



Review

Water-soluble polymeric xenobiotics – Polyvinyl alcohol and polyvinylpyrrolidone – And potential solutions to environmental issues: A brief review



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ABSTRACT

This paper describes a potential environmental problem closely linked with the global production of water-soluble polymers such as polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP). Both polymers make up the components of a multitude of products commonly utilized by industries and households. Hence, such a widespread use of PVA and PVP in the industrial sector and among consumers (the concentration of PVP in urban wastewater is approximately 7 mg/L) could pose a considerable problem, particularly to the environment. To this end, many publications have recently highlighted the poor biodegradability of PVA, in principle influenced by numerous biotic and abiotic factors. Facts published on the environmental fate of PVP have been scant, basically reporting that it is a biologically resistant polymer. As a result, the commercially produced water-soluble polymers of PVA and PVP are essentially non-biodegradable and possess the capacity to accumulate in virtually all environmental media. Consequently, there is a chance of heightened risk to the very environmental constituents in which PVA and PVP accumulate, depending on the routes of entry and transformation processes underway in such constituents of the ecosystem. This assumption is confirmed by the findings of initial research, which is worrying. Herein, PVA was detected in a soil environment, while a relatively high concentration of PVP was found in river water. A review of the literature was conducted to summarize the current state of knowledge concerning the fate of PVA and PVP in various environments, thereby also discerning potential solutions to tackle such dangers. This paper proposes methods to enhance the biodegradability of materials containing such materials; for PVA this means utilizing a suitable polysaccharide, whereas for PVP this pertains to actuating applications that induce substances to degrade. Accordingly, while it is understandable that this work cannot fully address all the issues associated with polymeric xenobiotics, it can still serve as a guide to discerning an economically viable solution, and provide a foundation for further research.

1. Introduction

In terms of production volume, polymeric materials pertaining to all technical materials currently constitute the greatest proportion of manufacturing and consumption. Their enormous utilization by industries and consumers has resulted in significant environmental pollution; these materials rank among the most widespread foreign particles discovered in the environment (Horton and Dixon, 2018). To place them in context, they are referred to as polymeric xenobiotics in environmental literature (Moore, 2008). For substances of this type, it is useful to discern whether they are comprised of the following:

a) **Plastics** - This term generally relates to materials formed primarily of organic macromolecular substances (polymers). In addition to

substances that are polymeric in nature, plastics **contain additives** so as to elicit a specific modification to a process or subsequent property. A range of publications concern the environmental fate of these additives and their impact on the ecosystem, often confirming that such substances are persistent and bio accumulative (e.g., phthalates or brominated flame retardants) (Rist et al., 2018). Other negative impacts exerted by plastics and micro-plastics on ecosystems should not be ignored; for instance, if such plastic waste occurs in seas and oceans, it may be colonized by organisms that attach themselves to it, potentially leading to these organisms being introduced by marine currents into areas outside their native ranges, thereby distorting biodiversity and threatening native species. Additionally, the accumulation of plastics at the bottom of oceans and seas, or rivers and lakes, may restrict the diffusion of gases between

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the liquid and solid state of the bottom of said body of water, resulting in the inhibition of benthic organisms (Wright et al., 2013; Moore, 2008).

- b) **Polymers** – these relate to organic macromolecular substances that are applied in pure form in real life, i.e., **without additives**. Of these, water-soluble synthetic polymers form a specific group, one often ignored since they are essentially “invisible”. The majority of these have been subject to a number of clinical and toxicological studies. However, information of an environmental nature is completely absent, in contrast to compounds of the type referred to as persistent organic pollutants (POPs), because synthetic polymeric substances appear to be biologically inactive and generally non-toxic. Important examples include **polyvinyl alcohol (PVA)** and **polyvinylpyrrolidone (PVP)**. Since the second half of the twentieth century, both have been widely adopted by the industrial sector due to their physico-chemical and toxicological properties, recently entering into use in households, too. While they exhibit no direct toxic effect on organisms in the concentrations applied, the potential exists for them to increase the mobility of toxic metals or organic pollutants in the individual constituents of the environment; made possible through the complexation characteristics and surfactant effects of the said polymers. Furthermore, such xenobiotics may disturb the natural cycle of substances in the ecosystem.

The current state of pollution affecting ecosystems by polymer xenobiotics means that society has become aware in recent decades that necessary measures have to be taken. Data on the extent of the danger posed, if combined with study and analysis conducted in a holistic manner, shall afford the opportunity to either cease or slow down the current negative trend and formulate acceptable measures to ensure that the matter is under control. Although it is beyond the scope of the present study to detail every issue associated with water-soluble polymeric xenobiotics, it can still serve as a guide to discerning an economically viable solution, thus providing a foundation for further research.

2. Basic characteristics and the environmental importance of polyvinyl alcohol and polyvinylpyrrolidone

Polyvinyl alcohol (PVA, Mowiol[®], Poval[®], Sloviol[®], Elvanol[®], E 1203) was discovered in 1915 by F. Klatt. Under conditions of normal temperature and pressure, it takes the form of powdery white crystalline matter, usually produced by alkaline hydrolysis of polyvinyl acetate. From a chemical perspective, PVA primarily has the structure of 1,3-glycol and is classified as a polyvinyl acetate. Core variables affecting the behaviour of PVA in the environment comprise the extent of polymerization and hydrolysis/re-esterification, in addition to stereo regularity (Fukae et al., 1994) and crystallinity.

The solubility of PVA in water and resistance to organic solvents stand out as the most important and interesting qualities. However, it is important to realize that not every kind of PVA is soluble in water to the same extent. Such solubility depends upon various factors: the size of the macromolecules; the number of –OH groups that remain free in the

molecule; how many acetate groups (Fig. 1) and aldehyde radicals are bound to it; and the extent to which etheric bonds are created in the molecule. In general, PVA that possesses a higher molecular weight is less soluble than derivatives at a lower stage of polymeration. The solubility of PVA is highly reliant upon the quantity of acetate groups in the molecule. Products with 5% content of acetate groups are insoluble in cold water, and only dissolve at 65–70 °C. When the content of acetate groups equals 12%, the said PVA is highly soluble in cold water. Where the content of acetate groups measures 20%–30%, the precipitation of PVA from the solution occurs at 30–35 °C. If the content of acetate groups is more than 50%, such a PVA becomes insoluble in water.

Numerous products exist commercially that boast different degrees of hydrolysis and various molecular weights. For instance, to permit easier orientation, the German manufacturer Clariant GmbH labels its range of products by number, as follows: Mowiol[®] X-Y; where X indicates viscosity (Pa.s) corresponding to molecular weight, and Y denotes the degree of hydrolysis (SH) of the said PVA.

PVA is also interesting from a biological perspective, as it is highly reminiscent of gelatine in behaviour. Consequently, it has been widely adopted in the medicinal sphere, among others, because the human organism is able to tolerate it without difficulty. Nevertheless, it has been reported that in such medicinal use, under certain circumstances, products boasting a high degree of polymeration may prove toxic to the human organism.

In terms of environmental protection, the aforementioned stereo regularity is also crucial, i.e., the arrangement of the polyvinyl alcohol chain that affects PVA synthesis. This was investigated by Fukae et al. (1994), who monitored the biodegradation of syndiotactic and isotactic PVA by micro-organisms present in activated sludge and by cultures adapted to PVA and identified as *Pseudomonas* sp. A-41. The said authors confirmed that enzymatic systems are more efficient in attacking arranged sequences and lesser polymeric fractions. PVA with high isotacticity (prepared in a laboratory) was easier to degrade in comparison with commercial PVA (Poval[®]HC, Kuraray Co. Ltd, Japan).

It is worth emphasizing the capacity PVA to adsorb into soil particles and naturally occurring minerals (Chiellini et al., 2000). Indeed, such naturally occurring minerals are often used as nano-fillers when preparing nano-composites based on PVA. According to research by Spiridon et al. (2008) and Tang et al. (2008), the given content of nano-fillers of the montmorillonite/diatomaceous earth type may negatively affect the biodegradability of such a nano-composite.

Polyvinylpyrrolidone (PVP, Povidone[®], Polyvidone[®], Povidonum[®], Kollidon[®], E 1201) was patented by W. Repp in 1939. Under conditions of normal temperature and pressure, PVP takes the form of a white or pale yellow powdery material, varied in particle size. Chemically, it is a polymeric lactam with an internal acid bond and is classified as a poly-N-vinylamide. Its amphoteric characteristic (Antić et al., 2011) is an important quality, which is determined by the structure of the monomer unit (Fig. 1). The heavily polar amide group boasts hydrophilic and polar properties. Non-polar methylene groups in the main chain and ring possess hydrophobic properties. The substances in which PVP dissolves well include water. Indeed, as molecular weight

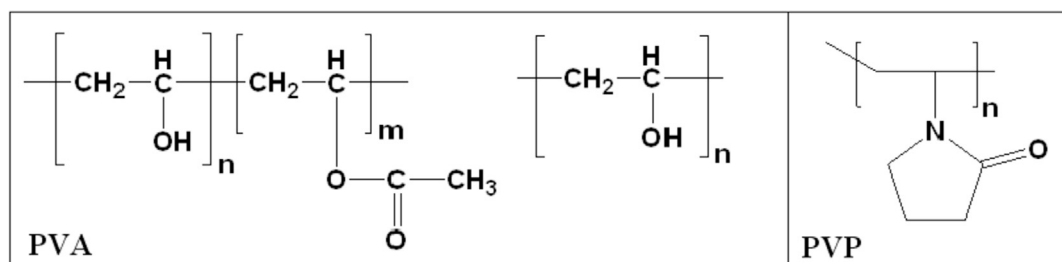


Fig. 1. Chemical structure of PVA (partially hydrolyzed – left, fully hydrolyzed – right) and PVP.

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