26 January 2022

Aquapak
Hollymoor Way, Rubery
Birmingham, B31 5HE
UK

Re: Consideration of PVOH as part of the solution to achieve circular economies for plastics

Plastics are amazing materials that have impacted and transformed most sectors of the economy with a huge diversity of products. One of the major sectors where plastics have had a profound and beneficial effect is in product packaging, which has established linkages between suppliers and consumers that now sustain many local and global markets.

The beneficial properties of plastics that make them extremely useful, inexpensive to produce, and inherently extremely stable also become their greatest liability, as their mismanagement at end-of-life has led to their accumulation as pollutants in the environment. Although some plastics are recycled, the vast majority currently follow a linear economic model whereby plastic production and use is followed by disposal and accumulation in landfills or incineration (UNEP 2018). It is therefore not desirable to promote a linear economy for any plastic material as the ultimate outcome is the loss of these valuable materials from future use. A particular issue of the current linear model is that approximately 2-4% of all plastics produced annually are accidentally or deliberately released into the environment (Jambeck et al 2015; Bucknall 2020).

Addressing the issues of plastics fits directly within the key tenets of the European Green Deal that include development of circular economies improved sustainability, reduction of pollution, and preservation of ecosystem and human health (EC 2020a). The environmental/human health issues of plastics have captured public attention, and because of lack of evidence, misinterpretation, or mis-representation of evidence effective communication of the realistic risks of plastics can be difficult to disentangle (Catarino et al., 2021).

Heriot-Watt University (HWU) has established a Consortium of Plastics and Sustainability (COMPASS; compass.hw.ac.uk) for unbiased, evidence-based, exploration of the global and societal challenges that will help map the future direction of plastics in the environment and world economy. This consortium provides the broad range of enabling knowledge and expertise necessary to underpin the drive towards a circular economy for plastics. Experts across our global campus work closely together and with external partners to provide solutions towards the global goals of recovering waste plastics, re-using, re-purposing, and recycling those waste plastics at the same time as reducing plastic use through product re-design and replacing where appropriate with better performing and more sustainable alternatives.

Investigating the potential environmental impacts of plastics including PVOH across their life cycle is important and it is critical that this is done within the broad context of alternative materials as well. Considerable work is needed to understand how to establish genuine circular economies for all of these materials and put the mechanisms in place to have these realized.

Polyvinyl alcohol (PVOH) is a polymer with unique properties that has the potential to contribute to the future direction of plastics within a circular economy and reduction of environmental impacts. Results of our investigations of the environmental implications of dissolved PVOH are consistent with previous reports that this material is innocuous to aquatic life for the variety of organisms that have been tested.

Further investigation into the decomposition of PVOH within the environment by abiotic and biotic factors is ongoing to establish rates and processes. These analyses will enhance understanding of how the attractive properties and unique opportunities of PVOH could be part of the solution to achieve circular economies for plastics.

Sincerely,

Theodore B. Henry   David Bucknall   TAGutierrez

Theodore B. Henry, PhD
Professor of Environmental Toxicology

David Bucknall
Professor of Materials Chemistry

Tony Gutierrez
Assoc Prof of Environmental Microbiology & Biotechnology

References

Bucknall DG. 2020. Plastics as a materials system in a circular economy. Phil. Trans. R. Soc. A 378: 20190268. http://dx.doi.org/10.1098/rsta.2019.0268).

Catarino AI, Kramm J, Völker C, Henry TB, Everaert G. 2021. Risk posed by microplastics: Scientific evidence and public perception. Current Opinion in Green and Sustainable Chemistry 29 (100467).

EC 2020a- European Green Deal https://ec.europa.eu/info/strategy/priorities-2019-2024/european-green-deal_en SBN 978-3-9820301-0-4 DOI 10.26356/microplastics.

Jambeck JR, Geyer R, Wilcox C, Siegler TR, Perryman M, Andrady A, Narayan R, Law KL. 2015 Plastic waste inputs from land into the ocean. Science 347, 768–771. (doi:10.1126/science.1260352).

UNEP, 2018. Single-Use Plastics: a roadmap for sustainability.

Knowledge Transfer Partnership

Heriot-Watt x Aquapak

Exploring the impact of plastics on marine environment through an investigation of the environmental implications of Aquapak's Hydropol™ polymers [formulations PVOH] considering physicochemistry, microbial decomposition, and ecotoxicology

HERIOT WATT UNIVERSITY

"Results from our investigations of the environmental implications of these two Hydropol™ formulations are consistent with previous reports that PVOH is of low toxicity to aquatic life for the variety of organisms and endpoints that have been tested."

Forward by Aquapak Polymers

The issue of single use plastics has highlighted a great number of environmental problems, and we have found that there is a lack of independent data in this area, particularly in marine ecosystems. Aquapak Polymer's Knowledge Transfer Partnership with Heriot-Watt University was therefore created to explore the impact of plastics on marine environment.

Phase one of this study, on which this report is based, focused on two formulations of Hydropol™, Aquapak's patent-protected speciality polymer that is a thermally-processible polyvinyl alcohol (PVOH). It considered its physicochemistry, microbial decomposition, and ecotoxicology.

Whilst COVID-19 initially impacted the lab research that could be undertaken, it allowed a more in-depth review of the pre-existing knowledge of PVOH was made, which confirmed it has low toxicity.

Results from the KTP's investigations of the environmental implications of two Hydropol™ formulations are consistent with previous reports that PVOH is of low toxicity to aquatic life for the variety of organisms and endpoints that have been tested.

Further research (now ongoing) is now needed assess ecotoxicity of PVOH standards in comparison with other water-soluble polymers to enable comparison of relative toxicity.

NEW PLASTICS ECONOMY Global Commitment

Heriot Watt Report

Executive summary report on the Knowledge Transfer Partnership (KTP) project between company partner Aquapak and academic partner Heriot-Watt University (HWU)

Project dates: March 2020 – March 2022
KTP Associate: Joel Kuhn
Project supervisors: Theodore B. Henry, Tony Gutierrez, David Bucknall

Project focus: Investigation of the environmental implications of Aquapak's Hydropol™ polymers [formulations of polyvinyl alcohol (PVOH)] considering physicochemistry, microbial decomposition, and ecotoxicology

Summary: Polyvinyl alcohol (PVOH) is a polymer with unique properties that has the potential to contribute to reducing the environmental impacts of plastics and improving the future direction of plastics within a circular economy. In this project, the physicochemistry, microbial decomposition, and ecotoxicology of two formulations of PVOH (Aquapak's Hydropol™ 33104 and Hydropol™ 30164) were investigated with the development of standardized tests. Ecotoxcity tests with the model saltwater invertebrate brine shrimp Artemia sp. demonstrated acute toxicity [lethal concentration predicted to kill 50% of test organisms (LC_{50})] at concentrations of 25 mg/L and 34 mg/L for Hydropol™ 30164 and Hydropol™ 33104 respectively. Likewise, acute toxicity tests with zebrafish larvae demonstrated small but statistically significant differences between Hydropol™ 30164 and Hydropol™ 33104 with LC_{50} values of 55 mg/L and 63 mg/L respectively. Observations of brine shrimp and zebrafish behaviour indicated that lethality was likely a consequence of physical disruption of organism swimming and respiratory movements due to high viscosity of the test solutions.

The small but significant difference in toxicity between the two Hydropol™ formulations could be related to water solubility or solution viscosity differences that result from the two formulations. Acute toxicity occurred in zebrafish embryos prior to hatching with LC_{50} of 40 mg/L for Hydropol™ 30164.

After hatching, heart rate of zebrafish larvae increased with age and with concentration (0.5-20 mg/L) of exposure to Hydropol™ 30164. Microbial decomposition tests indicated that the Hydropol™ formulations did not inhibit the growth of model marine bacterial strains or native marine microbial communities; however, decomposition of the polymers was not evident either because decomposition did not occur or because the detection methods were not sufficiently sensitive.

More sensitive decomposition tests, perhaps with use of isotopically-labelled PVOH could be considered to determine polymer decomposition, either by identifying the products of decomposition and/or the organisms carrying out this process, as well as determine rates of decomposition.

Results from our investigations of the environmental implications of these two Hydropol™ formulations are consistent with previous reports that PVOH is of low toxicity to aquatic life for the variety of organisms and endpoints that have been tested. Toxicity was evident only at aqueous concentrations that are orders of magnitude higher than those expected to occur in the environment from releases of Hydropol™.

Sincerely,

Theodore B. Henry

Theodore B. Henry, PhD

Professor of Environmental Toxicology

David Bucknall

David Bucknall

Professor of Materials Chemistry

T A Gutierrez

Tony Gutierrez

Assoc Prof of Environmental Microbiology & Biotechnology

NEW PLASTICS ECONOMY Global Commitment

Introduction

The accumulation of plastic debris in the environment is among the most prominent environmental issues of our time and finding solutions to this global crisis requires re-consideration of the plastic polymers that are produced and how these polymers are used. Widely used synthetic plastics such as polyethylene, polypropylene, and polystyrene have numerous beneficial properties; however, linear-use disposal pathways and high persistence in the environment lead to their environmental accumulation. The development of alternative polymers and a circular economy for plastics are methods to address these environmental challenges, and the Aquapak company has positioned itself to engage in some of these potential solutions with their Hydropol™ polymer. The Hydropol™ polymer is based on a formulation of polyvinyl alcohol (PVOH), which when treated with hot (>60°C) water, dissolves and can be recovered (i.e., for circular use-reuse applications) or released into waste streams or the environment in the aqueous phase. Release of PVOH into the aquatic environment presents a potential for exposure and negative effects in aquatic organisms that needs to be understood.

The water solubility of PVOH is a physicochemical property that influences the environmental fate of the polymer and its interaction with organisms. The polymer is produced in various forms for commercial use including PVOH beads, fibres, membranes, and films. Depending on the desired characteristics of these products, the PVOH can have different molecular weights and polydispersity, degrees of hydrolyzation as well as be compounded with a variety of additives that confer specific properties. Water solubility can be tuned by adjusting PVOH molecular weight and/or hydrolyzation. At elevated aqueous concentrations of PVOH, the solution becomes more viscous and over time settlement of the aqueous polymers in quiescent solutions can be observed at the bottom of the container. It is evident that at these high concentrations, PVOH tends to deposit to solid surfaces and consequently will settle on any exposed surface, such as sediments and aquatic organisms, if released into aquatic environments.

The environmental outcome (fate etc.) of PVOH will depend on the potential for the polymers to be decomposed by microorganisms, their rate of decomposition and the toxicity and residence time of any by-products produced.

Exposure of aquatic organisms to PVOH will occur in the water column and on/within sediments, and relevant routes of organism exposure include respiratory surfaces, ingestion, and dermal contact.

The rate and processes by which PVOH decomposes in the environment and exerts toxicity to organisms will impact the potential for the polymer and new PVOH formulations (e.g., the Hydropol™) to contribute to solving the global plastics crisis. Investigations of the microbial decomposition of PVOH in laboratory cultures of single and mixed bacterial species have been conducted, but results of decomposition rates, biochemical pathways, and decomposition products remain inconclusive. Further information is required to assess PVOH decomposition in environmentally relevant scenarios and by relevant microbial consortia (e.g., those present in marine ecosystems) to determine the fate of these polymers in the environment. Studies of the toxicity of PVOH in mammalian models have been reviewed (DeMerlis and Schoneker 2003), and the polymer was found to have low toxicity after investigations considered numerous exposure routes (oral, intravenous, rectal, intravaginal, subcutaneous) and toxic effect endpoints. A previous study with ^{14}C labelled PVOH demonstrated minimal accumulation after ingestion with the vast majority (>98%) passing unaffected through the gut and being detected in faeces within 48 h. The ecotoxicity of PVOH has previously been tested as part of a mixture in aqueous exposures with various fish and aquatic invertebrate toxicity test models; however, pure PVOH was not tested on its own and the contribution of PVOH to toxicity of the mixture could not be determined (Arfsten et al., 2004). No other PVOH ecotoxicity test results were found in the published literature.

The overall aim of this project was to provide information to assess the environmental implications of release of aqueous PVOH into the aquatic environment.

Specifically, our objectives were to

1. assess interactions of Hydropol™ with marine bacteria and the potential for microbial decomposition of the polymer,
2. develop standardized test procedures for conducting ecotoxicity tests with Hydropol™
3. investigate the toxicity of two forms of Hydropol™ in early life history stages of zebrafish, and
4. assess toxicity of two formulations of Hydropol™ in brine shrimp nauplii (i.e. early stage larvae).

Materials and Methods

The PVOH polymers were provided as solid pellets by Aquapak in two Hydropol™ PVOH polymer formulations designated as "warm" (Hydropol™ 33104) and "hot" (Hydropol™ 30164) referring to the relative temperatures at which aqueous dissolution occurs. Detailed procedures for preparing the aqueous solutions of Hydropo™and conducting ecotoxicity tests were provided as Standard Operating Procedures (SOPs) developed during the project and delivered to Aquapak. Briefly, aqueous solutions were prepared by dissolving 5 g of Hydropol™ pellets into 50 mL OECD water and heating (<100°C) with constant stirring to prepare a stock solution that was cooled to room temperature and subsequently diluted to the required concentration for toxicity tests. Zebrafish embryos or newly hatched larvae were individually exposed to 1 mL of various concentrations of Hydropol™ solutions in covered 24-well plates. For brine shrimp ecotoxicity tests, the procedure was identical except 10 brine shrimp were exposed in each well of the 24-well plates. Sub-lethal endpoints and mortality were assessed every 24 h during zebrafish and brine shrimp ecotoxicity tests. Statistical analyses of the dependent variable (e.g., mortality or hatching) relative to the independent variable Hydropol™ concentration or the second independent variable Hydropol™ type ("warm" or "hot") were conducted with logistic regression (R software for statistical analyses).

Results and Discussion

Standardized operating procedures (SOPs) for investigating the ecotoxicology of PVOH formulations were developed and applied to Aquapak Hydropol™ products. Test solutions over the concentration range of 0.5-100 mg/L were used to determine toxicity to occur in organisms. Evidence of changes in solution viscosity and some sedimentation of polymers out of solution to the bottom of containers at highest concentrations was observed. It is possible that non-homogeneous exposure solutions can impact toxicity test results if organisms reside in the water overlying accumulations of polymers that have settled to the bottom of the container at higher test concentrations. Nonetheless, clear concentration-responses were evident for all the tests conducted, test results were reproducible, and results are an accurate reflection of the toxicity under the conditions tested.

Test organism mortality increased with Hydropol™ concentration and differed between the two Hydropol™ formulations for both brine shrimp nauplii and zebrafish larvae (Figure 1 and 2). The order of acute toxicity (i.e., LC_{50} values) was the same for both species with Hydropol™ 30164 being more toxic than Hydropol™ 33104. Observations of both test organisms in exposure solutions identified inhibition of swimming and respiratory movements that were particularly evident at higher test concentrations for which increased solution viscosity was also visible. The mechanism of toxicity is suspected to be associated with physical disruption of tissue surfaces rather than by polymer absorption, bioaccumulation, or chemical toxicity. It is possible that the formulations of Hydropol™ 30164 and Hydropol™ 33104 differ in the molecular weights of PVOH in addition to their degrees of hydrolyzation and these differences influence test solution viscosity and thereby the observed effects on organism locomotion and respiratory movements. Nonetheless, the toxicity of Hydropol™ 30164 and Hydropol™ 33104 is low overall for the test-effect endpoints considered and occur at concentrations that are orders of magnitude higher than those expected to occur in the environment from releases of Hydropol™.

Survival of zebrafish embryos to hatching decreased with Hydropol™ 30164 exposure concentration (Figure 3) giving an LC_{50} value of 40 mg/L. Observations of embryos during exposure indicated shrinkage of the chorion around the embryo, which increased with Hydropol™ concentration.

Shrinkage of the chorion was also observed in unfertilized eggs (in Hydropol™ solution) and suggested that changes in the appearance of the chorion was a consequence of osmotic disturbance (i.e., differences in osmotic pressure between the perivitelline space and the external solution) leading to collapse of the chorion. An effect of osmotic pressure at higher polymer concentrations could also impact embryo survival and perhaps physical effects of compressed chorion on a developing embryo could be detrimental to survival. The LC_{50} (40 mg/L) for acute toxicity in embryos was consistent to that of zebrafish larvae (55 mg/L).

Of the effect endpoints that were tested, heart rate of zebrafish embryos was affected at the lowest Hydropol™ 30164 exposure concentrations tested. During normal zebrafish embryonic development (i.e., unexposed controls), heart rate increases with age from 24 h to 96 h postfertilization. The increase in heart rate with Hydropol™ 30164 concentrations over 0.1 mg/L suggests that development of embryos was accelerated by exposure to the polymer. No developmental or morphological abnormalities were observed during development and the consequences of accelerated development are unknown.

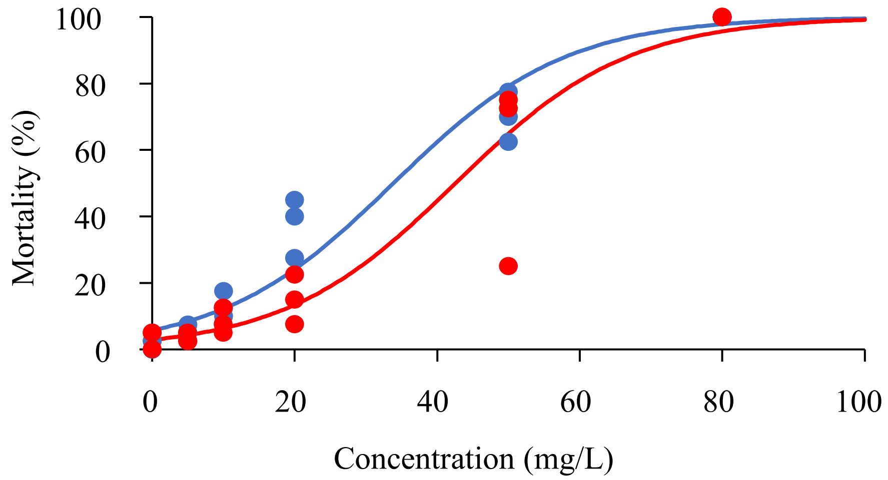

Figure 1. Mortality (%) of brine shrimp after 48-h exposure to "Hot" Hydropol™ 30164 (Blue) and "Warm" Hydropol™ 33104 (Red). There was a significant difference in brine shrimp mortality between the Hydropol™ types with "Hot" more toxic than "Warm", and the computed concentrations that induced 50% mortality (LC_{50}) were 25 mg/L and 34 mg/L respectively.

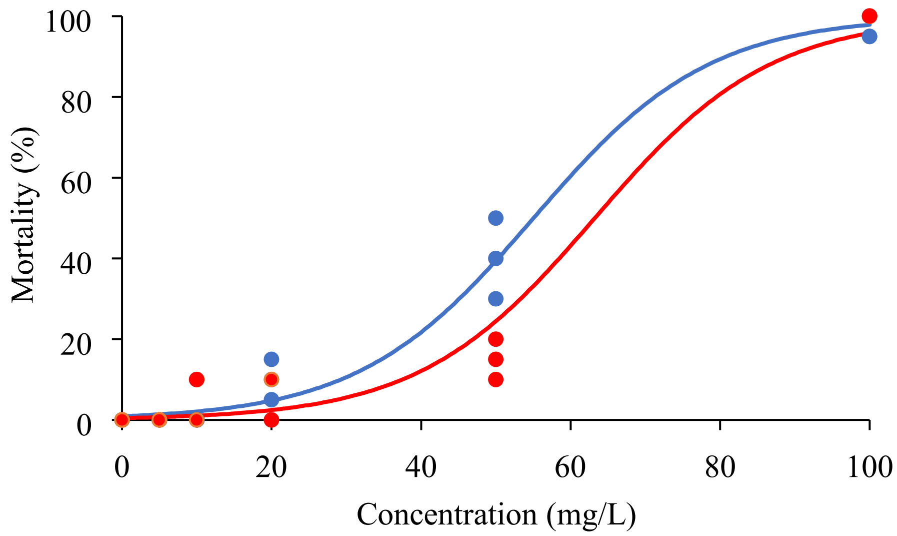

Figure 2. Mortality (%) of zebrafish after 72-h exposure to "Hot" Hydropol™ 30164 (Blue) and "Warm" Hydropol™ 33104 (Red). There was a significant difference in zebrafish larvae mortality between the Hydropol™ types with "Hot" more toxic than "Warm", and the computed concentrations that induced 50% mortality (LC_{50}) were 55 mg/L and 63 mg/L respectively.

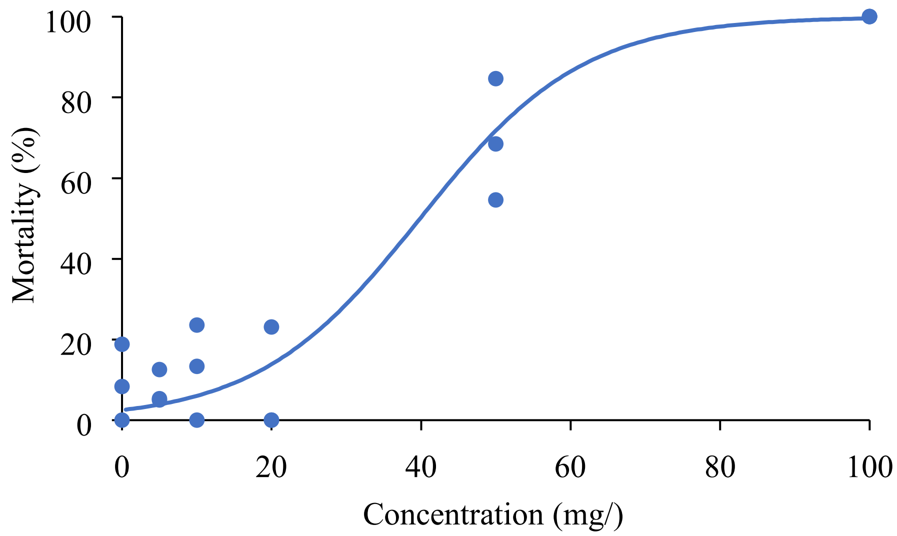

Figure 3. Mortality (%) of zebrafish embryos (prior to hatching) exposed to Hydropol™ 30164. The computed concentration that induced 50% mortality (LC_{50}) was 40 mg/L.

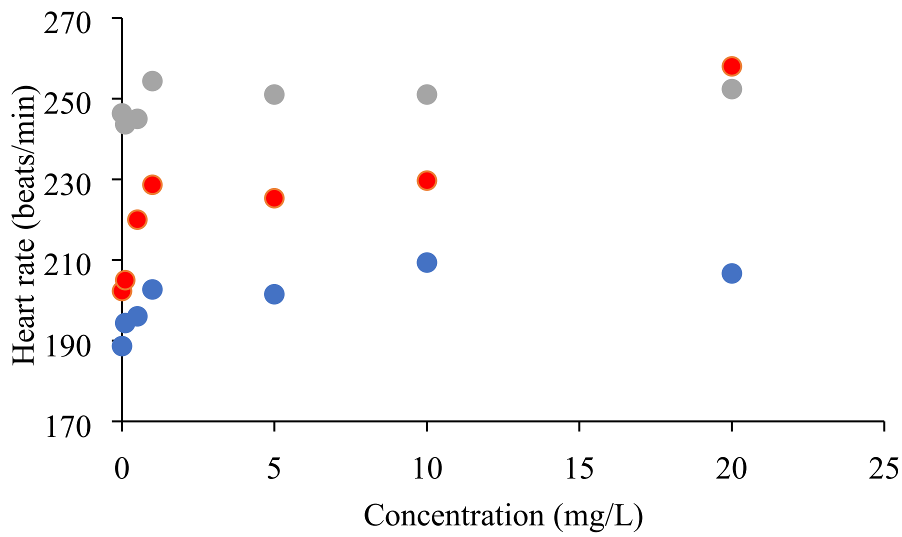

Figure 4. Heart rate (beats per min) of zebrafish embryos relative to Hydropol™ 30164 concentration at 48h (blue), 72h (red), and 96h (gray) after fertilization. Heart rate increased with age as expected in unexposed controls and increased with Hydropol™ 30164 concentration.

Ongoing research

Ongoing research is underway to assess ecotoxicity of PVOH standards in comparison with other water-soluble polymers to enable comparison of relative toxicity.

Draft manuscripts

The following draft manuscripts have been written relating to this summary, that will be finalised in the near future:

- Literature review collating the environmental behaviour and ecotoxicology of PVOH and other water-soluble polymers
- Research paper comparing the ecotoxicology of several water-soluble polymers (including PVOH) in various test organisms.

Literature cited

Arfsten DP, Burton DT, Fisher DJ, Callahan J, Wilson CL, Still KR, Spargo BJ. 2004. Assessment of the aquatic and terrestrial toxicity of five biodegradable polymers. Environmental Research 2004, 94:198-210.

DeMerlis CC, Schoneker DR. 2003. Review of the oral toxicity of polyvinyl alcohol (PVA). Food and Chemical Toxicology 2003, 41 (3), 319-326.