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Polymer Chemistry

Adhesion Peptide-Functionalized Biobased Microgels for Controlled Delivery of Pesticides

Abdulkadir Yayci[+], Tim Sassmann[+], Alexander Boes, Felix Jakob, Alexander Töpel, Anne Loreth, Carolin Rauch, Andrij Pich, and Ulrich Schwaneberg**

Abstract: Widespread use of plant protection agents in agriculture is a major cause of pollution. Apart from active ingredients, the environmental impact of auxiliary synthetic polymers should be minimized if they are highly persistent. An alternative to synthetic polymers is the use of natural polysaccharides, which are abundant and biodegradable. In this study, we explore pectin microgels functionalized with anchor peptides (P-MAPs) to be used as an alternative biobased pesticide delivery system. Using copper as the active ingredient, P-MAPs effectively prevented infection of grapevine plants with downy mildew under semi-field conditions on par with commercial copper pesticides. By using anchor peptides, the microgels tightly bind to the leaf surface, exhibiting excellent rain fastness and prolonged fungicidal activity. Finally, P-MAPs are shown to be easily degradable by enzymes found in nature, demonstrating their negligible long-term impact on the environment.

Introduction

Soil pollution with synthetic polymer particles (microplastics) and derived compounds is becoming a serious environmental burden. Sources of pollutants in soil are manifold and include packaging in landfills, wastewater sludge used as fertilizer and erosion from consumer products.[1] In all of these cases, soil pollution results from accidental discharge into the environment, sometimes caused by inappropriate protective measures. However, there are also practices that deliberately release synthetic polymers into the environment, particularly into soil. One of these deliberate sources of pollution is the use of fertilizers and pesticide formulations in agriculture. In the EU alone, approx. 10,000 t/year of synthetic polymers are willfully released into soils.[2]

Commercial pesticides commonly contain synthetic polymers as adjuvants, which improve the storage stability, water-solubility and long-term efficacy of the active ingredients. For instance, surfactants are used in pesticides to ensure even coverage of the plant surface, while adhesion-promoting agents improve the binding and rainfastness of pesticides to crops.[2a] Other uses of synthetic polymers include the stabilization of multi-component mixtures as well as controlled release formulations (CRFs) in which the polymer retains the bulk active ingredient, either by entrapment or interaction with active compound itself, conveying lasting protection against pests.[2b]

In some cases, adjuvants make up a major part of the bulk pesticide by weight, indicating their crucial role in pesticide efficacy.[3] While the examples given above demonstrate the benefits of using synthetic polymers in pesticides, these recalcitrant compounds can accumulate and may only be slowly degraded by the natural soil microbiota.[1,4] Long-term application of polymer-containing plant protection products can therefore lead to polymer accumulation in soil and groundwater, causing adverse effects on food chains as well as biodiversity and microbial activity.[5] Although data for the effects of long-term exposure to agricultural adjuvants is scarce, evidence of these substances causing harm to plants, soil microbiomes and vertebrates has emerged.[6]

An alternative to synthetic compounds is the use of biopolymers. Biopolymers are either natural polymers (such

[*] Prof. Dr. U. Schwaneberg
Institute of Biotechnology
RWTH Aachen University
Worringerweg 3, 52074 Aachen (Germany)
E-mail: u.schwaneberg@biotec.rwth-aachen.de

T. Sassmann,[+] Dr. A. Töpel, Prof. Dr. A. Pich
Institute of Technical and Macromolecular Chemistry
RWTH Aachen University
Worringerweg 2, 52074 Aachen (Germany)
E-mail: pich@dwi.rwth-aachen.de

Dr. A. Yayci,[+] T. Sassmann,[+] Dr. A. Boes, Dr. F. Jakob, Dr. A. Töpel, Prof. Dr. A. Pich, Prof. Dr. U. Schwaneberg
DWI - Leibniz-Institute for Interactive Materials
Forckenbeckstrasse 50, 52056 Aachen (Germany)

A. Loreth, C. Rauch
Julius-Kühn-Institute
Institute for Plant Protection in Fruit Crops and Viticulture
Geilweilerhof, 76833 Siebeldingen (Germany)

[+] These authors contributed equally to this work

as pectin, cellulose, lignin etc.) or biobased mimetics of synthetic polymers (made from natural resources). Natural polymers are environmentally benign and can be decomposed by organisms present in soil, predominantly bacteria, yeasts and fungi, e.g. by employing degrading enzymes such as pectinases.[7] In addition, natural polymers can be readily extracted from industrial waste streams, incentivizing upcycling. In recent years, biopolymers are increasingly investigated as an alternative to be used as adjuvants in agricultural pesticides due to their abundance and low impact on local ecosystems.[2b,8] Also, biopolymers can be used to manufacture microparticles containing a range of pesticides, as has been shown *inter alia* for lignin,[9] chitosan,[10] and pectin.[11] However, common methods to crosslink polysaccharides use toxic compounds such as periodates, which are environmentally harmful and require elaborate work-up procedures.[12]

In previous work, we showed successful delivery of micronutrients as well as biobased pesticides via polymer-based poly(*N*-vinylcaprolactam) (PVCL) microgels functionalized with anchor peptides.[13] While the microgels acted as a reservoir for the active ingredient, the anchor peptides enabled rainfast binding to the leaf surface, reducing run-off and increasing the availability of the compounds contained within the microgel.

Here, we report on a novel pesticide delivery system based on pectin microgel-anchor peptide conjugates (P-MAPs). P-MAPs are made from biobased building blocks and are designed to be biodegradable in nature. A novel and more sustainable reaction mechanism based on ADH/EDC chemistry to crosslink pectin in a one-step synthesis was developed, enabling downstream breakdown in the environment and substantially simplifying the production process while reducing its ecological footprint. In addition, we established a novel, peptide-based adhesion technology that enables rainfast adsorption of microgels to leaves. Adhesion peptides self-assemble on pectin microgels under mild conditions and do not require additional processing, further lowering the environmental impact of the system presented here.

Results and Discussion

Pectin is a heteropolysaccharide consisting of mostly galacturonic acid (GA) units with various degrees of side chain functionalization by other sugars. Pectin was used as the starting material since it is biodegradable, cheap and available in large quantities as an agricultural byproduct. In addition, this polysaccharide is easily modifiable as it contains abundant, accessible hydroxyl and carboxyl groups. We used carboxyl groups to crosslink pectin polymer chains, creating a covalently crosslinked polymer network. Adipic acid dihydrazide (ADH), used as the crosslinker here, was first incorporated into pectin solution. Subsequently, 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) was added, activating accessible carboxyls of pectin and immediately reacting with ADH, forming the hydrogel (Figure 1A). Due to the specificity of both activator and crosslinker, the reaction proceeds almost instantaneously and can be performed as a one-pot synthesis in water at ambient conditions without intermediate purification.

However, for the use case presented here, a hydrogel would not be suitable. Therefore, a droplet production unit (DPU) was used to produce defined microgels at high throughput (Figure 1B). In contrast to typical microfluidic devices, the DPU used here creates droplets in air by alternating chamber pressure so that the capacity is not limited by the flow through the device. The droplets are captured in an immiscible solvent to stabilize their spherical shape in an emulsion and allow crosslinking to complete. Indeed, pectin microgels produced with the DPU were efficiently crosslinked and showed long-term stability (Figure 1C). This process allows the production of pectin microgels on a 10–100 g/day (dry mass) scale. In addition, the solvent can be almost fully recycled as it is efficiently separated from the microgels with sieves prior to clean-up.

To investigate the influence of the crosslinker/activator ratio on the properties of the microgels, pectin was mixed with varying concentrations of EDC as well as ADH and processed with the DPU. The size and size distribution of generated pectin microgels was determined by light microscopy (Table 1).

Interestingly, after transferring the microgels to water, their size varied significantly between the different EDC/

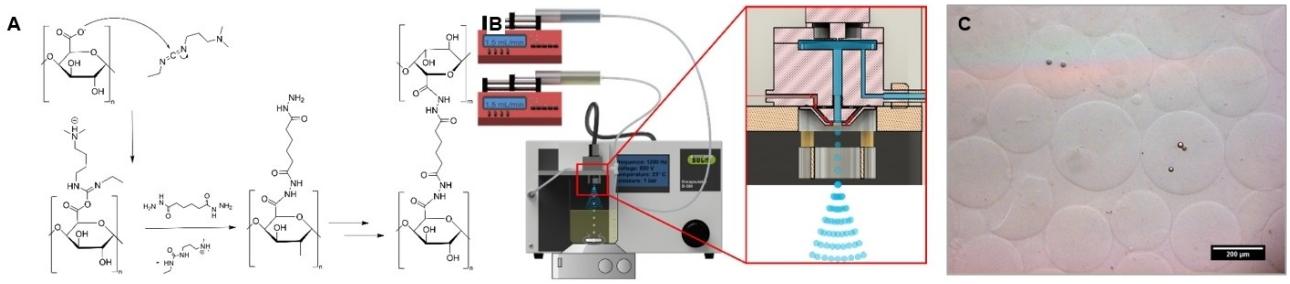

Figure 1. **A**: Reaction scheme to synthesize pectin hydrogel from citrus based pectin with EDC and ADH. **B**: Droplet generation unit (DPU) used for the production of pectin-based microgels. Two syringe pumps loaded either with EDC in buffer or pectin and crosslinker converge in the DPU. In focus, the air assisted nozzle system is shown, with liquid phase in blue and air stream with red arrows. **C**: Light microscopy images of pectin microgels (5 wt% ADH, 20x excess EDC).

Table 1: Size distribution of pectin microgels synthesized with varying activator/crosslinker ratios.

m (ADH) [wt%]	n(EDC)/n(ADH): 20 Ø size [µm]	deviation [µm]	n(EDC)/n(ADH): 40 Ø size [µm]	deviation [µm]
2,5	253	±93	390	±200
5	304	±83	217	±64
7,5	167	±59	124	±54

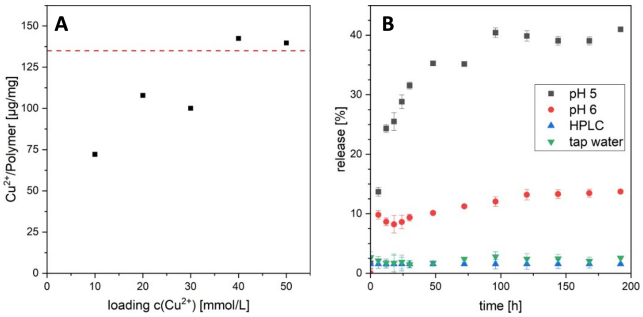

Figure 2. Uptake and release of copper ions from pectin microgels at room temperature (23 °C). **A**. Mass of Cu^{2+} per polymer loaded at different Cu^{2+} concentrations. Red line indicates the theoretical maximum. **B**: Released Cu^{2+} in surrounding media over time

ADH concentrations. With increasing number of crosslinks, the size of the microgel decreases, indicating reduced flexibility of the polymer network and therefore lower swelling. In fact, we noticed that some microgels synthesized at high crosslinker concentrations (7.5 wt% ADH) are damaged, which we attribute to the gel becoming too brittle to handle with the setup presented here (Figure S5, SI).

Corroborating, for low concentrations of ADH (2.5 wt%), microgels were comparably large with a 1.51 and 3.14-fold increase in size compared to 7.5 wt% ADH, respectively. However, microgels produced at low crosslinker concentrations were less homogeneous in size, which may be due to less efficient stabilization of the non-cured droplets directly after production, leading to agglomeration or fusion of droplets. Pectin microgels produced with 5 wt% ADH and 20x EDC excess were employed for all further studies, since they were homogeneous in size and exhibited best stability over long storage time.

Low-methoxylated pectin is known to naturally chelate divalent cations. In brief, two polymer chains enclose and coordinate cations via deprotonated carboxyls in an alternating fashion, which is also referred to as the egg-box model.[14] While these interactions themself are sufficient to gel pectin, the cations are only moderately bound and can be washed out into the surrounding solution, which leads to hydrogel collapse or dissociation. We exploited the innate binding capacity of pectin to incorporate copper ions into microgels. Copper is an essential active agent in agriculture since it protects plants against a broad spectrum of fungal and bacterial pathogens.[15]

To be able to confirm Cu^{2+} binding to pectin, the microgels were treated with different concentrations of copper acetate, washed and metal uptake was validated by an absorbance-based assay. Cu^{2+} content in the microgels increased up to a maximum between 40–50 mM Cu^{2+} in the loading solution, showing that the EDC/ADH treatment preserved the ability of pectin to bind cations. Maximum loading capacity was determined to be 140 µg Cu^{2+}/mg pectin. This is in good accordance with the theoretical loading maximum (135 µg Cu^{2+}/mg pectin), which was calculated by considering the fraction of galacturonic acid in pectin, the degree of methoxylation and the depleted carboxylic groups used for crosslinking (Figure 2A). Therefore, the microgels are naturally saturated when using a 50 mM Cu^{2+} solution. The theoretical loading maxima for 2.5% and 7.5 wt% ADH were 144 µg/mg and 125 µg/mg Cu^{2+}/polymer, respectively, indicating that the crosslinking degree does not have a significant impact on Cu^{2+} loading. We also noticed the formation of a bluish precipitate, likely corresponding to $Cu(OH)_2$ at higher copper concentrations, so that in all further experiments 135 µg/mg pectin copper loading was used.

Next, we investigated the release of Cu^{2+} from pectin microgels for up to two weeks. ICP-OES analysis showed that under selected experimental conditions (no continuous water exchange surrounding dialysis bag containing microgels) at a pH value of 5, nearly 40% of the loaded Cu^{2+} is released within around 3 days (Figure 2B). No further Cu^{2+} is released from the microgels during the next 5 days due to the accumulation of free Cu^{2+} in the dialysis water. However, the remaining Cu^{2+} can be released from the microgels when surrounding Cu^{2+} concentration is decreased by dilution or continuous water exchange. This effect suggests that the Cu^{2+} release from the microgels can be triggered by the dilution with water or sequential rain events in the field and thus the active ingredient can be released over long time periods. In addition, as shown in Figure 2B at the beginning of the experiment conducted at pH = 5, there is a burst-like release within the first few hours. This behavior might be favorable since rainwater is commonly acidic with a pH ranging from 4.2–6 (within Europe),[16] enabling a quick and targeted release over days during a rain event. This is especially useful since fungal infection events on leaves most commonly occur in humid conditions so that the fungicide is released when pest pressure is at its peak.[17] In contrast, the microgels almost fully retain their copper content in water at neutral pH over long periods of time which might also be desirable since pesticides are frequently dispersed in tap water with nearly neutral or slightly basic pH; therefore, no copper is released prior to target application.

Although the pectin microgels present a favorable balance between holding and releasing copper as their cargo, the microgel itself can be easily washed off from leaves, thereby leading to the loss of fungicidal activity on the plant. To avoid this scenario, we developed a peptide-based system to enable strong binding of the microgels to the plant surface. The concept is shown in Figure 3A: two separate binding domains, each highly specific for the respective target, are fused via a spacer-sequence. Since both domains

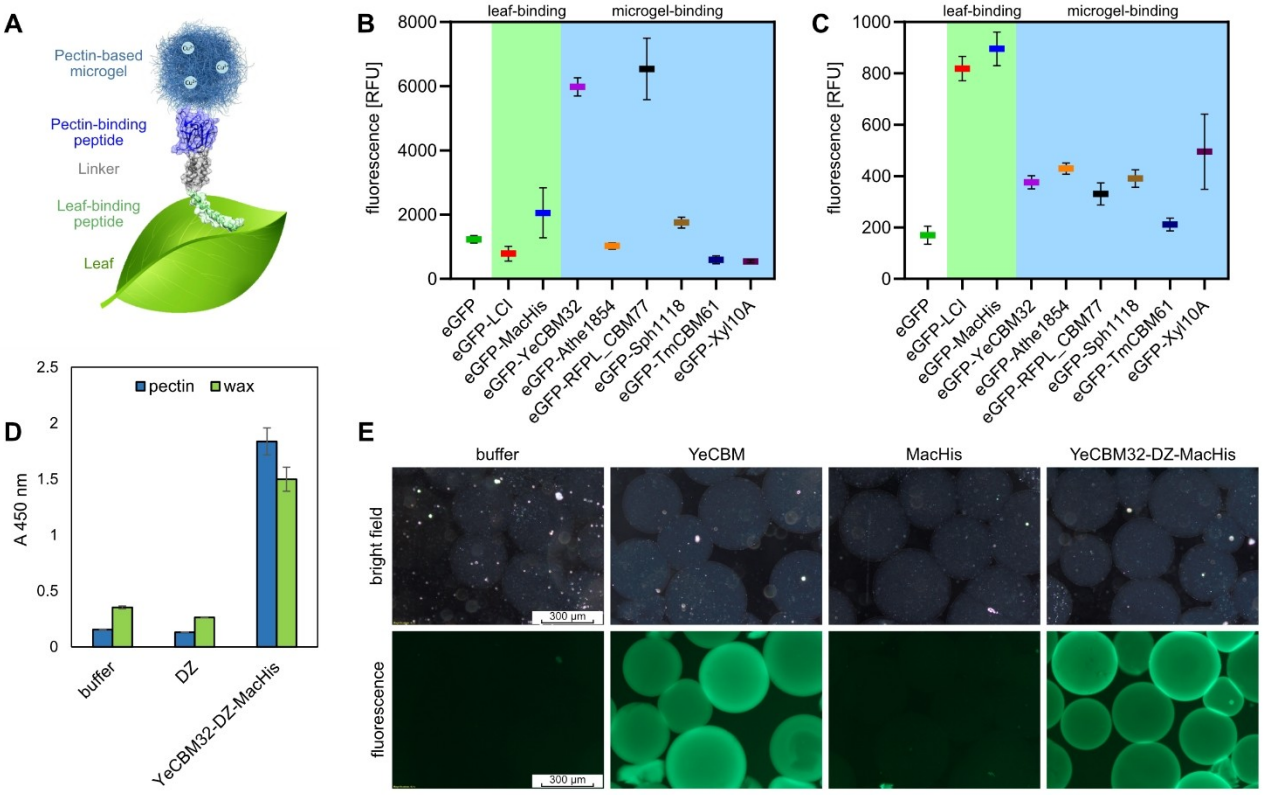

Figure 3. Development of a biadhesive anchor peptide. **A**: Overall strategy to bind microgels to the surface of leaves. Pectin-based microgels, containing complexed Cu^{2+} ions, are functionalized with a biadhesive peptide that binds specifically with one domain to the pectin of the microgels and with the other domain to the epicuticular wax of plants (here: grapevine). To minimize interference, both domains of the binding peptide are spatially separated by incorporating a linker. Figure not to scale. **B**: Binding behavior of selected anchor peptides on pectin hydrogels. Pectin was solidified into a hydrogel by Ca^{2+} treatment and used as a matrix to bind different eGFP-anchor peptide fusion proteins. Each box shows data of 3 independent binding studies. Whiskers indicate standard deviation. **C**: Binding study of selected anchor peptides on grapevine wax. Grapevine leaves were treated with chloroform and the extracted waxy mixture used as the substrate to bind eGFP-anchor peptides to. Each box shows data of 3 independent replicates. **D**: Validation of YeCBM32-DZ-MacHis on pectin and wax. Similar to **B** and **C**, binding matrices were prepared and peptides were added. An immunoassay was performed to quantify binding of the proteins. **E**: Fluorescence microscopy pictures of pectin microgels with selected anchor peptides. Microgels were functionalized with anchor peptides and subsequently treated with anti-His6 Alexa488-coupled antibody.

strongly prefer binding to only one of the surfaces, the final biadhesive peptide enables targeted and oriented binding.[18]

In order to develop the biadhesive peptide, in a first step binding peptides for both pectin (binding to microgels) as well as for grapevine wax (binding to leaves) were identified. Six carbohydrate binding modules (CBMs) that were reported to bind to pectin as well as two anchor peptides that were reported to bind to plant leaves[19] were selected and produced as eGFP fusion proteins in *E. coli*. The eGFP fusion proteins as well as eGFP only as control were added to the binding matrices (pectin or leaf wax). After thoroughly washing the binding matrices, eGFP fluorescence was determined, indicating the binding propensities of the different peptides (Figure 3B and 3C).

For pectin hydrogels, two equally well performing binding domains were found: YeCBM32 and RFPL_CBM77. These domains, expressed as eGFP fusions, showed significantly higher fluorescence on pectin hydrogel after 10 washing steps compared to eGFP alone (Figure 3B). YeCBM32 and RFPL_CBM77 are known to be CBMs expressed by pectin-degrading bacteria, with studies suggesting the ability to bind to pectin, however without being catalytically active.[20] Due to their native role, these peptides were evolved by nature for efficient pectin binding. Interestingly, the sequence similarity between both YeCBM32 and RFPL_CBM77 is very low, indicating that both domains evolved the capacity to bind pectin independently (Table S2). Similarly, all other tested CBMs exhibit low homology to each other. On a structural level, YeCBM32 and RFPL_CBM77 show a template modeling (TM) score of 0.48, indicating mild structure congruence (Table S3 and S4).[21] However, other CBM pairs had similar TM scores, even though at least one performed poorly in the pectin binding assay (e.g. YeCBM32 and TmCBM61, TM score = 0.49). Taken together, this indicates that different pectin-binding motifs are successful at binding under the conditions tested here. Further structure-function studies

would enable highlighting key design features that are needed to convey binding of peptides to crosslinked pectin.

An advantage of both YeCBM32 and RFPL_CBM77 is that the fusion to a non-native protein domain (here: eGFP) does not inhibit the ability of the CBMs to bind to pectin. In addition, the initial fluorescence of both peptides prior to washing was notably higher than for eGFP alone as well, indicating higher affinity of the eGFP-CBM fusions to pectin (Figure S6, SI). Since we found eGFP-YeCBM32 to be more easily producible in *E. coli* compared to eGFP-RFPL_CBM77, we decided to employ YeCBM32 as the pectin-binding module for all further studies.

Similarly to the pectin binding studies, we investigated the binding of the selected eGFP fusion proteins to extracted grapevine leaf wax using an established protocol.[19] As expected, the two anchor peptides MacHis and LCI significantly increased the fluorescence on grapevine leaf wax when expressed as eGFP fusions, whereas all five eGFP-CBMs showed only a low to moderate effect (e.g. 2.4-fold higher fluorescence intensity of eGFP-MacHis compared to eGFP-YeCBM32; Figure 3C). Likewise, eGFP-MacHis showed approx. the same fluorescence intensity as the negative control eGFP on pectin, illustrating that MacHis and YeCBM32 are specific for their respective target, allowing for oriented binding. For MacHis, key residues involved in binding to the epicuticular wax of apple leaves have been identified in a previous study, corroborating that MacHis is an efficient leaf binding peptide.[19] Taken together, MacHis was used as the wax-binding anchor peptide in further experiments.

The two binding domains YeCBM32 and MacHis were genetically fused and separated by a stiff spacer (domain Z of protein A from *Staphylococcus aureus*; DZ[22]) to minimize intramolecular interactions between both binding modules and produced as a fusion protein in *E. coli.* In order to test the functionality of the biadhesive peptide, binding assays were repeated on pectin and wax. Since eGFP is not included in the biadhesive peptide, these binding tests are based on an antibody immunoassay that detects the His_6-tag. Figure 3D illustrates that the biadhesive fusion peptide YeCBM32-DZ-MacHis adheres to pectin as well as grapevine wax whereas the spacer DZ (negative control) does not show any binding to either target. Therefore, the fusion of both domains in YeCBM32-DZ-MacHis retains their individual ability to bind to pectin and grapevine wax, respectively. The performance of YeCBM32-DZ-MacHis was further tested on pectin microgels and analyzed by fluorescence microscopy. Microgels were incubated with the respective binding peptide, washed and subsequently incubated with Alexa488-conjugated anti-His_6 antibody, which enables the visualization of bound protein by fluorescence. Figure 3E shows bright field and fluorescence images of microgels after treatment. Both peptides containing the pectin-binding domain YeCBM32 clearly bind to the microgels, while the anchor peptide MacHis provided virtually no binding to pectin. It can therefore be concluded that YeCBM32-DZ-MacHis binds not only to the pectin model substrate (hydrogel, Figure 3D), but also to the final pectin microgel product crosslinked by EDC/ADH. Importantly, this allows for the functionalization of the microgels without requiring an additional conjugation reaction (e.g. using click chemistry), which has been used in previous studies to covalently attach anchor peptides to microgels.[13a] The anchor peptides self-assemble in an oriented manner on the pectin-microgels in aqueous solution and under mild conditions, eliminating the need for elaborate activation and post-processing steps, which in turn reduces waste and emissions.

In order to verify that the biadhesive peptide conveys stronger and more resistant binding of the pectin microgels to the leaf surface, we assessed the binding of functionalized microgels to grapevine leaf disks. The microgels were either left untreated or incubated with YeCBM32 or YeCBM32-DZ-MacHis (the latter generating P-MAPs), respectively. For visualization, eGFP-YeCBM32 was added to all samples so that the microgels can easily be detected by the green fluorescence of eGFP. These microgels were added to leaf disks freshly cut from grapevine leaves and left to dry, simulating the coating procedure in an agricultural setting. Then, to mimic a rain event, the leaf disks were washed and subsequently analyzed by fluorescence microscopy (Figure 4A) as well as by a plate reader to quantify surface fluorescence (Figure 4B). The microgels only stayed on the surface of the leaf disks when functionalized with YeCBM32-DZ-MacHis, withstanding the simulated rain event. Functionalization of the microgels with YeCBM32 does not provide significant binding fastness, which is in line with the relatively weak binding of YeCBM32 to grapevine leaf wax (Figure 3C). Since MacHis alone does not bind to the microgels (Figure 2E), it can be concluded that specific and oriented binding of the biadhesive peptide occurs and conveys wash-resistant binding to the leaf surface. It is worth noting that after drying and subsequent rehydration by washing, the microgels appear as a pronounced 3D layer with some spherical structures still visible. It therefore seems like the microgels merge into a superstructure that covers the majority of the leaf disk without any major spare spots (under the conditions tested here). This also shows that the microgels spontaneously distribute on the surface without the need for spreading agents, which are commonly added to commercial agricultural pesticides and often contain polymers that are resistant to degradation,[23] illustrating another benefit of the pectin microgel-anchor peptide formulation used here.

Following binding assays under laboratory conditions, we investigated whether the Cu^{2+}-loaded P-MAPs (P-MAPs $+ Cu^{2+}$) protect grapevine plants against fungal infection. Grapevine pot plants were sprayed with either water, a commercial copper-containing pesticide currently approved for organic viticulture or P-MAPs $+ Cu^{2+}$, employing a commercially available spraying device used in agriculture. The plants were left outdoors for two days and leaf disks were harvested. The disks were treated with spore suspensions of *Plasmopara viticola*, the pathogen causing downy mildew. After infection, the leaf disks were incubated for 5–7 days, after which infection success was analyzed by visual inspection of the leaf disks for *Plasmopara sporangia.* As shown in Figure 5A and 5B, leaf disks harvested from plants

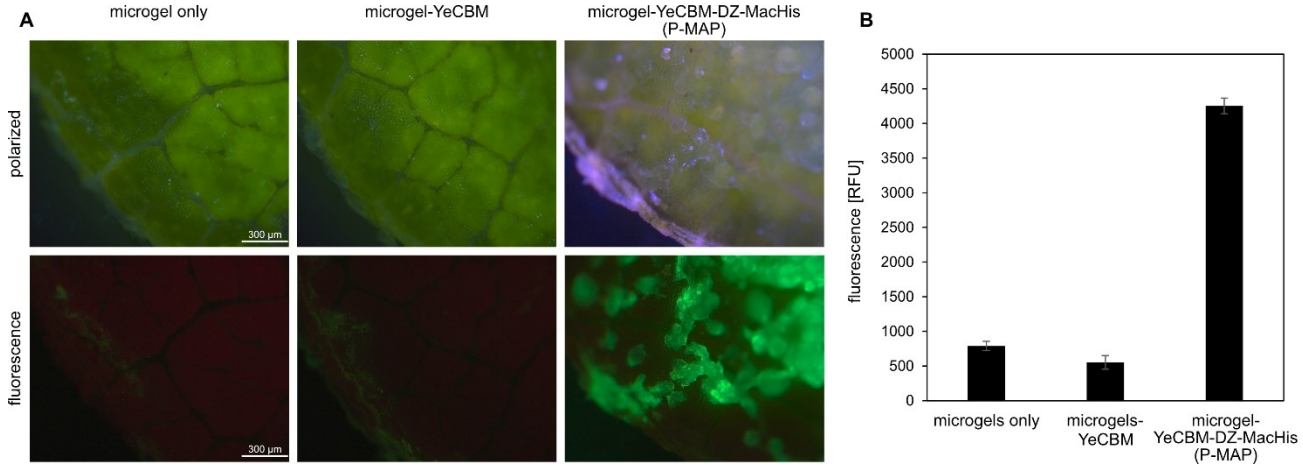

Figure 4. Biadhesive peptides bind pectin microgels to grapevine leaves. **A**: fluorescence microscopy pictures of grapevine leaf disks treated with differently functionalized pectin microgels. Microgels were treated with the same molar ratio of anchor peptide to pectin as well as eGFP-YeCBM as a fluorescence marker. Microgels were added onto the leaf and analyzed by microscopy. **B**: fluorescence quantification of leaf disks shown in A. After analysis by microscopy, leaf disk fluorescence was measured by a plate reader. Data was collected from 3 different leaf disk treatments.

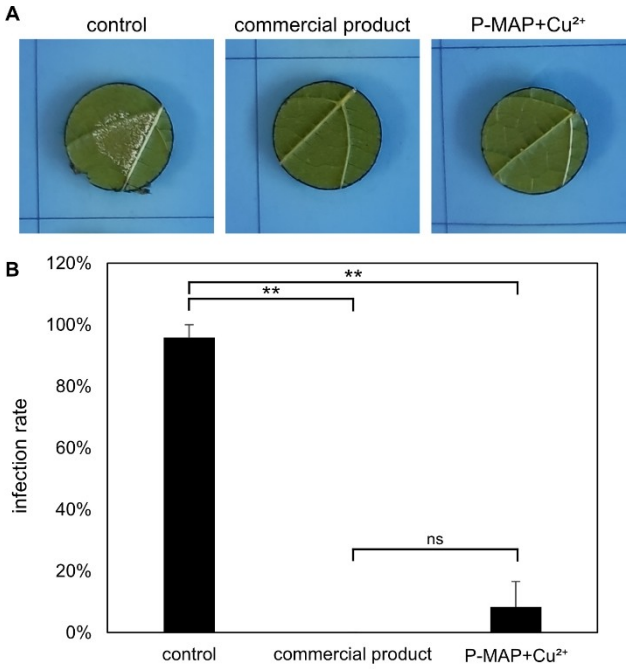

Figure 5. Functionalized pectin microgels prevent infection of grapevine leaves by *Plasmopara viticola*. **A**: leaf disks after infection with *Plasmopara viticola*. Grapevine pot plants were treated either with water (control), a commercial copper pesticide formulation or the Cu^{2+}-containing pectin microgels presented here. Plants were left outdoors for 2 days without any further treatment, during which medium rain events occurred (33 mm and 11 mm of precipitation, respectively). Leaf disks were cut from two leaves per plant (5 plants = 10 in total per run) and were infected with *Plasmopara* spores. After 5–7 days, infection rates of the disks were determined by visual examination. **B**: quantification of infection assays as described in **A**. Each bar represents data from 20 leaf disks collected in 2 treatment campaigns. During both campaigns, the plants were subjected to medium rainfall after pesticide treatment. (**: $p < 0.01$; ns: not significant).

only sprayed with water were fully colonized by *Plasmopara*, while both the commercial copper product as well as the P-MAPs + Cu^{2+} formulation developed in this study greatly protected the plants against *Plasmopara viticola* infections.

There was no significant difference in infection rates between the commercial product and the P-MAPs + Cu^{2+}, showing that the formulation developed in this study matches the performance of state-of-the-art pesticides. It is worth noting that the plants used here were subject to rain (33 mm and 11 mm, respectively) during outdoor incubation, indicating again that, by using biadhesive anchor peptides, the microgels are tightly bound to the surface and withstand medium intensity rain events.

Finally, we assessed the biodegradability of the P-MAPs by enzyme treatment. Pectinases are enzymes that are able to hydrolyze the pectin backbone into oligo- and eventually into monosaccharides, yielding compounds to be used as carbon sources.[24] Thus, pectinases are produced by numerous bacteria and fungi present in the soil, contributing to the overall carbon cycle and remineralization of plant matter.[25]

To determine biodegradability, P-MAPs were incubated with varying concentrations of pectinase and degradation was measured over time by dispersion analysis (Figure 6A). The microgels were quickly broken down in a pectinase concentration-dependent manner at ambient conditions. For high concentrations of pectinase (> 0.5 mg/ml), virtually complete degradation was observed within 24 h. Analysis of individual microgels by light microscopy shows the swift disintegration upon contact with pectinase (Figure 6B). Eventually, the microgels degrade to a degree that no colloidal structures can be identified anymore.

While the pectinase concentration used here is higher than the expected concentration in soil and on plants, it shows the potential of rapid degradation of P-MAPs. Considering the extracellular concentration of pectinases produced by microorganisms and comparing it to the lifetime of the microgels tested here, we estimate the

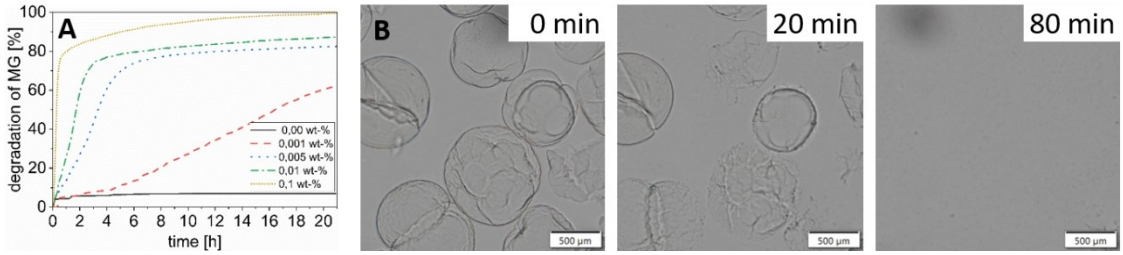

Figure 6. Degradation of pectin microgels. **A**: Degradation with varying amounts of pectinase over 24 hours at 20 °C. Following pectinase concentrations were used: **grey**: 0,00 wt% **red**: 0,001 wt% **blue**: 0,005 wt% **green**: 0,010 wt% **purple**: 0,050 wt% **yellow**: 0,100 wt% **B**: Degradation of pectin microgels with high concentration of pectinase over 1.5 hours at 20 °C. The complete degradation process can be found in SI.

lifetime of the P-MAPs to be in the range of several weeks to months when used in an agricultural setting.[26]

Conclusion

In summary, we developed a biobased, biodegradable and rainfast pesticide delivery system on the basis of pectin microgels and tailor-made biadhesive peptides. The microgels can be fabricated at medium scale under laboratory conditions and from inexpensive and renewable raw materials, allowing for the upcycling of plant-derived pectin to be re-used in agriculture. The biadhesive anchor peptide technology enables rainfast binding, reducing run-off and thereby pollution with copper as well as extended protection, minimizing the overall workload. The biadhesive peptides provide specific and oriented binding on the respective surfaces, enabling targeted and tailored adhesion of the microgels. In addition, the system presented here quickly self-assembles and does not require chemical activation of surface groups of the pectin microgels to attach the binding peptide, adding to the overall low-impact nature of the microgel-peptide system. Future studies will have to assess the stability of the pesticide system under conditions as close as possible to an application in agriculture and the impact of the local microbiome to degradation.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: anchor peptide · microgel · pesticide · delivery system · biodegradability

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