

Slow Release of Water-Soluble Salts from Polymers

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Synopsis

Release rates of NaCl and NaF from mixtures with polystyrene, polyethylene, thermosetting polyester, and crosslinked polyethylene have been studied. Salt/polymer granules were prepared by melt mixing under different conditions. The release process was studied in batch as well as continuous systems. The salt release from polymer into water depends on such parameters as salt content, temperature, water flow rate, and salt particle size.

INTRODUCTION

The idea of coating solid particles for protection or to control release is not new.^{1,2} Small amounts of solids, liquids, or gases can be enclosed by microencapsulation techniques to yield capsules ranging from a micron to a centimeter in diameter. The encapsulation techniques can be applied to systems containing nutrients, vitamins, drugs, deodorants, pesticides, fertilizers, etc.

Water-soluble inorganic salts dispersed in polymers can be leached out when the polymer/salt particles are brought into contact with water. This idea was employed by Fossey³ to produce polyethylene foams and by Gregorian⁴ to prepare crosslinked microporous polyolefin films. Long periods were required to leach out dispersed NaCl particles from polyethylene, and essentially open-cell foams were formed. Fossey suggests that the open-cell structure is due to osmotic pressure buildup in the cells (which become filled with concentrated NaCl solutions) resulting in bursting of the cell walls. The exact mechanism of salt release from the polymer is still in doubt, and the relative roles of bursting as opposed to diffusion or other factors are a subject for future studies.

Water chemists are interested in methods for dosing of chemicals into water by passing it through packed columns. Packed columns are often used in water treatment units where chemical reactions (ion exchange) as well as physical separations (adsorption on carbon black) take place.

In the present paper, preliminary data are presented on polymer/salt model systems. One of the end goals of this research will eventually be to conclude whether specific water treatment steps can be executed in packed columns functioning on the principle of controlled release.

EXPERIMENTAL

Granules of polystyrene (PS) and polyethylene (PE) with sodium chloride or sodium fluoride particles were prepared by mixing on a heated two-roll mill and

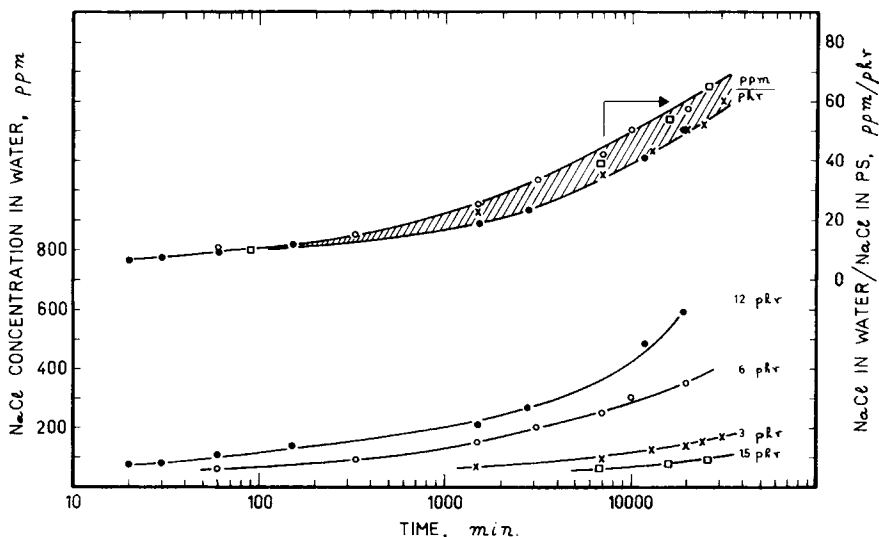


Fig. 1. NaCl release from PS/NaCl samples into a fixed volume of water.

subsequently grinding in a plastic mill. Several samples were mixed on the two-roll mill, followed by extruding and granulating. In addition, a mixture of polyethylene, peroxide, and NaCl was mixed on the two-roll mill to yield rough sheets which were then crosslinked in a compression mold. Polyester/NaCl samples were prepared by casting liquid polyester containing dispersed NaCl particles between glass plates. The plaques obtained were then ground. NaCl or NaF was used in concentrations up to 12 parts salt per 100 parts polymer (phr).

Salt concentration in water solution was measured with a Methron conductivity instrument using various types of electrodes, including a very sensitive one for dilute solutions (about 1 ppm).

Salt release experiments were carried out in batch and continuous systems. A batch system consisted of a 250-cc beaker containing 2 g polymer/salt granules, 200 cc water, and a magnetic stirrer. A continuous system consisted of a 1.6-cm-I.D. glass tube (tube and shell type) packed with 20 g polymer/salt particles. Water was pumped into the packed tube at a rate of 250 cc/hr from a constant-temperature bath. Water maintained at the same temperature was pumped from a separate reservoir through the annulus to keep the column at a constant temperature.

Salt content in the polymer/salt granules before and after contact with water was determined by drying at 105°C followed by combustion at 600°C.

RESULTS AND DISCUSSION

The phenomenon of releasing chemicals dispersed in polymers can be used to produce plastic foams, porous pipes, and membranes as well as dosing systems based on controlled release. Release is a serious drawback in cases where the presence of a dispersed chemical in a plastic is vital to its specific role. Understanding of the mechanism of migration is important for preparation of improved products of better slow-release characteristics on the one hand and practically no migration on the other.

In the present work, the feasibility of polymer/salt model pairs as controlled-release systems has been studied. The parameters investigated were those which seemed to have a major influence.

The effect of salt concentration in a polymer on its release rate into water was studied in batch as well as continuous experiments. Figure 1 exhibits data on PS/NaCl samples which release NaCl into a fixed volume of water so that the salt concentration in the water increases with time. Qualitatively, it is clear that higher NaCl contents in polystyrene result in higher concentrations in water after equal periods of time. The data of Figure 1 are replotted as shown by the upper curve in that figure. In this case, NaCl concentration in water (ppm) divided by the initial corresponding concentration in polystyrene (phr) is plotted versus time and, for practical purposes, a single curve is obtained. Thus, the relative NaCl concentration as defined (ppm/phr) increases with time in the closed system and is practically independent of the initial NaCl content in polystyrene. This conclusion was further verified in continuous experiments; results are shown in Table I for the two extreme salt concentrations studied, i.e., 1.5 and 12 phr NaCl.

TABLE I
Effect of Initial NaCl Content in Polystyrene on its Release into Water^a

Time, min	NaCl in water discharge, ppm		NaCl ratio, ppm (12 phr)/ ppm (1.5 phr)
	12 phr sample	1.5 phr sample	
5	1970	460	4.3
15	440	65	6.8
25	280	40	7
35	213	25	8.5
45	173	19	9.1
55	148	18	8.2
85	118	13	9
105	81	10	8.1
135	71	9	7.9
165	64	7	9.1
210	43	4.5	9.5
270	26	4	6.5

^a Water flow rate, 250 cc/hr; water temperature, 21°C.

TABLE II
Residual Salt in Various Polymers^a

Polymer	Initial NaCl, phr	Time, weeks	Residual NaCl, %
PS	1.5	8	20
PS	3	8	20
PS	6	6	16
PS	12	6	22
PE	10	2	93
CLPE	10	2	84
Polyester	10	4	82

^a Batch experiments: 2 g particles/200 g water; water temperature, 21°C.

The ratio of initial NaCl concentrations in polystyrene is equal to 8 (12/1.5). Table I shows that roughly the same ratio is obtained for the corresponding NaCl concentrations in water. In a continuous system, therefore, the relative NaCl concentration (ppm/phr) in the discharge water decreases with time and is practically independent of the initial NaCl content in PS. Samples of granules were taken from the columns after 6 hr of continuous operation, and their salt contents were determined by drying and subsequent combustion at 600°C. The residual NaCl concentrations found in PS were 77% and 81% for the 1.5- and 12-phr samples, respectively. This result again confirms that the relative concentration of NaCl is independent of initial NaCl content in PS. The same conclusion is also clear from determinations of residual NaCl in PS granules which were in contact with fixed amounts of water for long periods, as shown in Table II. The residual NaCl contents in PS are roughly independent of their initial contents.

Table II also summarizes data for polyethylene, crosslinked polyethylene (CLPE), and thermosetting polyester. It is evident that the type of polymer

TABLE III
Continuous Experiment Showing Constant NaCl Release from 8 Hours to 7 Days.
Polyester/NaCl Sample^a

Time	NaCl in water discharge, ppm
5 min	5680
15 min	2780
43 min	650
78 min	180
120 min	46
215 min	16
330 min	7.5
8 hr	5.5
25 hr	5.5
51 hr	5.5
5 days	5.5
6 days	5.5
7 days	5.5

^a Flow rate, 250 cc/hr; temperature, 32°C.

TABLE IV
Effect of Flow Rate on NaF Release from PS^a

Time, min	NaF in water discharge, ppm		NaF ratio, ppm ($Q = 250$)/ ppm ($Q = 1200$)
	$Q = 250$ cc/hr	$Q = 1200$ cc/hr	
15	855	16	53
25	435	15	29
35	170	12	14
65	57	11	5.2
85	37	9	4.1
120	30	7	4.3

^a 10 phr Sample; temperature, 32°C. Q = flow rate.

being used has a significant influence on the ease of salt release into water. The data, although of a preliminary character, show that polyethylene binds NaCl best. The retention capability of polymers given in Table II is found as follows in descending order: PE > CLPE > polyester > PS. The exact location of CLPE in this series will be reexamined since its behavior in release is expected to depend on its crosslinking degree.

One of the most important practical conclusions of the present work is that, in continuous experiments, the NaCl concentration in the discharge water attains a constant value after certain periods of time depending on the specific polymer/salt system and operating conditions. In the present investigation, constant rates of release were achieved after 6 to 48 hr of continuous operation and extended for rather long periods (in terms of weeks) thereafter. The concentration plateau region is shown in Table III for a polyester NaCl sample. The number of experiments carried out for long periods of time is still very limited, and the relationship of the plateau value to the initial NaCl content in the polymer is still to be assessed.

The effect of water flow rate through the packed column is shown in Table IV. As expected, at a higher flow-rate of water, the NaCl concentration in the discharged water is reduced. The ratio of flow rates shown in Table IV is 4.8, and similar NaCl concentration ratios are obtained in the 65- to 120-min range. Nevertheless, quantitative relationships describing the effect of flow rate on salt release are still lacking.

The effect of water temperature in flow systems is shown in Table V. Again as expected, at the higher temperature more salt is released. The size of NaCl particles affects the release process; however, the picture is incomplete. In some cases the concentration-time curves intersected, and narrow size ranges will, therefore, be used in future experiments.

Finally, it should be noted that methods and conditions of preparation of the polymer/salt granules are also important. Roll-milled and extruded samples exhibited increased retention compared with samples that were roll milled only. The molding pressure is also important, with increased retention for higher pressures. Thermosetting polyester contains polar groups, and it is cast at atmospheric pressure so that easier salt release might be expected; however, the experimental evidence contradicts this (compare polyester with PS in Table II).

TABLE V
Effect of Temperature on NaF Release from PS^a

Time, min	NaF in water discharge, ppm		NaF ratio, ppm ($T = 50^\circ$) / ppm ($T = 32^\circ$)
	$T = 32^\circ\text{C}$	$T = 50^\circ\text{C}$	
5	640	990	1.5
15	270	360	1.3
25	205	250	1.2
35	145	205	1.4
45	72	140	2
55	47	96	2
85	23	39	1.7
140	9	28	3.1

^a 6 phr Sample; flow rate, 250 cc/hr.

It is, therefore, likely that the three-dimensional structure of the matrix is the controlling factor in this case.

The research reported herein is of a preliminary nature. More experimental data are required in order to better assess qualitative trends and quantitative relationships wherever possible.

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