

## Material Compatibility of Polymers with Low GWP Refrigerants and Lubricant

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### ABSTRACT

Polymers are critical materials used in the construction of heating ventilation, air conditioning and refrigeration (HVAC&R) equipment. Understanding of the compatibility of these materials with new low global warming potential (GWP) refrigerants and lubricants is necessary to ensure reliable equipment operation over 10-20 years. AHRTI (Air-Conditioning Research Technology Institute), with funding from the US Department of Energy Building Technology Office, and NYSERDA (New York State Energy Research & Development Authority) sponsored the second phase of the AHRTI Project 9016 to continue the study of Low GWP (global warming potential) refrigerants. Phase II of this project expanded upon the chemical stability testing with more system materials of construction and included material compatibility of common non-metallic materials used in refrigerant containing systems.

This paper will focus on the material compatibility results of polymers with R-1233zd(E) and R-1224yd(Z) with and without mineral oil, R-1336mzz(E), R-514A, R-515B, R-516A, and R-454B with and without PAG (polyalkylene glycol), POE (polyol ester), and PVE (polyvinyl ether) lubricants.

### 1. INTRODUCTION

A comprehensive understanding of chemical stability and material compatibility of a refrigerant and lubricant with the materials used in HVAC&R equipment is critical to ensure reliable operation over the lifetime of the equipment. Phase I of the AHRTI 9016 research program was completed in 2021 to investigate chemical and thermal stability of a wide range of new low GWP refrigerants (Sorenson et al., 2021). Based on the findings in this study, Phase II of the AHRTI 9016 research program was started in 2022 focusing on expanding the chemical stability and materials compatibility understanding of low GWP refrigerants with additional materials. Material compatibility evaluations were conducted with various elastomers, gaskets, polymers & motor materials to further characterize these refrigerant systems as part of this project.

A similar program screening material compatibility was completed under AHRI MCLR Project #08007 which assessed the compatibility of R-1234yf and R-1234ze(E) with comparable materials tested under the AHRTI 9016 test program (Majurin et al., 2014a). This study revealed that many elastomers, gaskets, and polymers that were used in HFC (hydrofluorocarbon) systems are suitable for use with low GWP HFO (hydrofluoroolefin) refrigerants; however, the project recommended additional motor material studies for R-1234ze(E) to better understand system level implications. The same recommendations were not made with R-1234yf since it showed satisfactory compatibility with all evaluated materials. AHRTI Project 9016 Phase II included assessments of 8 elastomers, 3 flat sheet gaskets, 9 polymers and 7 motor materials with HCFO (hydrochlorofluoroolefins), HFO, and HFO blended refrigerants (R-1233zd(E), R-1224yd(Z), R-514A, R-1336mzz(E), R-515B, R-516A, and R-454B and limited materials were evaluated with R-466A). Materials selected were the same or similar to materials evaluated in AHRI MCLR Project #08007. Most refrigerants were evaluated with PAG, POE, and PVE lubricants, with the exception of R-1233zd(E) and R-1224yd(Z), which were evaluated with a white naphthenic mineral oil (MO), and R-466A, which was evaluated with an additized POE. The POE was unadditized except for low levels of an antioxidant,

common in synthetic lubricants, while the PVE and PAG lubricants were evaluated with additive packages designed to stabilize the lubricant with the refrigerant.

This paper will focus on the material compatibility results of polymers with R-1233zd(E) and R-1224yd(Z) with and without mineral oil, R-1336mzz(E), R-514A, R-515B, R-516A, and R-454B with and without PAG, POE, and PVE lubricants. These results will be summarized and further discussed in the AHRTI 9016 Phase II final report.

## 2. EXPERIMENTAL

Table 1 summarizes the times and temperatures for the exposures of these polymer materials. Test conditions for the exposures of these polymer materials deviate slightly from testing performed in AHRI MCLR Project #08007. Lubricant free conditions were tested at temperatures lower than the critical temperature of the refrigerant to ensure the material was fully submerged in liquid refrigerant at the test temperature. Lubricant containing conditions were tested at higher temperatures to align with previous studies of materials used in hermetic motors (Doerr and Kujak, 1993) than conditions selected in AHRI MCLR Project #08007 (Majurin et al., 2014a). Specifically, lubricant containing conditions were tested at 90°C in 2014, whereas this study conducted testing of all materials at the elevated motor material temperature of 127°C to align with studies by Doerr and Kujak in 1993.

**Table 1:** Refrigerant – Lubricant Test Conditions

| HCFO Conditions                    |                     | HFO Conditions                              |                     | HFO-Containing Blend Conditions |                           |  |  |
|------------------------------------|---------------------|---|---------------------|---------------------------------|---------------------------|--|--|
| Description                        | Exposure Conditions | Description                                 | Exposure Conditions | Description                     | Exposure Conditions       | Nominal Composition (% wt.)                                  |  |
| 100% R-1233zd(E)                   | 90°C<br>21 Days     | 100% R-1336mzz(E)                           | 90°C<br>21 Days     | 100% R-514A                     | 90°C<br>21 Days           | R-1336mzz(Z)<br>(74.7%)<br>R-1130(E)<br>(25.3%)              |  |
| 50% R-1233zd(E)<br>50% Mineral Oil | 127°C<br>21 Days    | 50% R-1336mzz(E)<br>50% PAG Oil             | 127°C<br>21 Days    | 50% R-514A<br>50% PAG Oil       | 127°C<br>21 Days          |  |  |
| 100% R-1224yd(Z)                   | 90°C<br>21 Days     | 50% R-1336mzz(E)<br>50% POE Oil             |                     | 50% R-514A<br>50% POE Oil       |                           |  |  |
| 50% R-1233zd(E)<br>50% Mineral Oil | 127°C<br>21 Days    | 50% R-1336mzz(E)<br>50% PVE Oil             |                     | 50% R-514A<br>50% PVE Oil       |                           |  |  |
|                                    |                     | 100% R-1234yf <sup>1</sup>                  | 90°C<br>21 Days     | 100% R-515B                     | 90°C<br>21 Days           | R-1234ze(E)<br>(91.1%)<br>R-227ea<br>(8.9%)                  |  |
|                                    |                     | 50% R-1234yf <sup>1</sup><br>50% POE Oil    | 90°C<br>21 Days     | 50% R-515B<br>50% PAG Oil       | 127°C<br>21 Days          |  |  |
|                                    |                     | 50% R-1234yf <sup>1</sup><br>50% PVE Oil    | 90°C<br>21 Days     | 50% R-515B<br>50% POE Oil       |                           |  |  |
|                                    |                     | 100% R-1234ze(E) <sup>1</sup>               | 90°C<br>21 Days     | 50% R-515B<br>50% PVE Oil       |                           |  |  |
|                                    |                     | 50% R-1234ze(E) <sup>1</sup><br>50% POE Oil | 90°C<br>21 Days     | 100% R-516A                     | 90°C<br>21 Days           | R-1234yf<br>(77.5%)<br>R-134a<br>(8.5%)<br>R-152a<br>(14.0%) |  |
|                                    |                     | 50% R-1234ze(E) <sup>1</sup><br>50% PVE Oil | 90°C<br>21 Days     | 50% R-516A<br>50% PAG Oil       | 127°C<br>21 Days          |  |  |
|                                    |                     |   |                     | 50% R-516A<br>50% POE Oil       |                           |  |  |
|                                    |                     |   |                     | 50% R-516A<br>50% PVE Oil       |                           |  |  |
|                                    |                     |   |                     |                                 | 100% R-454B               | 60°C<br>21 Days  | R-32<br>(68.9%)<br>R-1234yf<br>(31.1%) |
|                                    |                     |   |                     |                                 | 50% R-454B<br>50% PAG Oil | 127°C<br>21 Days   |  |
|                                    |                     |   |                     |                                 | 50% R-454B<br>50% POE Oil |  |  |
|                                    |                     |   |                     |                                 | 50% R-454B<br>50% PVE Oil |  |  |

<sup>1</sup>Data collected in AHRI MCLR Project #08007 (Majurin et al., 2014).

The samples selected for study are either materials that are currently in use or have been previously assessed for use in HVAC&R systems. Table 2 summarizes the polymer materials selected for this work. Polymer samples were received as ASTM D638 Type I specimens, with the exception of the PTFE material which was tested with ASTM D1708 microtensile specimens due to the requirements of the material supplier. All tensile test samples were exposed in their condition as received. Samples for weight and volume measurements were cut from the ends of the tensile specimens so that they could be fit into adequately sized test vessels, approximately 1.75"x0.75" (4.45 cm x 1.91 cm) rectangles. The microtensile samples were tested as whole samples for appearance, weight, and volume change because they were already an appropriate size for the test vessel.

Polymer samples tested in this study were exposed in a variety of combinations. Pieces used for weight, volume, and bakeout testing were exposed in individual vessels in the lubricant free test conditions to determine the extract content for each material. In the lubricant containing test conditions, all polymers were combined into a single vessel for each condition. Tensile test samples were combined into a single vessel for both the pure refrigerant and lubricant containing test conditions, as extract content was already determined using the weight and volume pieces of polymer.

**Table 2:** Materials and Testing Summary of Polymer Materials

| Polymer Material  | Appearance Change | Weight Change | Volume Change | Extract Content <sup>1</sup> | Post-Bakeout Appearance Change | Post-Bakeout Weight Change | Tensile Property Changes |
|---|-------------------|---------------|---------------|------------------------------|--------------------------------|----------------------------|--------------------------|
| Polytetrafluoroethylene (PTFE)<br>Parker 0100 - Unfilled            | X                 | X             | X             | X                            | X                              | X                          | X                        |
| Polyester<br>BASF Ultradur® B2550 - Unfilled                        | X                 | X             | X             | X                            | X                              | X                          | X                        |
| Nylon 6,6<br>BASF Ultramid® A3K BK00464 - Unfilled                  | X                 | X             | X             | X                            | X                              | X                          | X                        |
| Polyether Ether Ketone (PEEK)<br>Solvay Ketaspire® 820NT - Unfilled | X                 | X             | X             | X                            | X                              | X                          | X                        |
| Polyphenylene Sulfide (PPS)<br>Ryton® PPS R-7-120 - Filled          | X                 | X             | X             | X                            | X                              | X                          | X                        |
| Polyamide-imide (PAI)<br>Torlon® 4203L HF - Unfilled                | X                 | X             | X             | X                            | X                              | X                          | X                        |
| Polyetherimide (PEI)<br>Ultem® 1000                                 | X                 | X             | X             | X                            | X                              | X                          | X                        |
| Phenolic<br>Plenco® 4485  | X                 | X             | X             | X                            | X                              | X                          | X                        |
| Polybenzimidazole (PBI)<br>Celazole® TU-60                          | X                 | X             | X             | X                            | X                              | X                          | X                        |

<sup>1</sup>Extract content was tested only after exposure in 100% refrigerant conditions.

### 3. RESULTS AND DISCUSSION

Materials tested in this study were assessed and given risk levels as defined in Table 3, which are directly related to the tables published in previous work (Majurin et al., 2014b). The authors of that study created the risk levels based on results from critical tests and experience from system applications. It is noted that, in addition to the general requirements listed in Table 3, other factors should be considered during material selection, such as application intent and other material specifications. Lastly, other original equipment manufacturers (OEMs) and test labs may have different ranking criteria and selection processes than those reported here. A full presentation of results will be found in the AHRTI Project 9016 Phase II final report, which will provide more detail on the test results and discussion to provide insights into a materials compatibility with next generation refrigerants used by the industry. All risk levels for the materials, except polyester, and conditions tested in this study are summarized in Table 4; changes in elongation for these same materials were summarized in Table 5. Due to additional testing conducted with the polyester material, results were presented separately in Tables 6 and 7. For all materials, noteworthy trends and results are discussed in the following subsections. As a note, materials noted as high risk for a given attribute may also have additional attributes that would fall under medium or low risk categories.

For the discussion of tensile test results in this study (tensile strength change from control, percent elongation changes from control), it is assumed that changes in these properties of  $\pm 15\%$  are considered within the error of the testing method, sample reproducibility, and sample repeatability. This is because variations in the molding process, the curing process, and the tensile test procedure itself can result in batch-to-batch variation of the physical properties of the tensile bars. The tensile strength was much more consistent for each polymer tested so it was determined to define risk levels for only tensile strength change. Discussion on percent elongation change is limited to if a polymer exhibited elongation change outside of the range of  $\pm 15\%$  from control and was not a determining factor in the risk level of a polymer in a test condition. Elongation risks are dependent on if the elongation increased or decreased and vary from application to application. Elongation increases indicate that the sample became more ductile which could lead to lower long term creep resistance and difficulty maintaining tight dimensional tolerance. A decrease in elongation indicates that the sample became more brittle. Embrittlement of the polymer indicates that it could be at a higher risk for impact or contact related failures in the application. Therefore, it is recommended to fully understand and review the application of a polymer in tandem with the elongation data and risk levels of the other properties defined here before selecting a polymer for use in a low-GWP refrigerant environment. Due to these reasons, elongation values were included separately for review in Tables 5, 6 and 7.

For comparison purposes, HFO containing blend results are compared against results for R-1234ze(E) and R-1234yf (where applicable) published in the AHRI MCLR Project #08007 report. Three materials tested (PEI, Phenolic, and PBI) were not tested as a part of that work, so there are no data comparisons to the single components of R-1234yf and R-1234ze(E). Additionally, PTFE was only tested for weight and volume change in the previous study and not tested for tensile property changes, so no comparisons can be made for these results (Majurin et al., 2014a).

**Table 3:** Classification of polymer materials.

| <b>Material Risk Category</b> | <b>Weight &amp; Volume Change</b> | <b>Tensile Strength Changes</b> | <b>Appearance Change</b>   |
|-------------------------------|-----------------------------------|---------------------------------|--|
| High                          | >20% Increase<br>or >2% Decrease  | >50% Decrease                   | Significant material changes such as cracking, crazing, or blistering      |
| Medium                        | 10% - 20% Increase                | 15% - 50% Decrease              | Marginal material changes such as color change or minor extractables (>5%) |
| Low                           | 0% - 10% Increase                 | 0% – 15% Decrease               | No notable material changes  |

**Table 4:** Risk classification of polymer materials.

| Test Condition           |        | PTFE              | Nylon 6,6         | PEEK | PPS | PAI | PEI | Phenolic          | PBI |
|--------------------------|--------|-------------------|-------------------|------|-----|-----|-----|-------------------|-----|
| Refrigerant              | Oil    |                   |                   |      |     |     |     |                   |     |
| HCFO Refrigerants        |        |                   |                   |      |     |     |     |                   |     |
| R-1233zd(E)              | No Oil | Low               | Low               | Low  | Low | Low | Low | Low               | Low |
|                          | MO     | Med. <sup>2</sup> | High <sup>2</sup> | Low  | Low | Low | Low | Low               | Low |
| R-1224yd(Z)              | No Oil | Low               | Low               | Low  | Low | Low | Low | Med. <sup>3</sup> | Low |
|                          | MO     | Med. <sup>2</sup> | Low               | Low  | Low | Low | Low | Low               | Low |
| HFO Refrigerants         |        |                   |                   |      |     |     |     |                   |     |
| R-1336mzz(E)             | No Oil | Low               | Low               | Low  | Low | Low | Low | Low               | Low |
|                          | PAG    | Med. <sup>2</sup> | Low               | Low  | Low | Low | Low | High <sup>1</sup> | Low |
|                          | POE    | Low               | Low               | Low  | Low | Low | Low | Low               | Low |
|                          | PVE    | Med. <sup>2</sup> | Low               | Low  | Low | Low | Low | Low               | Low |
| HFO Blended Refrigerants |        |                   |                   |      |     |     |     |                   |     |
| R-514A                   | No Oil | Low               | Low               | Low  | Low | Low | Low | Low               | Low |
|                          | PAG    | Med. <sup>2</sup> | Low               | Low  | Low | Low | Low | Low               | Low |
|                          | POE    | Low               | Low               | Low  | Low | Low | Low | Low               | Low |
|                          | PVE    | Med. <sup>2</sup> | Low               | Low  | Low | Low | Low | Low               | Low |
| R-515B                   | No Oil | Med. <sup>2</sup> | Low               | Low  | Low | Low | Low | Low               | Low |
|                          | PAG    | Low               | Med. <sup>2</sup> | Low  | Low | Low | Low | Low               | Low |
|                          | POE    | Med. <sup>2</sup> | High <sup>2</sup> | Low  | Low | Low | Low | Low               | Low |
|                          | PVE    | Med. <sup>2</sup> | High <sup>2</sup> | Low  | Low | Low | Low | Low               | Low |
| R-516A                   | No Oil | Med. <sup>2</sup> | Low               | Low  | Low | Low | Low | Low               | Low |
|                          | PAG    | Med. <sup>2</sup> | Low               | Low  | Low | Low | Low | Low               | Low |
|                          | POE    | Med. <sup>2</sup> | Low               | Low  | Low | Low | Low | Low               | Low |
|                          | PVE    | Low               | Low               | Low  | Low | Low | Low | Low               | Low |
| R-454B                   | No Oil | Med. <sup>2</sup> | Low               | Low  | Low | Low | Low | Low               | Low |
|                          | PAG    | Med. <sup>2</sup> | Low               | Low  | Low | Low | Low | Low               | Low |
|                          | POE    | Med. <sup>2</sup> | Low               | Low  | Low | Low | Low | Low               | Low |
|                          | PVE    | Med. <sup>2</sup> | Low               | Low  | Low | Low | Low | Low               | Low |

<sup>1</sup>Placed in this risk category due to weight change.

<sup>2</sup>Placed in this risk category due to tensile strength change.

<sup>3</sup>Placed in this risk category due to appearance change.

### 3.1 Polytetrafluoroethylene (PTFE)

The PTFE material did not show any notable material changes after removal from the exposure vessel and minimal changes (<5%) in volume and weight change were observed in all conditions. Additionally, minimal extract (<0.5% by weight) was noted in 100% refrigerant exposures with the exception of R-1224yd(Z) with an extract of 3% by weight. However, this is still considered low risk per Table 3. In general, the majority of conditions exhibited a tensile strength decrease of greater than 15%, resulting in a medium risk classification. No comparisons were able to be made to the single components data from AHRI MCLR Project #08007 because sample configurations were inconsistent.

For elongation change, only five conditions were within  $\pm 15\%$  of control (100% R-1233zd(E), 100% R-1224yd(Z), 100% R-514A, 100% R-1336mzz(E), and R-1336mzz(E)/POE), while all other conditions showed decreases in elongation greater than 15%.

### 3.2 Nylon 6,6

The Nylon 6,6 material did not show any notable material changes or extract after removal from the exposure vessel and minimal changes (<5%) in volume and weight change were observed in all conditions. Only four conditions showed a decrease in tensile strength resulting in quantifiable risk (R-1233zd(E)/MO and R-515B with all lubricants), while all other conditions showed increases in tensile strength and are considered low risk. R-515B

showed a significant decrease in tensile strength, which is contrasted with increases seen in previous testing with R-1234ze(E). The difference in behavior could be due to the differences in test temperature between the two studies or the addition of the R-227ea component. These differences are an opportunity for future study. Generally, R-516A and R-454B behaved similarly to R-1234yf, as all three increased in tensile strength. Finally, R-514A and R-1336mzz(E) also behaved similarly indicating the presence of R-1130(E) does not impact the material's compatibility.

For elongation change, all conditions decreased by more than 15%. R-515B showed significantly higher decreases than R-1234ze(E) in all conditions. In the lubricant free and POE conditions, R-1234yf showed increases in elongation while the R-454B and R-516A conditions both decreased indicating the HFC blend component may impact the elongation. Like tensile strength, the change in elongation was consistent between R-514A and R-1336mzz(E).

**Table 5:** Elongation changes (% from control) seen in polymer materials.

| Test Condition           |        | PTFE | Nylon 6,6 | PEEK | PPS  | PAI  | PEI  | Phenolic | PBI  |
|--------------------------|--------|------|-----------|------|------|------|------|----------|------|
| Refrigerant              | Oil    |      |           |      |      |      |      |          |      |
| HCFO Refrigerants        |        |      |           |      |      |      |      |          |      |
| R-1233zd(E)              | No Oil | NC   | -55%      | -17% | NC   | NC   | -86% | -15%     | NC   |
|                          | MO     | -30% | -97%      | -30% | NC   | -25% | -92% | -31%     | NC   |
| R-1224yd(Z)              | No Oil | NC   | -54%      | -12% | NC   | NC   | NC   | NC       | NC   |
|                          | MO     | -22% | -75%      | -31% | NC   | -19% | -86% | +25%     | NC   |
| HFO Refrigerants         |        |      |           |      |      |      |      |          |      |
| R-1336mzz(E)             | No Oil | NC   | -46%      | NC   | NC   | NC   | -70% | NC       | NC   |
|                          | PAG    | -19% | -60%      | -26% | +27% | -16% | -89% | -20%     | +15% |
|                          | POE    | NC   | -61%      | -27% | NC   | NC   | -88% | NC       | +18% |
|                          | PVE    | -21% | -61%      | -35% | +24% | NC   | -84% | NC       | NC   |
| HFO Blended Refrigerants |        |      |           |      |      |      |      |          |      |
| R-514A                   | No Oil | NC   | -23%      | NC   | +16% | NC   | NC   | NC       | +25% |
|                          | PAG    | -36% | -53%      | -33% | +17% | -16% | -50% | NC       | +29% |
|                          | POE    | -19% | -50%      | -31% | NC   | NC   | -91% | -25%     | NC   |
|                          | PVE    | -29% | -53%      | -22% | NC   | NC   | -88% | -16%     | NC   |
| R-515B                   | No Oil | -46% | -38%      | NC   | NC   | NC   | -52% | -20%     | -20% |
|                          | PAG    | -21% | -96%      | -22% | +26% | NC   | -89% | NC       | NC   |
|                          | POE    | -35% | -97%      | -33% | +34% | NC   | -88% | NC       | NC   |
|                          | PVE    | -37% | -98%      | -35% | NC   | NC   | -83% | NC       | NC   |
| R-516A                   | No Oil | -21% | -55%      | NC   | NC   | NC   | -69% | NC       | NC   |
|                          | PAG    | -18% | -57%      | -30% | NC   | -20% | -88% | NC       | +23% |
|                          | POE    | -39% | -57%      | -36% | NC   | -17% | -89% | NC       | NC   |
|                          | PVE    | -26% | -56%      | -32% | NC   | -21% | -87% | -20%     | NC   |
| R-454B                   | No Oil | -43% | -30%      | +42% | NC   | NC   | NC   | -20%     | NC   |
|                          | PAG    | -44% | -22%      | NC   | -24% | -16% | -92% | -28%     | NC   |
|                          | POE    | -40% | -24%      | NC   | NC   | NC   | -91% | -30%     | NC   |
|                          | PVE    | -45% | -30%      | NC   | -25% | NC   | -91% | -27%     | NC   |

### 3.3 Polyether Ether Ketone (PEEK)

The PEEK material did not show any notable material changes or extract after removal from the exposure vessel, minimal changes (<5%) in volume and weight change, and minimal changes in tensile strength were observed in all conditions and as a result, all conditions were classified as a low risk. When comparing to previous test results with single components R-1234yf and R-1234ze(E), R-454B behaved similarly to the single component results, however, R-516A and R-515B had increases in tensile strength compared to their respective single component HFO results. Several conditions exhibited an elongation change within 15% of the control (100% R-1224yd(Z), 100% R-514A, 100% R-1336mzz(E), 100% R-515B, and 100% R-516A and all lubricant containing conditions with R-454B). All

other conditions decreased by more than 15%, with the exception of 100% R-454B, which increased by around 40%, approximately half of the increase seen in R-1234yf in previous studies. Also, in comparison to previous studies, R-515B and R-516A showed higher decreases than seen with their single components. Finally, R-514A and R-1336mzz(E) performed similarly.

### 3.4 Polyphenylene Sulfide (PPS)

The PPS material did not show any notable material changes or extract after removal from the exposure vessel and minimal changes (<5%) in volume and weight change were observed in all conditions. Additionally, all conditions exhibited a low risk change in tensile strength. An increase in tensile strength was observed in select conditions (R-1336mzz(E)/PAG, R-515B/PAG, and R-515B/POE) while remaining conditions exhibited tensile strength  $\pm 15\%$  from control. R-1234yf and R-1234ze(E) containing blends showed higher increases in strength than the individual components based on results from previous studies, while R-514A and R-1336mzz(E) behaved similarly.

A mix of elongation results were observed across the conditions tested. For example, two conditions showed elongation decreases greater than 15% (R-454B/PAG and R-454B/PVE) while six conditions showed an increase in elongation greater than 15% (100% R-514A, R-514A/PAG, R-1336mzz(E)/PAG, R-1336mzz(E)/PVE, R-515B/PAG, and R-515B/POE). The remaining conditions exhibited elongation values  $\pm 15\%$  from control. In general, R-1234yf and R-1234ze(E) containing blends showed much less elongation change than was previously observed with the single components. Finally, R-1336mzz(E) and R-514A showed similar elongation change.

### 3.5 Polyamide-imide (PAI)

The PAI material did not show any notable material changes or extract after removal from the exposure vessel and minimal changes (<5%) in volume and weight change were observed in all conditions. Additionally, all conditions exhibited a low risk change in tensile strength. In comparison to previous work with R-1234ze(E) and R-1234yf, blends with these components behaved similarly to the single components in testing.

Most of the test conditions showed elongation change within 15% of control with the exception of R-1233zd(E)/MO, 100% R-1224yd(Z), and all lubricant containing conditions with R-516A which exhibited elongation decreases greater than 15%. The R-1234yf and R-1234ze(E) containing blends tested in this study showed much less elongation change than the single components tested previously.

### 3.6 Polyetherimide (PEI)

The PEI material did not show any notable material changes or extract after removal from the exposure vessel and minimal changes (<5%) in volume and weight were observed in all conditions. Additionally, all conditions exhibited a low risk change in tensile strength with all values  $\pm 15\%$  from the control.

Apart from the 100% R-1224yd(Z), 100% R-514A, and 100% R-454B conditions, all PEI conditions showed significant decreases in elongation (>50%). The R-1234yf containing blends, R-454B and R-516A, showed similar levels of decrease in each condition while R-514A and R-1336mzz(E) show similar decreases in the POE and PVE conditions, but not in the lubricant free and PAG conditions where R-1336mzz(E) showed much higher decreases.

### 3.7 Phenolic

Unlike the other polymers previously discussed, minor visual appearance changes were noted of the phenolic material after exposure. The most significant change was noted in the 100% R-1224yd(Z) condition where a white residue was observed on the test pieces. This visual observation resulted in categorizing the risk as medium. Minimal extract and changes (<5%) in volume and weight were observed in all conditions, with only one condition (R-1336mzz(E)/PAG) showing a high risk weight loss of 2.1%. Many other conditions showed decreases in weight and volume change (1-2%) which is on the edge of acceptability before increasing in risk (Table 3). All conditions exhibited a low risk change in tensile strength, with most conditions increasing up to 15%.

Approximately half of the test conditions resulted in no change in elongation after exposure. Only one condition increased in elongation (R-1224yd(Z)/MO) while the remaining conditions decreased in elongation (100% R-515B, R-1233zd(E)/MO, R-1336mzz(E)/PAG, R-514A/POE, R-514A/PVE, R-516A/PVE, and all R-454B conditions). When reviewing the R-1234yf containing blends, R-516A did not show as much decrease in elongation as R-454B.

While R-1336mzz(E) decreased more than R-514A in the lubricant free and PAG conditions, it decreased less than R-514A in the POE and PVE conditions.

### 3.8 Polybenzimidazole (PBI)

The PBI material was noted to be slightly lighter in color after exposure in all conditions containing lubricant; however, this was still classified as low risk due to the minimal change. Minimal extract, weight, volume, and tensile strength changes were observed resulting in a low risk classification for all test conditions.

Many of the test conditions had no change in the elongation after exposure ( $\pm 15\%$  from control). Only one condition exhibited a decrease in elongation greater than 15% (100% R-515B), while four conditions exhibited an increase in elongation greater than 15% (100% R-514A, R-514A/PAG, R-1336mzz(E)/POE, R-516A/PAG). It was noted that the elongation results were dissimilar between the R-516A and R-454B in the PAG and POE conditions (where the R-516A increased and R-454B decreased), while they performed similarly in the lubricant free and PVE conditions. No clear trends were seen between the R-514A and R-1336mzz(E) conditions.

### 3.9 Polyester

In the original testing, all polymer pieces and tensile bars were exposed in a single vessel. During this testing, the PBT polyester material exhibited significant material changes in the lubricant containing conditions; all pieces exhibited changes in color from white to yellow/orange, and they became so embrittled that they could not be tensile tested. The weight and volume changes seen in the lubricant containing conditions were acceptable, despite the embrittlement, but after bakeout many pieces showed significant cracking and deterioration.

Although this material was tested similarly and combined with all polymers in the lubricant free conditions, these samples did survive the exposure and tensile testing was completed. In these conditions, the material exhibited low weight and volume changes as well as minimal extract; however, most conditions experienced tensile strength changes resulting in a classification of medium risk with the exception of 100% R-516A and R-1336mzz(E) which are classified as low risk. Risk assessments and elongation results are shown in Table 6.

**Table 6:** Risk classification of polyester material in pure refrigerant conditions.

| Refrigerant              | Risk Level          | Elongation Change (%) |
|--------------------------|---------------------|-----------------------|
| HCFO Refrigerants        |                     |                       |
| R-1233zd(E)              | Medium <sup>1</sup> | +131%                 |
| R-1224yd(Z)              | Medium <sup>1</sup> | +90%                  |
| HFO Refrigerants         |                     |                       |
| R-1336mzz(E)             | Low                 | -11%                  |
| HFO Blended Refrigerants |                     |                       |
| R-514A                   | Medium <sup>1</sup> | +133%                 |
| R-515B                   | Medium <sup>1</sup> | +75%                  |
| R-516A                   | Low                 | +30%                  |
| R-454B                   | Medium <sup>1</sup> | +174%                 |

<sup>1</sup>Placed in this risk category due to tensile strength change.

R-1234ze(E) and R-1234yf containing blends showed larger decreases in tensile strength than the single components tested previously. Conditions containing R-514A showed more change in material properties than R-1336mzz(E), indicating the R-1130(E) component may be impacting the compatibility of this material.

All elongation, with the exception of R-1336mzz(E), showed significant increases, with the highest being R-454B at nearly 175%. This is in direct contrast to the results in the AHRI MCLR Project #08007 project, where pure R-1234yf was found to decrease the elongation by nearly 100%. However, in that study, a three refrigerant blend of equal parts by weight of R-1234yf, R-1234ze(E), and R-32 was tested where the polyester exhibited an elongation increase greater than 200%, see Figure 1. This suggests that R-32 could be impacting this property.



Due to the significant degradation of the polyester samples when combined with the other polymers in lubricant containing conditions, additional study was pursued to compare results of testing the polyester material individually versus combined with the other polymeric materials. Because the PBT in the polyester can undergo hydrolysis in the presence of moisture and heat (Loyer et al., 2020), it was hypothesized that moisture was being extracted from the other polymers in the vessel at the high exposure temperatures (127°C) or by the lubricants themselves resulting in hydrolysis of the polyester material and causing embrittlement. This may have not been seen in AHRI MCLR Project #08007 because the test temperature of the polymers in lubricant containing conditions was lower (90°C) and there were less polymers tested in the same vessel (6) from which moisture could be extracted. A test of this hypothesis was done in each lubricant type by exposing the polyester material to R-1224yd(Z)/MO, and R-454B with each of the PAG, POE, and PVE lubricants. Polyester material was placed in the exposure vessels and tested for three weeks at 127°C. After exposure, the pieces were found to be intact and strong enough for tensile testing.

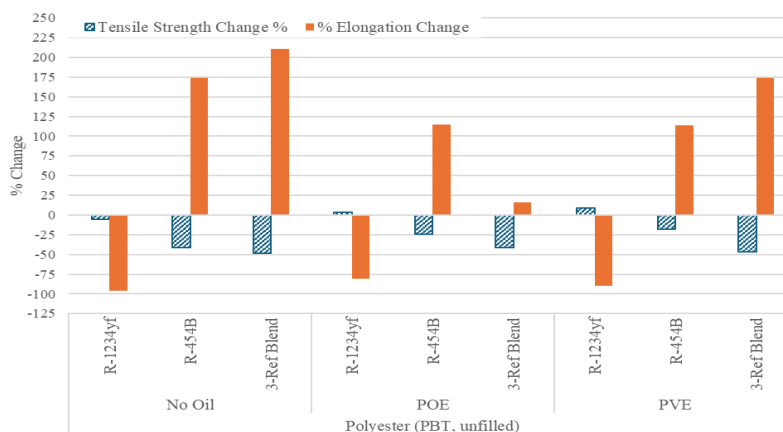
In these single-material exposures, minimal appearance changes and minimal weight or volume changes were observed. When exposed to R-1224yd(Z)/MO, minimal change in tensile properties was observed, resulting in a classification of low risk. A decrease in tensile strength was observed in the R-454B/PAG, R-454B/POE, and R-454B/PVE, but not greater than 50% allowing this material to be classified as a medium risk. In all cases, the elongation increased, most significantly in the presence of POE and PVE lubricant. Similar behavior to the lubricant free conditions was observed when compared to previous work. R-1234yf decreased significantly in elongation, while R-454B showed significant increase (Figure 1). Risk assessments & elongation results are provided in Table 7.

Similar behavior of the polyester would likely be observed with other refrigerants and lubricants, however, given these findings, future studies may be recommended to investigate this further.

**Table 7:** Risk classification of polyester material in lubricant containing conditions tested independently.

| Test Condition    | Risk Level          | Elongation Change (%) |
|-------------------|---------------------|-----------------------|
| R-1224yd(Z)<br>MO | Low                 | +40%                  |
| R-454B<br>PAG     | Medium <sup>1</sup> | +71%                  |
| R-454B<br>POE     | Medium <sup>1</sup> | +114%                 |
| R-454B<br>PVE     | Medium <sup>1</sup> | +114%                 |

<sup>1</sup>Placed in this risk category due to tensile property change.



**Figure 1.** Graphical comparison of tensile property changes of polyester material.

## 5. CONCLUSIONS

Structural polymer materials were tested for identifying material compatibility concerns of materials typically used in HVAC&R construction. They were tested with refrigerants R-1224yd(Z), R-1233zd(E), R-514A, R-1336mzz(E), R-515B, R-516A, and R-454B with and without lubricant. Risk criteria were determined and applied to each test condition. Risk categories were not applied to elongation change results because of the application-specific requirements that elongation change can affect and positive or negative changes in elongation can have different effects on the polymer. Four materials tested (PTFE, Nylon 6,6, Phenolic, and Polyester) had medium risk behavior in at least one condition tested, while the other materials (PEEK, PPS, PAI, PEI, and PBI) exhibited low risk behavior in all conditions tested when elongation change was not defined. Additional comparisons were made between R-514A and R-1336mzz(E) containing conditions, where most polymers exhibited similar property changes in all properties except for elongation, which could suggest that the R-1130(E) component affects the compatibility of these materials.

Additionally, comparisons were made between R-1234yf and R-1234ze(E) containing blends and the results of the single components tested in AHRI MCLR Project #08007. Many tensile properties were different between the single components and the blended refrigerants, which could be indicative of the blend or the effect of the exposure being a higher temperature than in that study. Lastly, it was discovered that hydrolysis of the PBT material in polyester could contribute to significant degradation of that material and could merit further study as the industry moves towards higher operating temperatures. Overall, the results suggest that polymeric materials in HVAC construction should be properly reviewed and assessed for their application before use with these low GWP refrigerants.

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## NOMENCLATURE

|      |             |    |           |
|------|-------------|----|-----------|
| Med. | Medium Risk | NC | No Change |
|------|-------------|----|-----------|

## REFERENCES

- Doerr, R.G., and Kujak, S.A., 1993, Compatibility of Refrigerants and Lubricants with Motor Materials. Report DOE/CE/23810-13. Air-Conditioning and Refrigeration Technology Institute, Arlington, VA, USA.
- Loyer, C., Régnier, G., Duval, V., Ould, Y., Richaud, E. (2020). PBT plasticity loss induced by oxidative and hydrolysis ageing. *Polymer Degradation and Stability*, 181, 109368.
- Majurin, J.A., Sorenson, E., Staats, S.J., Gilles, W., and Kujak, S.A., 2014, Material Compatibility and Lubricants Research for Low GWP Refrigerants – Phase II: Chemical and Material Compatibility of Low GWP Refrigerants with HVAC&R Materials of Construction. AHRI Report No. 08007-01. Air Conditioning, Heating, and Refrigeration Technology Institute, Inc., Arlington, VA, USA.
- Majurin, J., Gilles, W., and Staats, S., 2014, “Materials Compatibility of HVACR System Materials with Low GWP Refrigerants”. 15<sup>th</sup> International Refrigeration and Air Conditioning Conference at Purdue, July 14-17, 2014. Paper 2132.
- Sorenson, E., Kujak, S., Leehey, M., Robaczewski, C., Stellpflug, T. 2021. Material Compatibility and Lubricants Research for Low GWP Refrigerants – Chemical Stability of Low GWP Refrigerants with Lubricants. Report AHRI 09016. Arlington, VA: Air Conditioning, Heating, and Refrigeration Technology Institute, Inc.