Study into the Biodegradation and Ecotoxicity of Hydropol-coated paper in recycling mills

Scope

Paper recycling within the UK is a success story with over 80% of paper and board packaging recovered for recycling into new products such as corrugated boxes and e-commerce packaging. The need to extend food shelf life and to protect the packaged goods from damage during transit has required paper and board to be combined with other materials, such as plastic, to increase resistance to oil and grease, water, gas ingress/egress and to improve cushioning properties. Recycling of multi-material packaging is a challenge to high volume recycling mills as it increases reprocessing costs and generates a plastic-rich 'reject' stream (Figure 1). At best, mill rejects are conditioned and burnt for energy or worse, are disposed of to landfill.

Figure 1 Plastic-rich pulper rejects

High volume recycling paper mills would prefer all plastics to be avoided - particularly polymers with low shear strength that break down in the pulper into microplastics which may pass through the mill water effluent plant and discharged into the water course or pass into and contaminate the finished products. CPI guidance is available to help retailers and brands specify and design paper-based packaging that can easily be recycled at high volume recycling papermills and notes that '*...fully soluble, bio-digestible barrier systems would be welcomed*'. Multi-material paper-based packaging makes up ~ 3% of paper-based packaging which includes plastic laminated food packaging and 'on the go' sandwich packs[1]. These packs contain valuable 'once-used' virgin fibres which add strength to recycled paper but the presence of plastic means that such packaging is not a desirable fibre feedstock for high volume recycling paper mills.

Hydropol coatings, deployed as functional barriers or paper strength enhancers are designed to be compatible with the paper recycling infrastructure and allow paper packaging to be recycled:

- Consumers can deposit their Hydropol coated papers alongside other papers for recycling kerbside and be confident that the packs will be recycled back into recycled-content papers
- Recycling paper merchants and MRF's identify Hydropol coated packaging as paper for recycling which can baled or sent loose to mills
- Hydropol solubilizes at the repulping temperatures and durations used by high volume recycling paper mills and facilitates rapid fibre dispersion. Hydropol is not substantive to fibre and passes through to the mills effluent plant where it is biodegraded as part of the intended use. For manufacturers of recycled corrugated case materials which deploy

anaerobic digestion to treat their waste waters, there is the potential that Hydropol could be mineralized to biogas which is cleaned and the methane burnt in the mills combined heat and power plant to generate heat and electricity for the paper making process. Methane generated by the on-site AD plant offsets the purchase of natural gas from the grid.

This document examines primary and secondary information sources to assess the fate of Hydropol (polyvinyl alcohol-PVOH) used as a paper barrier coating following its dissolution during the repulping process and release for biological treatment. Secondary research examined available scientific and trade literature from suppliers of PVOH in detergent applications as well as sizing agents used in the textile industry. Primary research input includes Aquapak commissioned testing which was carried out by AquaEnviro, a specialist waste water treatment test house and consultancy[2].

This document provides insights into the fate of Hydropol following the paper repulping process. Additionally, the document is intended to stimulate interest from the paper and packaging sector who want to deploy repulpable and biodegradable barrier coatings to improve the circularity of their paper packaging products.

Summary of findings

In summary:

1. Effluent treatability studies reported in the literature confirm high rates of PVOH biodegradation within acclimatized activated sludge biological treatment processes which are operated at 15°C and above. Standardised aerobic and anaerobic biodegradability tests which were carried out by Aqua Enviro demonstrated high rates of Hydropol removal within acclimatized and non-acclimatized aerated activated sludge (94.6% and 99.3% respectively). Anaerobic digestion of Hydropol was noted to be slower with 34.3% removal in Biomethane Potential tests
2. Absence of acute and chronic toxicity effects. Acute toxicity data and its extrapolation to evaluate chronic effects indicate low ecotoxicity. PVOH is inherently biodegradable and does not persist in the environment. Carbonaceous and nitrification inhibition tests carried out by AquaEnviro confirmed that Hydropol did not inhibit bacterial respiration rate (ie no acute toxicity)
3. The potential contribution from soluble Hydropol coatings to effluent organic strength (as measured by Chemical Oxygen Demand - COD) is considered. Estimates suggest that low percent increases in COD (~1.5%) would be observed when using Hydropol coated paper packaging at 1% of fibre furnish
4. Potential to reduce plastic-rich pulper rejects and increase fibre yield from the Mixed Paper grade. Most paper plastic packaging laminates will enter the mill from comingled household collected paper which is sorted into a 'Mixed Paper' grade. In the scenario considered in this document, if Hydropol coated paper makes up 1% of the mills total fibre furnish, this could amount to 5% of the comingled collected paper with a subsequent 5% reduction in waste pulper rejects.

Background to the study

Hydropol solubilizes at the repulping temperatures and durations used by high volume recycling paper mills and facilitates rapid fibre dispersion. The dissolved Hydropol is discharged for effluent treatment as part of its intended use, where it is mineralized (biodegraded) together with other biodegradable organics which are generated during the paper recycling process.

A highly polluted effluent is generated during the recycling of paper which is treated by a dedicated on-site effluent treatment facility before safe discharge.

Using soluble and repulpable barrier coatings, such as Hydropol for paper packaging improves fibre yield and reduces plastic rejects. However, three important questions remain:

1. Once dissolved, is Hydropol biodegraded within the biological treatments used by recycling papermills?
2. Are there any acute and chronic environmental impacts from the usage of Hydropol?
3. Will the use of a repulpable biodegradable Hydropol coating change the recycling mill effluent characteristics, overload the effluent treatment plant or increase treatment costs making their use difficult to justify technically and economically?

Effluent treatability of Hydropol

Schonberger et al (1997)[3] compiled extensive laboratory test data, including continuous laboratory effluent treatment plant tests and Zahn Wellens/EMPA tests which confirms the inherent aerobic biodegradation of PVOH within activated sludge treatment plants. Of the 15 tests described, the extent of biodegradation was noted as follows:

- 7 tests (90% biodegradation or higher)
- 5 tests (80% biodegradation or higher)
- 2 tests (60-75% biodegradation)
- 1 test (29% biodegradation).

It was noted that an activated sludge which is acclimatized to PVOH together with effluent temperatures in excess of 15°C were required if high rates of biodegradation were to be achieved. AquaEnviro tests determined the inherent aerobic biodegradability of Hydropol to acclimatized and non-acclimatized aerated activated sludge. Bio Methane Potential tests were also carried out to estimate the amount of methane that can be produced from anaerobically digesting PVOH at mesophilic temperatures. Activated sludge and anaerobic UASB granules were both supplied by a UK-based high-volume recycling mill which manufactures corrugated case medium.

Within the Zahn Wellens testing, Hydropol was almost completely removed by the non-acclimatized activated sludge with 99.3% COD reduction respectively. No additional removal of Hydropol was observed through pre-acclimatisation of the biomass prior to testing. In the case of the non-acclimatised sludge, the Hydropol concentration (measured as COD) was reduced from 897mg/l to 17mg/l over the test period (Figure 2).

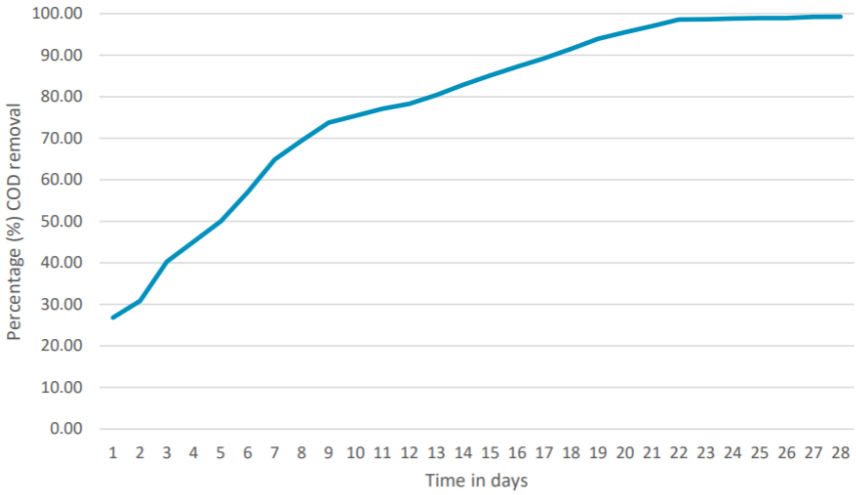

Figure 2 Percentage soluble COD removal curve for aerobic non-acclimatised mixed liquor test

Hydropol was noted to be slowly biodegradable under anaerobic conditions with 34.3% removal in the BMP test (Table 1; Figure 3).

Table 1 Feedstock parameters and methane yield

Sample	COD (mg/l)	Volume of Sample added (ml)	CH_4 produced (ml)	Methane yield (L.CH_4/kg.COD applied)	% COD Destruction
PVOH	3.8	207	94	120	34.3%

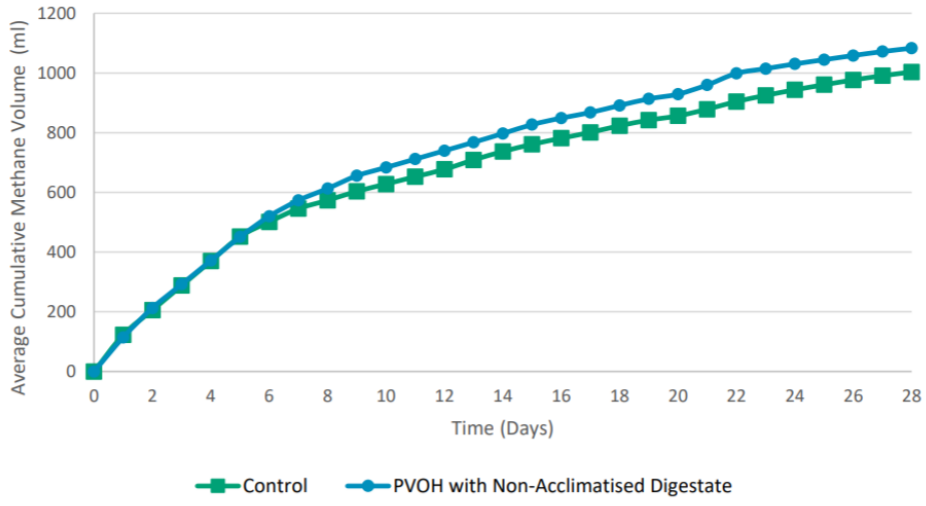

Figure 3 Methane evolution profile for PVOH and non-acclimatised digestate

Pilot testing would be required to determine whether this biodegradability would be replicated under the process conditions of a full-scale mill and whether Hydropol could be treated without any impacts on the process.

Assessment of acute and chronic effects

P&G first introduced its Tide Pod range of laundry detergent pods, with a soluble PVOH coating in 2012 [4]. Since then, soluble PVOH coatings have been widely adopted by many companies for the delivery of 'unit-dose' chemicals for domestic and commercial dishwashers and washing machines.

Soluble coatings are discharged into the environment as part of the intended use and as such their environmental impacts need to be quantified. Henkel carried out an in-depth environmental safety assessment of PVOH associated with its liquid laundry detergent[5]. An extensive set of aquatic toxicological and biodegradation information was collated to develop scenarios on detergent use and to assess the risk associated with the raw material use in the respective scenarios. Dual tests which examined Total Organic Carbon and mineralization to CO_2 qualified PVOH as inherently biodegradable and that a significant proportion would be removed from sewage during biological treatment. The REACH regulations classify persistent substances as those that display a half-life of 60 days or more in aquatic environments[6]. Since PVOH is inherently biodegradable it was concluded that PVOH is not persistent and does not accumulate in aquatic environments. Acute toxicity data against algae and *Daphnia magna* revealed low toxicity. When extrapolated, it was concluded that chronic effects would not be expected for a range of end-use scenarios. Henkel concluded for all scenarios addressed, that the use of PVOH with its liquid laundry detergent was safe.

AquaEnviro investigated the inhibition of respiration of carbonaceous and nitrifying activated sludge bacteria when exposed to wastewater generated from paper hand sheets made from Hydropol coated paper[7]. Test data showed an absence of inhibition to bacterial respiration. These results are consistent with those obtained by Henkel.

Estimate of Hydropol loadings on paper mill wastewaters-scenario development

Aquapak estimates show that a stand-up pouch measuring 26x23cm (front and back) and base measuring 23x9cm (total area 1,404 cm^2) and made from 40gsm paper with a 15µm Hydropol barrier coating weighs 64.54g of which 8.42g is Hydropol. In this scenario, a mill takes in 300,000 tpa of paper for recycling and discharges $5m^3$ water per tonne of product. If 1% of the mill's furnish is Hydropol coated paper (ie 3,000 tonnes per annum) then the concentration of PVOH within the effluent is estimated to be ~301mg/l with a COD of 400mg/l. Post primary treated effluents from recycled packaging mills have COD values anywhere upto 25,000mg/l[8]. The Hydropol coating would account for just over 1.5% of the total loading to the AD plant where indicative data suggest that around a third would be converted to valuable biogas and the remainder biodegraded by the activated sludge plant.

Pulper rejects reduction

Most paper plastic packaging laminates enter the mill from comingled collections from households which is sorted into a 'Mixed Paper' grade. Mixed Paper can make up ~ 20% of the fibre furnish of a recycling mill. In the scenario considered in this document, Mixed Paper could amount to 60,000 tpa for a mill reprocessing 300,000 tpa of paper for recycling. Should Hydropol coated papers make up 1% of the mills fibre furnish (3,000 tpa), then there is potential to reduce the mill's rejects by 5% (3,000/60,000*100 = 5%). This reduces environmental impacts, disposal costs and also decreases the quantity of valuable fibre which is entrained in pulper rejects and lost from the process.

Conclusions

Hydropol repulpable barrier coatings offer potential to increase fibre yield and reduce cost associated with the disposal of plastic rich rejects. The evidence presented in this document demonstrates that the PVOH used to make the Hydropol barrier coated paper packaging would contribute a small percentage increase to mill effluent organic load, where around one third would be converted to valuable biogas and then mostly be mineralized and removed by existing activated sludge systems, has low ecotoxicty and does not persist in the environment. Hydropol coatings offer the potential to increase fibre yield and reduce plastic-rich pulper rejects associated with comingled collected papers.

1 Confederation of Paper Industries. Paper and board packaging recyclability guidelines. Revision one: January 2020
2 PVOH Acclimatisation and determination of treatability SP460 August 2020. AquaEnviro report.
3 Schonberger, H; Baumann A and Keller W (1997). Study of Microbial Degradation of Polyvinyl Alcohol (PVA) in Wastewater Treatment Plants. American Dyestuff Reporter
4 https://www.freedoniagroup.com/Content/Blog/2017/08/03/Water-Soluble-PVOH-The-Material-Behind-the-Booming-Detergent-Pod-Market
5 Meier F, Stelter N, Zeese NJ and Tolls J (2013). Raw material supplier and detergent manufacturer cooperate in Environmental Safety Assessment of a new detergent raw material – a case study
6 EC (2004) Regulation (EC) No 648/2004 of the European Parliament and of the Council of 31 March 2004 on detergents, Offic. J EU. L104,1
7 Process Investigation Testing SP370 April 2019. AquaEnviro report.
8 BAT Reference Document for the production of pulp, paper and board 2015 Available at: https://eippcb.jrc.ec.europa.eu/reference/production-pulp-paper-and-board