&p_p_state=normal&p_p_mode=view&p_p_col_id=column-1&p_p_col_pos=1&p_p_col_count=2&_disslists_WAR_disslistsportlet_javax.portlet.action=searchDissLists

generally lies within 1-100 mg/L for the three substances (except for L3, which shows a slightly lower toxicity (EC50 = 120 mg/L)).

Data for L4, L5 and L6 are solely QSAR data. These data predict that the substances are not ready biodegradable. However L5 is predicted to be inherently biodegradable. L4 is expected to have the highest toxicity where the EC50 for algae and daphnia is expected to be 7 mg/L and 29 mg/L respectively. None of these three substances are expected to bioaccumulate (Log Kow <3).

RadiSurf states that the substances are disposed of as chemical waste, so there is no problem for the aquatic environment. If the substances were to be discharges off via wastewater, a threshold would be given in the discharge permit to the emissions of the substances, which are not readily biodegradable and which have a toxicity between 1-100 mg/L.

Oxygen scavengers

Ac1 and Ac3 have a very comparable structure. [redacted]. The substances are ready biodegradable and are not expected to be bioaccumulative. They have no classification that addresses the environment and health.

Ac2 is an inorganic substance and therefore it is not relevant to look at biodegradation data for this substance. Ac2 will dissociate and hydrazine itself hydrolyses very readily in the aquatic environment. Ac2 has a high toxicity to algae, crustaceans and fish with E(L)C50 values <1mg/L. In addition, a NOEC value for algae of 0.006 mg/L has been reported. Ac2 is not included in any of the reviewed lists and it has no harmonized classification addressing human health and the environment. However a notified classification is available allocating the classification H350 (Carc. 1b) which is given to substances presumed to have carcinogenic potential for humans. The classification in this category is largely based on animal evidence, animal experiments for which there is sufficient evidence to demonstrate animal carcinogenicity. If possible, the substance should be substituted for another substance or the use and disposal must be done under controlled conditions.

Ac7 a harmonized classification that addresses both the environment (H412) and human health (H341). The substance is not readily biodegradable and has a relatively high toxicity, which explains the classification as H412. If possible, the substance should be substituted for another substance or the use and disposal must be done under controlled conditions.

Ac5 and Ac6 are both characterized by a low toxicity (E(LC)50 >> 100 mg/L). They have no classification addressing human health and the environment and are not included in any of the reviewed lists.

RadiSurf states that the substances are disposed of as chemical waste, so there is no problem for the aquatic environment. If the substances were to be discharges off via wastewater, a threshold would be given in the discharge permit to the emissions of the substances, which are not readily biodegradable and which have a toxicity between 1-100 mg/L. Ac7, which has the harmonized classification H341 and Ac2 wich has a notified classification of H350 would not be allowed to be released via waste water.

Table 10. Environmental and human health assessment of nitrogen containing ligands

Substance	L1	L3	L2	L4	L5	L6
CL (harmonised/notified) /1/	H302 (Acute Tox. 4)		H301 (Acute Tox. 3)	H302 (Acute Tox. 4)	no results	no results
	H311 (Acute Tox. 3)		H310 (Acute Tox. 2)			
	H314 (Skin Corr. 1B)	H314 (Skin Corr. 1B)	H314 (Skin Corr. 1B)			
			H318 (Eye Dam. 1)			
			H370 (STOT SE 1)			
Environmental fate /2/	Not ready biodegradable	No /10/	NO, expected to be inherently biodegradable /10/	NO /10/	inherently biodegradable /10/	NO /10/
	OECD 301E					
Ecotoxicity /2/	LC50 (fish): 157 mg/L	LC50 (fish): >1000 mg/L /10/		LC50 (fish): 392 mg/L /10/	LC50 (fish): 423 mg/L /10/	LC50 (fish) >1000 mg/L /10/
	EC50 (Daphnia) 54.9 mg/L	EC50 (Daphnia):120 mg/L /10/		EC50 (Daphnia): 29 mg/L /10/	EC50 (Daphnia): 218 mg/L /10/	EC50 (Daphnia) >1000 mg/L /10/
	ErC50 (algae): 78,3 mg/L	EC50 (algae): 20 mg/L /10/		EC50 (algae): 7 mg/L /10/	EC50 (algae): 79 mg/L /10/	EC50 (algae) >1000 mg/L /10/
	NOErC: 42 mg/L					
Log Kow /2/	<-2,1	.-0.59 /10/	.-2,9 /10/	0.53 /10/	1.50 /10, exp./	.-8.29 /10/
PBT concusion /3/	Potentially P, not B, (based on Log Kow, CL and acute tox. No further assessment necessary)	NO	NO	Potentially P, not B, (based on Log Kow, CL and acute tox. No further assessment necessary)	NO	Potentially P, not B, (based on Log Kow, C&L and acute tox. No further assessment necessary)
vPvB conclusion /3/	Potentially Pv	NO	NO		NO	
Endocrine Disrupting Chemical (EDC) /4, 5, 6/	not included	not included	not included	not included	not included	not included
	not included	not included	not included	not included	not included	not included
	not included	not included	not included	not included	not included	not included

Substitute It Now (SIN list) /7/	Not included	Not included	Not included	Not included	Not included	Not included
REACH Candidate list/SVHC /8/	Not included	Not included	Not included	Not included	Not included	Not included
EU list of allergenic substances /9/	Not included	Not included	Not included	Not included	Not included	Not included

ref /1/ C&L inventory (search by CAS no.)

ref /2/ ECHA reg. database (search by CAS no.)

/3/ Guidance on Information Requirements and Chemical Safety Assessment; Chapter R.11: PBT/vPvB assessment; Version 3.0 June 2017

/4/ Annex 13: List of 146 substances with endocrine disruption classifications prepared in the Expert meeting http://ec.europa.eu/environment/archives/docum/pdf/bkh_annex_13.pdf

/5 / G. Petersen, D. Rasmussen, K. Gustavson (2007) Study on enhancing the endocrine disrupter priority list with a focus on low production volume chemicals. http://ec.europa.eu/environment/chemicals/endocrine/pdf/final_report_2007.pdf

/6/ http://ec.europa.eu/environment/chemicals/endocrine/strategy/substances_en.htm#priority_list

/7/ SIN List: http://chemsec.org/business-tool/sin-list/

/8/ SVHC: https://echa.europa.eu/da/candidate-list-table

/9/ EU list of 26 allergenic substances classified in accordance with Directive 1272/2008

/10/ Epi-suite QSAR calculation (Epi-Web 4.1) calculation based on CAS number

/11/Aquire ecotox database

/12/ chemicalbook search by CAS number

Table 11. Environmental and human health assessment of catalyst activators

Substance	**Ac1**	**Ac2**	**Ac3**	**Ac4**	**Ac5**	**Ac6**	**Ac7**
CL (harmonized/notified) /1/	not classified	H301-H312-H314-H317-H330-H350-H410	not classified	no results	not classified	not classified	H302 (Acute Tox. 4)
							H312 (Acute Tox. 4)
							H332 (Acute Tox. 4)

							H341 (Muta. 2)
							H412 (Aquatic Chronic 3)
Environmental fate /2/	ready biodegradable /2/	dissociates and hydrolyses /dor/	ready biodegradable /10 (see Ac1)/	dissociates	dissociates	ready biodegradable	not ready biodegradable
Ecotoxicity /2/	LC50 (fish): 1020 mg/L	LC50 (fish): 0,61 mg/L	LC50 (fish) >17 mg/L /11/	)> 100 mg/L (fish, daphnids and algae (NOEC (algae) > 100 mg/L	LC50 (fish): 7100 mg/L	LC50 (fish): 440 mg/L	LC50 (fish) > 10 mg/L (<35 mg/L)
	EC50 (Daphnia): 74 mg/L /10/	EC50 (Daphnia):0.16mg/L			LC50 (Daphnia): 4100 mg/L	LC50 (Daphnia): 1535 mg/L	LC50 (Daphnia) > 10 mg/L (<35 mg/L)
	ErC50 (algae) >74 mg/L	ErC50 (algae): 0.017 mg/L				NOEC (Algae) 425 mg/L	ErC50 (algae) 4.3 mg/L
	NOErC≥74 mg/L	NOErC: 0.006 mg/L					NOErC (algae) 1.53 mg/L
Log Kow /2/	.-4,2	-0.16	.-1.85 /10, exp/	NA	NA	.-0.2	.-0.47
PBT concusion /3/	Not PBT	Potentially T	Not PBT		Not PBT	Not PBT	T, potentially P
vPvB conclusion /3/	Not vPvB	Not vPvB	Not vPvB		Not vPvB	Not vPvB	Not vPvB
Endocrine Disrupting Chemical (EDC) /4, 5, 6/	not included	not included	not included	not included	not included	not included	not included
	not included	not included	not included	not included	not included	not included	not included
	not included	not included	not included	not included	not included	not included	not included
Substitute It Now (SIN list) /7/	Not included	Not included	Not included	Not included	Not included	Not included	Not included
REACH Candidate	Not included	Not included	Not included	Not included	Not included	Not included	Not included

list/SVHC /8/							
EU list of allergenic substances /9/	Not included	Not included	Not included	Not included	Not included	Not included	Not included

ref /1/ C&L inventory (search by CAS no.)
ref /2/ ECHA reg. database (search by CAS no.)
/3/ Guidance on Information Requirements and Chemical Safety Assessment; Chapter R.11: PBT/vPvB assessment; Version 3.0 June 2017
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/5 / G. Petersen, D. Rasmussen, K. Gustavson (2007) Study on enhancing the endocrine disrupter priority list with a focus on low production volume chemicals. http://ec.europa.eu/environment/chemicals/endocrine/pdf/final_report_2007.pdf
/6/ http://ec.europa.eu/environment/chemicals/endocrine/strategy/substances_en.htm#priority_list
/7/ SIN List: http://chemsec.org/business-tool/sin-list/
/8/ SVHC: https://echa.europa.eu/da/candidate-list-table
/9/ EU list of 26 allergenic substances classified in accordance with Directive 1272/2008
/10/ Epi-suite QSAR calculation (Epi-Web 4.1) calculation based on CAS number
/11/Aquire ecotox database
/12/ chemicalbook search by CAS number

Appendix 2.2 Health and environmental evaluation of a RadiSurf product

Note that blank pages and page of content of the report are left out in this appendix. Also note that names of substances are proprietary information and have been left out of this report.

Health and environmental evaluation of a RadiSurf product

Miljøstyrelsen/RadiSurf/TI

Technical Note

August 2019

The expert in **WATER ENVIRONMENTS**

Health and environmental evaluation of a RadiSurf product

Prepared for	Miljøstyrelsen/RadiSurf/TI
Represented by	-

Project manager	Dorte Rasmussen
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Project number	11823884
Classification	**Confidential**.

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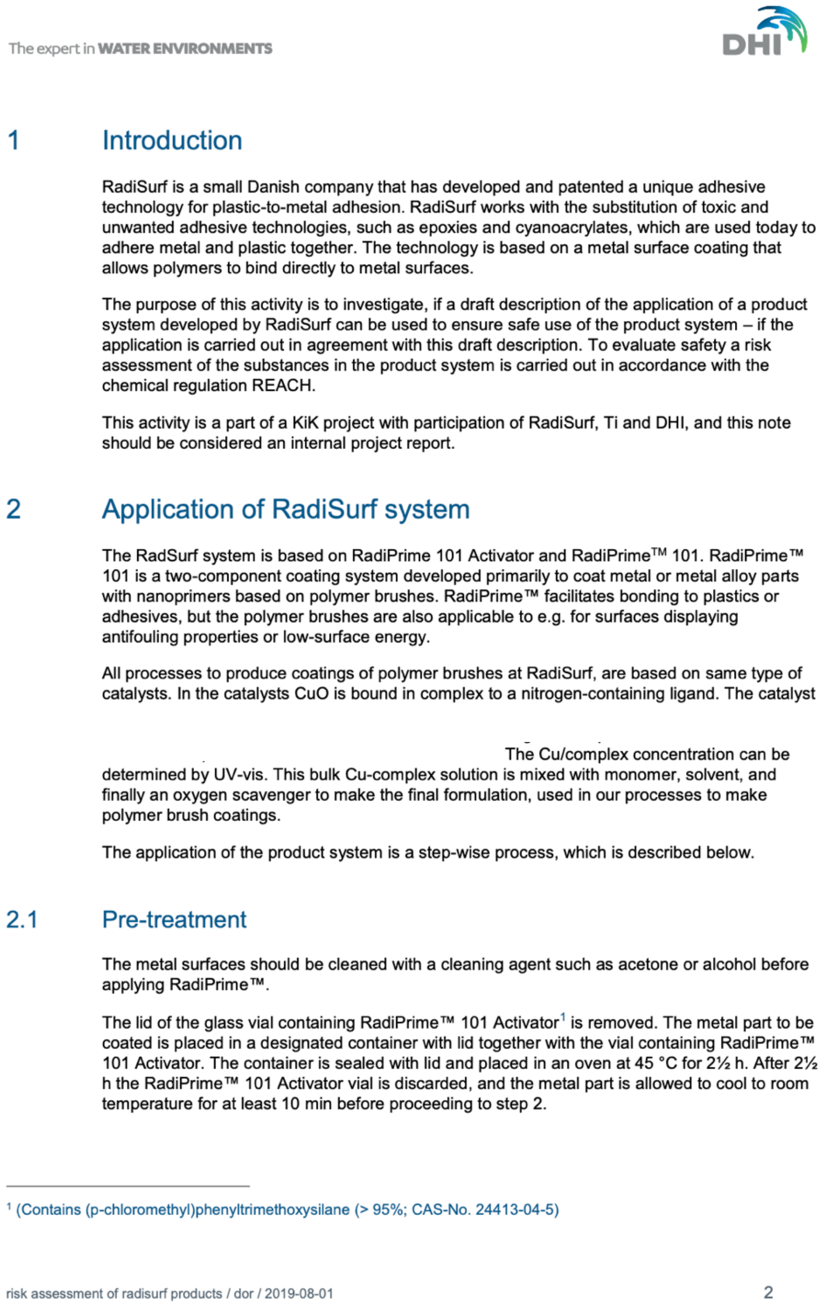

1 Introduction

RadiSurf is a small Danish company that has developed and patented a unique adhesive technology for plastic-to-metal adhesion. RadiSurf works with the substitution of toxic and unwanted adhesive technologies, such as epoxies and cyanoacrylates, which are used today to adhere metal and plastic together. The technology is based on a metal surface coating that allows polymers to bind directly to metal surfaces.

The purpose of this activity is to investigate, if a draft description of the application of a product system developed by RadiSurf can be used to ensure safe use of the product system – if the application is carried out in agreement with this draft description. To evaluate safety a risk assessment of the substances in the product system is carried out in accordance with the chemical regulation REACH.

This activity is a part of a KiK project with participation of RadiSurf, Ti and DHI, and this note should be considered an internal project report.

2 Application of RadiSurf system

The RadSurf system is based on RadiPrime 101 Activator and RadiPrime^{TM} 101. RadiPrime™ 101 is a two-component coating system developed primarily to coat metal or metal alloy parts with nanoprimers based on polymer brushes. RadiPrime™ facilitates bonding to plastics or adhesives, but the polymer brushes are also applicable to e.g. for surfaces displaying antifouling properties or low-surface energy.

All processes to produce coatings of polymer brushes at RadiSurf, are based on same type of catalysts. In the catalysts CuO is bound in complex to a nitrogen-containing ligand. The catalyst [redacted] The Cu/complex concentration can be determined by UV-vis. This bulk Cu-complex solution is mixed with monomer, solvent, and finally an oxygen scavenger to make the final formulation, used in our processes to make polymer brush coatings.

The application of the product system is a step-wise process, which is described below.

2.1 Pre-treatment

The metal surfaces should be cleaned with a cleaning agent such as acetone or alcohol before applying RadiPrime™.

The lid of the glass vial containing RadiPrime™ 101 Activator[1] is removed. The metal part to be coated is placed in a designated container with lid together with the vial containing RadiPrime™ 101 Activator. The container is sealed with lid and placed in an oven at 45 °C for 2½ h. After 2½ h the RadiPrime™ 101 Activator vial is discarded, and the metal part is allowed to cool to room temperature for at least 10 min before proceeding to step 2.

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[1] (Contains (p-chloromethyl)phenyltrimethoxysilane (> 95%; CAS-No. 24413-04-5)

2.2 Application of nanoprimer

0.9 g RadiPrime™ 101 B dissolved in 2 mL water are added per 100 mL RadiPrime™ 101 A. RadiPrime™ 101 B is dissolved in water in a separate container or flask and is hereafter slowly added to RadiPrime 101 A while stirring.

Mix ratio	Volume	Weight
RadiPrime 101 A	100 mL	
RadiPrime 101 B		0.9 g dissolved in 2 mL water

The metal part to be coated is placed in a designated container with lid. The combined RadiPrime solution is poured into the container with the metal part, and the container is sealed with the lid. The solution should be stirred or shaken gently for 40 min at room temperature (it may turn grey or slightly cloudy).

After 40 min, the coated metal part is removed from the solution and flushed or washed with (1) water and (2) acetone. If an ultrasonic bath is available, the coated part may be cleaned further by ultrasonication in acetone for 10 min. Otherwise, soaking in acetone for 1 h is recommended to remove physisorbed polymer. Afterwards, the coated part is left to air dry in a ventilated area.

Risk assessment

A risk assessment of the processes has been carried out. For this purpose, the activities have been characterised by assigning a PROC to its main activity. The PROCs are a part of the use descriptor system /1/ developed by ECHA and is used to enable a uniform description of uses across industry and countries. Furthermore, the PROCs can be used as input parameter into the ECETOC TRA model /2/, which also have been used in the present occupational risk assessment. It should be noted that the ECETOC TRA is developed for industrial processes – and it probably will result in a to high predicted exposure level for the smaller scale uses, e.g. on a laboratory scale.

A short overview of the activities, assigned PROCs, operational conditions (e.g. temperature) and risk management measures (RMM) for the activities is given in Table 1.

Information on product composition has been available and that the assessment is based on knowledge of the intrinsic properties of the individual substances. The applied values are given in Table 2.

The levels at which no effects are expected are also given in the table (for humans, the DNEL = Derived No Effect Level is used and for the environment PNEC = Predicted No Effect Concentration is used). The predicted exposure levels and risk characterisation ratios (RCR) = exposure level/(DNEL: for human exposure, PNEC for environmental exposure) are given in Table 3.

In addition, an ABC-evaluation of the substances is prepared (see /3/). This evaluation is commonly applied for assessing if used products could be discharged of to the sewer after use and is based on the hazard of the substance. The ABC score divides substances into 3 categories, where A-substances are the most hazardous and C-substances are the least hazardous substances. The score is assigned according to whether the substances can cause very severe health effects (carcinogenic, mutagenic or toxic to reproduction properties) and on its environmental properties (biodegradability at aerobic and anaerobic conditions, acute ecotoxicity and potential for bioaccumulation).

								ors with enhanced general ventilation	Gloves APF 10	-	Eye protection	

								al ventilation	No contact	-	no contact	The used mixture is discarded of as chemical waste

XPhTMS L1 Ac1
L1 L1

2h EC50 (mg/L): 11.9.

		XPhTMS			L1	L1	Ac1	L1
DNEL (dermal)	mg/kg bw/d	no data	343	0.01276	0.3		n.r.	137

been carried out.

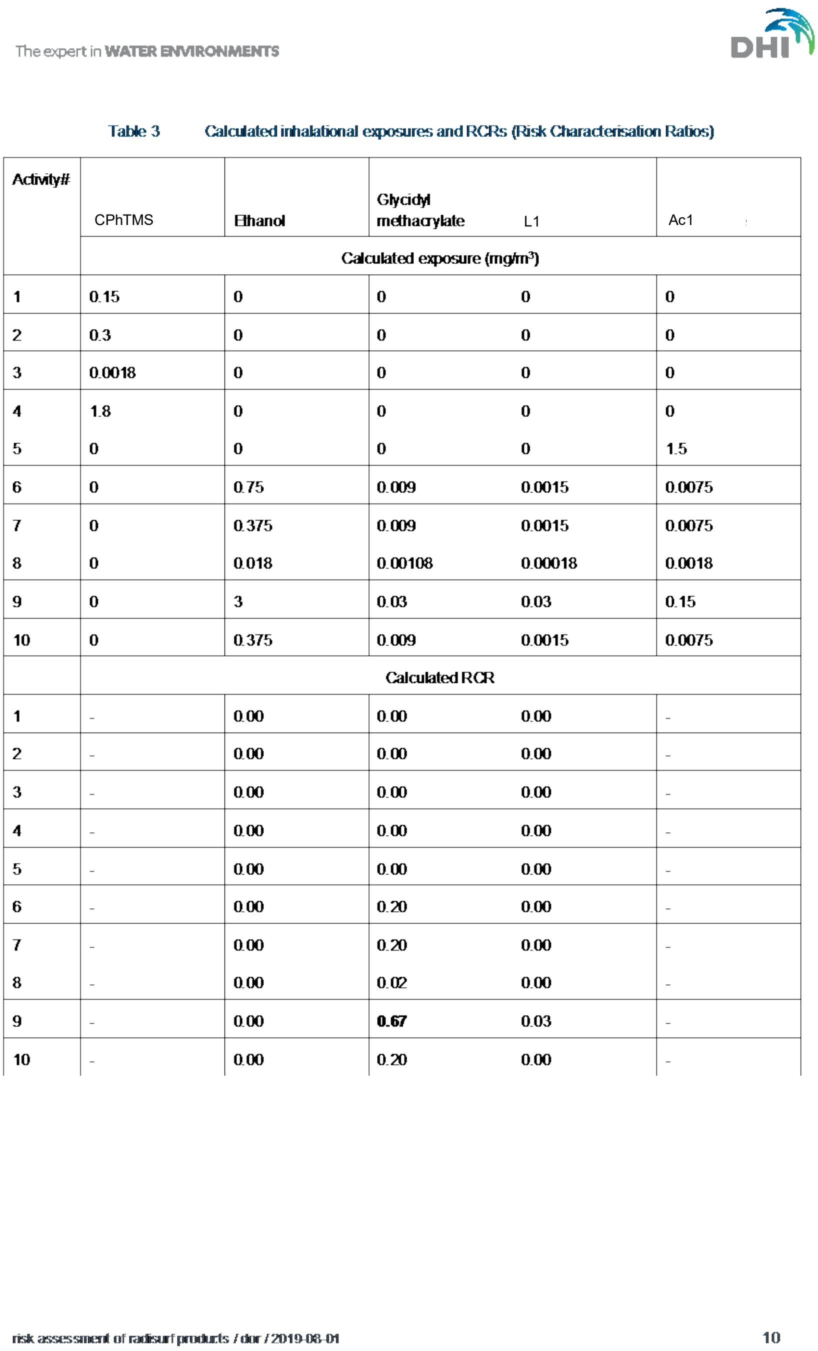

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Table 3 Calculated inhalational exposures and RCRs (Risk Characterisation Ratios)

Activity#	CPhTMS	Ethanol	Glycidyl methacrylate	L1	Ac1
	Calculated exposure (mg/m^3)				
1	0.15	0	0	0	0
2	0.3	0	0	0	0
3	0.0018	0	0	0	0
4	1.8	0	0	0	0
5	0	0	0	0	1.5
6	0	0.75	0.009	0.0015	0.0075
7	0	0.375	0.009	0.0015	0.0075
8	0	0.018	0.00108	0.00018	0.0018
9	0	3	0.03	0.03	0.15
10	0	0.375	0.009	0.0015	0.0075
	Calculated RCR				
1	-	0.00	0.00	0.00	-
2	-	0.00	0.00	0.00	-
3	-	0.00	0.00	0.00	-
4	-	0.00	0.00	0.00	-
5	-	0.00	0.00	0.00	-
6	-	0.00	0.20	0.00	-
7	-	0.00	0.20	0.00	-
8	-	0.00	0.02	0.00	-
9	-	0.00	**0.67**	0.03	-
10	-	0.00	0.20	0.00	-

risk assessment of radisurf products / dor / 2019-08-01 10

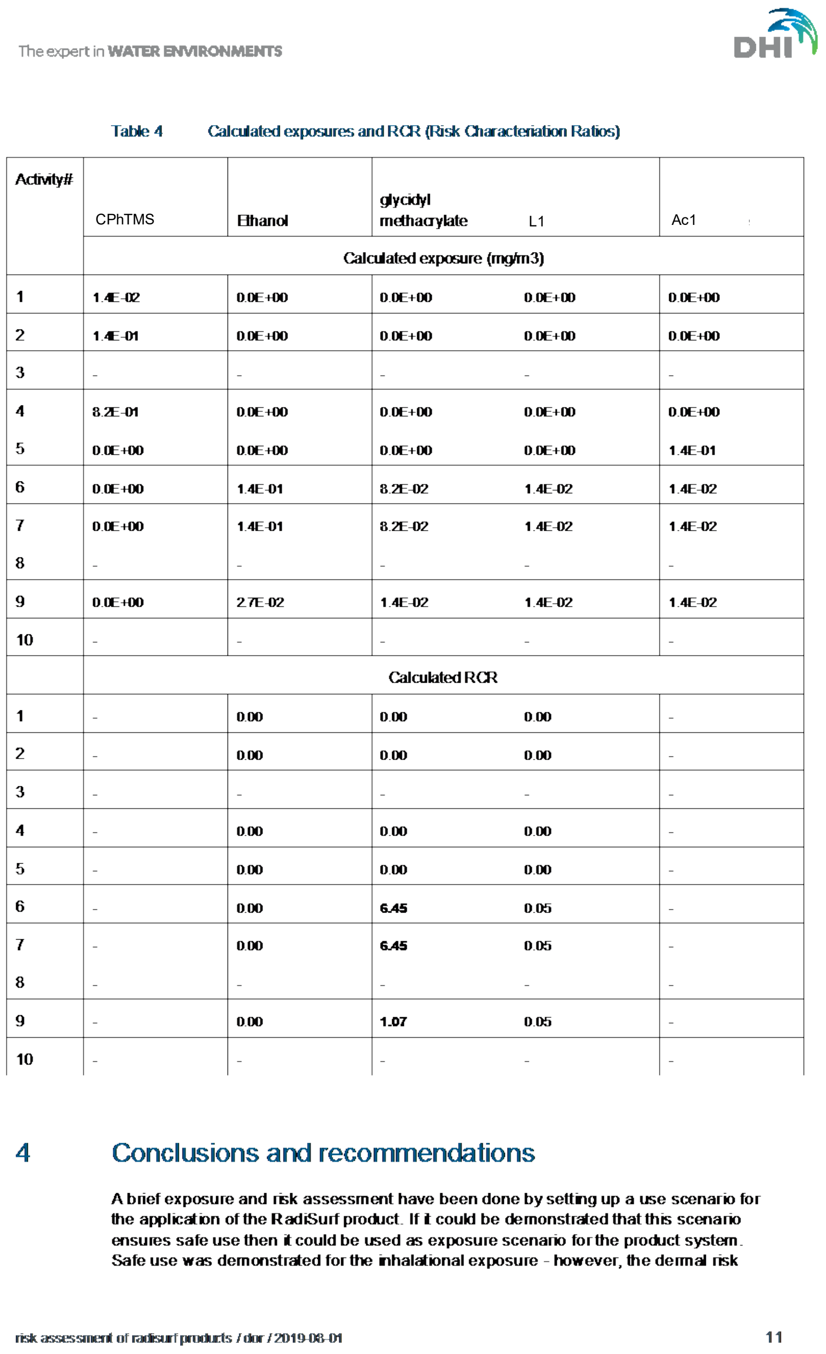

Table 4 Calculated exposures and RCR (Risk Characteriation Ratios)

Activity#	CPhTMS	Ethanol	glycidyl methacrylate	L1	Ac1
	Calculated exposure (mg/m3)				
1	1.4E-02	0.0E+00	0.0E+00	0.0E+00	0.0E+00
2	1.4E-01	0.0E+00	0.0E+00	0.0E+00	0.0E+00
3	-	-	-	-	-
4	8.2E-01	0.0E+00	0.0E+00	0.0E+00	0.0E+00
5	0.0E+00	0.0E+00	0.0E+00	0.0E+00	1.4E-01
6	0.0E+00	1.4E-01	8.2E-02	1.4E-02	1.4E-02
7	0.0E+00	1.4E-01	8.2E-02	1.4E-02	1.4E-02
8	-	-	-	-	-
9	0.0E+00	2.7E-02	1.4E-02	1.4E-02	1.4E-02
10	-	-	-	-	-
	Calculated RCR				
1	-	0.00	0.00	0.00	-
2	-	0.00	0.00	0.00	-
3	-	-	-	-	-
4	-	0.00	0.00	0.00	-
5	-	0.00	0.00	0.00	-
6	-	0.00	**6.45**	0.05	-
7	-	0.00	**6.45**	0.05	-
8	-	-	-	-	-
9	-	0.00	**1.07**	0.05	-
10	-	-	-	-	-

4 Conclusions and recommendations

A brief exposure and risk assessment have been done by setting up a use scenario for the application of the RadiSurf product. If it could be demonstrated that this scenario ensures safe use then it could be used as exposure scenario for the product system. Safe use was demonstrated for the inhalational exposure - however, the dermal risk

g. Vejledning fra
Miljøstyrelsen, Miljøstyrelsen Nr. 2 2006 (in Danish).

/4/ EPisuite

/5/ DTU QSAR

Substitution of Organic Solvents in Production of new Adhesion Technology as an Alternative to Hazardous Gluing Processes

Hazardous and problematic chemicals was eliminated from RadiSurf's polymer brush nanoprimer process. Today the 2-step process only uses water/alcohol solvents, a low concentration of a benign CuO catalyst, and it even has oxygen tolerance. The results show that the nanoprimer displays high adhesive strength resulting in cohesive fracture when binding PMMA and PC materials to metals.

A health and environmental assessment of process steps involved in the nanoprimer application was undertaken and the first test of a future commercial nanoprimer kit was done, both to support the steps towards selling RadiSurf's nanoprimer agents globally. Finally, results demonstrated that nanoprimers in combination with a thermoplastic sheet in many cases will be able to replace problematic adhesives such as epoxy in the assembly of metal-to-metal.

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