

Chemical Compatibility Screening Results of Plastic Packaging to Mixed Waste Simulants *

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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 (U.S. 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 national 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 for hazardous and radioactive materials has been addressed. This program has been described in considerable detail in an internal SNL document, Chemical Compatibility Test Plan & Procedure Report (Nigrey 1993) and in a companion paper (Nigrey 1995) of this conference.

In this paper, we present the results of the first phase of this testing program. This phase involved the screening of five candidate liner and six seal materials to four simulant mixed wastes, respectively. The testing protocol involved exposing the respective materials to ~ 3,000 gray (3 kGy) of gamma radiation followed by 14-day exposures to the waste types at 60°C. The seal materials were tested using Vapor Transport Rate (VTR) measurements while materials suitable for liner applications were tested using specific gravity measurements. For these tests, a screening criteria of ~1 g/m²/hr for VTR and a specific gravity change of 10% was used as a metric (Nigrey 1995). 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.

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EXPERIMENTAL

The properties which were evaluated to assess the suitability of potential seal and liner materials in mixed waste packaging designs were the magnitude of Vapor Transmission Rates (VTR) and specific gravity changes. In this section, we describe the experimental aspects of the screening phase of the chemical compatibility testing program.

The four simulant mixed waste forms selected were (1) an aqueous alkaline simulant tank waste, (2) a chlorinated hydrocarbon mixture, (3) a simulant scintillation fluid, and (4) a ketone mixture. The aqueous simulant contained 179 g sodium nitrate, 50 g sodium nitrite, 82 g sodium hydroxide, 32 g sodium carbonate, 17 g cesium chloride, and 16 g strontium chloride dissolved in 1 L of deionized water. The cesium and strontium salts were meant to simulate radioactive components. The chlorinated hydrocarbon simulant consisted of a mixture of 500 mL trichloroethylene, 250 mL chlorobenzene, 240 mL carbon tetrachloride, and 30 g cerium (III) 2-ethyl hexanoate. The cerium(III)-containing compound simulated uranium by virtue of its similar ionic radius. The simulant scintillation fluid was a mixture of 333 mL toluene, 333 mL xylene, 323 mL dioxane, and 1 mL water. The ketone simulant was a mixture of 600 mL methyl ethyl ketone, 390 mL methyl isobutyl ketone, and 30 g cerium acetyl acetonate hydrate. The rationale for the selection of these waste forms is described in the companion paper (Nigrey 1995).

Because none of the current mixed waste packaging concepts have received approval, a program was developed to test various properties of a broad range of liner and seal materials. The selected materials were ten plastics having known chemical resistance to a large number of classes of chemicals. The term plastic, as used in this paper, refers to polymeric materials, which includes both seal and liner materials. The selected plastics were butadiene-acrylonitrile copolymer rubber (Nitrile), cross-linked polyethylene (XLPE), epichlorohydrin rubber (EPI), ethylene-propylene rubber (EPDM), fluorocarbons (VITON™ or Kel-F™), tetrafluoroethylene (TEFLON), high-density polyethylene (HDPE), isobutylene-isoprene copolymer rubber (Butyl rubber), polypropylene (PP), and styrene-butadiene rubber (SBR).

Sample Preparation. Standardized test methods were used to cut, condition, and test the materials. The geometry of the material samples was specified by the test method. The samples were cut using an expulsion press and dies (Part # 22-16-00) manufactured by Testing Machines Inc., Amityville, NY. For example, the rectangular (1" x 2" x 0.125") samples required for specific gravity measurements were cut in the expulsion press fitted with an Expulsion Straight Edge Die (Part #23-10-06). Similarly, the circular samples (2.69" diameter x 0.125" thick) required for VTR measurements were cut in the expulsion press fitted with an Expulsion Die specifically designed for use in the American Society for Testing and Materials (ASTM) Standard Test Method D814 testing (Part # 23-00-00). The use of the press and dies permitted the cutting of multiple samples of uniform dimensions. The individual samples were visually checked to assure that none had nicks or other imperfections prior to their use. As recommended by ASTM D618, the plastics were conditioned at a standard temperature of 23°C (73.4°F) and a relative humidity of 50% for at least 24 hours prior to the testing process. This was done by storing the cut samples in a desiccator (Fisher Scientific, Part # 08-615) filled with magnesium nitrate hexahydrate (Fisher Scientific, Part # M46-500, 500 g) and saturated with water. Procedures for generating this constant relative humidity environment are described in ASTM E104. During conditioning, the samples were stacked atop each other and separated from each other using a metal spiral (Slinky Jr., James Industries, Inc., Part # 126).

Sample Irradiation. The pre-cut liner and conditioned seal samples were first exposed to gamma radiation from an underwater ^{60}Co source at SNL using a water-tight stainless steel canister (volume ~ 4 Liters). All the samples (of one candidate material) required for compatibility testing in each of the four simulant waste streams were placed in one canister. This involved 12 samples for VTR measurements or 20 samples for specific gravity measurements. The samples were loaded into a metal basket in the same configuration as was used to condition the samples, i.e., the samples were stacked atop each other and separated by a metal spiral. The basket was inserted into the canister and the canister was sealed. The loaded canister was lowered into the pool to a depth of 6 feet, purged with slow steady flow (~ 30 mL/min) of dry air, and allowed to come to thermal equilibrium at 60°C (Gillen 1982). Once thermal equilibrium was obtained, the canister was lowered into its irradiation location in the pool and the exposure time was started to obtain the desired radiation dosage. The highest dose rate currently available at the Low Intensity Cobalt Array (LICA) Facility is ~ 2 kGy/hr. Thus for a screening study where a gamma-ray dose of 2.86 kGy was required, the samples were exposed for approximately 1.5 hours. After the samples received the calculated radiation dosage, the canister was removed from the pool and the samples were again placed in the conditioning chamber. No more than 24 hours elapsed between the time the samples had been exposed to radiation and when they were exposed to the simulant wastes.

Sample Exposure to Chemicals. The general exposure protocol for specific gravity involved placing four specimens of each plastic material into a container (cell), and exposing them to each of the wastes for 14 days at 60°C. The four specimens were bundled together using nylon cable ties. Within each bundle, the specimens were separated through the use of ~1/16" (~ 2 mm) metal pins as spacers. This allowed for the ready access of the waste simulant to all surfaces of each specimen. A tapered pint glass canning jar (Kerr Group, Inc., Los Angeles, CA, Part # 70610-00518) was loaded with the five bundled test specimens and then filled with 300 mL of the test solution. Care was taken to ensure that sufficient waste was present to expose the entire surface area of all the samples. For relatively insoluble materials, ASTM D543 recommends about 10 mL/in² (~1.6 mL/cm²). After filling with liquid waste, the metal lid and band were attached to the jar and tightened. The jar was placed in secondary container which was then placed in an oven (Blue M, Model OV-490A-2) maintained at 60°C. The container was kept in this oven for 14 days.

VTR measurements were performed according to the procedures describes in ASTM D814. Here is a general description of the methodology. For specific experimental details, the standard test method should be consulted. The VTR cells consisted of 1/2 pint glass Mason jars (Kerr Group, Inc., Los Angeles, CA, Part # 70610-00105B). Each of the three jars was filled with approximately 200 mL of the test solution. For elastomeric materials, ASTM D543 recommends about 40 mL/in² (~6.2 mL/cm²). The seal specimen and metal band were loosely attached. The three jars were placed in an upright configuration (seal and metal band facing up) into the oven thermostated at 60°C. These jars were held at this temperature for one hour. They were then removed from the oven, sealed tightly, and then weighed on an analytical balance (Mettler-Toledo Inc., Hightstown, NJ, Model AT200 or PM2000). The respective weight of each jar was recorded and the jars were returned to the oven. At this time however, the jars were placed in the oven in an inverted position, i.e., with the seal and metal band facing down. The jars were again removed from the oven and reweighed after 24 hrs. They were then returned to the oven and kept in the oven for the remainder of the 14 days. After this time period, the jars were removed from the oven and reweighed. It should be noted that where flammable and toxic organic materials were used, e.g., the simulant scintillation fluids, the ketone simulants, and the simulant chlorinated hydrocarbon mixture, the jars

were placed in a metal paint can (Wellborn Paint Manufacturing Company, unlined paint can, gallon capacity, Part # 3239001) and the can was tightly sealed.

DISCUSSION AND RESULTS

The main threats to seals and liners are judged to come from strong aqueous base, chlorinated solvents, hydrocarbon solvents, and ketones (Nimitz 1994). Because few polymers are resistant to all these materials, it is possible that different polymers will be chosen as container components for the different waste streams being transported. The candidate liner and seal materials chosen were known to be chemically resistant to the above described waste forms.

The material properties that should be evaluated to assess the suitability of potential seal and liner materials in mixed waste packaging designs are mass and density changes, VTR, hardness, modulus of elasticity, tensile strength, elongation, compression set, and stress cracking (Nigrey 1993). Since the measurement of all these material properties was expected to be costly and time-consuming, screening tests with relatively severe exposure conditions such as high temperatures and high radiation levels were implemented to quickly reduce the number of possible materials for full evaluation. The evaluation parameters used in the screening study consisted of specific gravity changes in liners and changes in permeability rates (VTR) in seals. These parameters were evaluated using standardized test methods such as those developed by the American Society for Testing and Materials (ASTM). For specific gravity changes, ASTM D792 was used. In evaluating VTR, ASTM D814 was used. The criteria and the rationale for their selection are described below.

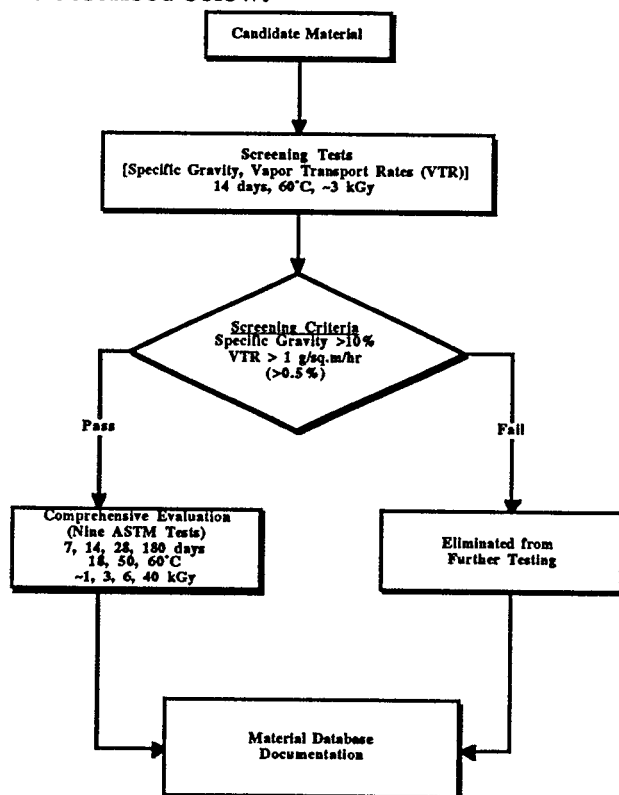


Figure 1. Screening Strategy

The proposed testing strategy shown in Figure 1, 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/m²/hr for 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 liner applications. As shown in Figure 1, 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 is compiled in a material database which is 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 these tests 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 in sealing applications is certainly obvious. What may not be as obvious is the $\sim 1 \text{ g/m}^2/\text{hr}$ pass/fail criteria value 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 its use.

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 cannot be directly converted to traditional permeability values, the VTR values can be used to give a figure of merit for permeability. For the purposes of these screening tests, these values of VTR were used as a criteria for determining whether the material passed or failed the exposure protocol.

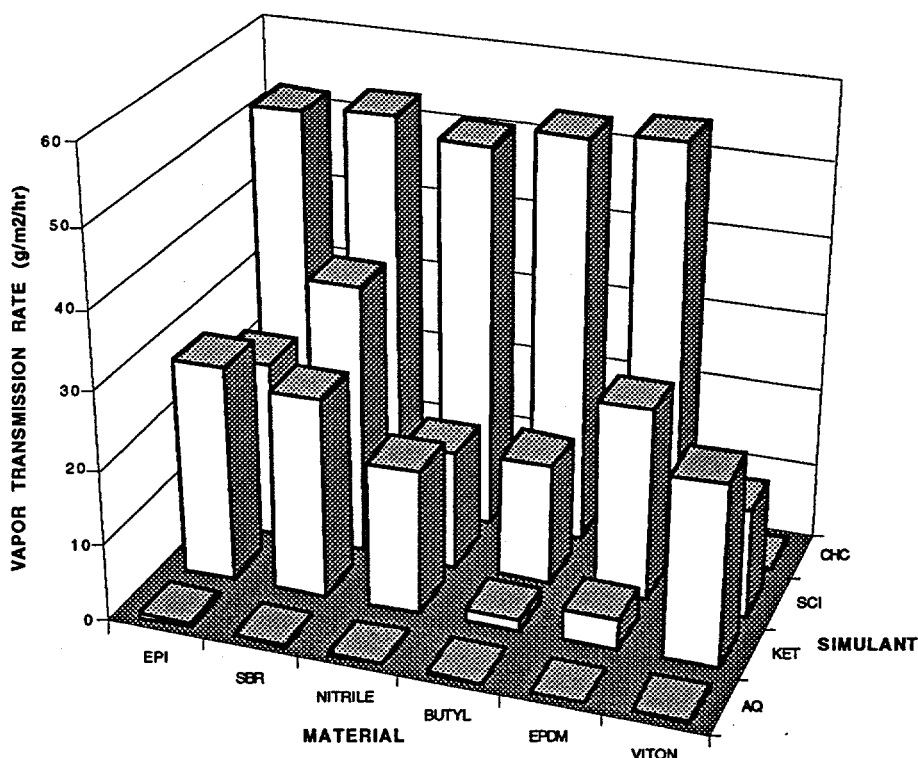


Figure 2. VTR of six seal materials exposed to the four simulant mixed wastes at 60°C.

The results of the screening of six seal materials exposed to the four simulant mixed wastes for 14 days at 60°C is shown in Figure 2. As can be seen from the data, while all seal material passed exposure to radiation and the aqueous simulant mixed waste, the EPDM rubber exhibited the lowest VTR of $0.05 \text{ g/m}^2/\text{hr}$. When exposed to radiation and chlorinated hydrocarbon simulant mixed wastes, only VITON passed these screening tests

with a value of 0.25 g/m²/hr. None of the seal materials tested passed the screening tests in either the simulant scintillation fluid mixed waste or the ketone mixture simulant waste. However, VITON and Butyl had the lowest VTR values, respectively, in these wastes. These results are consistent with chemical compatibility data reported in the literature (Park 1993). However, since these screening tests combined radiation and chemical effects, it can be concluded that radiation effects, i.e., γ -radiation at a dose of ~3 kGy, plays little, if any role in affecting the resistance of these materials to these chemicals at 60°C. It should, however, be mentioned that a different conclusion might have been reached had some other evaluation criteria been used. For example, if tensile property changes had been selected instead of VTR values, different conclusions might have been reached.

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 can give some indication of whether the material has changed in mass and/or in volume. These changes in turn might indicate whether the environment to which the material has been exposed has affected the material's composition. For example, leaching of various components of the material such as plasticizers or other constituents 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.

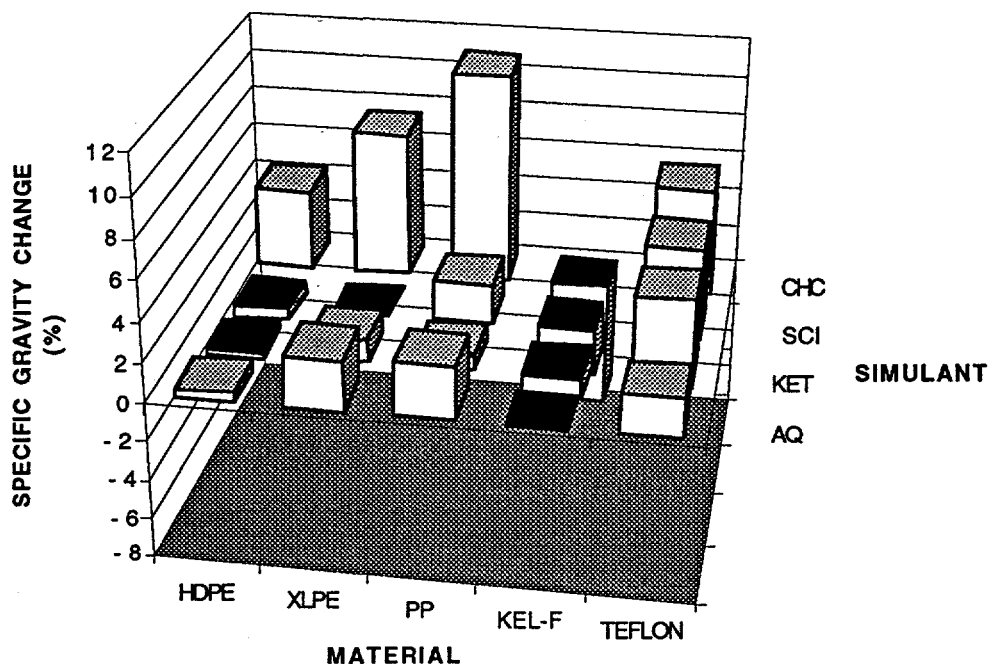


Figure 3. Specific gravity changes in liner materials exposed to the four simulant mixed wastes at 60°C.

The specific gravity data for the five liner materials is presented in Figure 3. The data shows that, while all materials with the exception of polypropylene (in chlorinated hydrocarbons) passed the screening criteria of 10% specific gravity change, Kel-F, HDPE, and XLPE were found to offer the greatest resistance to the combination of

radiation and chemicals. In spite of the fact that most materials exhibited a positive change in specific gravity, three materials (HDPE, XLPE, and Kel-F) had samples which exhibited negative changes in specific gravity. The samples which exhibited this behavior can be recognized in the graph by a completely blackened area. We provide a discussion of this phenomenon here. Since the determination of specific gravity by ASTM D792 involves only the measurement of sample mass, a negative value for specific gravity would suggest that the effected samples had lost some buoyancy, i.e., a loss in mass or volume. However, a close examination of the data for the affected samples revealed that these actually had an increase in mass. Without performing additional measurements on these materials, the origin of the negative specific gravity change can only be speculated upon. One such speculation is that the observed mass gain is due to adsorption effect. In such a process, the sorbed species causes a greater increase in the volume of the sample. If the volume component of the sample increases to a greater extent than does the mass, a net decrease in the specific gravity would be observed. Since the test method did not involve dimensional measurements, it was not possible to confirm this hypothesis. Another explanation of this effect is that during the exposure to the wastes, a component of the material was leached from the sample. This preferential leaching of material components could be masked by the simultaneous uptake of chemical species. It is not unreasonable that a desorbed species would have a greater specific gravity than an adsorbed species. However, since the meaning of these negative specific gravity changes are not understood at this time, the selection of these materials by packaging designers is questionable.

As was established by the VTR measurements, the results of the specific gravity measurements are consistent with what has been generally reported in the literature about the chemical resistance of materials used in liner applications (Britton 1989). However, based on the screening strategy described here, this work has demonstrated that those materials met the criteria are resistant not only to chemicals alone but also to a combination of radiation and chemicals. Since such data is not available in the literature, this work provides valuable data to supplement the chemical compatibility literature.

CONCLUSIONS

We have developed a chemical compatibility program for the evaluation of transportation packaging components which may be used in transporting mixed waste forms. Consistent with the methodology outlined above, we have performed the first phase of this experimental program to determine the effects of simulant mixed wastes on packaging materials. This effort involved the screening of 10 plastic materials in four liquid mixed waste simulants. The 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 rubbers were tested using VTR measurements while the liner materials were tested using specific gravity as a metric. For these tests, a screening criteria of ~1 g/m²/hr for VTR and a specific gravity change of 10% was used. Based on this work, it was concluded that while all seal materials passed exposure to the aqueous simulant mixed waste, EPDM and SBR had the lowest VTRs. In the chlorinated hydrocarbon simulant mixed waste, only VITON passed the screening tests. In both the simulant scintillation fluid mixed waste and the ketone mixture simulant mixed waste, none of the seal materials met the screening criteria. It is anticipated that those materials with the lowest VTRs will be evaluated in the comprehensive phase of the program. For specific gravity testing of liner materials the data showed that while all materials with the exception of polypropylene passed the screening criteria, Kel-F, HDPE, and XLPE were found to offer the greatest resistance to the combination of radiation and chemicals.

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