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Project Summary

Fundamental Approach to Service Life of Flexible Membrane Liner's (FML's)

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Predicting the service life of flexible membrane liners (FML's) exposed to chemicals has usually been done by physical or mechanical changes after exposure. The report summarized here presents an alternative approach--that to water for periods up to fifteen months were tested by five different chemicals and transport related measurements. The results indicated that monitoring the transport properties of FML's exposed to particular chemicals over a reasonable exposure time could be considered as one possible method for predicting an FML's lifetime.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Because of the extremely large amounts of waste disposed to landfills each year, it is essential that when FML's are the liner of choice, they be sound. Predicting the service life of FML's exposed to chemicals has been attempted by measuring physical or mechanical property changes after periodic exposure times (EPA 9090). Here five different mass transport measurements are evaluated as a function of exposure time to simple chemicals.

Experimental Design

Four experimental techniques were employed:

1. Water vapor transmission (WVT)
2. Diffusion coefficient determinations
   - Water absorption (WA)
   - Water vapor absorption (WVA)
   - Radioactive tracer measurement (RT)
   - Benzene adsorption (BA)
3. Microstructural observations
4. Differential scanning calorimetry (DSC)

Four FML's were chosen for the study:

1. Polyvinyl chloride (PVC)
2. Chlorinated polyethylene (CPE)
3. Ethylene propylene diene monomer (EPDM)
4. High density polyethylene (HDPE)

Five liquids were used:

1. Water, as a control
2. 10% sulfuric acid (in water), a strong acid solution
3. 10% sodium hydroxide (in water), a strong base solution
4. 100% xylene, a common solvent
5. 10% phenol (in water), a common and troublesome byproduct of many commercial processes.

The FML's were taken from the exposure tubs, cut to the appropriate size for measurement, and sealed in properly identified plastic bags. Before actual measurements, many samples were taken from the plastic bags and desiccated in a vacuum desiccator for 1 month to attempt to ensure they were completely dry.

Water Vapor Transmission

To see if changes indicating instability of the FML structure could be observed, WVT tests were run according to ASTM E-96-80. A commercial humidity/temperature chamber was used to maintain the required ASTM temperature and humidity environment.

Diffusion Coefficient Determinations

There are no standard tests for diffusion coefficient determinations. Following a literature survey, the methods researchers found most satisfactory and reliable were used.

Water Absorption

To determine the diffusion coefficient of water in a particular FML, the FML was immersed in water and the weight gain was monitored as a function of time.

Water Vapor Absorption

The WVA test followed that of the liquid WA test. Instead of suspending an FML directly in a controlled temperature bath, however, the FML was placed in a separate glass cylinder with water in the bottom; this, in turn was suspended in the water bath. This, 100% humidity conditions were present, and water vapor entered the FML as a function of time. The increase in weight was plotted against time.

Radioactive Tracer Measurements

RT measurements were employed to determine the diffusion coefficient of a particular molecule. Although tritiated water would be the preferred diffusant, it is difficult to work with. Benzene with ^{14}C was, therefore, used. Although benzene is a very good swelling agent for rubber-type materials and swelling agents have unusually high values for apparent diffusion coefficients, the method's value is not lessened because it does determine the relative changes in diffusion properties of PVC, EPDM, and CPE samples.

Benzene Absorption

BA was used (in Phase II) for HDPE because HDPE has a low solubility. Relatively large amounts of radioactivity would have been needed to produce a high enough count rate for the Geiger-Mueller tube detection used here.

Microstructural Observations

To see if severe chemical attack could be monitored on a small (microstructural) scale with the use of SEM (Scanning Electron Microscopy), observations were made on as-received PVC and on PVC exposed to methylene chloride.

Differential Scanning Calorimetry Measurements

DSC measurements were made to see if a chemically induced structural change could be detected with this method.

Six-Month Exposure Results, Phase I

The six-month exposure results for WVT and for RT are summarized in Table 1.

Water Vapor Transmission

For PVC, exposure to NaOH and H_2SO_4 had little effect on the WVT; phenol and xylene, which leach plasticizer from PVC, definitely lowered the WVT. For EPDM, exposure to the four chemicals had little effect on the WVT, but phenol exposure significantly increased WVT. Because xylene destroyed CPE in a few days, no results are given for CPE and xylene. Thus, the WVT depended on the chemical to which the FML was exposed.

Diffusion Coefficient

Water Absorption and Water Vapor Transmission

Because the FML's did not in general achieve a constant equilibrium weight during a long immersion time and because the diffusion coefficient cannot be determined without this final weight, WA and WVA presented problems. The uptake process was more complicated than simple diffusion and may be complicated by surface absorption effects. These and other problems made WA and WVA unreliable methods with which to determine diffusion coefficients of water in commercial FML's.

Radioactive Tracer

For PVC, the results genera agreed with those for WVT: exposure acid and base do little to the diffusi coefficient, but leaching agents (phe and xylene) leach out the plasticizer a the PVC becomes stiffer and the diffusi coefficient is reduced.

For EPDM, the results agre exactly with those for WVT with resp to relative change. Unfortunately, t agreement for PVC and EPDM do r extend to CPE. Agreement for acid a base are good, but for phenol t agreement is poor.

Microstructural Observations

SEM photos of samples soaked methylene chloride for various times (o minute to ten minutes) and magnifie 100, 300, and 3000 times indicated change. Although these observatio were preliminary, the results showed little promise that further work in this ar was halted.

Differential Scanning Calorimeter Results

That xylene removes plasticizer fr PVC is seen vividly on the DSC trac After one month's exposure, the mate is noticeably stiffer and shows a ve definite glass transition. The DSC resu for CPE exposure to phenol are al shown. The structure becomes evid as the CPE is exposed to phenol o month, three months, and six mont The longer the exposure, the mo structure in the DSC traces.

Fifteen-Month Exposure Results, Phase II

The fifteen-month results from Pha II are summarized in Table 2. Becau Table 2 involved different lots of t same FML (as were used in Phase I), t two sets of data cannot be present together on a continuous basis.

The exposure matrix for Phase included the following:

HDPE was exposed to water, NaO H_2SO_4, phenol, and xylene,

CPE was exposed to water, NaO H_2SO_4, and phenol; and

EPDM, PVC, CPE, and HDPE we exposed to water.

Table 1. *Percent Change (from 0 to 6-mo. exposure) in Transport Properties for WVT[a] and RT[a]*

FML	WVT % Change	WVT Data Trend at 6 Mo.	RT % Change	RT Data Trend at 6 Mo.
PVC:				
H_2SO_4	+12%	Steady	+4%	Steady
NaOH	+10%	Steady	-11%	Steady
Phenol	-30%	Steady	-50%	Steady
Xylene	-25%	Steady	-85%	Steady
EPDM:				
H_2SO_4	+138%[b]	Rising[b]	+37%	Rising
NaOH	+1000%	Steady	+20%	Steady
Phenol	+70%	Steady	+17%	Steady
Xylene	-[c]	-[c]	-[c]	-[c]
CPE:				
H_2SO_4	+54%[b]	Steady	+15%	Rising
NaOH	+46%	Steady	-11%	Steady
Phenol	+260%[b]	Rising[b]	-9%	Steady
Xylene	-[c]	-[c]	-[c]	-[c]

[a] Water vapor transmission, radioactive tracer
[b] An arbitrary, but reasonable, criteria for a degrading effect from a particular exposure is a large, absolute increase and a continuing upward trend at 6 mo.
[c] No data; xylene destroyed CPE after a few days

Table 2. *Percent Change (from 0 to 15-mo. exposure) in Transport Properties for WVT[a], and RT[a], and BA[a]*

FML	WVT % Change	WVT Data Trend at 15 Mo.	RT % Change	RT Data Trend at 15 Mo.
PVC:				
H_2SO_4	-28%	Rising	+50%	Decreasing
NaOH	-25%	Rising	+42%	Decreasing
Phenol	+56%	Rising[b]	+100%	Rising[b]
Water	-25%	Steady	+44%	Rising
HDPE:				
H_2SO_4	-12.5%	Rising[b]	+23%	Steady
NaOH	+12.5%	Decreasing	+54%	Rising
Phenol	+12.5%	Steady	+23%	Decreasing
Xylene	-12.5%	Decreasing	+23%	Steady
Water	-12.5%	Rising	+23%	Steady
FML's in Water:				
EPDM	0%	Steady	+35%	Steady
PVC	-5%	Steady	+6%	Steady
CPE	-29%	Steady	+50%	Steady
HDPE	0	Steady	+50%	Steady[c]

[a] Water vapor transmission; radioactive tracer; benzene absortpion.
[b] An arbitrary, but reasonable, criteria for a degrading effect from a particular exposure is a large, absolute increase and a continuing upward trend at 15 mo.
[c] Liquid benzene absorption was used for HDPE

The major finding of Phase II was that CPE showed a significant increase in WVT and RT diffusion coefficient with exposure to phenol.

Conclusions

1. WVT and RT were found to be quite reliable test methods, whereas WA and WVA techniques experienced serious problems in regard to obeying simple, one-dimensional diffusion theory.
2. The BA method worked well for HDPE.
3. The various transport coefficients showed all the expected types of behavior with chemical exposure:
   - constancy with exposure (acids and bases on most all FML's and all chemicals on HDPE)
   - decrease with exposure (plasticizers leaching from FML's)
   - increase with exposure (phenol-treated CPE).
4. The WVT and RT results were generally complementary to one another. The transport approach was quite successful in predicting the instability of CPE exposed to phenol. This instability was further verified by DSC measurements.
5. The work lends credence to the use of mass transport measurements to determine structural change in FML's. The EPA 9090 method includes physical and mechanical testing of the compatibility of FML to prospective chemicals. Mass transport measurements could be added to or be complimentary to EPA 9090 testing, because transport of waste leachate through the FML is the property of paramount importance

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The complete report, entitled "Fundamental Approach to Service Life of Flexible Membrane Liners (FML's)," (Order No. PB 90-263 856/AS; Cost: $17.00, subject to change) will be available only from:
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