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Effects of Hanford Tank Simulant Waste on Plastic Packaging to Components *

P. J. Nigrey and T. G. Dickens

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

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 towards 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) at this conference.

In this paper, we present the results of the second phase of this testing program. This phase involved the comprehensive testing of five candidate liner materials to an aqueous Hanford Tank simulant mixed waste. The comprehensive testing protocol involved exposing the respective materials a matrix of four gamma radiation doses (1.43, 2.86, 5.71, and 36.7 kGy), three temperatures (18, 50, and 60°C), and four exposure times (7, 14, 28, and 180 days). Following their exposure to these combinations of conditions, the materials were evaluated by measuring five material properties. These properties were specific gravity, dimensional changes, hardness, stress cracking, and mechanical properties.

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EXPERIMENTAL

In this section, we describe the experimental aspects of the comprehensive phase of the chemical compatibility testing program.

Materials. The selected materials were five 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. The selected plastics were high-density polyethylene (HDPE), cross-linked polyethylene (XLPE), polypropylene (PP), fluorocarbon (Kel-F™), and polytetra-fluoroethylene (TEFLON).

Simulant Preparation. The simulant mixed waste form used in this testing phase was an aqueous alkaline simulant Hanford Tank waste. It was prepared by dissolving 179 g (2.10 moles) of sodium nitrate and 50 g (0.73 moles) sodium nitrite in deionized water (600 mL) using a 4 L beaker. After these salts had completely dissolved, 82 g (2.05 moles) sodium hydroxide was added under stirring and slight heating using a magnetic hotplate (Corning, Model PC-320). To this hot (~ 70°C) stirred solution, 17 g (0.107 moles) cesium chloride and 16 g (0.0952) strontium chloride was added. Finally, 32 g (0.301 moles) of sodium carbonate was added to the solution. This later addition resulted in the formation of a copious amount of white precipitate. Based on its insolubility, it is believed that this precipitate is strontium carbonate. To the resulting mixture was added another 400 mL of deionized water to bring the total volume of water used to 1 L. After cooling to near ambient temperature, the stirred mixture was stored in Amber Glass Bottles (Fisher Scientific, #03-327-6). It should be mentioned that the procedure described above was scaled up three-fold to give 3L batches of the simulant. All chemicals used in the preparation of the waste simulant were ACS reagent grade chemicals.

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 (Part # 22-16-00) and dies manufactured by Testing Machines Inc., Amityville, NY. For example, the rectangular (1" x 2" x 0.125") samples required for specific gravity and hardness measurements were cut in the expulsion press fitted with an Expulsion Straight Edge Die (Part #23-10-06). Rectangular (1" x 3" x 0.125") samples required for dimensional measurements were cut in the expulsion press fitted with an Expulsion Straight Edge Die (Part #23-10-07). Rectangular (1/2" x 1 1/2" x 0.125") samples required for stress cracking measurements were cut in the expulsion press fitted with an Expulsion Straight Edge Die (Part #23-14-36). Similarly, the Type IV samples required for tensile testing were cut in the expulsion press fitted with an Expulsion Die (Part # 23-14-23) specifically designed for the American Society for Testing and Materials (ASTM) Standard Test Method D638. The use of the press and dies permitted the cutting of multiple samples of uniform dimensions. When attempting to cut out the harder materials such as HDPE, PP, and Kel-F with the expulsion press, considerable difficulty was encountered. This problem necessitated machining the required "dog bone" samples of the materials to Type IV specifications. The individual samples were visually checked to assure that none had nicks or other imperfections prior to their use. A matrix was developed for labelling samples according to test method, sample number, and testing conditions. The samples were individually labelled with the use of 1/8" steel letter and number stamp sets (Siebenthal Inc., Part #'s YOU03273 and YOU03093, respectively). Due to the limited space available, the tensile testing samples were labelled with 1/16" steel letter and number stamp sets (Siebenthal Inc., Part #s YOU01271 and YOU01091, respectively). 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. A humidity/temperature pen (Fisher Scientific, Part # 11-661-14) was used to monitor these conditions. 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).

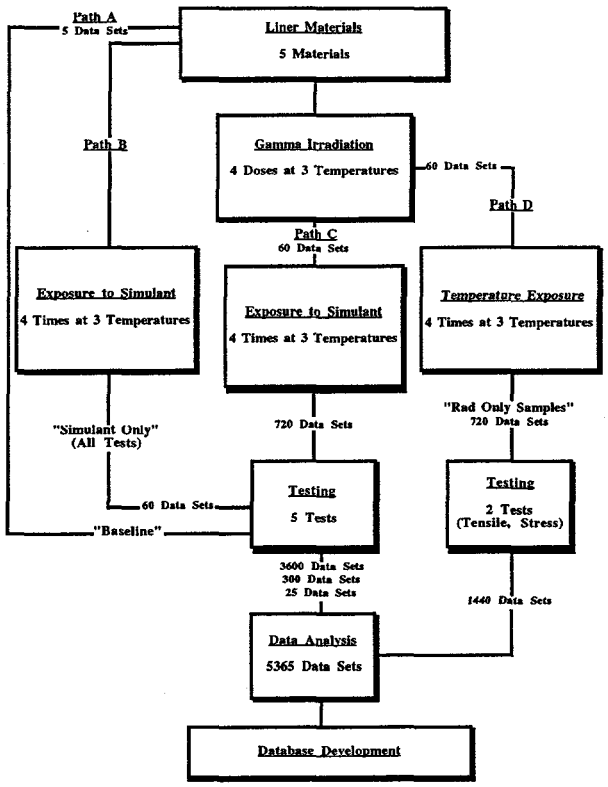
Sample Irradiation. For specific gravity measurements, 20 samples (4 samples per material, with 5 materials used) were cut out for each radiation dose, temperature, and time exposure for a total of 420 samples. For dimensional measurements, 180 samples were prepared. Hardness measurements involved 180 samples. Stress cracking measurements involved 1200 samples while tensile testing involved 2400 samples. The above mentioned sample numbers include only those samples which were exposed to gamma radiation from an underwater ^{60}Co source at SNL. These 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 then inserted into a water-tight stainless steel canister (volume ~4 L). The canister was sealed and 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 either ambient, 50, or 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 irradiations where a gamma-ray dose of 1.43 kGy was required, the samples were exposed for approximately 0.75 hours. For doses of ~3, 6, and 40 kGy, the corres-ponding longer exposure times were needed. After the samples received the calculated radiation dosage, the canister was removed from the pool and the samples were again placed in the conditioning chambers. No more than 24 hours typically 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 the specific testing conditions. The four specimens were bundled together using 7-1/2" nylon cable ties (Siebenthal Inc., Part # GRA6X753). 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 2 L glass bottle (Fisher Scientific, Part # 03-321-1E) was loaded with the 4 bundled test specimens and then filled with 1600 mL of the test solution. Care was taken to ensure that sufficient simulant waste was present to expose the entire surface area of all the samples. After adding the liquid simulant waste, the plastic lid was attached to the jar and tightened. The jar(s) were placed in the respective enviromental chambers maintained at 18, 50, and 60°C. The jar(s) were kept in these environmental chambers for 7, 14, 28, and 180 days. Similar procedures were followed for each of the other four testing procedures, i.e., dimensional testing, hardness testing, stress cracking tests, and tensile tests. In the case of stress cracking experiments, the samples were held in specially designed stainless steel specimen holders described in ASTM D1693. The samples held in the specimen holders were placed in the the jars containing the aqueous waste simulant.

DISCUSSION

The material properties that should be evaluated to assess the suitability of potential liner materials in mixed waste packaging designs are mass and density changes, hardness, modulus of elasticity, tensile strength, elongation, and stress cracking in polyethylene

materials. 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 results of these screening studies have been described in a companion paper (Nigrey and Dickens 1995) at this conference. From this screening study it was found that all of the selected liner materials had passed the screening criteria in the aqueous simulant mixed waste. This then resulted in the testing of five materials that were exposed to a matrix of four radiation doses, three temperatures, and four times in the simulant waste. In view of the extensive number of materials and exposure conditions, this second phase of the program is refered to as the "Comprehensive Testing" Phase that is still in progress. The evaluation parameters used in this comprehensive testing phase consisted of measuring the specific gravity changes, dimensional changes, hardness changes, stress cracking in polyethylene materials, and tensile property changes of potential liner materials. 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 dimensional changes, ASTM D471 was used. For hardness changes, ASTM D2240 was used. In evaluating stress cracking in polyethylene materials, ASTM D1693 was used. Finally, for evaluating tensile property changes, ASTM D638 was used.



Before describing the results of this study, we will describe the comprehensive testing strategy. This strategy is shown in the adjacent flow diagram. Five liner materials (HDPE, XLPE, PP, Kel-F, and Teflon) were evaluated. These materials were subjected to four different protocols (Paths A-D). To determine the intrinisic properties of the materials, the "Baseline" samples (Path A) were prepared for each of the five tests. In order to differentiate the effects on the materials by radiation and chemicals, one series of samples was only exposed to the simulant (Path B), while the other series of samples were exposed to both radiation and the simulant (Path C). The first series of samples is described as "Simulant Only" in the flow diagram. It should be noted that both series of samples were exposed for the four time periods (7, 14, 28, and 180 days) at three different temperatures (18, 50, and 60°C). For two testing protocols, tensile testing and stress cracking, where the effects of radiation and temperature alone could have significant impact on the properties, a series of samples described as "Radiation Only" is shown in the flow diagram (Path D). What may not appear obvious from the flow diagram is the large number of samples being tested in this comprehensive testing phase of the program. An attempt has been made in the flow diagram to demonstrate the total sample quantities. This can be seen by the number of data sets being generated after each exposure protocol. The total data sets being analyzed after testing are nearly 5400! Since the number of samples in each data set varies depending on the method, i.e., hardness tests are performed in triplicate while stress cracking tests include ten samples, the total number of

samples tested in this phase is significantly larger than 5400. In view of the large number of samples analyzed, we will only present the results of conditions where material properties have significantly changed. These conditions were at the highest gamma radiation dose (~40 kGy) and the highest temperatures (60°C).

RESULTS

Before describing the results of the analyses to date, it should be mentioned that a complete data analyses of all testing performed to date has not been completed. The principle reason for this is that a number of the 180 day experiments are still in progress. Until all experiments are completed, it is not possible to fully understand the implications of these studies. In Figure 1, we present the results of four measurements, specific gravity changes, dimensional changes (volume changes), hardness changes, and tensile strength changes. In the case of specific gravity changes shown in Figure 1a, it can be seen that most materials with the exception of TEFLON changed ~ 1% from baseline values.

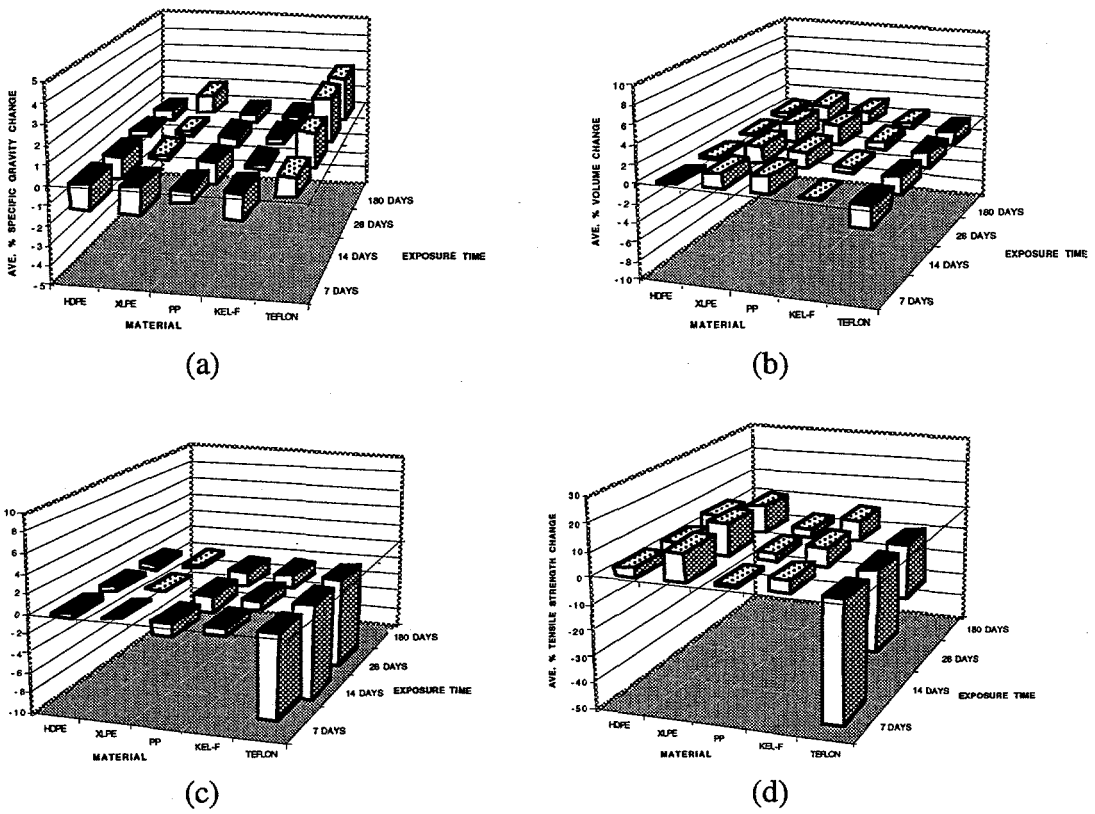


Figure 1. Comprehensive testing results of five liner materials after exposure to ~40 kGy of gamma radiation and the aqueous simulant waste at 60°C (a) specific gravity changes, (b) dimensional changes, (c) hardness changes , and (d) tensile strength changes.

Some of these changes, were negative, i.e., the material's specific gravity decreased. These data points can be recognized by the darkened areas in the bar graph.

The data for dimensional changes is summarized in Figure 1b. This bar graph shows volume changes rather than dimensional changes since volume is inclusive of all three dimensions, length, width, and thickness. As with specific gravity changes, the volume changes appear to be less than 2%. The greatest contributor to the change in volume was change in thickness.

The data for hardness changes is shown in Figure 1c. For this property, all materials with the exception of TEFLON exhibited changes less than 2%. TEFLON stands out in these measurements in that this material had changes in excess of 8%. As found previously for specific gravity, nearly all of these materials had negative property changes; most samples became softer after this exposure protocol.

The tensile strength changes are shown in Figure 1d. All materials with the exception of TEFLON exhibited changes less than 5% while TEFLON had changes in excess of 20%. For TEFLON these changes indicate that the material has a lower tensile strength after the exposure protocol.

The standard test method for stress cracking applies only to polymeric materials in the polyethylene class. Since this study only includes two such materials, HDPE and XLPE, we have omitted this data in this paper. However, to summarize the results of these measurements, HDPE is severely effected under these conditions of radiation exposure and temperature. In point of fact, after seven days of exposure at these conditions, 30% failures were observed for HDPE. At 14 days, 90% failures were observed. XLPE, on the other hand stood up much better at these conditions with failures in the 50% range.

Based on the limited results presented here, it is worthwhile to attempt to identify the one material which displayed the greatest chemical compatibility towards the simulant mixed waste under these conditions. In order to accomplish this, some ranking scheme needed to be developed. In this instance, we chose to sum the property changes and derive an average value over the four exposure times. That material which was calculated to have the lowest average property change value, i.e., changed the least, was assigned an arbitrary value of one. The other materials were then given values from two to five in the order of increasing average property change values. The ranking scheme developed in this manner is given in Table 1 The material with the best response should have the lowest changes in all the properties measured. This can be determined by adding the rankings for each material and chosing the material with the lowest value. As can be seen in Table 1, this very simplistic approach has selected the fluorocarbon Kel-F™ as the material which is most compatible with this simulant mixed waste under these conditions.

Table 1. Material Ranking

Property	HDPE	XLPE	PP	Kel-F	Teflon
Specific Gravity Changes	4	1	3	2	5
Dimensional Changes	3	5	4	1	2
Hardness Changes	2	1	4	3	5
Tensile Strength Changes	2	4	1	3	5
Total	11	11	12	9	17

However, the other well-known engineering plastic, HDPE, could equally well be identified as being compatible by virtue of its good performance (a high ranking value of two) in two out of the four properties evaluated. Since packaging designers may have other criteria for selecting materials, the data in Table 1 can be used in different ways.

CONCLUSIONS

We have developed a chemical compatibility program for the evaluation of plastic packaging components which may be incorporated in packaging for transporting mixed waste forms. Consistent with the methodology outlined in this paper, we have performed the second phase of this experimental program to determine the effects of simulant Hanford Tank mixed wastes on packaging materials. This effort involved the comprehensive testing of five plastic liner materials in the aqueous mixed waste simulant. The testing protocol involved exposing the respective materials to ~1, 3, 6, and 40 kGy of gamma radiation followed by 7, 14, 28, 180 day exposures to the waste simulant at 18, 50, and 60°C. From the limited data analyses performed to date in this study, we have identified the fluorocarbon Kel-F™ as having the greatest chemical compatibility after having been exposed to 40 kGy gamma radiation followed by exposure to the Hanford Tank simulant mixed waste at 60°C. The most stricking observation from this study was the poor performance of Teflon under these conditions.

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