Poly(Vinyl Alcohol) Membrane Systems for the Controlled Release of Chlorinated Isocyanurates

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SYNOPSIS

The applicability of membrane-reservoir devices based on cold water insoluble, fully hydrolyzed poly(vinyl alcohol) (PVA) membranes for the controlled release of chlorinated isocyanurates into aqueous media has been demonstrated. In addition to providing a prolonged constant rate of release, fully hydrolyzed PVA membranes also exhibit good stability in the presence of saturated solutions of chlorinated isocyanurates. The apparent resistance to degradation by chlorine and the significant retention of wet mechanical strength of these membranes have been attributed to the semicrystalline nature of PVA. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Chlorinated isocyanurates, because of their bactericidal and algicidal properties, have been commonly employed as topical antiinfectives[1] and disinfectants for water cooling systems or swimming pools.[2] A cyanurate-stabilized hypochlorite system, derived either from cyanuric acid plus a suitable source of hypochlorite chlorine or from one of the chlorinated isocyanurates, has been shown to be one of the most effective systems for water disinfection.[3] Conventional delivery methods for such chlorinated isocyanurates generally rely on the direct dissolution of solid active ingredients in water. In some cases, mechanical means such as a perforated plastic pouch and canister, and other types of flow-restraining devices are used to regulate the dissolution rate of these chlorinating agents. Because dissolution depends to a large extent on the solid shape and surface area as well as flow rate, pH, and temperature, a first-order release mode with a diminishing release rate is generally observed, primarily due to the decrease in solid surface area with time. As a result, an excess amount of chlorinating agent is usually delivered at the beginning and an insufficient chlorine level is subsequently experienced at a later stage.

When dissolved in water, chlorinated isocyanurates provide both cyanuric acid and available chlorine in the form of hypochlorous acid, HOCl, according to the hydrolysis scheme similar to the one given below for trichloroisocyanuric acid:

$$HOCl \rightleftharpoons H^+ + ClO^-$$
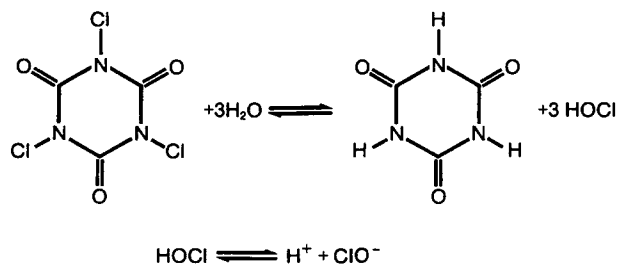
Here, the resulting hypochlorous acid acts as the bactericide and algicide in water treatment. For effective disinfection purposes, the presence of a minimum level of available chlorine is generally required. However, because of the continuous elimination of available chlorine by various environmental factors such as temperature fluctuations, exposure to sunlight, wind, and organic contaminants, it is often desirable to deliver the chlorinating agent at a uniform rate in order to replenish and maintain the required chlorine level. This can be achieved potentially with a membrane-reservoir system capable of providing a prolonged zero-order release (or constant-rate release) via the rate-con-

trolling membrane as long as a saturated reservoir of active ingredient can be maintained.[4] In the present case, the relatively low solubility of chlorinated isocyanurates makes them particularly suitable for such delivery devices to maintain a saturated reservoir.

A viable membrane for the controlled release of chlorinated isocyanurates into the aqueous environment has to exhibit strong mechanical strength both in the dry and wet state, good resistance to chlorine oxidation and pH changes, and a reasonable chlorine release rate. We have found that among various commercially available polymers, the cold-water insoluble, fully hydrolyzed poly(vinyl alcohol) (PVA) appears to meet most of the above requirements as a suitable membrane material. In this paper, we report the diffusional release and stability characteristics of such a PVA membrane system for the controlled release of chlorinated isocyanurates.

EXPERIMENTAL

Materials

Trichloroisocyanuric acid (ACL-85), sodium dichloroisocyanurate (ACL-60), potassium dichloroisocyanurate (ACL-59), and monotrichlorotetra-(monopotassium dichloro)-isocyanurate (ACL-66) were obtained from Monsanto. Calcium hypochlorite was obtained from Aldrich. The amount of available chlorine that the chlorinated isocyanurates yield in solution is generally characterized in their grade designation by the manufacturer. For example, ACL-85 provides about 85% available chlorine in solution. As a comparison, calcium hypochlorite provides about 65% available chlorine.

Cold-water insoluble PVA membranes of thicknesses ranging from 0.05 to 0.13 mm were obtained as general purpose and mold release 1-000 series PVA films from Mono-Sol Division, Chris Craft Industries, Inc. These films contained about 16% polyol plasticizer and were all based on fully hydrolyzed PVA (M_w of 115,000; M_n of 40,000; and a dispersity of about 2.9 as determined by gel permeation chromatography). The equilibrium water swelling of these PVA films was about 60%, corresponding to a crystallinity of about 30%.[5-7] These films exhibited heat sealability and extremely high dry tensile strength.

Methods

The release systems studied were in the form of PVA membrane pouches containing powdery or granular

chlorinated isocyanurates. The dry PVA pouches were carefully vacuum-sealed on a laboratory heat-sealer. Pouch dimensions ranging from 2 × 2 cm to 18.7 × 18.7 cm and loadings of chlorinating agent ranging from 5 to 453.6 g were used. The release experiments were carried out by suspending the PVA pouches in well-stirred water tanks with capacities ranging from 1 to 32 gal to ensure the minimization of boundary layer effect and the approach to a perfect sink condition. Aliquots were taken periodically and the concentrations determined on a Beckman ACTA C-III UV-visible spectrophotometer. For cyanuric acid, the solutions were buffered to pH 8 and absorbances read at 214 nm. For hypochlorous acid, a method based on the quantitative oxidation of methyl orange in acidic solution and subsequent measurement of the loss of absorbance at 507 nm was used.[8] The tensile strength of wet PVA membranes was measured on an Instron Model 1123 Tensile Tester following Test Method A (a static weighing, constant-rate-of-grip separation test) of the ASTM D-882 standard test methods. All experiments were carried out in triplicate at 25°C.

RESULTS AND DISCUSSION

Release experiments using chlorinated isocyanurates have been conducted on pouches made of initially dry PVA membrane of different thicknesses. As expected, the results show prolonged constant-rate release behaviour up to 80% or more of the total release for the duration when a saturated reservoir was maintained. Typical cumulative and rate data for the release of ClO^- and cyanuric acid from a ACL-85/PVA membrane system are shown in Figures 1 and 2. Other release results comparing the effects of active agent solubility, PVA membrane thickness, loading-to-pouch volume ratio, and added NaCl are summarized in Table I, where the pouch volume is calculated from an equivalent spherical volume in a fully expanded pouch of known dimension. Because a finite amount of osmotic water uptake will occur in the reservoir, above a threshold loading-to-volume ratio, the resulting increase in internal pressure may eventually lead to pouch failure. Thus, the loading-to-volume ratio determines not only the duration of the release but also the stability of the PVA pouch. In the present study, the loading-to-volume ratios were kept below a threshold range of 0.64–0.8 g/cm³.

In the dry state, unplasticized PVA has a glass-transition temperature (T_g) reported to be between 70 and 80°C that is reduced to near room temper-
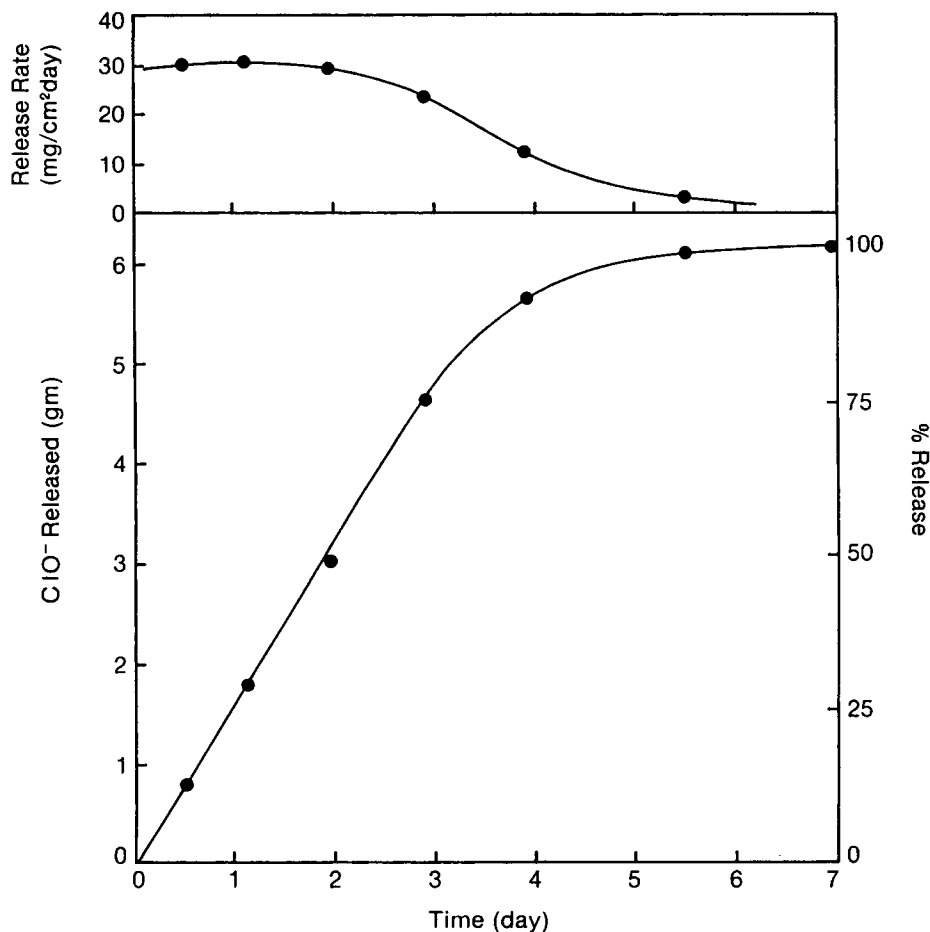
Figure 1   Release of ClO$^-$ from ACL-85/PVA membrane system. Loading: 9.1 g; loading/ volume: 0.16 g/cm^3; PVA dry thickness: 0.08 mm.

ature with 15% glycerol as plasticizer.[9] Under normal ambient temperature, the present PVA pouch is practically impermeable to most gaseous material due to the low gas permeability of PVA [$< 10^{-13}$ cm^3 · cm/cm^2 · s · cmHg; at least 1–2 orders of magnitude less than that of poly(vinylidene chloride)][9,10] hence eliminating the irritating fumes during the direct handling of the chlorinating agent. In the wet state, water plasticizes the PVA membrane by lowering its T_g and thereby increases the diffusion rate of active ingredients through the membrane to a useful level. It has been reported that the T_g of unplasticized PVA can be lowered to room temperature, with only 6% by weight of water.[11] In the fully swollen state, PVA films become rubbery with an elongation of over 240%.[9] Upon activating by water, such a PVA pouch containing chlorinated isocyanurates of limited solubility can achieve a constant release for a prolonged period of time by providing a constant diffusional driving force

across the PVA membrane. From Fick's law of diffusion, it can be shown that the steady-state membrane diffusion rate is directly proportional to the concentration difference across the membrane and inversely proportional to the membrane thickness.[4,12] In other words, the release rate is directly related to the concentration gradient across the membrane. In the present system, the ability to maintain a saturated reservoir, and therefore a constant concentration gradient, is directly responsible for the observed zero-order release.

As shown in Table I, the ClO$^-$ release rate is observed to increase with decreasing membrane thickness and increasing solubility of the chlorinated isocyanurate, as would be predicted from the resulting changes in the diffusional driving force. Here, the concentration gradient is increased by either reducing the membrane thickness or increasing the upstream concentration (i.e., solubility). Thus, for a given PVA membrane thickness, the release rate
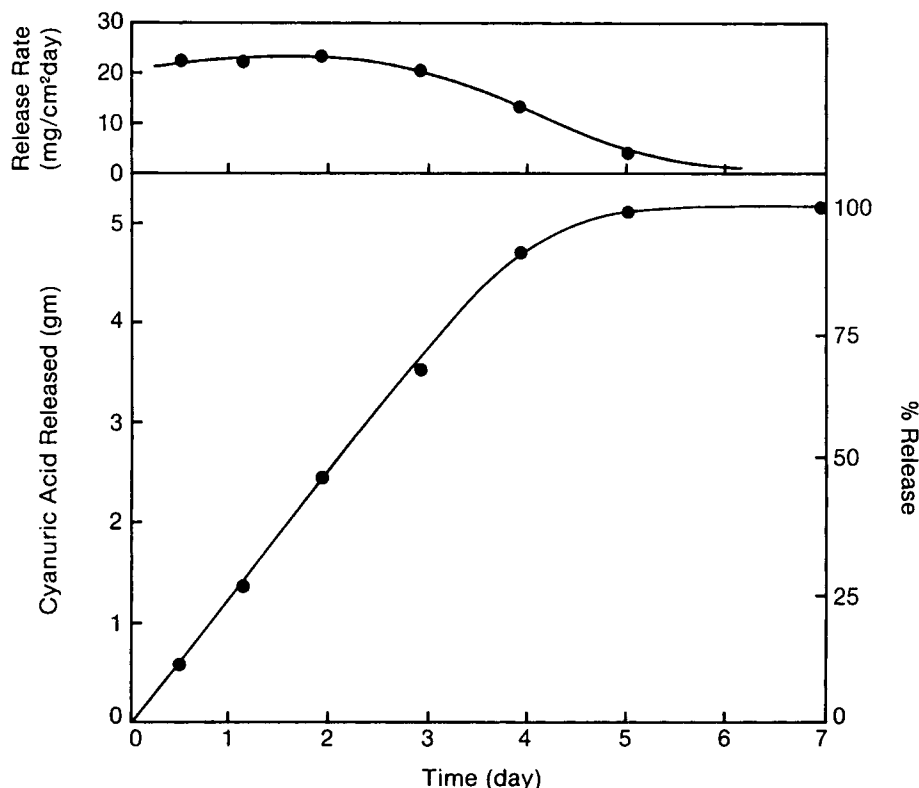
Figure 2   Corresponding release of cyanuric acid from ACL-85/PVA membrane system of Figure 1.

from the ACL-85/PVA membrane system is the smallest followed by that from the ACL-66, ACL-59, and ACL-60 systems, consistent with the increasing trend in their respective solubilities. The release results for a 20/80 ACL-85/ACL-59 mixture have also been included in Table I since this physical mixture has the same chemical composition as that of ACL-66. The resulting ClO⁻ release rate appears to be slightly higher for the physical mixture as a result of its higher aqueous solubility. The transition period required for the initially dry PVA membrane to become fully swollen and for ClO⁻ to diffuse across the swollen membrane will vary according to the solubility of the chlorinated isocyanurate and the thickness of the PVA membrane. Typically, periods of up to 1 h may be required to initiate the release. The incorporation of a small amount of NaCl into the reservoir of chlorinated isocyanurate has been found to reduce the initial release time lag substantially by facilitating the osmotic water intake. The release results of ACL-66 in the presence of various amounts of NaCl are also included in Table I. A comparison of ACL-66 release data, with and without added NaCl, shows that the incorpo-

ration of NaCl causes a slight increase in ClO⁻ release rate when the amount of NaCl is low (5–10%). Apparently, the facilitation of osmotic water intake by the added NaCl promotes more efficient contact between the reservoir and the PVA membrane. However, at higher NaCl contents, the ClO⁻ release rate appears to decrease somewhat with increasing NaCl content, possibly a consequence of the more rapid osmotic dilution of the reservoir.

The physical integrity of PVA membranes in contact with saturated solutions of various chlorinated isocyanurates has also been examined. The test results are presented in Table II. The failure of PVA pouches in contact with calcium hypochlorite and the relatively short stability limit for PVA pouches containing trichloroisocyanuric acid are attributed to polymer erosion and degradation resulting from the extreme solution pH of these compounds and their strong oxidizing power. The oxidation of PVA is known to be facilitated under such extreme acidic or alkaline conditions.[9] To further examine the corresponding changes in mechanical strength, a tensile test based on Method A of the ASTM D-882 standard test methods was conducted on wet PVA mem-

Table I   Release Characteristics of Chlorinated Isocyanurates From PVA Membrane Systems

Compound	Solubility (%)	PVA Dry Thickness (mm)	Loading (g)	Loading/ Volume (g/cm³)	NaCl Content (%)	ClO⁻ Release Rate (mg/cm²·day)
ACL-85	1.2	0.08	5	0.29	—	30.97
		0.10	5	0.29	—	23.21
ACL-60	25	0.08	23.6	0.59	—	261.20
ACL-59	11	0.08	10	0.44	—	81.04
		0.10	6.8	0.40	—	64.03
ACL-85/ACL-59		0.08	8.2	0.35	—	51.45
Mixture (20/80)	3.1	0.10	6.8	0.50	—	39.32
			10	0.55	—	37.31
ACL-66		0.08	3.2	0.31	—	48.95
	2	0.08	3.2	0.35	—	43.04
		0.08	10	0.43	—	49.30
		0.10	5.9	0.18	—	24.00
ACL-66 with		0.08	5	0.44	5	51.00
NaCl		0.08	10	0.12	10	53.95
		0.08	10	0.64	15	58.27
	2	0.08	10	0.48	20	45.26
		0.08	10	0.46	30	44.80
		0.10	5	0.20	5	25.95
		0.10	5	0.23	5	29.34
		0.10	5	0.37	5	38.07

branes that had been in contact with saturated solutions of various chlorinated isocyanurates for 2 weeks. From results shown in Table III, it is clear that the wet tensile strength of PVA membrane is reduced to less than 20% of the original in the ACL-85 treated system whereas about 50–60% of the original tensile strength is retained in the ACL-66 and ACL-85/ACL-59 mixture treated systems. Such apparent resistance to degradation by chlorine and the significant retention of wet mechanical strength can be directly attributed to the semicrystalline nature of the present PVA membranes. Here, the PVA crystallinity is estimated to be about 30% from its initial equilibrium water swelling of 60%, based on the correlation reported.[5–7] These semicrystalline PVA membranes are most likely undergoing both oxidative chain scission and dissolution of crystalline regions in concentrated solutions of chlorinated isocyanurates, similar to the effect generated by concentrated hydrogen peroxide as reported by us recently.[7] The rates of both these processes and the initial crystallinity of PVA will undoubtedly determine the extent of wet mechanical strength.

To investigate the extent of applicability of these PVA pouches in water chlorination, we also carried out scaled-up release experiments in 10- and 32-gal water tanks with a constant water overflow of 300 mL/min to simulate the elimination process. The PVA pouches, containing 453.6 g of ACL-66 each with or without 10% added NaCl, were constructed from 0.10-mm thick PVA membrane. The loading to volume ratio was 0.25 g/cm³, well below the stability threshold value. As shown in Figure 3, the resulting hypochlorous ion levels are quite uniform for a period over 10 days. No pouch failure was observed during the entire releasing period. The slightly higher ClO⁻ level here for the system containing 10% NaCl is in agreement with the observed increase in ClO⁻ rate at low levels of added NaCl (Table I).

In summary, the feasibility of utilizing cold-water insoluble, fully hydrolyzed PVA membranes for the controlled release of chlorinated isocyanurates has been demonstrated. The apparent resistance to disintegration by chlorine and the significant retention of wet mechanical strength of PVA membranes after prolonged contact with saturated solutions of chlorinated isocyanurates, has been attributed to the semicrystalline nature of PVA. By controlling the PVA membrane thickness, area, and loading of active agent, various release rates and duration have been achieved. This heat-sealable PVA membrane

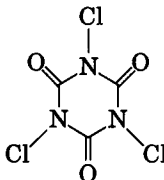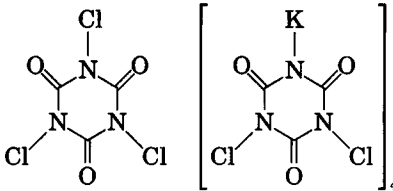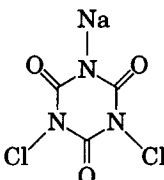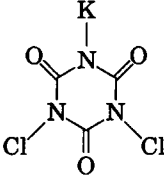**Table II   Stability of PVA Membrane in Saturated Solutions of Chlorinated Isocyanurates**

Compound	Solubility (%)	pH of Saturated Solution	PVA Dry Thickness (mm)	Time to Pouch Failure (Days)
Trichloroisocyanuric acid (ACL-85)	1.2	2.6–3.0	0.05 0.08 0.13	10 24 30
Monotrichloro-tetra(monopotassium dichloro)–isocyanurate (ACL-66)	2	4.4–4.6	All	Stable indefinitely
Sodium dichloroisocyanurate (ACL-60)	25	7.0	All	Stable indefinitely
Potassium dichloroisocyanurate (ACL-59)	11	6.0	All	Stable indefinitely
Ca(OCl)$_2$Calcium hypochlorite	>25	12.3	All	Rapid disintegration

Table III   Tensile Strength of Swollen PVA Membranes

Sample	Wet Thickness (mm)	Tensile Strength ($\times10^6$ N/m^2)
PVA control	0.09	3.63
PVA treated with ACL-66 + 10% NaCl	0.08	1.28
PVA treated with ACL-66 + 10% NaCl	0.11	1.41
PVA treated with ACL-85/89 (20 : 80)	0.08	1.63
PVA treated with ACL-85	0.08	0.66

All samples except the control were treated with saturated ACL formulations in water for 2 weeks.

system offers the advantage of eliminating over-chlorination generally associated with a simple dissolution system while maintaining a constant available chlorine level for an extended and prescribed period of time. In addition, the gas impermeable nature of dry PVA membrane makes the elimination of irritating fumes and direct handling of chlorinating agent by the present PVA membrane system an added advantage.

The applicability of this PVA membrane system is not limited to the controlled release of chlorinating agent. In fact, it is useful in the controlled release of a variety of water-soluble active ingredients such as herbicides, insecticides, disinfectants, chelating agents, detergents, and dye stuffs into aqueous media.[13]
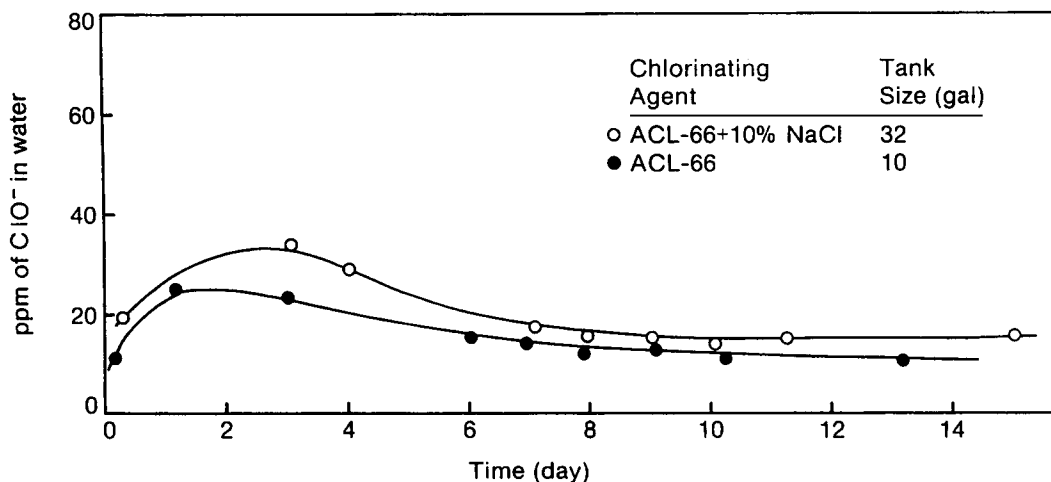
Figure 3   Release characteristics of ACL-66 from scale-up PVA membrane systems. Flow rate: 300 mL/min; loading: 453.6 g; loading/volume: 0.25 g/cm^3; PVA dry thickness: 0.10 mm.

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