EFFECTS OF SIMULANT HANFORD TANK WASTE ON PLASTIC PACKAGING COMPONENTS *

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ABSTRACT

In this paper, we describe a chemical compatibility testing program for packaging components which might be used to transport mixed wastes. We will mention the results of the screening phase of this program and then present the results of the second phase of this experimental program. 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 -140, 290, 570, and 3,670 krad of gamma radiation followed by 7, 14, 28, 180 day exposures to the waste simulant at 18, 50, and 60°C. From the data analysis performed to date in this study, we have identified the fluorocarbon Kel-F™ as having the greatest chemical compatibility after being exposed to gamma radiation followed by exposure to the Hanford Tank simulant mixed waste. The most striking observation from this study was the poor performance of Teflon under these conditions. The data obtained from this testing program will be available to packaging designers for the development of mixed waste packagings. The implications of the testing results on the selection of appropriate materials as packaging components are discussed.

I. INTRODUCTION

Hazardous and radioactive materials packagings are to permit such materials to be transported without posing a threat to the health or property of the general public. To achieve this aim, regulations 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. 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 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, the point can be made that a Chemical Compatibility Testing Program is the means to assure any regulatory body that the issue of packaging compatibility towards hazardous and radioactive materials has been addressed with respect to these simulants.

II. EXPERIMENTAL

A. 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...
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polyethylene (XLPE), polypropylene (PP), fluorocarbon (Kel-F™), and polytetrafluoroethylene (Teflon).

B. 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. To this hot (~70°C) stirred solution, 17 g (0.107 moles) cesium chloride and 16 g (0.0952) strontium chloride were added. Finally, 32 g (0.301 moles) of sodium carbonate was added to the solution. This latter 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. It should be mentioned that the procedure described above was scaled up threefold to give 3-L batches of the simulant. All chemicals used in the preparation of the waste simulant were ACS reagent grade chemicals.

C. 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 labeling samples according to test method, sample number, and testing conditions. The samples were individually labeled with the use of 1/8” steel letter and number stamp sets. Due to the limited space available, the tensile testing samples were labeled with 1/16” steel letter and number stamps. As recommended by ASTM D618®, the plastics were conditioned at a standard temperature of 23°C (73.4°F) and 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 filled with magnesium nitrate hexahydrate (500 g) and saturated with water. A humidity/temperature sensor 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 metal spacers.

D. Sample Irradiation

For specific gravity measurements, 20 samples (four samples per material, with five 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 1,200 samples while tensile testing involved 2,400 samples. The above mentioned sample numbers include only those samples which were exposed to gamma radiation from an underwater ⁶⁰Co 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 a slow steady flow ( ~30 mL/min) of dry air, and allowed to come to thermal equilibrium at either ambient, 50, or 60°C. 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 ~200 krads/hr. Thus for irradiations where a gamma-ray dose of ~140 krads was required, the samples were exposed for approximately 0.75 hours. For doses of ~290, 570, and 3,700 krads, the corresponding 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.

D. Sample Exposure to Simulants

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. Within each bundle, the specimens were separated through the use of ~1/16" metal pins as spacers. This allowed for the ready access of the waste simulant to all surfaces of each specimen. For relatively insoluble materials, ASTM D5439 recommends about 10 mL/in² (~1.6 mL/cm²). A 2-L glass bottle was loaded with the four bundled test specimens and then filled with 1,600 mL of the test solution. After adding the liquid simulant waste, the plastic lid was attached to the jar and tightened. The jar(s) were placed in the respective environmental 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[10]. The samples held in the specimen holders were placed in the jars containing the aqueous waste simulant.

III. DISCUSSIONS

The purpose of a Chemical Compatibility Program is to provide a scientifically defensible methodology for measuring the chemical compatibility of 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 testing program was to assess the current state of chemical compatibility testing technology and direct the thinking of all those concerned toward routes that might lead to satisfactory, comprehensive, and reliable chemical compatibility data for use by the U. S. DOE in its Office of Environmental Management.

The results of the first phase of this testing program have been presented at other conferences[11,12]. We will only summarize the results in this paper. The 1st 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 ~290 krads of gamma radiation followed by 14-day exposures to the waste types at 60°C. 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, screening criteria of ~1 g/m²/hr for VTR and a specific gravity change of 10% were used as metrics[13]. 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.

The screening studies concluded that while all seal materials passed exposure to the aqueous simulant mixed waste, ethylene propylene rubber and styrene butadiene rubber 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. 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 the four simulant mixed waste chemicals.

With the completion of the screening phase of the program several years ago, the comprehensive phase of this program has been in progress. Since all seal and liner materials passed the screening tests when exposed to the simulant Hanford Tank Waste, ten materials needed to be subjected to the test matrix. This would result in an extremely large sample set. In view of manpower and budget constraints, the comprehensive testing phase of the program was further subdivided into the testing of liner materials and seal materials. The results of liner testing will now be discussed.

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, dimensions, 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. 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. 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 Figure 1.

![Figure 1. Comprehensive Testing Strategy](image-url)

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 intrinsic 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 5,400! 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 10 samples, the total number of samples tested in this phase is significantly larger than 5,400. 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 (~3,670 krads), the highest exposure duration (180 days) and the highest exposure temperatures (60°C).

IV. RESULTS

Figure 2 shows the specific gravity changes of five liner materials exposed to 3,600 krads of gamma ray doses followed by exposure to the aqueous simulant waste at 60°C for 7, 14, 28, and 180 days.

![Figure 2. Specific gravity (S.G.) measurements](image)

It should be noted that the scale for % S.G. Change is rather small, e.g., from 1 to 5%, and either positive or negative. The sign of the specific gravity indicates whether specific gravity has increased or decreased when compared to the pristine materials, i.e., the material’s specific gravity at ambient conditions. Therefore, changes in the magnitude and the sign of specific gravity values indicate changes in this property. The greater the absolute values of the changes the more the materials are affected by this set of environmental conditions. Since properly engineered packaging components are not expected to be affected by contents of the package, i.e., the mixed wastes, materials exhibiting the least changes in specific gravity should be selected as packaging components. The results in Figure 2 show that all materials with the exception of Teflon exhibited specific gravity changes less than 2%. These results are significantly different from those found for materials exposed to the lower radiation doses and temperatures. Under the less aggressive conditions S.G. changed less than 1%. Teflon stood out in that increases in S.G. of more than 2% were observed. Increases in S.G. (or relative density) suggest that either the mass increased or the volume of the samples decreased. As can be seen in Figure 3, the latter situation is the case for Teflon.

Figure 3 gives the volume changes for five liner materials exposed to 3,600 krads of gamma ray doses followed by exposure to the aqueous simulant waste at 60°C for 7, 14, 28, and 180 days.

![Figure 3. Dimensional (Volume) measurements](image)

Since volume represents the product of length, width, and thickness, the evaluation of volume changes provides a concise picture of these environmental effects. The data shows that for HDPE and Kel-F™ minimal volume changes occur. Teflon exhibits decreases in volume at all exposure times.
In Figure 4, we give the hardness changes of five liner materials exposed to 3,600 krad of gamma ray doses followed by exposure to the aqueous simulant waste at 60°C for 7, 14, 28, and 180 days.

As was seen in the previously discussed measurements, Teflon stands out in its response to a combination of high radiation and elevated exposure temperatures. Teflon showed decreases in hardness up to ~14%. This means that the material has become softer. For certain applications in transportation packagings this may or may not be desirable.

Consistent with all the previous measurements, all materials had small tensile strength changes while Teflon had a decrease in tensile strength of nearly 80%.

Based on the results presented in this paper, 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, a ranking scheme needed to be developed. For this purpose, 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 (1). The other materials were then given values from two (2) to five (5) in the order of increasing average property change values. This can be seen visually by closely inspecting the results given in Figures 2 - 5. For example, in Figure 4, XLPE would appear to be first, i.e., assigned a value of 1, HDPE (2), Kel-F™ (3), PP (4), and Teflon (5). By adding the respective values for all four radiation doses and three temperatures, a total value for each measurement can be obtained. The ranking scheme developed by this process is given in Table 1. The material with the best overall response should have the lowest changes in all the properties measured. This can be determined by adding the rankings for each material and choosing the material with the lowest total value. As can be seen in Table 1, this very simplistic approach has identified the chlorofluorocarbon Kel-F™ as the material which is most compatible with this simulant mixed waste under these conditions. However, the well-known engineering plastic, HDPE, could equally well be identified as being very compatible by virtue of its good performance when specific gravity and tensile strength are used as the metric. For these two measurements, HDPE could be ranked first by virtue of this materials low total value for these two properties. Since packaging designers may have other criteria for selecting materials, the data in Table 1 can be used in different ways.

Since HDPE might be selected by some based on the data presented here, it is worthwhile to discuss the issue of stress cracking. Environmental stress cracking is a form of chemical attack in which a chemical that does not appreciably attack or dissolve a polymer in an unstressed state will cause catastrophic failure.
Table 1. Material Ranking

<table>
<thead>
<tr>
<th>Property</th>
<th>HDPE</th>
<th>XLPE</th>
<th>PP</th>
<th>Kel-F</th>
<th>TEFLOxN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity Changes</td>
<td>26</td>
<td>31</td>
<td>32</td>
<td>31</td>
<td>60</td>
</tr>
<tr>
<td>Dimensional Changes</td>
<td>43</td>
<td>46</td>
<td>32</td>
<td>29</td>
<td>31</td>
</tr>
<tr>
<td>Hardness Changes</td>
<td>39</td>
<td>22</td>
<td>37</td>
<td>22</td>
<td>60</td>
</tr>
<tr>
<td>Tensile Strength Changes</td>
<td>21</td>
<td>32</td>
<td>26</td>
<td>31</td>
<td>55</td>
</tr>
<tr>
<td>Total</td>
<td>129</td>
<td>131</td>
<td>127</td>
<td>113</td>
<td>206</td>
</tr>
</tbody>
</table>

when the polymer is stressed in its presence. The stress cracking phenomenon is a recognized potential problem with some varieties of HDPE and other semi-crystalline polymers. For this reason, a specific standardized test, ASTM D 1693 has been developed.

and 3,600 krad of gamma ray doses followed by exposure to the aqueous simulant waste at 60°C for 7, 14, 28, and 180 days. Figure 6b, shows the stress cracking failures for XLPE subjected to the same conditions. These results show quite clearly that XLPE has superior stress cracking performance.

V. CONCLUSIONS

We have described 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 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 ~140, 290, 570, and 3,600 krad of gamma radiation followed by 7, 14, 28, 180 day exposures to the waste simulant at 18, 50, and 60°C. From the data analyses performed, we have identified the fluorocarbon Kel-F™ as having the greatest chemical durability after having been exposed to gamma radiation followed by exposure to the Hanford Tank simulant mixed waste. The most striking observation from this study was the extremely poor performance of Teflon under these conditions.

ACKNOWLEDGMENTS

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REFERENCES


4. Kel-F is a trademark product for polychlorotrifluoroethylene (CTFE) formerly manufactured by 3M. Daikon America now manufactures this material under the tradename Neoflon.


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Effects of simulant Hanford tank waste on plastic packaging components

SUBJECT-DESCRIPTORS

RADIOACTIVE WASTES:T1; PACKAGING:Q1; TRANSPORT:Q1; COMPATIBILITY:Q1, Q2, Q3, Q4, Q5; LINERS; CONTAINERS; RADIOLYSIS:Q2, Q3, Q4, Q5; LIQUID WASTES; HAZARDOUS MATERIALS; MATERIALS TESTING; POLYETHYLENES:T2; POLYPROPYLENES:T3; TEFLOM: T4; KEL-F:T5; DENSITY; HARDNESS; TENSILE PROPERTIES; MORPHOLOGICAL CHANGES
In this paper, the authors describe a chemical compatibility testing program for packaging components which might be used to transport mixed wastes. They mention the results of the screening phase of this program and then present the results of the second phase of this experimental program. 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 approximately 140, 290, 570, and 3,670 krad of gamma radiation followed by 7, 14, 28, and 180 day exposures to the waste simulant at 18, 50, and 60 °C. From the data analysis performed to date in this study, they have identified the fluorocarbon Kel-F® as having the greatest chemical compatibility after being exposed to gamma radiation followed by exposure to the Hanford Tank simulant mixed waste. The most striking observation from this study was the poor performance of Teflon under these conditions. The data obtained from this testing program will be available to packaging designers for the development of mixed waste packagings. The implications of the testing results on the selection of appropriate materials as packaging components are discussed.