



Chemical resistance testing of geomembrane liners

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Abstract

There are many accepted methods to ascertain the integrity of a Geomembrane Liner (GM) by subjecting it to a battery of physical, mechanical and chemical testing. This work used a new test system that combined physical testing with chemical exposure. Three permeants were chosen to represent a range of aggressiveness towards HDPE (High-Density Polyethylene); a number of test conditions were evaluated. Cyclic loading, in particular, showed promise as test mechanism. A parameter, the 'delta modulus', was devised that was shown descriptive of the degree of chemical attack. The testing system utilized was able to resolve differences in degree of chemical attack in a relatively short time. GMs were found to be influenced by cyclic loading, with elastic properties nearly disappearing after less than six cycles. Strain enhanced chemical activity.

1. Introduction

Geomembranes (GMs) are a class of geosynthetic materials composed of essentially impervious synthetic polymers, elastomers and plastomers. Their uses include lining and covering of liquid storage facilities and solid and hazardous waste treatment, storage, and disposal facilities. The US government has established laws that prohibit migration of liquids from these facilities into the water systems. The US Environmental Protection Agency (EPA) has determined that GMs are the most practical way of minimizing pollutant release from hazardous waste facilities [1].

The study of GMs is of importance for several reasons. Although land disposal of hazardous waste is seen as the last resort, the practice will continue due to the lack of alternative management options. Additionally, many other hazardous materials facilities will be required to use GMs as barriers (e.g. storage, treatment and transfer areas).

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GMs are also increasingly being recommended for municipal solid waste landfills, due to the perceived impossibility of excluding hazardous wastes from municipal wastes. In the US, they are now required in new landfill cells.

To serve their purpose in protection of the environment, barriers employing GMs will have to last far longer than current experience with these materials. Additional study of GMs is needed because their long-term behavior is unknown. Unanticipated failure mechanisms may manifest themselves and be undetectable due to the liners' inaccessibility. This work showed the initial application of a new test system to produce chemical resistance data.

The results of the testing program conducted with this apparatus yielded a testing system that could more accurately represent the performance of these materials under the combination of conditions that they would expect to encounter in the field. Additionally, the system could be easily modified to test a variety of other conditions of exposure.

2. Background

There exists a considerable literature in the testing of GMs. An overview of existing tests, including concerns with the significance of resulting data, has already been presented [2]; only highlights and extensions are presented below.

2.1. Mechanisms of attack and failure

GMs are subject to a wide variety of stresses during installation and operation in a land disposal facility. The liner must be able to support its own weight during and after installation due to the slope of the sides of the cell and contours of the bottom required for drainage. These internal stresses are due to the characteristically low coefficients of friction in nontextured GMs; internal stresses arise when the GMs are placed on significant grades [3]. The passage of heavy equipment may cause cyclic straining in the GM during the placement of wastes. Finally, the landfill applies its considerable weight, compressing the liner. If the earth underneath the landfill is not properly prepared, localized subsidence can occur to which the liner must conform in order to remain intact.

In addition to these stresses, fluid heads may occur subjecting the material to additional loads. These heads may be from a fluid containing components that attack the liner. Chemical attack may occur in conjunction with the physical attack mechanisms discussed above. When under chemical attack, the polymer can swell and soften if it absorbs wastes, but there is little knowledge of the long-term effects on the mechanical resistance to stress from these combined mechanisms of attack [1].

2.2. Existing testing of physical properties

A large array of physical, chemical and mechanical property tests have been codified by the American Society for Testing and Materials [4]; they have been

combined into a sequence of procedures in EPA's Method 9090 [5]. Most of these tests were derived directly from materials engineering; they can be categorized as index tests that elicit a single material property.

Performance tests that attempt to reflect service conditions have been under development [6], several have recently been codified. The most sophisticated of these tests grip the sample in a ring and deform it normal to its surface. The deforming force is most often applied hydrostatically; the material is forced against various granular media below [7–10]. The Geosynthetic Research Institute at Drexel University has been a great leader in the development of these tests, and in having such tests made part of the ASTM standards. Of particular interest is ASTM 5397, Evaluation of Stress Crack Resistance of Polyolefin Geomembranes... [4]. Of greatest significance is that physical testing is very rarely combined with chemical exposure.

2.3. Geomembrane chemical characteristics key to attack

The semi-crystalline structure of some polymers, factors influencing the degree of crystallinity and cross-linking are all important to the interpretation of chemical resistance test results. High-density polyethylene (HDPE), a semi-crystalline polymer, is the most popular material used in lining of waste disposal facilities. Thus, discussion will focus on its properties.

The key structural aspects of HDPE are shown in Fig. 1 [11]. With each order-of-magnitude increase in magnification, different aspects of the structure are illustrated. Lamellae exist within spherulites. The lamellae constitute the basic arrangement of the polymer chains. The lamellae are thin, flat sheets in ribbon form.

Chemical attack is first evinced by disruptions of the bonding between lamellae. These linkages may be healed if a volatile aggressor is allowed to volatilize. More irreparable structural damage occurs if the structure of the lamellae themselves is damaged. Gross parameters discussed above, such as swelling, are indicative of adsorption of the attacking chemical by the polymer.

A convenient measurement of the permeability of a liquid into a polymer is the solubility parameter, δ . Hildebrand first defined this parameter as the square root of the cohesive energy density, which is defined as the energy needed to eliminate the attraction forces binding together one mole of a polymer [12–14].

$$\delta = \sqrt{CED} = \sqrt{\frac{E_v}{V_M}} = \sqrt{\frac{\rho(\Delta H_v - RT)}{M}}, \quad (1)$$

where ΔE_v is the molecular cohesive energy, V_M is the molar volume, ρ is the density, ΔH_v is the heat of vaporization, R is the universal gas constant, T is the Kelvin temperature, and M is the molecular weight. The units are $(\text{cal}/\text{cm}^3)^{1/2}$, typically denoted as the Hildebrand unit, h . Eq. (1) readily defines the solubility parameter of most liquids. The Hansen solubility parameter was developed to take into account the effect of dipole–dipole interaction and hydrogen bonding, which can be considered more relevant to polymer applications. This parameter is a three-dimensional

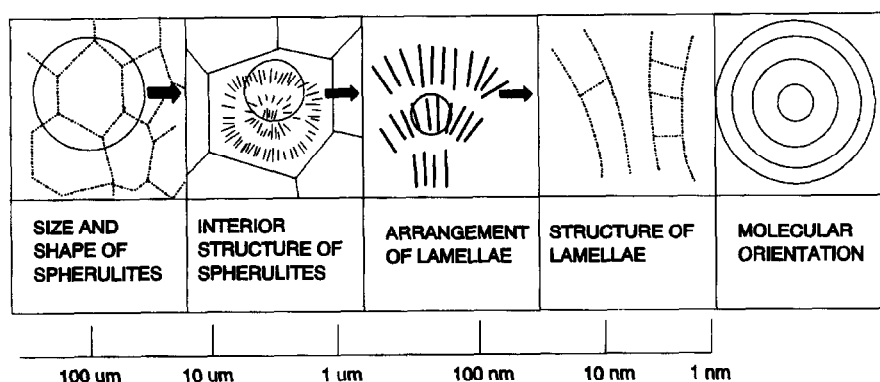


Fig. 1. Structural features of semi-crystalline polyethylene as a function of scale.

representation of a substance's solubility and is expressed as a vector.

$$\delta_f^2 = (\delta_d)^2 + (\delta_p)^2 + (\delta_h)^2 \quad (2)$$

The first component of the vector, δ_d , represents the van der Waals dispersion forces, the second component, δ_p , represents the dipole interaction and the third component, δ_h , represents the hydrogen bonding [12]. Hildebrand's solubility parameter gives a good indication of the permeability of a membrane to a liquid or vapor; it is the most widely used, even though the Hansen parameter, δ_f , is theoretically more representative.

Fig. 2 displays the general relationship between the solubility parameter of a particular polymer and a range of solvent solubility parameters. The maximum sorption indicates equilibrium, and hence, the solubility parameter for that polymer. Fig. 2 also shows that a completely amorphous polymer will have infinite sorption of a liquid with identical solubility parameters while a polymer containing some degree of crystallinity will reach a finite sorption level for that liquid. This is because crystalline regions will tend not to sorb liquids.

Further factors such as crosslinking, crystallinity, and plasticizing agents within the polymer make physical testing a necessity. Noncrystalline and un-crosslinked polymers will dissolve in a solvent within 1.8 Hildebrand units of the polymer. Polymers will swell when exposed to solvents with solubility parameters within 3.2 units of the polymer. When the volume of the penetrant within the polymer reaches 1% of the polymer volume, the polymer becomes solvated. The polymer is considered saturated and the process of diffusion is increased. As the concentration of the solvent is increased in the polymer, solute-solvent interactions begin to take place and polymer chain segments are separated by the solute.

Because molecular transport of a solvent through a polymer material involves separation and movement of polymer chain segments, any mechanism that hinders these movements will have an effect on the permeation rate for the polymer material. Two such mechanisms are: the degree of crystallinity and strain-induced orientation

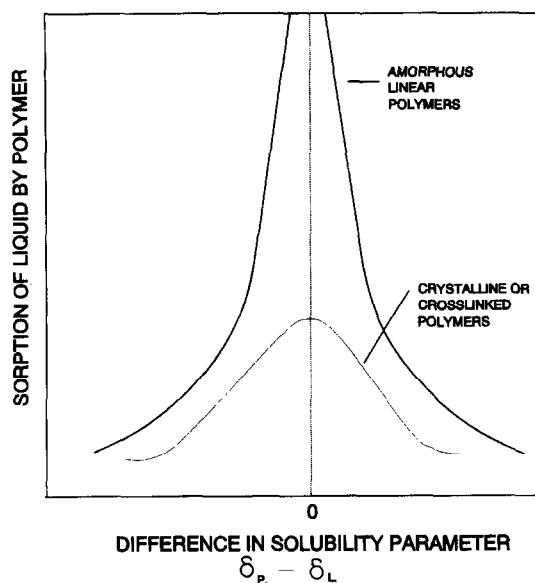


Fig. 2. A conceptual view of the difference between solubility parameters for amorphous and crystalline polymers.

of the polymer [15, 16]. In the case of the latter, cold-drawing the polymer in the machine direction tends to reduce permeability; adding strain in the lateral direction increased permeability [10]; in multi-axial testing, both occur.

2.4. Chemical resistance

Chemical resistance is often tested by devising a method to expose samples to liquids representative of leachates, followed by strength-of-materials tests. Immersion, or coupon, testing requires placing a coupon of GM in a dish of leachate, simulated leachate, or leachate component; the material is then cleaned and dried, and subjected to physical tests discussed above [17]. This test sequence forms the basis of the US Environmental Protection Agency's Method 9090 [5]. Among the concerns in using this test expressed to the first writer by members of the design community are:

- (1) During the time permitted between chemical exposure and physical testing, a HDPE sample can be held in a low-density polyethylene bag. The bag would then be likely to be less chemically resistant than the sample it contained. Volatile materials having an effect on the sample could volatilize through this bag, permitting a degree of return of the sample to pre-exposure conditions. The resulting physical test would not be representative.
- (2) Both sides of the sample are exposed, which is not the case in an initially sound sample.

(3) Method 9090 and the like do not simultaneously test immersion and the effect of stress [18]. Method 9090 now recommends the addition of a static-tension test that attempts to elicit behavior called 'environmental stress cracking'.

(4) It is not physically reasonable to apply loads sufficient to deform the membrane by applying compressed air above an aggressive liquid. Such pressures would represent at least 9 m of head. Thus, multi-axial performance tests as currently constituted, should not be used for chemical resistance testing.

Chemical exposure tests are new enough that it is quite difficult to gather enough data to make comparisons across techniques. Haxo [12] has conducted a series of chemical resistance tests. The one-sided, or pouch, test involved making a pouch of the sample and filling that pouch with leachate; the tub test lined a plywood tub with the sample prior to filling it with leachate; the immersion test completely submerged a sample in leachate; the exposure test exposes the sample to leachate at the bottom of a lysimeter. The polymers were elasticized polyolefin (ELPO) and epichlorhydrin (CO). The variable, percent retention of stress is commonly produced by relaxation tests: here the material is stretched to twice its original length, and the reduction in force over time reported. This combination of GMs and tests provided the widest consistent data base for comparison among different types of exposure available in the literature. Table 1 shows the lack of consistency among the data. It is difficult to determine the connection between any existing test and the barrier capabilities of the GM [14].

Testing seeks to assess physical attributes of a material relevant to its performance. Ideally, the measured physical attributes should help explain any diminution in performance. Testing costs argue for such determinations to be made quickly. Previous work [19] shows and discusses the significance of cyclic loading in testing without chemical resistance. In that work are discussed: the importance of cyclic loading to suspected causes of stress cracking, and the significance of the rapid loss of elasticity of HDPE membrane. In chemical resistance testing, the loss of elasticity

Table 1

Percent retention of stress at 100% elongation for matrecon 'Oily Waste 104' under different exposure conditions for two polymers; data from [12]

Test type	Duration (d)	Retention of stress (%)	
		ELPO	CR
One-sided	500	61	50
	1250	71	42
	1308	67	
Tub	2008		79
	240	99	91
Immersion	570	103	93
	248	62	46
Exposure	752	75	70

could assume added significance. Multi-axial cycling would have the mechanical effect of repeatedly spreading lamellae, providing repeated chances for permeant entrance and additive loss. In the viscous area of the stress/strain curves, the hysteresis shown in this work could serve as a measure of plasticizer loss. Additionally, multi-axial cycling would repeatedly strain the sample in its machine direction (direction of calendaring or extrusion, assumed to be the orientation of the majority of the polymer strands), providing rapid assessment of loss strength. Lower viscosities, shown by reduced forces, could suggest loss of cross-linkage. Thus, cyclic testing was determined to have the greatest potential as a rapid test method for assessment of the effect of a potentially aggressive leachate constituent on a GM.

To represent accurately the field conditions involved with the combined stresses, a test system should be able to simultaneously do the following:

- (1) Apply a compression to simulate the weight of the landfill.
- (2) Allow application of fixed amounts of displacements for stress/strain, cyclic and relaxation testing.
- (3) Allow application of fixed amount of force to conduct creep tests.
- (4) Be fully instrumented to read forces and displacements and store those data.
- (5) Allow independent application of fluid head, possibly employing suspected aggressive chemicals; this was the focus of this work.

This work sought to develop and use such an apparatus.

3. Apparatus development

Much of the work reported herein involved development of the test system used to obtain the results presented. During this process, it was possible to make several observations concerning GM properties.

The experimental system was designed to deform a 150 mm (6 in) diameter disk of membrane material in a clamped ring. Fig. 3 shows the test cell in the Material Testing System (MTS). The MTS is capable of standard displacement testing, as well as cyclic loading. The cell was constructed by modifying a standard Soiltest 150 mm (6 in) permeameter. The system encased the GM sample in granular material that simulated the underlying and overlying protective layer. The granular medium in contact with the membrane was standard Ottawa sand, representative of the best field construction. It compacts slightly during testing, which is recorded by a displacement transducer on the inner load frame. Together, the independent testing frame and the testing machine allowed a wide variety of forces to be applied to the sample in different manners. After a test, the system was carefully dis-assembled to make certain that the sand layer was completely intact between the piston and the sample, avoiding direct exposure to metal components. Fig. 4 shows a sketch of the design of the grips holding the sample. Taking those two figures in combination, it can be seen that, to deform the membrane downwards relative to the grips, the test cell is lifted up by the MTS's ram. Construction materials were limited to corrosion-resistant metals, Teflon[®] and Viton[®] because of the potential use of aggressive chemicals.

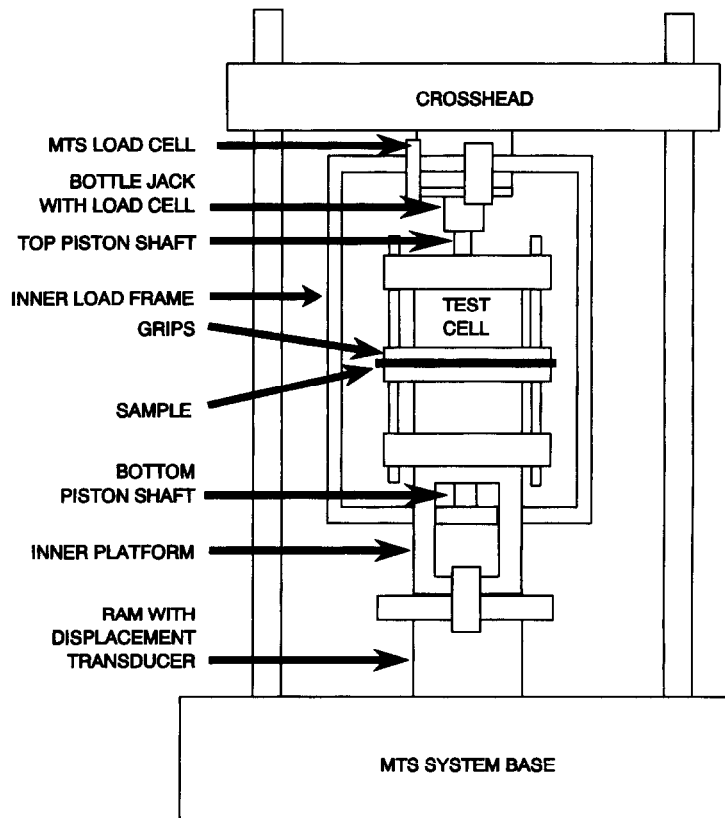


Fig. 3. Test cell in compression tester.

In developing the system, it was important to make certain that GM failures were not a result of peculiarity of the testing system. Surface tension theory indicates [2] that, upon allowing pressure of a deformable membrane on one side of a sample to exceed pressure on the other side, the resulting deformation of the membrane would form a smooth spherical section due to equilibration of force within the membrane. A principal objective of the design of the grips and pistons was to produce this geometry in the membrane, allowing for the presence of, and load applied through, granular media. Attainment of a spherical section at the center of the sample was ascertained by examining the samples after each individual test. The piston shape and the configuration of the granular media layers were thus developed so as to evenly distribute stress over the surface of the tested sample.

Fig. 5 shows the system used to apply fluid to the test cell. The regulated air pressure determined the fluid head. The system allowed the upper chamber to be entirely filled with fluid before applying pressure. The activated carbon filter was

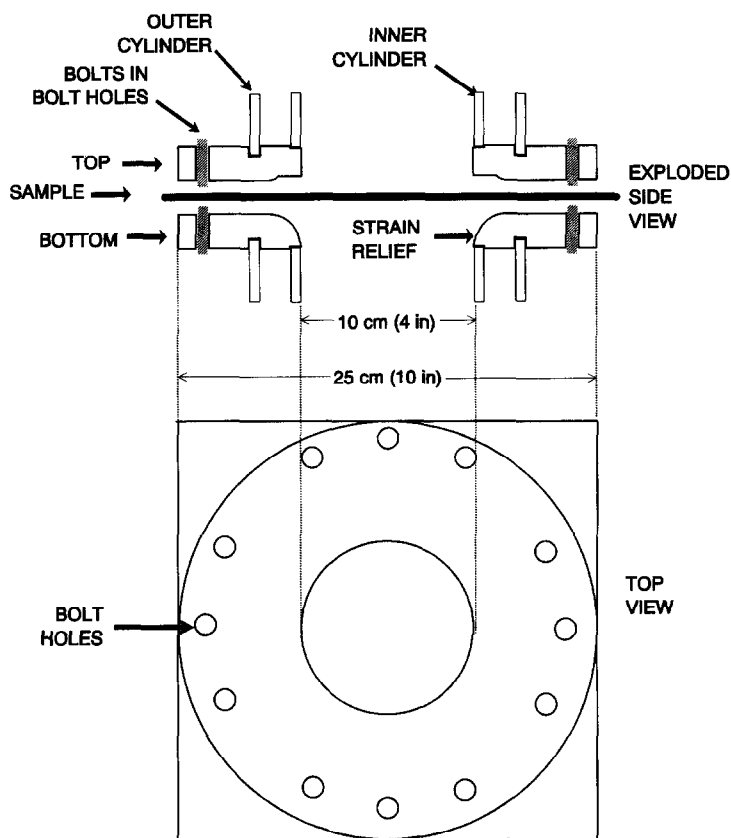


Fig. 4. Top and side view of sample grips.

provided to prevent discharge of organic vapors to the laboratory environment. No pressure would be detected by the pressure transducer without movement of or failure in the membrane.

Data were gathered electronically. The MTS provided its own stress and strain readout corresponding to movement of its ram (see Fig. 3). The inner load frame was instrumented with its own Omega load cell (LCG-10K). Pressure in the lower chamber was detected by the use of an Omega pressure transducer (PX181-200G54). Data gathering was automated by use of computerized data conversion (DT2801 A/D board) and storage. A micro-computer was adapted to read and store the data from the testing procedures.

Preliminary tests were run to aid in the development of the GM testing system. Observations during these tests were used to further develop the testing method.

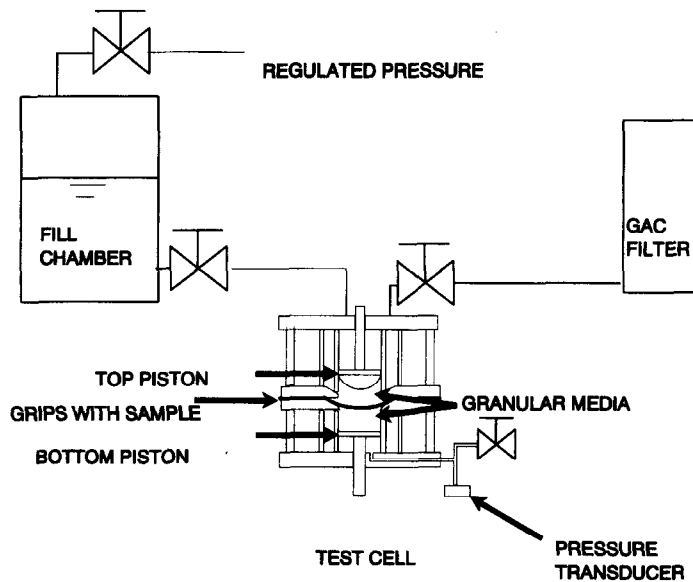


Fig. 5. System to apply liquid to top of sample.

4. Method

In order to make comparisons with current standardized testing parameters, the new testing procedure used strain rates and values from current ASTM testing method procedures. The standard method recommended for semi-crystalline membranes is ASTM D638 which states values to be reported should include tensile force at yield and break, and elongation (%) at yield and break. The tensile strength data reported measures the force in Newtons applied over the GM's original cross-sectional surface area in square meters. These tensile strength values are reported in Pascals. In this multi-axial testing, load applied via the vertical displacement was resisted by tension within the membrane. Thus, the force reacting to that applied by the vertical displacement of the test system is radial within the circular sample, which is fixed along its circumference. Materials testing practice calls for measuring stress as the applied force divided by the area normal to that force. In this case, the area, A_T , over which the force in the membrane, F , was applied became the edge area of the sample, equal to the product of the circumference of the exposed sample disk ($2\pi r$) and its thickness (T)

$$\sigma = \frac{F}{A_T} = \frac{F}{2\pi rT}, \quad (3)$$

where σ is stress. The standard measure of stress is reported as a function of the original surface area; as opposed to 'true stress', which is a function of the resultant

surface area. The strain or elongation is measured as a percentage change in length divided by the sample's original length. Due to the unique application of force and displacement to the GM with the new test system, a relationship between surface area (as opposed to edge area) and strain (γ) was developed:

$$\gamma = \sqrt{\frac{A_D}{A_O}} = \sqrt{\frac{A_D}{\pi r^2}}, \quad (4)$$

where A_O is the surface area of the un-deformed sample. Although the geometry of the test system allowed deterministic evaluation of a recursive area relationship, it was recognized that the geometry was third-order, allowing a single equation to fit the geometry with great accuracy ($r^2 = 1.000$). To thus allow rapid calculation of the surface area of the deformed sample, A_D , as a function of the piston displacement, y , the following cubic was determined:

$$A_D = 182.03 + 14.89y + 4.8259y^2 - 0.27484y^3. \quad (5)$$

All dimensions are in cm. These values were then reported in a standard stress/strain graph.

Testing involved:

(1) The GM sample was cut and holes were punched to allow passage of bolts. The sample was then placed in the grips. Using a standard alternating/opposite bolt tightening pattern, the grips were tightened. It was found that it was very important to avoid any sample that had the slightest amount of small grooves visible in the surface.

(2) The grips were placed into the test cell, and the test cell assembled, including granular media. When fluid head was applied, an initial load of fluid was placed in the upper chamber prior to placement of the cell top. This was done in a hood when organics were employed.

(3) The test cell was placed into the inner load frame and MTS. Connections for fluid head and data gathering were made.

(4) The electronics, hydraulics, and data gathering systems were turned on and allowed to stabilize.

(5) The materials testing machine and data gathering systems were turned on. Initial sample displacement was made, as required.

Three chemicals were used as permeants. Haxo [12] showed that HDPE has a Hildebrand solubility parameter between 7.7 and 9.9 $\text{cal}^{1/2} \text{cm}^{-3/2}$; swelling should occur within 3.2 units of this value.

(1) For the neutral case, distilled, de-ionized water was employed (23.4 H).

(2) The US EPA simulates landfill leachate with a buffered acetic acid solution, as specified in their TCLP test [20]. Acetic acid itself has a Hildebrand solubility parameter of 10.1 H.

(3) Reagent-grade toluene having a Hildebrand solubility parameter of 8.9 H represented common organic solvents found in consumer products and resulting wastes.

Testing comprised a combination of physical tests and permeant exposure:

(1) Stress/strain without cycling. The standard displacement rate of 51 mm/min [4] was employed. The maximum displacement, 25 mm vertical displacement of the piston, corresponded to 110% strain.

(2) Cyclic testing. These tests involved an initial displacement of 19 vertical mm, followed by cycling with an amplitude of 6.4 mm, giving a maximum displacement of 25.4 mm, and a minimum of 12.6 mm. Employing the same rate-of-strain as in (1) yielded a frequency of 0.033 Hz. In application, cycling was begun prior to full displacement, and ramped to full displacement and amplitude so as to avoid causing membrane failure due to excessively fast movement. Prior work showed good agreement with punch-type tests, showing that friction within the sand in the test system had minimal effect on the application of load to the membrane [19].

(3) Fluid head was applied at 0, 0.344, and 0.689 MPa in both stress/strain and cyclic tests. These pressures corresponded to the elevated pressures used in testing clay liner materials.

A randomized block design was used to allow statistical evaluation of the results.

5. Results and discussion

Stress/strain, without cycling, was undertaken so as to compare performance of this system with its predecessors. The cyclic testing comprised the new chemical resistance testing system. Cyclic testing provided the reduction in testing time that would allow an adequate range of tests to be conducted in response to any individual question. Further, cyclic testing may well reflect exposure conditions [19]: the limited number of cycles required to cause a significant decrease in elastic behavior could be applied by the passage of heavy equipment during installation of subsequent liner layers, leachate monitoring and collection systems, and initial waste layers. The cyclic action places strain that separates polymer fibers (lamellae) and, as it pulls in all directions, also tensions the membrane in the direction of primary alignment of these strands. It is entrance of a potentially aggressive material into the membrane that causes a degradation of physical strength. Separation between and tensioning of the polymer strands can both speed permeant penetration, thus creating a faster assessment. Simultaneous monitoring of stress records the effect. While elevated temperatures may occur in leachates, their incorporation in current testing to speed manifestation of effects is fraught with confounding factors [2]. Separate assessment of heating, using the Comprehensive Test System discussed in this work, is planned for future research.

In the results given below, graphs are shown only of results that illustrate the points of discussion. Too many tests were undertaken to show all the resultant graphs. However, the results included all the test data, except where repeated equipment failure precluded complete testing. Significant parameters drawn from the tests, together with statistical parameters, are shown in the tables.

5.1. Stress/strain without cycling

In the randomized block design, the three block observations were: water, TCLP extraction fluid, and toluene. The three treatments were: 0, 0.34, and 0.69 MPa. A statistical comparison was performed on the stress at yield. Table 2 displays these data. Fig. 6 shows data gathered in stress/strain testing with water at different hydraulic pressures. Inspection shows that fluid head greatly confounds measurement of stress: departure from zero is nearly linear with fluid head. Inspection of Table 2 shows a similar relationship with the stress at yield, the important parameter measured. At 90% significance (0.1 level of significance, $F = 4.32$) there was no correlation between yield stress and chemical aggressor and no correlation between yield stress and pressure. However, the conclusion that chemical and pressure did not cause a significant change in the membrane, based solely on these data, would be in error. When testing the membrane using toluene at 0.689 MPa the membrane failed, permitting passage of toluene through the sample at a rate that caused a loss of pressure differential across the membrane. It was also interesting to note that the F value for the treatments (pressure) when compared to the F value at a 90% level of significance showed only a 0.18 difference. These results indicated that the combination of displacement and an aggressive permeant could cause a change in the integrity of a membrane at any fluid head in a short period of time.

5.2. Cyclic testing

Fig. 7 shows several different features of stress testing. The right hand side shows stress testing with water with a variety of fluid heads. Positive stress values correspond to load necessary to displace the membrane from its initial displacement to the low point in the cycle, in the direction of its initial displacement. In all cases, 2 min of data are shown prior to the beginning of cycling (this is when the transducers began recording). Cycling was ramped up over 1 min to its full amplitude. One would expect, with a perfectly elastic material, that the stress would never be negative; a negative

Table 2
Randomized block statistical results for yield stress from stress/strain testing

Pressure (MPa)	Stresses at yield (N/cm ²)		
	Water	TCLP	Toluene
0.0	1065.52	1026.18	1101.59
0.344	1042.57	1072.08	1108.14
0.689	783.57	1036.01	763.90
Source of variation	F value		
Treatments	4.14		
Blocks	0.39		

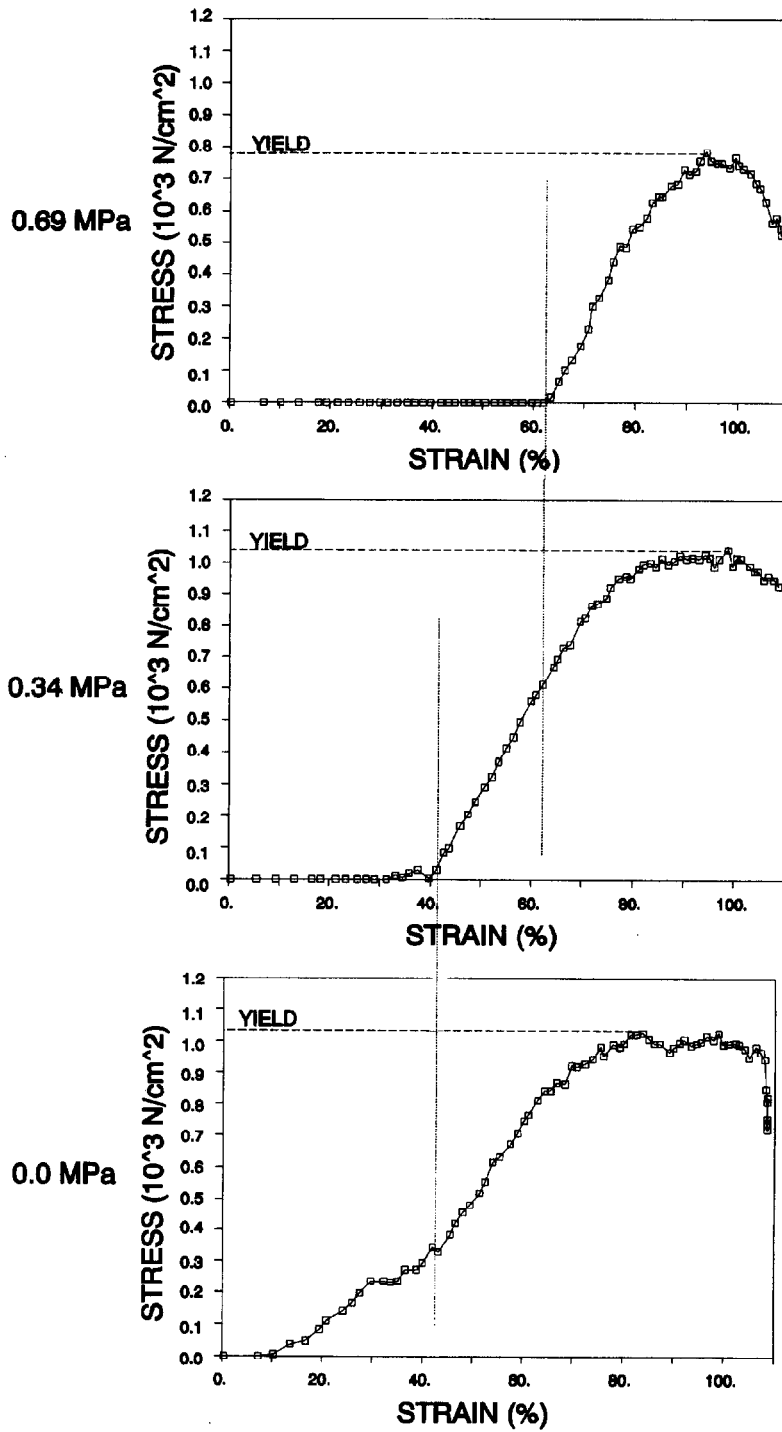


Fig. 6. One set of comparison graphs showing stress/strain test results with water at different pressures.

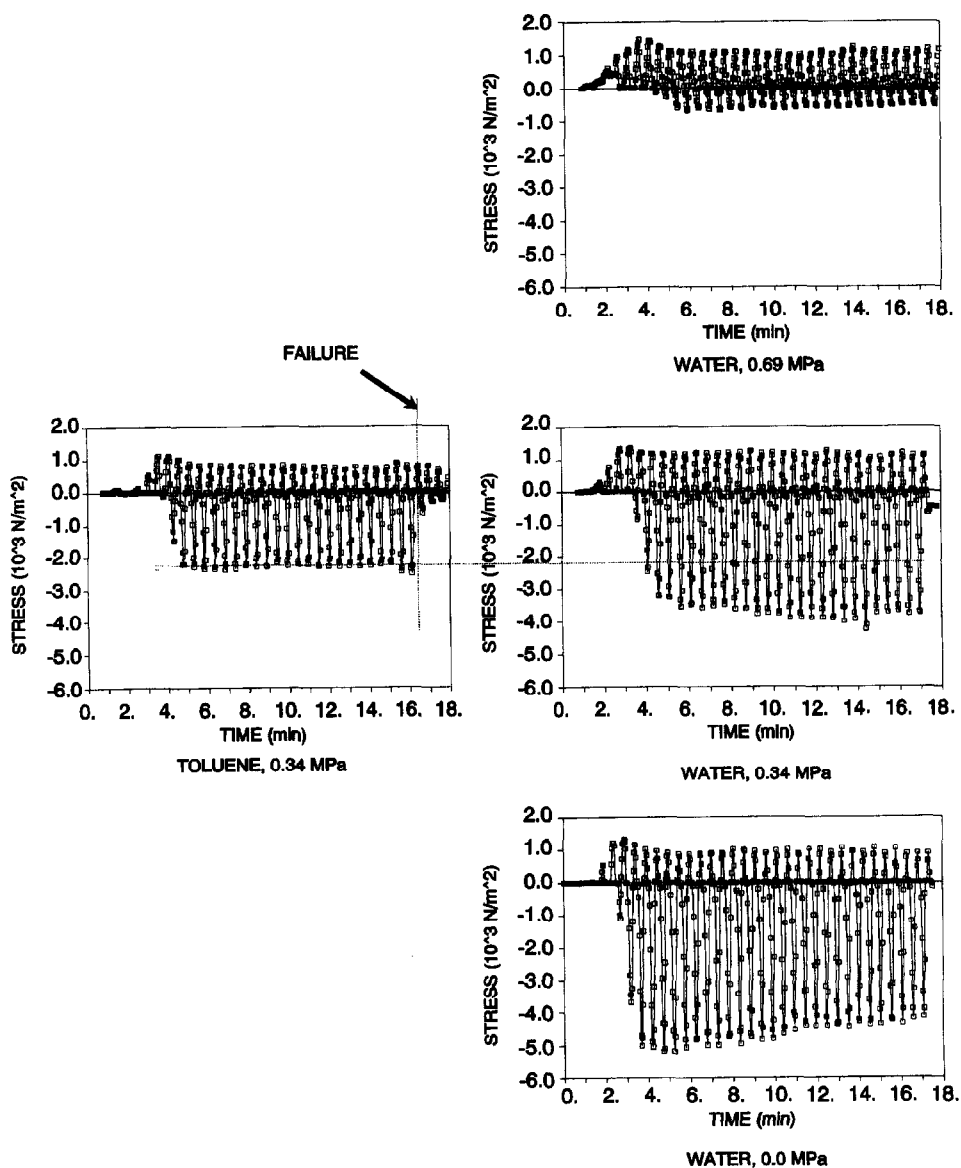


Fig. 7. Cyclic stress testing data comparing various permeant pressures with water and toluene.

number corresponded to the need to push the membrane back to its lowest displacement in the cycle. Even with no water pressure, the membrane lost its elasticity within 3 min (six cycles). Corresponding to Fig. 6, the influence of increasing the fluid pressure was seen by the increased force required to return the membrane to its datum position. Twenty minutes test duration was sufficient to observe failure with the aggressive permeants.

Analysis of the results determined that 0.69 MPa was too high a pressure for this testing. In the case of toluene, two tests at this pressure resulted in catastrophic failure; attendant equipment damage precluded the gathering of data. Thus, comparison between water and toluene is undertaken in Fig. 7 at 0 and 0.34 MPa. At both pressures, toluene caused a reduction in elasticity and an increase in plasticity by contrast with water. Contrasting the central parts of the graphs for the 0.34 MPa tests, the horizontal dotted line makes clear that toluene lowered the amount of force required to move the membrane. At 0.0 MPa, the lower piston was able to move the membrane back to its initial position without working also against fluid pressure. Without the applied fluid pressure, the force needed to return the membrane to the initial position increased from cycle to cycle as the membrane lost elasticity. This was attributed to loss of material strength: the plastic deformation after the 6th minute required less force. In the 0.34 MPa test with toluene, failure began just after the 16th minute. The first indication was disappearance of the need to exert a force to return the membrane to its initial position; this is seen in the cycle immediately following the dotted vertical line in Fig. 7. Immediately after this was noted, the test was terminated, so cycles following minute 17 were not significant.

The data from the 0.0 MPa tests were particularly interesting in conjunction with pressure readings. Fig. 8 shows bottom chamber gas pressure readings taken from the corresponding tests shown in Fig. 7. Data from tests with an intact membrane, such as that shown with water at 0.34 MPa, showed the pressure transducer detecting the cycling of the membrane; the membrane's cycling changed the volume of the sealed bottom chamber. As discussed above, failure was produced with toluene at the 0.34 MPa; the pressure in the bottom chamber then climbed to that of the liquid in the top chamber. It was particularly interesting to compare the case of zero pressure with toluene: the pressure data showed that the membrane did fail, at around 10 min. Failure was shown by the reduction in pressure: even though the membrane continued to oscillate about its displaced position, a hole allowed pressure in the bottom chamber to equilibrate with the top chamber. Careful examination of the corresponding graph in Fig. 7, comparing water with toluene, is required to determine that a change in stress also occurred at that time. Thus, the membrane could fail catastrophically under chemical attack without an easily detectable change in its physical properties.

Cyclic testing reveals the thixotropy of viscous materials. Fig. 9 compares stress/strain data for the three chemicals used to test liner resistance. As discussed above, with increased fluid pressure, the mechanical stress also increased. Since pressure was the same in all these tests, the difference shown in the amount of stress below the null value was due to different GM response to the permeants. The few initial cycles at full amplitude during which stress remained above zero (i.e., before the membrane had to be pushed back) are hidden; in the majority of the test, considerable force was required to overcome the fluid head, against which the decreasingly-elastic membrane was unable to return. Increasingly aggressive chemical attack was principally visible as increasing softness in the membrane. Shortly after initial displacement, the membranes relaxed quickly about their new minimum displacements; they then behaved plastically. The aggressive chemicals reduced the strength of the material, requiring less force for the plastic deformation.

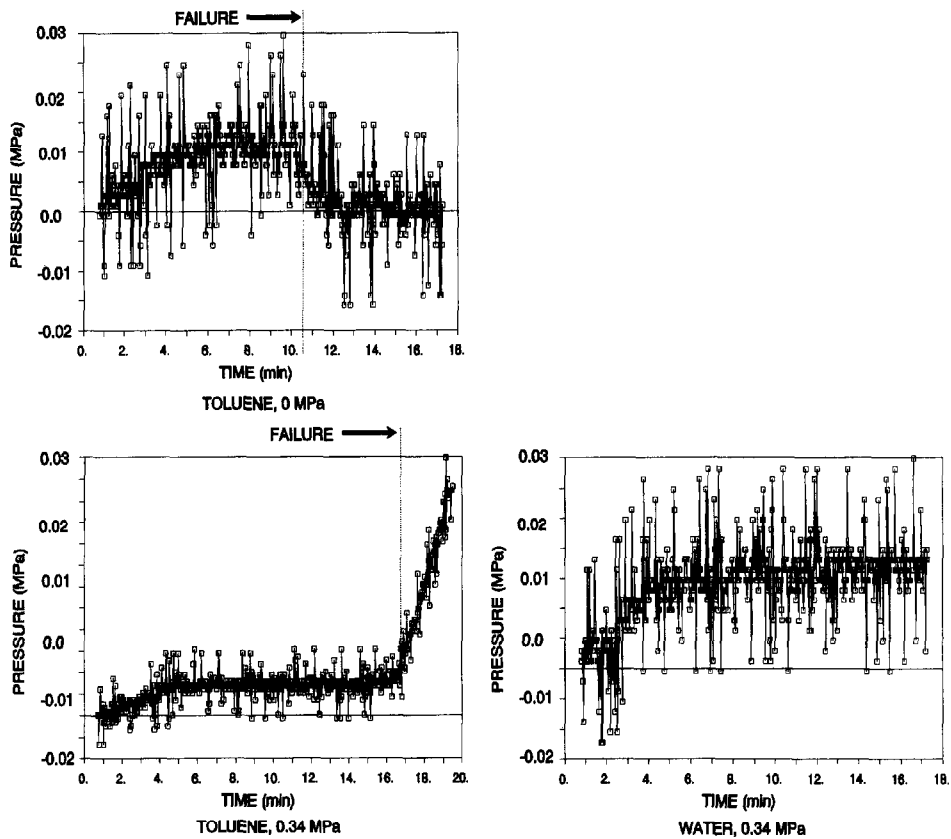


Fig. 8. Gas pressure in the test cell below the sample.

Care was taken in the experimental design to make certain that the membrane was tested during cycling, rather than failing due to the onset of cyclic motion. Thus, it was seen as crucial to examine the main core of the 'cyclones' in the stress-strain diagrams. Fig. 10 diagrams the analysis. By contrast to the behavior of the ideal elastic, thixotropy would cause positive stress to result in a different strain than negative stress; this changing of the straight line into an ellipse is indicative of the additional energy required to strain the material. Plasticity is shown by relaxation of the material, which would be revealed by a standard creep test.

A parameter was sought that would describe the spread of the 'cyclone', as a function of chemical attack. This parameter was named the 'delta modulus', ΔE , defined as the ratio of the average stress range to the average strain range:

$$\Delta E = \frac{\overline{\sigma_{\max}} - \overline{\sigma_{\min}}}{\overline{\gamma_{\max}} - \overline{\gamma_{\min}}} \quad (6)$$

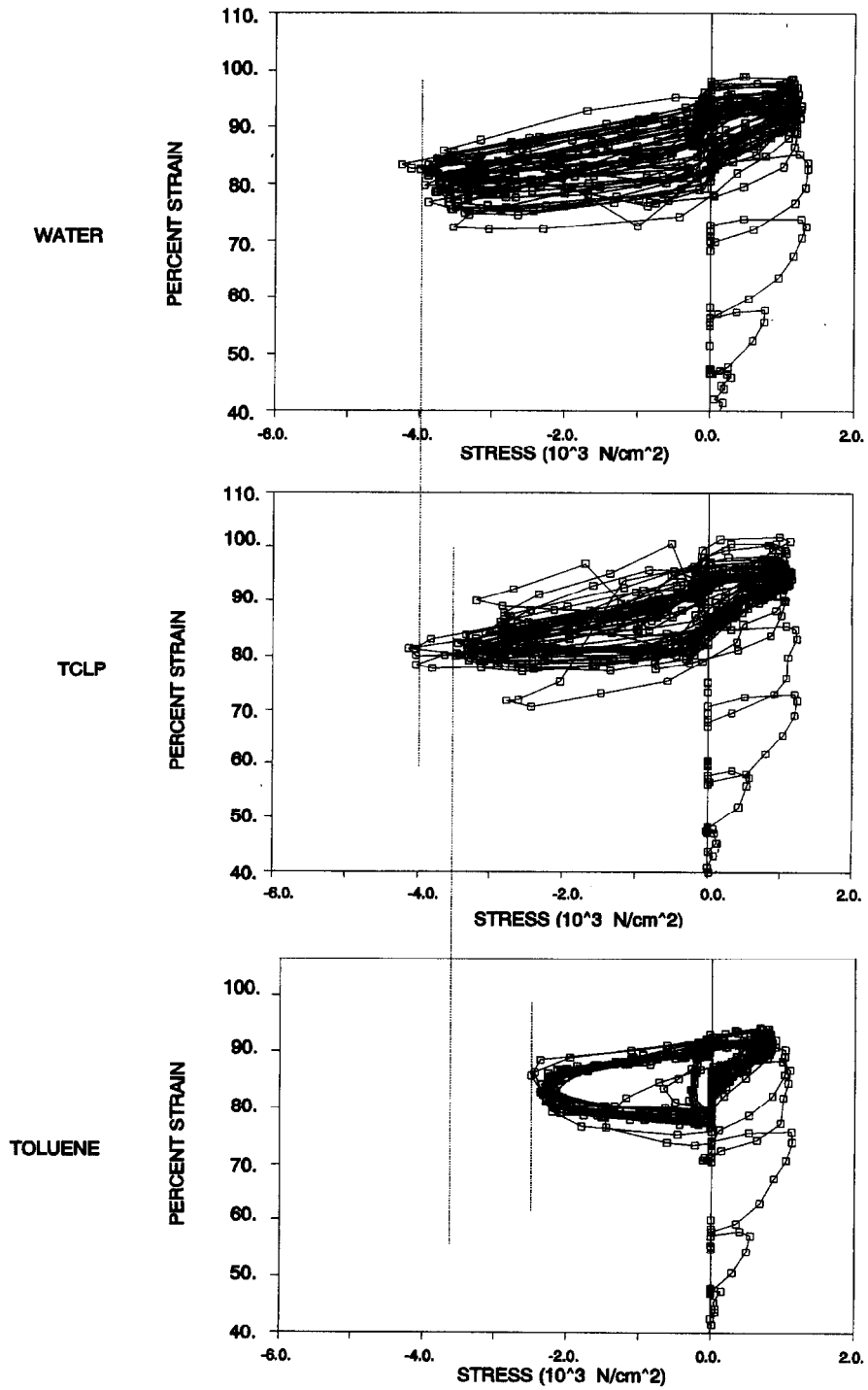


Fig. 9. Stress/strain test results for cyclic testing of with all three leachates at 0.34 MPa.

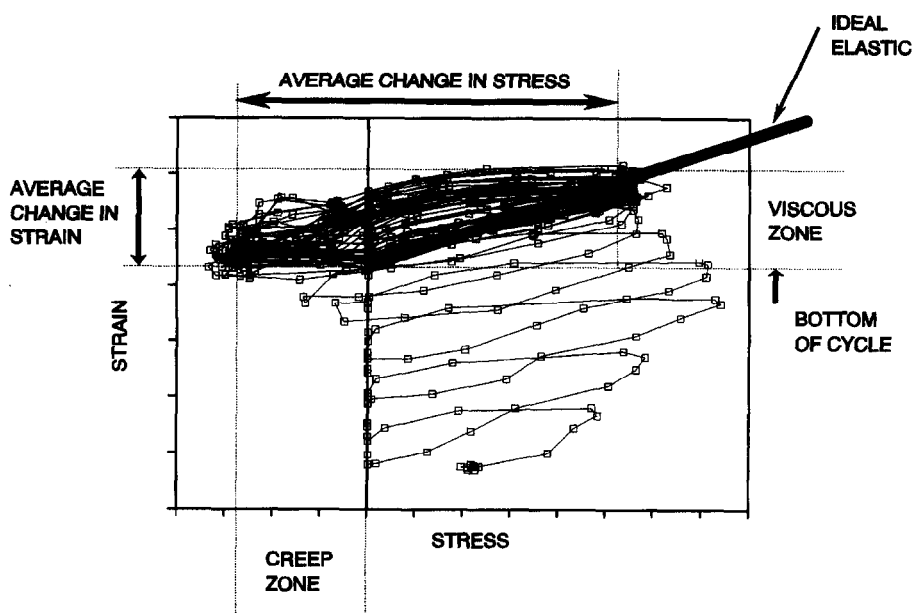


Fig. 10. Interpretation of cyclic stress/strain diagram.

where σ is the stress and γ is the strain. The phase angle between the stress and strain curves was found to be 23.7° . Because the phase angle did not deviate significantly throughout the tests, only the delta modulus was used in the statistical analysis. Randomized block statistics for the delta modulus are presented in Table 3. As discussed, it was not possible to use the highest pressure with toluene, precluding comparisons at that pressure among all tests.

At either pressure tested, ΔE decreased in the order of chemical aggression as predicted by the Hildebrand solubility parameter: distilled water was the least aggressive, followed by the TCLP mixture, and finishing with toluene as the most aggressive. The F value for treatment (varying pressure; $F = 8.53$) and for the blocks (14.49) and both exceeded 90% level of significance ($F = 9.00$). The data indicated that chemical aggressor did make a statistically significant difference in the modulus of the membrane. The data are graphed in Fig. 11 for 0.344 MPa.

5.3. Observations

As this work involved test development, observations during the experimentation gave further insight as to function. As discussed under Apparatus Development, great care was taken to be as certain as possible that failures were not a function of the equipment; all visible effects in the membrane samples were well away from grip edges. Elongation (necking normal to the plane) of the sample during stress/strain testing occurred in a circular region just below the piston head, passing through the center of

Table 3
Randomized block statistical results for delta modulus

Pressure (MPa)	Delta modulus (MPa)		
	Water	TCLP	Toluene
0.0	127.76	106.67	98.44
0.344	328.80	291.69	279.00
$\delta_p - \delta_L(H)$	14.6	1.3	0.1
Source of variation	F value		
Treatments	922.58		
Blocks	14.49		

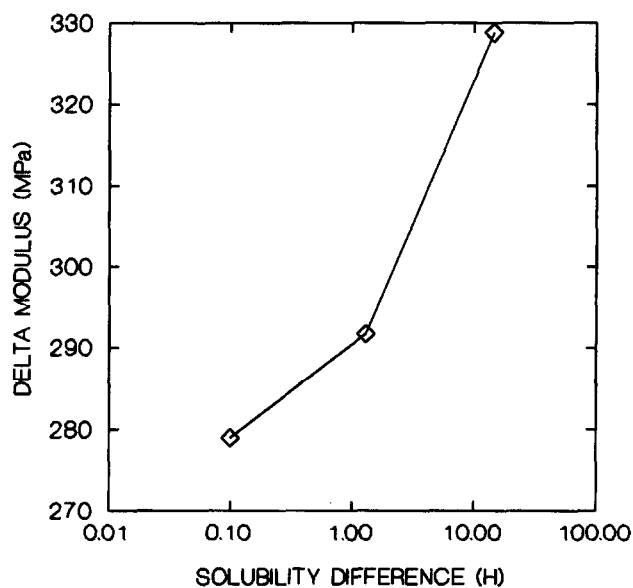


Fig. 11. Delta modulus (ΔE) as a function of solubility parameter difference ($\delta_p - \delta_L$) for 0.344 MPa.

the sample, for the samples exposed to the water or TCLP extraction fluid. The elongation areas were larger in the samples that were exposed to the higher pressures. Elongation in the case of the toluene samples formed a box shape with the sides of the box oriented in the machine and transverse directions. Again, the box was about 50 mm on a side, centered in the sample, well away from grips and lips. This shape was significant, as it showed that cyclic loading first spread the polymer chains, splitting in the machine direction; the resulting weakness then caused further failure of the cross-linking where stress concentrations occurred at the end of the initial tears. The membrane in these areas looked wrinkled. The samples in the 0.689 MPa test showed

several parallel strips of elongated material in both the machine and transverse directions. The sample had a small tear in the machine direction. The high-pressure test was repeated and the sample showed similar features.

After cyclic testing, the membrane samples that were exposed to the water or TCLP extraction fluid at any pressure had the same physical changes: an elliptical section just beneath the piston. This section was smooth and showed no preference as to development in either the machine or transverse directions. The toluene samples were different. At 0 MPa the sample had the smooth elongated circular section with a large tear running over 180° of the circle. Other smaller tears were apparent within the circle. All seemed to have first developed in the machine direction. At 0.344 MPa, the same circular elongated section developed, with slightly more wrinkling visible. A small tear developed in the machine direction just at the tip of the elongated section. At 0.689 MPa a very wrinkled elongated section developed in more of a box-like shape. A large tear developed in the machine direction.

Without an aggressive chemical such as toluene, this testing system did not produce wrinkling; its deformation does not extend to failure with less-aggressive chemicals. The wrinkled sections indicated that swelling occurred in the polymer during toluene testing. As the sample thinned, and became more exposed to the toluene, swelling caused the sheet to swell in the plane direction, causing the wrinkling. The appearance of thinning in the machine direction indicated weakening in bonding between crystalline sections, with the resultant weakening of the membrane sheet revealed by the thinning in the machine direction. Both the occurrence of wrinkling and the pattern of thinning were consistent with solvent attack. The thinned, wrinkled sections stiffened over approximately one-half hour after being removed from the testing apparatus. This would be consistent both with solvent evaporation and cooling of the sample. Thermal analyses, and study of the effect of temperature, are important directions for future research.

6. Conclusions

All established tests of exposure either do not incorporate strain or perform stress testing separately, after exposure. This testing showed weak correspondence between the hydraulic integrity of a membrane and multi-axial, noncyclic stress/strain testing. This research showed that chemical aggressors caused no significant change in the measured physical characteristics of the membrane using stress/strain tests. Data concerning pressure under the membrane showed that cyclic testing was capable of evaluating the strength of a membrane exposed to a leachate without the use of extreme fluid pressures not relevant to exposure conditions. Thus, the need to simultaneously expose and cyclically stress the sample was strongly suggested.

The new parameter, ΔE (delta modulus), provided a sound measure of the effect of a chemical upon the geomembrane test sample. Changes in ΔE were much in keeping with the theoretical understanding of chemical aggression by solvent action provided by solubility parameters. Many leachates are too complicated to speciate (hence Haxo's 'oily waste' in Table 1), so it was important to develop a test that could directly

indicate membrane susceptibility. ΔE could be used, comparing an unknown mixture to pure solvents or solvent combinations tested in the laboratory.

The failed membrane samples suggested that a combination of toluene and applied force had a significant effect on the membrane's hydraulic integrity. The crystallinity of a crystalline polymer membrane is altered during the stretching of the membrane, with crystals orienting in the direction of the stress. At the same time, toluene under a pressure and concentration gradient would be most likely of the tested materials to be forced into the amorphous regions surrounding the crystallites, thus allowing increased movement of the crystalline regions, and allowing further permeation, as well as easing attack of the crystallites. The result would be, finally, the tear in the material. The failures observed would indicate that failure had proceeded into the crystalline regions. Further exploration of these possibilities would require thermal analysis.

The tears always developed in the machine direction. The probable cause was a combination of the inherently-greater strength in the machine direction due to strand orientation, and the fine grooves in the machine direction which appeared to be a result of the material's manufacturing. This, despite every precaution taken to reject samples showing obvious fine scratches.

The cyclic testing results might have implications in design of a land disposal facility. A cyclic force applied to the membrane under an aggressive chemical caused failure of the membrane in as few as 3 cycles. If such cycling were found significant in field-scale testing, additional attention might be paid to preparation of highly-compacted, less compressible subgrades. The lack of connection between fluid head and ultimate failure would further suggest that limitations on leachate head over the liner would not reduce chemically-related failure; leakage after failure would, of course, be reduced with lower heads. Thus, if one wished to use an intact liner to store leachate prior to pumping, one could do so without jeopardizing the liner integrity.

Cyclic testing was able to accelerate manifestation of the effects of chemical attack. Comparison with solubility parameters showed that the delta modulus was related to chemical interactions. All failures with toluene were shown within 20 min. With a laboratory configured for this test system, experienced technicians could conceivably perform one evaluation per hour. This would provide considerable savings by comparison to the shortest test specified in Method 9090 of 30 d.

References

- [1] R.E. Landreth, Service life of geosynthetics in hazardous waste management facilities, in: I.D. Peggs (Ed.), *Geosynthetics; Microstructure and Performance*, ASTM STP, Vol. 1076, ASTM, Philadelphia, 1990, p. 26.
- [2] R.I. Stessel and P.M. Goldsmith, Flexible membrane liners in waste management, *J. Air Waste Management Assoc.*, 42 (1992) 1178.
- [3] G.N. Richardson and R.M. Koerner, *Geosynthetic Design Guidance for Hazardous Waste Landfill Cells and Surface Impoundments*, non-published report, US EPA, Cincinnati, OH, 1985.
- [4] ASTM, *Annual Book of ASTM Standards*, American Society For Testing and Materials, Philadelphia, 1991.

- [5] US EPA, Method 9090, Office of Solid Waste, US Environmental Protection Agency: Washington, DC, n.d.
- [6] US EPA, Lining of Waste Containment and other Impoundment Facilities, EPA/600/2-88/052, Risk Reduction Engineering Laboratory, US Environmental Protection Agency, Cincinnati, OH, 1988.
- [7] R.M. Koerner, *Designing with Geosynthetics*, Prentice-Hall, Englewood Cliffs, NJ, 1990.
- [8] H. Steffen, Report on two-dimensional strain/stress behavior of geomembranes with or without friction, Proc. Int. Conf. on Geomembranes, Industrial Fabrics Assoc. Int., St. Paul, MN, 1984, p. 181.
- [9] D. Fayoux and D. Loudiere, The behavior of geomembranes in relation to the soil, Proc. Int. Conf. on Geomembranes, Industrial Fabrics Assoc. Int., St. Paul, MN (1984) p. 175.
- [10] A.S. Michaels, W.R. Vieth and H.J. Bixler, Gas permeability of highly oriented dibutyl maleate-ethylene copolymer films, *J. Appl. Polymer Sci.*, 8 (1964) 2735.
- [11] H.G. Zachman and R. Gehrke, Advances in Indirect methods of polymer morphology characterization, in: *Morphology of Polymers: Proceedings, 17th Europhysics Conference on Macromolecular Physics*, Berlin, Walter de Gruyter, Berlin, 1986, p. 119.
- [12] H.E. Haxo Jr., T.P. Lahey and M.L. Rosenberg, Factors in Assessing the Resistance of Geomembrane Liners and Waste Liquids, Hazardous Waste Engineering Research Laboratory, US Environmental Protection Agency, Cincinnati, OH, 1986.
- [13] R. C. Weast (Ed.), *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 1980.
- [14] A.D. Schwope, W.J. Lyman, J.M. Bass and J.H. Ong, *Analysis of Flexible Membrane Liner Chemical Compatibility Tests*, Municipal Environmental Research Laboratory, US Environmental Protection Agency, Cincinnati, OH, 1983.
- [15] A.S. Michaels and H.J. Bixler, Membrane permeation, theory and practice, in: E.S. Perry (Ed.), *Progress in Separation Science*, Vol. 1, Interscience, New York, 1968, p. 143.
- [16] W.W. Brandt, Model calculation of the temperature dependence of small molecule diffusion in high polymers, *J. Phys. Chem.*, 63 (1959) 1080.
- [17] US EPA, Lining of Waste Containment and Disposal Facilities, SW-870, Office of Solid Waste and Emergency Response, US Environmental Protection Agency, Washington, DC, 1983.
- [18] H.E. Haxo and N.A. Nelson, Factors in the durability of polymeric membrane liners, Proc. Int. Conf. on Geomembranes, Industrial Fabrics Assoc. Int., St. Paul, MN, 1984, p. 287.
- [19] Paul Goldsmith and Richard Ian Stessel, Multi-axial testing of geomembranes, *Waste Management and Research*, forthcoming.
- [20] 40CFR268.20.