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Mixed Waste Chemical Compatibility: A Testing Program for Plastic Packaging Components*

P. J. Nigrey

Sandia National Laboratories, Albuquerque, New Mexico, United States of America

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INTRODUCTION

The purpose of hazardous and radioactive materials packaging is to enable these materials to be transported without posing a threat to the health or property of the general public. To achieve this aim, regulations in the United States have been written establishing general design requirements for such packagings. While no regulations have been written specifically for mixed waste packaging, regulations for the constituents of mixed wastes, i.e., hazardous and radioactive substances, have been codified by the U.S. Department of Transportation (DOT, 49 CFR 173) and the U.S. Nuclear Regulatory Commission (NRC, 10 CFR 71). The design requirements for both hazardous [49 CFR 173.24 (e)(1)] and radioactive [49 CFR 173.412 (g)] materials packaging specify packaging compatibility, i.e., that the materials of the packaging and any contents be chemically compatible with each other. Furthermore, Type A [49 CFR 173.412 (g)] and Type B (10 CFR 71.43) packaging design requirements stipulate that there be no significant chemical, galvanic, or other reaction between the materials and contents of the package. Based on these requirements, a Chemical Compatibility Testing Program was developed in the Transportation Systems Department at Sandia National Laboratories (SNL). The program attempts to assure any regulatory body that the issue of packaging material compatibility towards hazardous and radioactive materials has been addressed. This program has been described in considerable detail in an internal SNL document, the Chemical Compatibility Test Plan & Procedure Report (Nigrey 1993).

In this paper, we discuss the meaning of chemical compatibility and describe the methodology used for measuring the effects of simulant mixed wastes on polymeric materials. These polymeric materials are those which may be used in current and future container designs for the transportation of hazardous and mixed wastes throughout the U.S. Department of Energy (DOE). In these discussions, we will assess the current state of chemical compatibility testing technology and provide the rationale for the strategy used in this program. While discussions of the results of the screening phase and the comprehensive testing phase of the program will not be presented, these topics are discussed in companion papers at this conference (Nigrey and Dickens 1995a &b).

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BACKGROUND

The term used to describe whether a material has not had any of its properties altered significantly when exposed to chemicals or other agents is referered to as that material's chemical compatibility with that agent. A variety of other terms can be found in the literature which are synonymous with the meaning of chemical compatibility. A much used and popular term that has been used to describe a material's chemical compatibility is its chemical resistance. Regardless of the varied meaning of chemical compatibility, in the discussions of this paper, the term will focus on the response of polymeric materials when exposed to a specific combination of environmental conditions including gamma radiation and chemicals at different temperatures for different exposure times. Thus, it should be apparent that any material which has minimal response to these environmental factors will have a high degree of chemical compatibility.

The purpose of a Chemical Compatibility Program (CCP) is to provide a scientifically defensible methodology for measuring the chemical compatibility of potential polymeric liner and seal materials with hazardous wastes. These polymeric materials are those which may be used in current and future container designs for the transportation of hazardous and mixed wastes throughout the DOE complex. The approach for developing such a program was to assess the current state of chemical compatibility testing technology, and to suggest routes that might lead to satisfactory, comprehensive, and reliable chemical compatibility data for use by the U. S. DOE in its Transportation Management Division.

Based on a review of the large body of chemical compatibility testing information, it is important to be aware of the basic factors that play a role in determining the chemical compatibility of polymers (plastics) with various chemical environments. Polymer-environment interactions can be either reversible (absorption leading to plasticization and swelling) or irreversible (oxidative) in nature. In general, polymers are resistant to weak acids, weak bases, and salt solutions. Strong acids can oxidize polymers leading to embrittlement. Organic solvents cause swelling, softening, and eventually dissolution. Since most chemical degradation of any particular polymer in any fluid or gas depends on the type of polymer, it is unlikely that the chemical compatibility information between polymers and any mixed waste form will be found in the literature. To provide the regulatory assurance that materials are suitable for use in the design of transportation packagings, liner and seal materials require compatibility testing with simulated wastes to determine their chemical resistance to these substances.

APPROACH

Materials. The main threats to seals and liners from the anticipated waste forms are judged to come from strong aqueous base, chlorinated solvents, hydrocarbon solvents, and ketones (Nimitz 1994). The candidate liner and seal materials which are known to be chemically resistant to the above described waste forms, are butadiene-acrylonitrile copolymer, cross-linked polyethylene, epichlorohydrin, ethylene-propylene rubber, fluorocarbon, tetrafluoroethylene, high-density polyethylene, isobutylene-isoprene copolymer, polypropylene, and styrene-butadiene rubber.

Simulants. Because of the wide variety of waste compositions found throughout the DOE complex, it is not possible to choose one specific simulant waste composition in a CCP. In addition, since no specific transportation container has been selected or has been specified for certain waste compositions, it is not possible nor prudent to select a very specific waste composition. However, there is sufficient information in the open literature (Whyatt 1990) and in DOE reports (DOE 1992) that provides some guidance on the quantities and character of the larger waste streams found within the DOE complex. Four simplified compositions of these large volume waste streams were selected in this testing program. To simulate some of the tank wastes at the Hanford Site, a rather simple aqueous solution containing 2 molar sodium nitrate, 0.7 molar sodium nitrite, 2 molar sodium hydroxide, 5.5 molar sodium carbonate, 0.1 molar cesium chloride and 0.1 molar strontium chloride was chosen. The combination of nitrate and nitrite anions represented the oxidizing chemical species while the hydroxide and carbonate anions simulated the corrosive nature of the tank wastes. The last two constituents, cesium and strontium, simulated the radioactive component in this large volume waste stream. To simulate the sizable inventories of chlorinated hydrocarbons mixed wastes, a solution of 50% by volume of trichloroethylene, 25 % chlorobenzene, 24% carbon tetrachloride and 1% cerium (III) 2-ethyl hexanoate was selected. This mixture of chemicals was believed to qualitatively represent the chlorinated solvent waste streams at the DOE sites. The cerium salt simulated uranium and other actinide elements because of similarities in ionic radii and redox properties. Similarly, to simulate liquid scintillation fluids and/or fuel hydrocarbons, a solution of 33% toluene, 33% xylene, 32% dioxane with 1% water was used. The water component was meant to simulate tritiated water found in some mixed wastes. Finally, to simulate ketones, a solution of 60% methyl ethyl ketone and 39% methyl isobutyl ketone containing 1% cerium (III) acetyl acetonate hydrate was used. It should be mentioned that ketones were solvents frequently used in the nuclear fuel reprocessing cycle.

Testing Variables. The variables in chemical compatibility testing represent those factors that are meant to simulate the conditions under which the material will be used. Specifically, the more important of these variables include exposure temperature, exposure time, radiation dose, and waste liquid concentration.

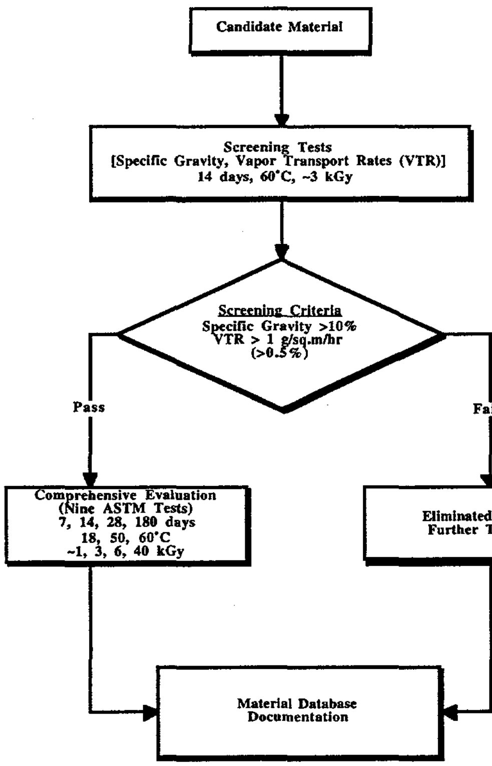
Some standard testing methods specify exposure temperatures of 23°C and 50°C. Since the purpose of this program was to evaluate the effects of hazardous materials on transportation container components, it is worthwhile to mention that the U.S. DOT regulations in 49 CFR 173.24 (e)(3)(ii) require chemical compatibility testing at temperatures of 18, 50, and 60°C. These temperatures were chosen in this program.

As with exposure temperatures, in standardized testing methods, the duration of exposure varies with each test method. However, regardless of the actual test duration, most groups involved in chemical compatibility testing agree that what is required is a three-level approach involving short-duration, intermediate, and long-duration exposure (Tratnyek 1985). We have selected exposure times of 7, 14, 28, and 180 days to include short and long duration exposure times.

With regard to the radiation dose that polymers should be exposed to, some international standards (IEC 1991) recommend that materials be exposed to absorbed doses ranging from 10^3 to 10^8 gray (Gy). These doses span a range where no effects in material properties are expected to where plastic materials are expected to be severely damaged. We have selected γ-radiation doses of 1.43, 2.86, 5.71, and 36.7 kGy from a ^{60}Co source. These radiation values were calculated based on γ-ray dose rate data available to us for the projected components of a pump submerged in a specific storage tank on the Hanford, WA reservation (Hey 1992). These data indicate a maximum γ-ray dose rate in the range of ~7.5 to 8.5 Gy/hr. The maximum dose rate of 8.5 Gy/hr was used in calculating the dose that container materials will receive from a ^{60}Co source at SNL. Using this dose rate and the four exposure times of 7, 14, 28, 180 day, the four doses described above were calculated.

A final variable for chemical compatibility testing is waste concentration. Practitioners of chemical compatibility evaluations generally believe that materials should be tested with the actual concentration of waste. This concentration is considered a good way to simulate a worst-case situation. For transportation containers, such a worst-case scenario could involve the partial evaporation of the contained waste, i.e., leakage of the more volatile components from a container. For this reason we selected a mixture of pure chemicals at their full strength as a worst-case condition.

Test Types. A variety of properties have been proposed and used for evaluating polymeric materials. For organizations concerned with mixed waste forms, the materials' resistance to both chemicals and radiation are of interest. Where low-levels of radiation are expected, resistance to chemicals may be of greater interest. Chemical compatibility is usually based on static physical test data obtained after exposure of the material to a chemical (leachate, surrogate, or simulant). The simplest of such testing involves changes in mass and dimensions. Since specific gravity measurements combine these two variables in one method, this method is particularly attractive for screening tests. Other static physical tests, led by hardness and tensile (stress/strain) properties, are used to indicate changes in the material and degradation. The stress/strain properties are related to the molecular makeup of the polymer, so that any attack or alteration in the polymer structure is manifested by changes in these properties.

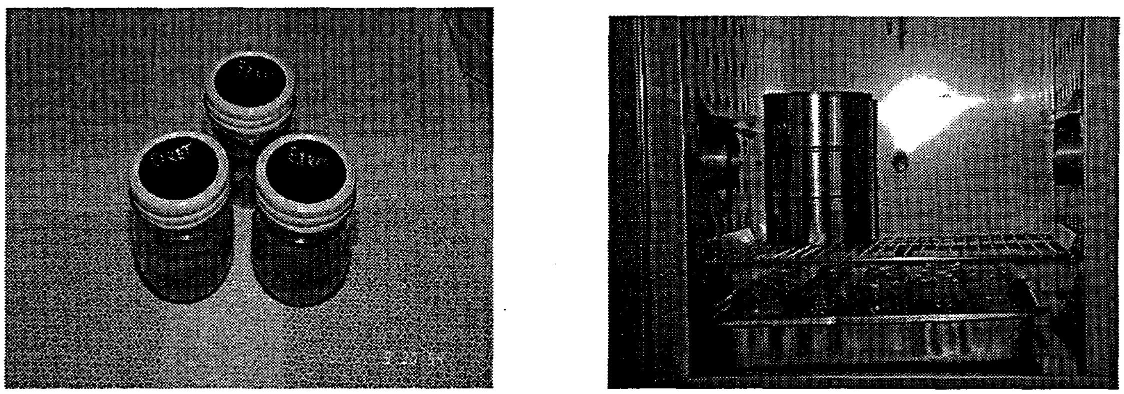


The proposed testing strategy shown in the adjacent flow-diagram uses a screening technique to limit the number of materials being subjected to more comprehensive testing. In this strategy, screening criteria values of 10% for specific gravity and ~1 g/m^2/h for Vapor Transport Rates (VTR) were selected. These values were chosen because they have been cited in the literature (Schwope 1985) as qualitative criteria in determining the chemical resistance of materials used in landfill liner applications. As shown in the flow-diagram, those materials which exhibit lower values are determined to pass the screening test while those with higher values fail the tests. These latter materials are then eliminated from further testing. All testing data are compiled in a standard spreadsheet format for eventual inclusion in a material database. Such a material database will be available to packaging designers or additional parties within and external to the DOE. The selection of specific gravity and VTR as screening tools is based on the availability of national standards, i.e., ASTM D792 and ASTM D814, that describe the use of these properties to test plastics. These tests can be easily performed with inexpensive laboratory equipment, and they provide data on materials consistent with their intended application. For example, where a material exhibits changes in specific gravity, i.e., changes its density, the materials may be losing some of the specific desirable properties for which they were selected. Such properties might include flexibility, radiation resistance, and chemical resistance.

Permeability evaluations of materials used for sealing applications is certainly obvious. What may not be as obvious is the ~1 $g/m^2/hr$ pass/fail criterion for permeability rates. While this value may be valid for flexible liners used in hazardous waste landfill applications, its application to packaging components may be tenuous. However, since rates of permeation are used in packaging regulations, i.e., by the U.S. DOT in Appendix B of 49 CFR 173, the use of related permeability rates provides validation for their use.

SCREENING TESTS

VTR Measurements. VTR testing provides a measurement of the rate of vapor transmission of a volatile liquid through a seal material. This type of testing provides a steady-state measure of the rate of vapor and liquid transmission through relatively thin plastics. While the calculated values of VTR can not be directly converted to traditional permeability values, the VTR values can be used to give a figure of merit for permeability. The experimental configuration for this measurement is shown in Figure 1. The measurements were performed according to the procedures described in ASTM D814.



(a) (b)

Figure 1. Vapor Transmission Rate experiments showing (a) a triplicate set of VTR cells and (b) the cells in a laboratory oven during the experiment.

Specific Gravity Measurements. Specific gravity testing provides a direct measurement of the density of the materials. Since density values reflect possible physical changes in materials, these measurement give some indication of whether the material has changed in mass and/or volume. These changes in turn indicate whether the chemicals to which the material has been exposed have affected the material's composition. Leaching of various components of the material such as plasticizers or other constituents of the plastic might occur. A change in the density of the material might also indicate swelling. Swelling can be important when selecting appropriate liner materials for packagings because liners can be structural components of the package. If liners swell, the change could have undesirable effects on the performance of the package.

COMPREHENSIVE EVALUATIONS

Those materials passing the screening tests will be evaluated using four different radiation doses, three temperatures, and four exposure times for each of the four waste forms described previously. The radiation levels chosen are 1.43, 2.86, 5.71, and 36.7 kGy of γ-radiation from a ^{60}Co source. The exposure temperatures are 18, 50, and 60°C. Exposure times of 7, 14, 28, and 180 days are used. In addition to the specific gravity, the response of the liner materials will be further evaluated based on their dimensional changes (ASTM D471), hardness changes (ASTM D2240), tensile property changes (ASTM D412 and D638), and stress cracking (ASTM D1693). Seal materials will also be evaluated by permeability changes (ASTM D814) and compression set changes (ASTM D395). For a detailed discussion of these measurements in liner materials, a companion paper in these Proceedings should be consulted (Nigrey and Dickens 1995a&b).

TESTING FACILITIES

The measurements described above for the screening tests and comprehensive testing necessitate the availability of a facility that has the capability of irradiating plastics with gamma radiation. A number of such facilities are conveniently available at SNL. One such facility, the Low Intensity Cobalt Array (LICA) Facility, is situated near the Environmental Testing Laboratory (ETL) where all other chemical compatibility testing is performed. The LICA Facility at SNL has the capability to irradiate materials using fixtures in which there is a linear array or a circular array of the Cobalt-60. Depending on the specific array, dose rates of 10 Gy/hr to 2 kGy/hr can be achieved. The test cans used for the irradiation experiments can be heated and purged with either air or inert gases. Figure 2 shows the LICA pool with its linear and circular arrays.

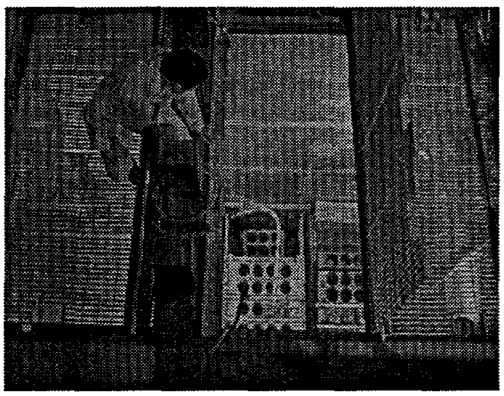


Figure 2. SNL LICA Pool

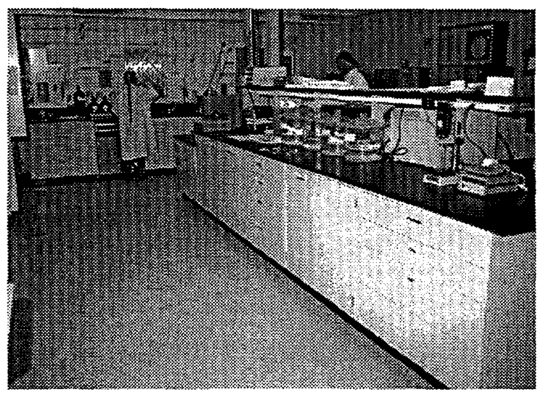


Figure 3. Testing Facilities

The ETL is a state-of-the-art laboratory which includes environmental chambers having the capability to routinely achieve temperatures from -80°C to 200°C. Mechanical testing equipment such as a Universal Testing machine and associated computerized control equipment can perform a variety of tensile and compression testing operations. Figure 3 shows a view of the ETL along with the previously mentioned capabilties. Not shown is equipment to perform Shore hardness measurements, stress cracking, specific gravity measuremsnts, and compression set measurements. In addition to this, more materials testing-related equipment, chemical fumehoods, gloveboxes, and analytical devices such as a Gas Chromatograph equiped with a Mass-Sensitive Detector (GC/MS) are available.

SUMMARY

We have developed a Chemical Compatibility Testing Program for the evaluation of transportation packaging components which may be used in transporting mixed waste forms. In this program, we have screened ten plastic materials in four liquid mixed waste simulants. These plastics were butadiene-acrylonitrile copolymer rubber, cross-linked polyethylene, epichlorohydrin rubber, ethylene-propylene rubber, fluorocarbons (Viton and Kel-F), polytetrafluoroethylene, high-density polyethylene, isobutylene-isoprene copolymer rubber, polypropylene, and styrene-butadiene rubber. The selected simulant mixed wastes were (1) an aqueous alkaline mixture of sodium nitrate and sodium nitrite; (2) a chlorinated hydrocarbon mixture; (3) a simulant liquid scintillation fluid; and (4) a mixture of ketones. The screening testing protocol involved exposing the respective materials to ~3 kGy of gamma radiation followed by 14 day exposures to the waste simulants at 60°C. The seal materials or elastomers were tested using Vapor Transport Rate measurements while the liner materials were tested using specific gravity as a metric. For these tests, screening criteria of ~1 $g/hr/m^2$ for VTR and specific gravity change of 10% were used. Those materials which failed to meet these criteria were judged to have failed the screening tests and were excluded from the next phase of this experimental program. We are presently completing the comprehensive testing phase of liner materials in simulant Hanford Tank waste.

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