Comparison of the Effects of Testing Conditions and Chemical Exposure on Geomembranes Using the Comprehensive Testing System

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ABSTRACT: Chemical compatibility tests were conducted on high-density polyethylene geomembrane samples using the Comprehensive Testing System (CTS) under low- and high-displacement conditions. CTS development between the two sets of data (low- and high-displacement) was found to significantly reduce the friction within the testing cell. This friction reduction was apparent from the decrease in delta modulus from the larger values obtained during low-displacement testing to the smaller values obtained during high-displacement testing. The results of the high-displacement testing showed statistically significant differences between delta modulus results at the 95% confidence interval (probability = 0.050), which was not possible with the low-displacement test configuration. Further, the high-displacement testing showed that the more soluble the test chemical was in polyethylene, the lower the resulting delta modulus. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2097–2110, 1998

Key words: geomembrane; high-density polyethylene; chemical compatibility; testing; landfill liner

INTRODUCTION

The Comprehensive Testing System (CTS) was developed at the University of South Florida for testing simultaneous application of mechanical loads, chemical exposures, and other environmental factors, such as elevated temperature, on geomembranes (GMs). This paper documents and compares the results of two separate testing programs conducted using the CTS. A key advantage of the CTS, exploited in both these test programs, was its ability to distinguish the effects of chemicals on the mechanical properties of the GM without causing catastrophic failure of the membrane. Such "nondestructive" laboratory testing differs sharply from standard practice that measures stress and strain at break, among other variables. The valuable information available from the comparisons of these two test programs is information concerning the effect of displacement. Attaining different displacements while striving to maintain the same type of material behavior required modification of the test system that produced useful test-development information.

This article describes the overall configuration of the CTS and its further development between the two test phases, permitting the use of greater displacement. Data from the two test programs are presented, where the manner of presentation is designed to ensure comparison of program

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data. Finally, results are discussed, producing conclusions concerning chemical interactions and recommendations for test programs.

CHEMICAL COMPATIBILITY TESTING

Chemical compatibility of GM liners is largely the result of the ability of the GM to resist permeation by solvents present in landfill leachate. Chemical compatibility tests involve exposure of the GM to solvents, and application of mechanical loads to the GM. The following sections discuss current test procedures used to evaluate GMs and the solubility of solvents in the polymer.

Geomembrane Testing

Standard GM testing methods are commonly divided into two categories: index and performance tests. While that terminology has not been formally accepted by American Society of Testing and Materials (ASTM) Committee D-35 on Geosynthetics, it is understood that the index test determines a physical property of the geosynthetic itself, regardless of the environment in which it is employed. It presents the geosynthetic property under standardized, isolated, and ideal conditions. A performance test describes how the geosynthetic performs in the environment in which it will be employed. This performance may fluctuate with the various environments.[1]

The Chemical Compatibility Test for Wastes and Membrane Liners, EPA Method 9090,[2] combines chemical exposure with a battery of mechanical tests to evaluate GM suitability for the proposed use. The test battery consists of standardized uniaxial index tests by the ASTM or by Federal Test Methods Standards (FTMS).

The key attribute of performance tests is multiaxial loading of the GM. Multiaxial tests use three-dimensional deformations, which are more representative of field conditions than are traditional uniaxial tests. In early multiaxial testing efforts, the GM is supported in a large vessel and subjected to a hydrostatic load normal to the plane of the sample until failure. The bulk of this multiaxial testing has been performed using either air pressure or hydrostatic pressure to deform the material. Fayoux and Loudiere[3] performed blister tests and hydraulic puncture tests. The blister test involved using hydrostatic pressure against a membrane supported by soil. Hydrostatic deformations require heads that would be the equivalent of up to 9 m, which is extreme.

Steffen[4] performed the first reported three-dimensional multiaxial tension test by removing the soil beneath a GM under pressure. One problem with these tests was that visual estimation of the extent of deformation had to be made, which introduced a degree of error. Results of these burst tests on high-density polyethylene (HDPE) indicate that there is a 9 to 15% strain at failure, which is only 1% of the strain measured uniaxially and 50% of the strain at the tensile yield point.

Koerner and colleagues,[5] with the Geosynthetic Research Institute (GRI), modified the pressure-vessel concept, using a vessel having a 24-in diameter, and included a center-point measuring stick. The vessel was capable of withstanding pressures of 2 MPa (300 psi). Strain percent was reported as a ratio of change in length of a chord along the surface of the sample to the original sample diameter. Studies by Frobel[6] reiterate the effect of three-dimensional tests on the yield stress of HDPE. While these studies are not yet standardized by ASTM, they are available as GRI standard GM-4. A clear emerging message is that an appropriate modeling of a field situation is absolutely necessary if a design-by-function approach is to be used.

Some researchers have suggested that the tensile characteristics of geotextiles should be tested under soil-confinement conditions.[7–10] Ling and associates[11] reviewed the previous research conducted to examine the tensile properties under soil-confined conditions. One of the important findings derived from these tests was that there was a significant increase in the stiffness and strength of the geotextile compared with the unconfined conditions. However, these testing methods failed to simulate on-site conditions because the soil was kept stationary inside a box, and the geotextile had to overcome the frictional resistance against the stationary soil before the tensile load in the geotextile could be applied. As a result, the measured load reflects the combined effects of the frictional force and the stress confinement, while on-site slippage at the soil–geotextile interfaces would not occur until a failure occurred. Therefore, these apparatuses overestimate the strength and stiffness of the geotextile. Ling and coworkers[11] developed an apparatus to measure the confined and unconfined tensile properties of geotextiles, however the shortcomings discussed above still existed. Furthermore, other important

Table I Cohesive Energy Density Data for Pure Chemicals Tested Using the Comprehensive Testing System and HDPE[14]

Compound	δ_d (MPa)$^{1/2}$	δ_p (MPa)$^{1/2}$	δ_h (MPa)$^{1/2}$	R_a^2 (MPa)
HDPE	17.6	0.0	0.0	
Benzene	18.4	0.0	2.0	6.56
Ethylbenzene	17.8	0.6	1.4	2.48
Toluene	18.0	1.4	2.0	6.60
Xylenes	17.8	1.0	3.1	10.77
Trichloroethene	18.0	3.1	5.3	38.34
Tetrachloroethene	19.0	6.2	2.9	54.69

environmental factors largely affecting liner performance, such as liquid-waste attack, were not considered in the testing. These tests, however, were developed for geotextiles, and their use with GMs has not been reported. The CTS was developed in response to recognized deficiencies in earlier GM test methods.[12] Its development in the context of this work and its attributes are discussed below.

Solubility of Solvents in Polymers

Solubility of a solvent in a polymer affects the mechanical properties of the polymer. This section provides background information on the solubility of a solvent in the polymer and the mechanism through which the solvent affects the polymer's properties. A measure of the solubility of a chemical in polyethylene is the distance from the solvent's cohesive energy density to the cohesive energy density of the polymer (R_a^2), which was calculated using the equation

$$R_a^2 = (2\delta_{d,P} - 2\delta_{d,S})^2 + (\delta_{p,P} - \delta_{p,S})^2 + (\delta_{h,P} - \delta_{h,S})^2 \quad (1)$$

where δ_d, δ_p, and δ_h are the cohesive energy densities due to dispersive, polar, and hydrogen bond-type interactions, respectively.[13] The values of δ_d, δ_p, and δ_h, as well as the value of R_a^2 for the solvents and polyethylene, are listed in Table I.[14]

In addition, polymer properties can be related to the mobility of polymer chains. Free volume is defined by considering each chain in a unit volume of polymer to be replaced by a sphere of the same volume. The volume of all spheres, taken together, represents the occupied volume. The difference between the occupied volume and the total volume of the polymer is the free volume. The free volume model envisages that the solvent diffuses by exchanging positions with holes in the polymer matrix that result from continuous redistribution of free volume due to thermal fluctuations of the polymer chains. Segmental mobility of polymer chains is responsible for the redistribution of free volume. Diffusivity and mechanical properties of the polymer are governed by the mobility of the system.[15,16]

COMPREHENSIVE TESTING SYSTEM

The CTS was developed to test the effects of multiaxial loads on GMs simultaneously with chemical attack. The CTS features a soil–GM interface and is capable of cyclic loading. These features of the CTS allow it to overcome the aforementioned disadvantages of previous multiaxial test systems. The following sections describe the CTS, its development, and its use in this work.

Development of the CTS

A simplified drawing of the configuration of the CTS test unit is shown in Figure 1. The CTS consisted of a test cell filled with granular media designed to apply loads to the GM through pistons mounted on a compression tester capable of applying cyclic loads. The cell was affixed to a support frame mounted to a Materials Testing System, Inc. (MTS, Minneapolis, MN), hydraulic ram. The CTS was originally constructed in 1987, and had undergone a series of modifications to attain its configuration at the start of the work reported here.

The CTS was originally developed because a need was believed to exist for multiaxial tests of GMs under field conditions. The existing mul-

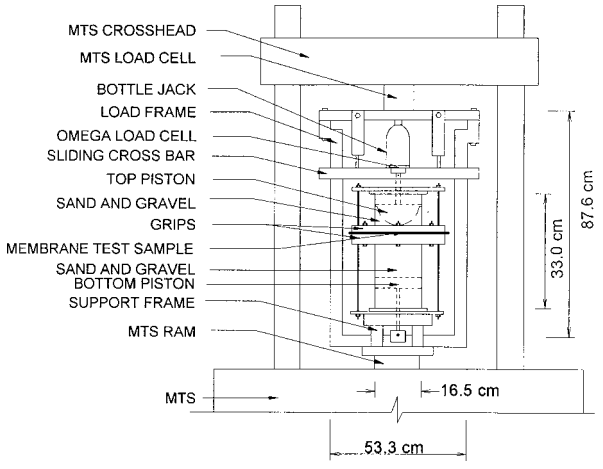

Figure 1 Comprehensive testing system.

tiaxial tests at the time the first CTS cell was constructed consisted of hydrostatic tests in which the membrane was deformed by exposure to elevated pressures of fluids on one side of the membrane.

The main objective of developing the CTS was to create a test capable of simulating the actual conditions a GM would encounter in the field, including mechanical loads, chemical attacks, and increased temperatures. The system needed to be able to simulate these conditions and provide useful data which could be directly related to field conditions. The CTS was designed to be capable of any combination of the following:

1. Apply compression to simulate the weight of the landfill;
2. Apply controlled displacements for stress–strain, cyclic, and relaxation testing;
3. Apply fixed forces to conduct creep tests;
4. Read and store forces and displacements;
5. Allow independent application of fluid head; and/or
6. Read and store pressure in the bottom chamber so as to detect membrane integrity by detecting fluid passage through the membrane.

CTS development for this work consisted of attempting to duplicate the application of overburden (waste) loads, hydraulic loads (leachate), and cyclic loads (test parameter, also potentially representative of the movement of heavy equipment) to the GM placed at the bottom of a sanitary landfill. The initial tests demonstrated that the CTS could apply a load and deform the membrane without causing failure to the membrane at the sample grips.[12] Failure at the grips, also called punch failure, was considered inappropriate because this type of failure meant that the sample was being sheared at the wall of the test cell. Inappropriate failure resulted when the granular media acted as a monolith and the GM sample resisted having this cylindrical monolith pushed through an orifice the same diameter as the monolith, shearing the sample around the ring where the orifice and monolith met. Stessel and Goldsmith[12] also demonstrated that when a sample is displaced, stress relaxation occurs, as expected from the viscoelastic nature of polymeric materials. They utilized a 10-cm (4-in)-diameter sample.

The next step in the development of the CTS was the addition of simulated leachate at various heads, combined with the application of cyclic and compressive loads. Later work tested GM samples with a combination of hydraulic head, overburden loads applied by a hydraulic jack, and cyclic loads.[17] This work also employed a 10-cm (4-in)-diameter test sample. The delta modulus was developed during this work as a test parameter by taking the ratio of the magnitude of cyclic strain to the range of stress observed:

$$\Delta E = \frac{(\bar{\delta}_{\max} - \bar{\delta}_{\min})}{(\bar{\epsilon}_{\max} - \bar{\epsilon}_{\min})} \tag{2}$$

where δ and ϵ are the stress and strain, respectively. The delta modulus provides a single-parameter measure of the material's elasticity/plasticity and strength as revealed under cyclic loading. It is capable of revealing differences in polymer behavior arising from changes in exposure conditions.

CTS Cell Configuration and Modifications

The CTS test cell began as a 15-cm (6-in)-diameter Soil Test, Inc. (Lake Bluff, IL), permeameter. Earlier data[12,17] were obtained using an insert, reducing the cell and grip diameter to 10 cm (4 in). This was later increased to utilize the entire 15-cm (6-in) permeameter diameter. The initial work reported here was conducted using the original permeameter walls; in the later work, the permeameter walls had been replaced completely by 15-cm (6-in) nominal diameter schedule-40 stainless-steel pipe machined to an inside diameter of 15.24 cm (6 in). Permeameter walls are

typically galvanized steel. The abrasion resulting from cyclic motion of the granular media against the rough, zinc-coated galvanized steel created friction, which caused removal of the zinc coating and permitted corrosion. Additionally, the machined stainless-steel walls were taller than those of the original permeameter, allowing displacements required for 20-cm (8-in)-diameter GM samples. Stainless steel was chosen as the material of construction for the cell components due to its chemical resistance.

The transmission of force from the piston to the sample was provided by the granular media. Originally,[12] the granular media was Ottawa sand, standard sieve size #10 to #60. However, the sand alone was found to migrate between the permeameter walls and the piston. The sand also made avoidance of punch failure very difficult due to the angular surfaces of the sand grains, which would cause the sand to move as a monolith and punch the GM at the grips. Therefore, a layer of larger granular media was added between the sand and the piston; it was finally determined that sand layered with Texas Blast gravel provided an adequate granular medium for testing and this was used for the initial, low-displacement testing.

As part of the later, high-displacement testing program, the sand was replaced with #4 glass beads (standard screen size 25/45) to decrease friction and permit increased displacements. The glass bead was smoother and more spherical, resulting in lower friction. The reduced friction alleviated the inappropriate failure at the grips. Initially, Texas Blast gravel was retained as a backing material to keep the small beads from migrating past the pistons, but the gravel was found to crush, bind, increase friction, and create slack in the cell. The Texas Blast gravel was replaced with 3.5- to 4.5-mm-diameter glass beads.

To further contain the small glass beads and reduce friction within the cell, glass fiber cloth and a glass fiber filter paper were added. Glass fiber cloth was placed next to the GM; the loose weave of the cloth was bunched during placement to allow the glass fiber to continue to cover the sample as the sample's area increased during displacement. The advantage of glass fiber cloth in testing was to further reduce friction between the granular media and the GM sample. In landfill applications, the glass fiber cloth also simulated the increasingly common use of geonet, replacing the soil drainage layer. Glass fiber filter has much smaller openings than glass fiber cloth. Use of glass fiber filter was necessary where it was important to prevent fine glass beads from falling to lower layers in the test cell; fine glass beads easily passed through ordinary glass fiber cloth. The glass beads were found to compact well during cell construction, which generally reduced the buildup of slack during testing. The glass beads also reduced friction substantially. Friction was further reduced by installing filter material during cell construction.

The final bottom cell construction, from the bottom piston up, consisted of the following sequence of materials:

- a Micropore® glass filter disk,
- glass fiber cloth,
- a Teflon® disk,
- large glass beads,
- a Micropore® glass filter disk,
- small glass beads,
- glass fiber cloth, and
- the geomembrane sample.

Above the sample, in the top cell, was the following sequence of materials:

- a piece of fiberglass cloth,
- small glass beads,
- another piece of fiberglass cloth,
- large glass beads, and
- the upper piston.

The cell construction is shown in Figure 2.

Before both low- and high-displacement programs, tests were conducted to determine the optimum total displacement, cyclic frequency, cyclic displacement, and cell configuration for the project. For the low-displacement work, the tests were conducted using a two-part load application: first, a total ramp displacement of 5.7 cm, followed by cyclic displacement at a rate of 1.3 cm/min (2.25 in at 0.5 in/min).

In the low-displacement testing, the ram was displaced to the maximum displacement and then the cyclic loading was initiated, as shown in Figure 3. Failure of the sample was believed to occur during initial ramping due to formation of a monolith of glass beads resulting from the loads required to displace a still-elastic GM. Additionally, due to the need to switch hydraulic ram control functions manually, there was time be-

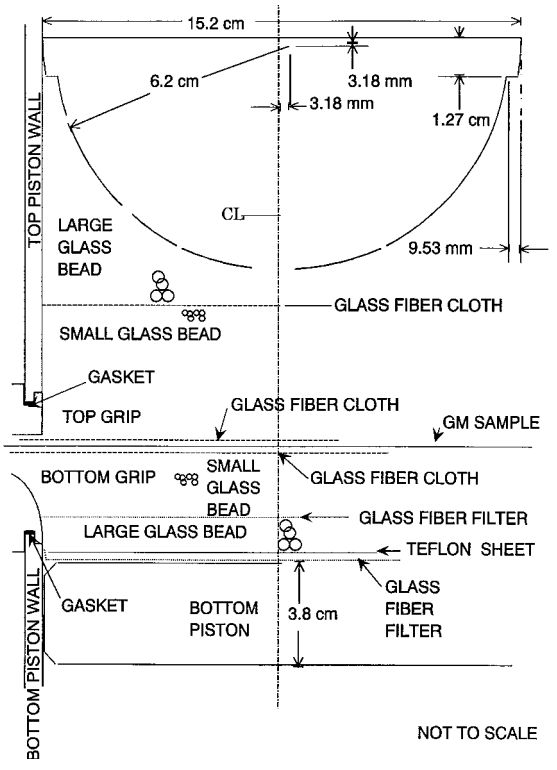

Figure 2 Cross-section view of the test cell setup and granular media.

tween the end of the initial ramp displacement and the start of cyclic loading that may have resulted in creep of the sample at the grips. The single large ramp displacement may have increased the likelihood of failure at the edge of the grip. To alleviate problems associated with the initial ramping followed by cyclic loading, ramp displacement procedures were modified so that the sample displacement was increased manually during cyclic loading until the total displacement was achieved. The sample displacement was increased manually at the bottom of the return stroke of cyclic loading until the total displacement of 6.35 cm (2.5 in) was achieved. Four manual ramp displacements of 0.63 cm (0.25 in) and a final manual ramp displacement of 1.27 cm (0.5 in) were performed. This resulted in a total manual ramping of 3.81 cm (1.5 in). This mode of displacement is shown in Figure 4. The cyclic displacement was 2.54 cm (1 in) in magnitude, resulting in a total displacement of the GM sample of 6.35 cm (2.5 in).

Changes in the CTS between the two data sets reported here were the modifications of the test cell and an increase in the total displacement to 6.35 cm (2.5 in) with a cyclic displacement of 2.54 cm (1 in) at a displacement rate of 3.9 cm per minute (1.5 in/min). The modifications of the test cell and changes in the initial and cyclic displacements allowed testing to be conducted that obtained results independent of the physical aspects of the test cell. The number of cycles required to achieve complete failure was found to be about 70 to 80.[18]

Conduct of CTS Tests

Data from the tests were recorded using a computerized data acquisition system. The MTS control panel provided outputs from the MTS's load cell and linear voltage displacement transducer (LVDT), which indicated the displacement and load on the GM. The MTS was calibrated prior to each test series; the load cell was within 1% of full range; and the MTS's LVDT within 1% of the reading for the range utilized. An Omega load cell (having an accuracy of 0.25% of full scale) and a Brainard–Kilman linear displacement transducer (having an accuracy of 0.10% of full scale) were mounted to the inner load frame, allowing determination of differences between the actual loads and displacement of the GM and the values recorded by the MTS's instrumentation. Differences between these readings indicated slack in

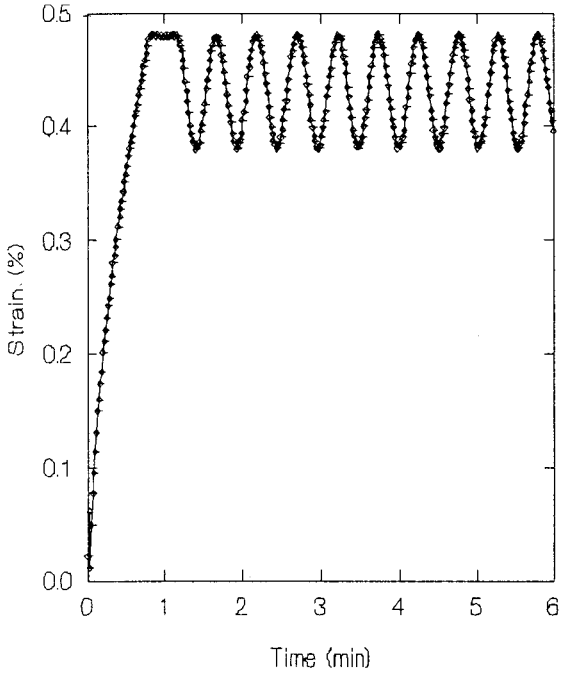

Figure 3 Initial ramp displacement followed by cyclic displacement.

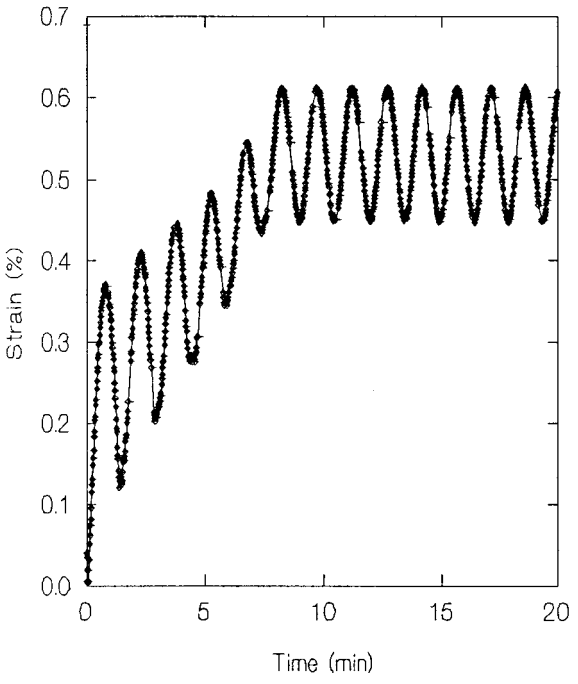

Figure 4 Manual displacement increases during cyclic loading.

the test cell. An Omega pressure transducer/indicator was attached to the lower cell to determine pressure in the cell, which would indicate a breach of the GM. These instruments were utilized in both the low- and high-displacement testing programs.

The outputs of these instruments were fed into a computerized data acquisition system consisting of a microcomputer equipped with an analog-to-digital converter card. The data from the analog-to-digital conversion card were then recorded in a Microsoft Excel spreadsheet. The spreadsheet was programmed to perform calculations of stress, strain, slack, and delta modulus. For the high-displacement testing, the spreadsheet was programmed to acquire the data directly and to display the results of the calculations on a near-real-time basis in graphic form on the screen during testing, greatly aiding the evaluation of test progress. All the data were stored on a diskette in Microsoft Excel format for further analysis.

The test was conducted by programming the desired displacement and frequency into the MTS's control panel as previously described. Displacement was a controlling variable. Strain was calculated from the displacement as the square root of the change in the surface area of the deformed sample as described below.

GM Test Samples

In order to evaluate a GM material typical of GMs commercially available in the United States, various liner materials were considered for testing. HDPE was selected as the liner material due to its widespread use in lining landfills. Current high-displacement recommendations support that the liner be 60 mil thick, so this thickness was selected. The material was to be evaluated as part of a composite liner system under a landfill, so slope stability was not an issue and thus a smooth material was selected. This also eliminated the possibility that the varying thickness of the textured materials would affect results due to stress concentrations at points in the sample relief. Finally, in selecting the liner material, the reputation of the manufacturer, history of support for EPA research, and product availability were evaluated.

The GM liner samples tested were 1.5-mm (60-mil)-thick HDPE obtained from GSE Lining Technology, Inc. (Houston, TX). Manufacturer's specifications for this material are presented in Table II.[19] Two separate bulk rolls of material were obtained, one for each phase of the testing. To reduce variation within the test phases, test samples for each testing program were obtained from the same roll of HDPE. Samples 40 by 40 cm (16 by 16 in) were cut from the roll and drilled for the passage of the NC threaded rods and bolts used for clamping the grips and the top and bottom clamping plates. Samples were inspected for surface imperfections that might lead to unwanted modes of failure during testing. Samples exhibiting imperfections, such as scratches or grooves, were rejected due to possible stress concentration at these defects.

Test Chemicals

Test chemicals for this project were selected based upon identification of environmentally significant landfill leachate constituents. The toxicity characteristic leaching procedure (TCLP) synthetic leachate represents aqueous leachate resulting from percolation of rainwater through the landfill. Motor oil and gasoline may be present in the landfill due to disposal of used motor oil, nonhazardous gasoline-contaminated media, or gasoline-powered engines. The chlorinated solvents may be present in the landfill due to disposal of small quantities of solvents used in residences and small businesses exempt from hazardous waste disposal regulations. Table III contains the

Table II Minimum Properties for Smooth GMs[19]

Property	Test Method	Minimum Property
Minimum thickness (mil)	ASTM D751, D1593 or D5199	54
Average thickness (mil)		60
Density (g/cc)	ASTM D792(b) or D1505	0.940
Carbon black content (%)	ASTM D1603	2.0–3.0
Carbon black dispersion	ASTM D3015	A1, A2, B1
Tensile properties (each direction)	ASTM D638 Type IV, 5 cm/min NSF 54, modified	
Tensile strength at yield (ppi)		130
Tensile strength at break (ppi)		243
Elongation at yield (%)	1.3-in gauge length	13
Elongation at break (%)	2.5-in gauge length	560
Tear resistance (lb)	ASTM D1004	45
Puncture resistance (lb)	FTMS 101, Method 2065	80
ESCR (h)	ASTM S1693, B	1,500
Dimensional stability (% change)	ASTM D1024 (1 h at 100°C)	±2

waste characterizations, Chemical Abstracts Service number, and other regulatory information for the chemicals used in this project.[20,21]

The chemicals used to evaluate the GMs in this project were obtained from various sources. The pure organic solvents were obtained from Fischer Scientific, Inc. (Pittsburgh, PA), and met American Chemical Society certification. The chemicals were benzene, ethylbenzene, trichloroethene, tetrachloroethene, and mixed (*ortho, meta,* and *para*) isomers of xylene. Motor oil, obtained from a local automobile parts store (Discount Auto Parts, Lakeland, FL), had a viscosity rating of SAE 10W30. Gasoline was obtained from a local Shell Oil Company retail outlet. The grade of gasoline was Super Unleaded with an octane number of 93 (R + M/2). The composition of gasoline and motor oil depends on a variety of proprietary factors, including source of the crude oil, processing techniques used in refining, blending of petroleum feedstocks, and time of year. For this reason, detailed chemical composition of the gasoline and motor oil were not determined.

The synthetic leachate used in the test was TCLP extraction fluid number 1.[20] Three batches, 20 L each, of the TCLP fluid were prepared. Glacial acetic acid was added to approximately 10 L of water in a 20-L Nalgene® carboy. Then, 1*N* sodium hydroxide was added to the contents of the carboy to adjust the pH to 4.93 ± 0.05 standard pH units. Finally, the remaining water was added to bring the total liquid to 20 L. Appropriate amounts of cadmium chloride and lead nitrate were dissolved in separate 20-L volumes of TCLP solution to create TCLP solution containing double the Safe Drinking Water Act maximum contaminant levels of lead (0.015 mg/L) and cadmium (0.005 mg/L). Therefore, the resulting TCLP solutions contained 0.030 mg/L lead and 0.001 mg/L cadmium. All reagents used in preparing the TCLP extraction fluid samples were obtained from Fischer Scientific. Separate chemical stocks were used in each of these testing programs, but the chemicals used were the same quality and were prepared identically.

Data Analysis

The data from an individual test consisted of the load applied, the sample displacement, and the test chemical. Stress is defined as the ratio of the load applied to the area perpendicular to the application of load. The cross-sectional area of the membrane was calculated as the product of thickness and circumference of the sample held within the grooved area of the grips. Stress could be mathematically represented as

$$\sigma = \frac{L}{2\pi r S} \tag{3}$$

where σ is the stress (N/cm^2), L is the applied load (N), r is the radius of the test sample held within the grooved area of the grips (cm), and S is the thickness of the sample (cm).

Table III List of Chemicals Used, Chemical Abstracts Service (CAS) Numbers, Synonyms, and Waste Characteristics[21]

Hazardous Substance	CAS Number	Synonyms	EPA Waste Number
Benzene	71432		U109, D018
Cadmium	7440439		D006
Ethylbenzene	100414		
Lead	7439921		D008
Multisource leachate			F039
Tetrachloroethene	127184	tetrachloroethylene, perchloroethylene	U210, D039
Toluene	108883	methylbenzene	U220
Trichloroethene	79016	trichloroethylene	U228
Xylenes, mixed isomers	1330207	dimethylbenzene	U239
F001. The following mixed solvents used in degreasing; all spent solvent mixtures/blends used in degreasing containing, before use, a total of 10% or more (by volume) of the above halogenated solvents or those solvents listed in F002, F004, and F005; and the still bottoms from the recovery of these spent solvents and solvent mixtures.			F001
A. Tetrachloroethylene			
B. Trichloroethylene			
F002. The following mixed solvents; all spent solvent mixtures/blends containing, before use, a total of 10% or more (by volume) of the above halogenated solvents or those solvents listed in F002, F004, and F005; and the still bottoms from the recovery of these spent solvents and solvent mixtures.			F002
A. Tetrachloroethylene			
B. Trichloroethylene			
F003. The following spent nonhalogenated solvents and the still bottoms from the recovery of these solvents:			F003
A. Xylene			
B. Ethylbenzene			
F005. The following spent nonhalogenated solvents and the still bottoms from the recovery of these solvents:			F005
A. Toluene			

Due to the multiaxial deformation of the sample, the strain was computed as the square root of the change in area divided by the original area of the test sample before deformation. Because the vertical displacement was the control parameter for the test, surface area had to be computed from this displacement value. The geometry of the deformation was assumed to consist of three portions; (1) the top portion of a torroidal area at the cell wall defined by the bottom grip, (2) a spherical area in the center of the GM, and (3) a right angle cone frustum joining the other two portions, as shown in Figure 5. The total displacement (h) was considered to be the sum of the displacements resulting from each of these three portions of the curve:

$$h_{\mathrm{TOTAL}} = h_{\mathrm{TORROID}} + h_{\mathrm{FRUSTUM}} + h_{\mathrm{SPHERE}} \quad (4)$$

Four simultaneous equations can be solved for the values of h_{TORROID}, h_{FRUSTUM}, h_{SPHERE}, and θ, based upon the actual measured total displacement. The surface area can be determined from these heights and θ using the appropriate equations. Because data reduction was performed in a spreadsheet, repetitive solving of simultaneous equations was not possible. The clear third-order geometry allowed curve-fitting of a polynomial with $r^2 = 1.00$. The resulting equation is

$$SA = 494.469 + 24.23(x) + 1.590(x^2) - 0.062(x^3) \quad (5)$$

where x is the vertical displacement of the test sample in centimeters, and SA is the resultant membrane surface area in square centimeters.

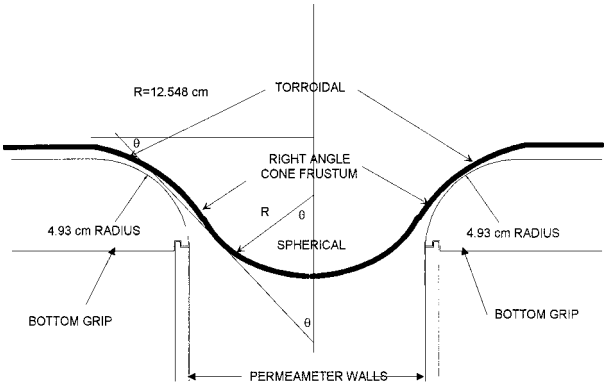

Figure 5 Geometry of GM deformation during CTS test.

The curve fit had an error of less than 0.025% for a displacement of 3.75 cm (1.5 in).[22]

Strain in the GM as a function of applied stress is shown in Figure 6. During cyclic testing, creep began to occur during the initial displacement. After a few cycles, the system reached steady state, where the loads (stresses) resulting from the displacement (strains) were relatively constant. The use of absolute modulus and phase angle, consistent with viscoelastic theory, was not feasible to describe the system. A parameter called the delta modulus (ΔE), developed by Stessel and Hodge,[17] was used:

$$\Delta E = \frac{(\overline{\delta_{\max}} - \overline{\delta_{\min}})}{(\overline{\epsilon_{\max}} - \overline{\epsilon_{\min}})} \tag{6}$$

where δ and ϵ are the stress and strain, respectively. The delta modulus provides a single-parameter measure of the material's elasticity/plasticity and strength as revealed under cyclic loading. The delta modulus value for a GM appears to depend on the initial displacement of the GM, magnitude of the cyclic displacement, and rate of displacement. By varying these parameters, the test can be adjusted to best determine the suitability of GMs for a given purpose.

Once the delta modulus values were calculated, the data were entered into Systat for Windows, version 5.0. Initially, Systat was used to prepare box plots of the data to identify trends in the data. Box plots can be ordered by median or other value, and adjacent box plots provide the easiest comparison of data.[23] With chemical exposure as the only treatment in both the low- and high-displacement tests, delta modulus calculated as above was subjected to analysis of variance (ANOVA) to determine whether statistically significant changes in the material property of the test sample occurred due to the treatment (test chemical). Multiple-comparison techniques were used to determine whether the population mean values of the tests conducted were significantly different within treatments (test chemicals). In multiple comparisons, the probability that each confidence interval contains its respective population means was determined. When means are tested for pairwise differences, the probability of finding one that is statistically significant based on chance alone increases rapidly with the number of pairs examined.[24] A powerful multiple-comparison technique involves the use of Bonferroni confidence intervals to determine the range of the population means based on the sample results. The Bonferroni confidence intervals for multiple comparisons are adjusted in size from the confidence intervals used for single comparisons based on the number of treatments performed. Tukey Studentized-range t-intervals are a refinement of Bonferroni's confidence intervals based on a balanced, one-way ANOVA where the number of observations for each treatment is the same. Tukey-Studentized t-intervals are used in Tukey's wholly (or highly) significant differences (HSD) test, and provide the shortest simultaneous confidence intervals for pairwise comparisons of the differences between means for balanced experiments.[25] Tukey HSD probabilities can then be compared to the 1-α significance level for rejection of the null hypothesis, where α is the probability that the mean value falls outside the individual confidence intervals.

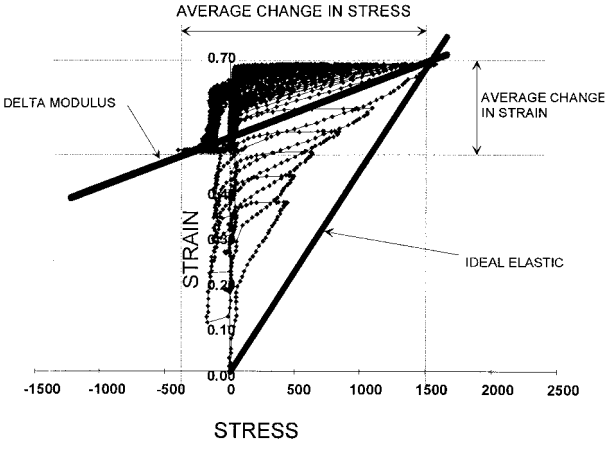

Figure 6 Typical stress–strain plot for CTS testing.

Table IV Delta Modulus Results in MPa from CTS Testing of GMs at Low and High Displacements

Chemical	Low Displacement (MPa)	High Displacement (MPa)
Benzene	188	32.77
	153	27.18
		31.62
Ethylbenzene	236	31.96
	200	24.73
		19.16
Gasoline	216	26.81
	220	23.09
		30.80
Motor oil	181	47.21
	174	42.73
		44.60
Tetrachloroethene	118	17.53
	202	9.95
		15.81
Trichloroethene	236	19.67
	228	13.15
		15.81
TCLP-Pb	185	28.38
	203	19.17
		22.53
TCLP-Cd	189	20.53
	184	18.46
		15.88
Water	221	35.20
	227	37.09
		30.41
Xylenes	217	47.35
	212	49.82
		45.77

RESULTS AND COMPARISONS

The tests conducted under low-displacement conditions utilized a 6-in nominal diameter permeameter as the test cell, sand and blast gravel as the granular media, and a 3.75-cm (1.5-in) initial ramp displacement followed by 1.25-cm (0.5-in) cyclic displacements. The tests conducted at high-displacement conditions utilized the glass beads as a granular media, and a total displacement of 6.25 cm (2.5 in) accomplished through application of four 0.625-cm (0.25-in) manual ramps and one 1.25-cm (0.5-in) manual ramp at the bottom of the cyclic displacement. The test results are presented in Table IV and presented graphically in Figure 7. Results of multiple-comparison ANOVA are included in Table V.

An inherent contradiction is clear when comparing test conditions and data: low-displacement testing produced higher moduli than high-displacement testing. As discussed above, friction clearly dominated low-displacement data. Further confirmation was derived from the rarity of significant differences in low-displacement data: no low-displacement test-result pairs were significantly different in multiple comparisons, compared with 23 significantly different results at the 95% confidence level (probability < 0.050). Clearly, low-displacement data were overwhelmed by noise from friction. With proper configuration, the lower friction present in high-displacement testing permitted greater displacement, albeit without catastrophic failure. The greater displacement also contributed to the increase of significant differences in the high-displacement testing. The results of low-displacement testing therefore showed greater delta modulus due to the larger forces required to overcome the greater friction in the test cell. The usefulness of friction reduction conducted after the low-displacement testing, for the high-displacement testing, was obvious when box plots delta modulus for the aromatic compounds tested—benzene, ethylbenzene, and xylenes—were ranked by values of R_a^2 in Figure 8. Comparing the results for the samples exposed to aromatic compounds, it could be seen that the low-displacement results showed no correlation between delta modulus and solubility parameter R_a^2 for the solvent and HDPE. From the high-displacement results,

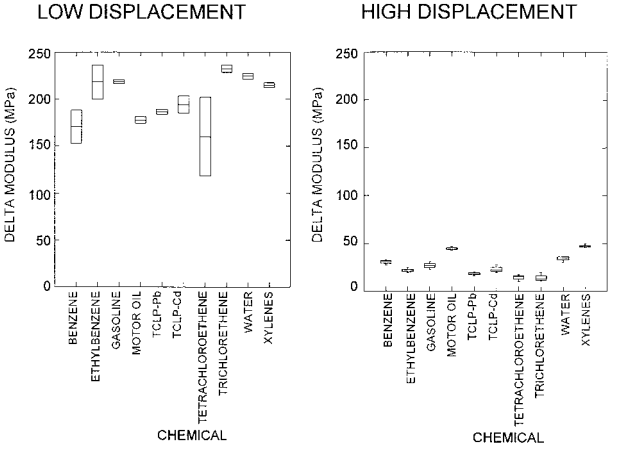

Figure 7 Box plots of low- and high-displacement delta moduli from CTS testing.

Table V Multiple Comparison Results of Differences Between Effects of Chemicals for Low- and High-Displacement Testing: Tukey HSD Multiple Comparisons

	Matrix of Pairwise Comparison Probabilities: Low-Displacement Tests									
	1	2	3	4	5	6	7	8	9	10
1	1.000									
2	1.000	1.000								
3	0.999	0.981	1.000							
4	0.902	0.978	0.556	1.000						
5	0.902	0.978	0.556	1.000	1.000					
6	1.000	0.998	1.000	0.724	0.724	1.000				
7	0.960	0.861	1.000	0.333	0.333	0.997	1.000			
8	0.604	0.781	0.274	1.000	1.000	0.400	0.147	1.000		
9	0.791	0.923	0.421	1.000	1.000	0.580	0.237	1.000	1.000	
10	0.946	0.992	0.640	1.000	1.000	0.802	0.400	0.997	1.000	1.000
	Matrix of Pairwise Comparison Probabilities: High-Displacement Tests									
	1	2	3	4	5	6	7	8	9	10
1	1.000									
2	0.803	1.000								
3	0.019	0.403	1.000							
4	0.434	1.000	0.774	1.000						
5	0.194	0.971	0.966	1.000	1.000					
6	0.000	0.000	0.004	0.000	0.000	1.000				
7	0.951	0.162	0.001	0.048	0.016	0.000	1.000			
8	0.999	0.405	0.004	0.149	0.054	0.000	1.000	1.000		
9	0.001	0.048	0.961	0.160	0.373	0.057	0.000	0.000	1.000	
10	0.000	0.000	0.001	0.000	0.000	0.994	0.000	0.000	0.008	1.000

1, TCLP-Cd; 2, TCLP-Pb; 3, benzene; 4, ethylbenzene; 5, gasoline; 6, motor oil; 7, tetrachloroethene; 8, trichlor; 9, water; 10, xylenes.

delta modulus could be clearly correlated to the solubility parameter for the aromatic compounds tested. The moduli obtained from testing chlorinated compounds trichloroethene and tetrachloroethene could not be explained by solubility (R_a^2). In the high-displacement testing, both halocarbons tested resulted in substantially lower moduli than the other compounds tested.

In low-displacement testing, the motor-oil result can be used as an indication of the effect of reducing friction within the cell. Motor oil is a viscous liquid capable of lubricating the cell walls and the granular media. The reduced friction between the cell wall and the granular media, and within the granular media, resulted in lower applied loads. This lower friction and the resulting applied loads reduced the delta modulus observed from motor oil in the low-displacement testing.

The overall lower friction in the high-displacement cell design provided test conditions for which interactions within the cell had been reduced to the point where the actual effect of the solvent on the GM could be observed. The high-displacement test results showed that the solubility of the solvent in the GM had a direct effect on the resulting delta modulus of the GM. The current CTS configuration is capable of allowing investigation into the interactions between chemicals present in leachate and into the effects of these interactions on the mechanical properties of the GM. This ability is clearly shown on Figure 8, where the delta moduli of high-displacement tested chemicals were found to be related to the solubility of the solvent in the polymer. Theoretically, increasing the solubility of the solvent decreases the polymers' mechanical properties.

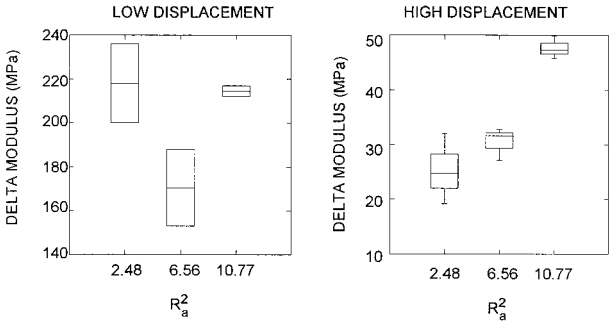

Figure 8 Box plot of low- and high-displacement delta moduli for aromatic compounds sorted by values of R_a^2.

SIGNIFICANCE AND RECOMMENDATIONS

The CTS has undergone a series of modification and improvements since its initial inception in 1987. Through these modifications, the test system has been refined and fine-tuned to allow the system to be sensitive to variations in the results, which can be traceable directly to polymer science. The CTS is the only multiaxial test that has, to date, been able to show direct relationships between its results and polymer–solvent interaction parameters.

The CTS is unique in deforming the sample using granular media; other multiaxial efforts use fluid pressure. Comparison of the two test series presented in this paper showed that the development of a granular-media displacement system was not trivial. The risks of retaining attributes that add friction were many. In addition, it was found to be very important that careful experimental procedures be followed to produce data that could be replicated. Only with this care taken were meaningful data produced. The second test sequence not only permitted increased displacement, but also permitted that displacement without ever causing the sample to fail, as defined by breaking. Under these conditions, the CTS proved capable of implementing granular-media displacement independent of fluid head to produce data that were theoretically meaningful and that identified (in both test phases) the unique characteristic of chlorinated solvents, requiring further study.

Further testing of polymers and solvents need to be conducted to expand the database of CTS test data. This database expansion will enable a more detailed look at the effects of solvents on polymers. Of particular interest is the effect of multicomponent leachates. These mixtures will allow greater insight into the mechanisms of GM degradation in the landfill environment.

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