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Project Summary

Factors in Assessing the Compatibility of FMLs and Waste Liquids

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This experimental research project studied various factors in the compatibility of flexible membrane liners (FMLs) with waste liquids and other hazardous substances that may be encountered in waste storage and disposal facilities. This work was conducted in three basic areas:

1. **Swelling of FMLs and other FML-related compositions in organics, and calculation of the solubility parameters of these compositions.**
2. **Distribution of organics between aqueous solutions, such as leachates, and FMLs.**
3. **Variables in EPA Method 9090 compatibility testing of FMLs and waste liquids.**

Equilibrium swelling of 28 FML-related polymeric compositions was determined in 30 organics and deionized water. These 28 polymeric materials included thermoplastic crosslinked and semicrystalline compositions, of which 22 were commercial FMLs or sheetings and six were known compositions prepared in the laboratory for this study. Basic polymer and compound variations (e.g., differences in polymer type, level of crystallinity, crosslink density, filler level, and amount and type of plasticizer) were assessed.

Crystallinity of the base polymer appears to be the dominant factor in reducing the swelling of an FML or an FML-related composition in all of the organics and to override both the solubility parameters and cross-linking. Among compositions based on amorphous polymers, the proximity of the component solubility parameters to those of the organics could be used in most cases to indicate the swelling and the probability of changes in properties. Nevertheless, empirically derived data are still necessary for untested combinations of organics and FMLs.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research 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

The compatibility of a proposed polymeric membrane liner with the waste to be contained is a principal requirement of the Resource Conservation and Recovery Act permitting process for the construction of a waste storage and disposal facility. The other principal requirements are low permeability and durability. Thus, a liner material must have low permeability to all the constituents of a waste liquid and must maintain its physical integrity, including seams, to contain the particular waste effectively for the required length of time.

In assessing the suitability of a polymeric product designed to be in contact with liquids and chemicals, it is common practice in the rubber and plastics industries to use solubility parameters to select the polymer compound and ultimately to expose the composition to the liquid with which it is to be in contact. The effects of the exposure upon the physical properties of the compositions are measured as a function of time. The swelling and dimensional changes that take place and the changes in mechanical properties, such as tensile strength, elongation at break, tear strength and modulus are normally measured. For many applications service life is estimated as the time of a percentage change in property relevant to its performance or one that has been correlated with performance. In the case of FMLs used in lining waste storage and disposal facilities, specific criteria for an allowable magnitude of change in specific properties beyond which an FML "fails" have not been developed.

The technology involving the use of polymeric membranes for lining storage and disposal facilities is relatively new. At present, information in the open literature regarding the compatibility of FMLs and waste liquids based on actual experience continues to be limited. On the other hand, considerable information regarding the compatibility of specific polymeric materials with specific organics and liquids is available which the engineer and designer can use to assess potential compatibility of given materials with given waste liquids. Because waste liquids can be complex mixtures with the possibility of detrimental effects due to the combination of components, the compatibility of a lining material with a specific waste liquid needs to be determined. Reliable test protocols are needed so that correct assessment of the liner-waste compatibility can be made by the permit writer when reviewing a permit application.

Among properties that appear to be related to FML performance, the swelling or loss in weight in service is one of the most useful tools in assessing its compatibility with wastes. Associated with these changes in weight are changes in most of the physical properties, such as tensile strength, tear strength, modulus, hardness, permeability, puncture resistance, and fatigue resistance.

Matching the solubility parameter values of an FML with those of a specific waste liquid and its constituents has been suggested as a means of predicting the swelling that might take place in an FML on exposure. Determination of the applicability of the solubility parameter values to estimate the compatibility of FMLs and specific wastes and to estimate the service lives of FMLs was one of the principal objectives of this project.

In addition to the possible use of solubility parameters for predicting compatibility and service lives of FMLs as liners in specific waste storage and disposal facilities, there are several other factors which can affect the magnitude of swelling and possibly the ultimate service life. The compositional factors include:

- Degrees of crystallinity of the polymer.
- Level of crosslinking of the polymer.
- Amount of filler in the compound formulation.
- Amount of plasticizer in the compound.
- Amount of waste soluble constituents in the compound.

The environmental factors include:

- Concentration of the organics and the partitioning of an organic dissolved in the waste liquid with a polymeric liner.
- The effect of strain or stress on a liner in service.

This project was undertaken to investigate and quantify the various factors that contribute to the performance of FMLs and their compatibility with waste liquids in waste storage and disposal facilities and to investigate factors involved in predicting long-term compatibility and service life.

Objectives

The four principal objectives of this project were:

- To develop a methodology that can be used to predict the compatibility of FMLs with specific waste liquids and to estimate their service lives for lining waste storage and disposal facilities.
- To determine the solubility parameters of polymeric FMLs and to explore their use for determining the compatibility of FMLs with waste liquids of different types.
- To assess the different factors that affect the magnitude of swelling of an FML in contact with waste liquids.
- To determine the effects of swelling on mechanical and permeability characteristics of FMLs in service.

In addition to the above, this project had the following secondary objectives:

- To assess the effects on polymeric FMLs of organics in dilute solutions and determine whether threshold levels for organic species in waste liquids can be set.
- To assess the effects on polymeric FMLs of exposure to waste liquids, such as in the testing of environment stress-cracking resistance.
- To determine the importance c crosslink type and crosslink densit upon FML behavior in wast impoundment environments.
- To determine the applicability c higher exposure temperatures i performing compatibility tests and i estimating the service life of an FM as a liner in a waste storage an disposal facility.

Summary and Conclusions

The work conducted on this projec was in three major areas relating to th chemical compatibility of FMLs wit waste liquids and leachates:

- Swelling of FMLs in organics an calculations of the solubilit parameters of the FMLs and relate compositions.
- Distribution of organics in aqueou solutions between water and FMLs.
- Study of variables in FML/waste liqui compatibility testing.

Swelling of FMLs in Organics and Calculations of the Solubility Parameters of the FMLs and Related Composition

Equilibrium swelling of 28 FML related polymeric compositions wa determined in 30 organics and deionize (DI) water. These 28 polymeric material included thermoplastic, crosslinked, an semicrystalline compositions, of which 2 were commercial FMLs or sheetings an six were laboratory-prepared com positions. Within these 28 composition basic polymer and compound variation were included, such as polymer type level of crystallinity, crosslink density filler level, and amount and type c plasticizer.

The organics covered a wide range c Hildebrand solubility parameters as we as the component solubility parameter i.e., the dispersive ($_d$), polarity ($_p$), an hydrogen-bonding ($_h$) components. Th organics were selected by a compute program from a list of 131 organics o which the solubility parameter data wer available and which covered the range of component solubility parameter value as well as the Hildebrand parameter.

Equilibrium swelling was measured b weighing specimens of polymeri compositions that had been immersed i the individual neat organics until ther was essentially no change in weigh Each of the solubility parameter including the Hildebrand and componer parameters, were then calculated fror the swelling data for each of the olymeric compositions through a computer program which generated the curve that best fit the data for that parameter.

The most significant results of this swelling study were:

- The crystallinity of the polymer appeared to be the dominant factor in reducing the swelling of the polymeric composition in all of the organics and appeared to override both the crosslinking and the solubility parameters.
- The crosslinking of an amorphous polymer reduced swelling in all of the organics compared with the uncrosslinked polymer. Increasing the crosslinking density reduced the swelling.

  Note: The crystallinity and crosslinking factors are not additive. The introduction of crosslinking in semicrystalline polymeric compositions tends to reduce the amount of crystallinity.
- Though the magnitude of swelling of amorphous polymers could, in many instances, be estimated from the proximity of the values of the component solubility parameters of the polymer and those of the organic, the swelling of the FML in many combinations could only be roughly estimated based upon the type of organic. The matching of the Hildebrand solubility parameter values remains a necessary but not sufficient condition for swelling. The swelling tests should be performed to ensure that an amorphous FML will not swell in a particular organic. Thus, empirically derived data are still needed for untested combinations of organics and FMLs.
- With waste liquids that contained dissolved organics, the organics were absorbed by the FML; the amounts absorbed depended on: (1) the relationship of the solubility parameters of the organic and the FML, and (2) the solubility of the organic in water.

Distribution of Organics in Aqueous Solutions Between Water and FMLs

A series of experiments was performed to study the distribution of organics from dilute aqueous solutions to FMLs and the permeation of these organics through the FMLs. Three preliminary experiments were performed to explore the movement of organics with respect to water and FMLs and to assess gas chromatography as a means of measuring the concentrations of organics so that their movement from one solution into another could be followed. These experiments were as follows:

- Measurement of the distribution of seven organics in mixtures at different ratios with water between the organic phase and water. The mixtures included organics having a wide range of solubilities in water from miscibility to almost complete insolubility.
- Measurement of the distribution of organics between water and a paraffinic oil which was selected to simulate polyethylene because of their chemical similarity.
- Measurement of the distribution of organics in a dilute aqueous solution of organics and a high-density polyethylene FML which was immersed in the solution.

A series of six additional and more extensive experiments was conducted to assess the distribution of organics between water and FMLs:

- To determine the distribution of organics between saturated aqueous solutions of individual organics and a polyethylene FML.
- To determine the distribution of organics between organic-saturated FML specimens and deionized water.
- To determine, in a two-compartment test apparatus, the distribution and transmission of nine organics in a dilute aqueous solution through a linear low-density polyethylene FML.
- To determine, in the two-compartment test apparatus, the distribution of trichloroethylene (TCE) in a dilute aqueous solution among the air-spaces, the water layer, and the FML separating the two compartments.
- To determine, in a vapor-tight three-compartment test apparatus, the distribution of the trichloroethylene and toluene from a dilute solution to the vapor, water, and FML layers.
- To determine the distribution, in the three-compartment test apparatus separated by polyethylene FMLs, of six volatile organics initially in a dilute aqueous solution. These organics covered the range of solubility parameters from an alkane to an organic acid.

The results of these experiments demonstrated that the organics, based upon their solubility parameters, will transfer from a dilute aqueous solution to the FML with which the solution is in contact and, if volatile, permeate into the airspace on the opposite side of the FML as a vapor. The ultimate ratio, at equilibrium, of the concentration of the organics in the FML to that in the water can vary over hundreds of orders of magnitude, depending on the solubility parameters of the organics.

A multi-compartment test apparatus with FML specimens between the compartments to simulate the condition of a waste liquid in service appears to be an appropriate means of measuring the movement of organics from dilute solutions and transmission through FMLs. The concentration of the organics in the various zones of the test apparatus can be followed by gas chromatographic analysis of the vapors and liquids and headspace gas chromatographic analysis of the FML.

The solubility of an organic in water appears to have been a significant factor in its movement through the apparatus. For example, n-octane, when added to water in the three-compartment test apparatus, tended to volatilize and be transported into the airspace above the top FML rather than into the lower FML and the airspace below the dilute aqueous solution of organics. TCE, which is highly volatile and yet has a relatively high solubility in water, was transmitted relatively fast throughout the three compartments of the test apparatus, thus showing its high mobility.

Considerable time was required for the organics originally in the dilute solution in the apparatus to reach equilibrium in the vapor, the water, and the FMLs layers. This indicates the need for relatively long exposure periods, e.g., four months, for conducting compatibility tests of FMLs in dilute solutions and waste liquids. Because of the long exposure period, vapor-tight exposure tanks should be used.

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***Robert E. Landreth** is the EPA Project Officer (see below).*
The complete report, entitled "Factors in Assessing the Compatibility of FMLs and Waste Liquids," (Order No. PB 88-173 372/AS; Cost: $19.95, subject to change) will be available only from:
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