Polymerization of HFO – a Problem to Be Reckoned With?

Some months ago, we received at KTH, from an industrial contact, a refrigerant cylinder containing **R513A**. This is a blend consisting of **44% HFC-134a** and **56% HFO-1234yf**. The problem with this particular cylinder was that it released a **white foam** which immediately hardened upon contact with air (Figure 1). We had previously heard that this can occur, but had not seen it ourselves, nor heard of such events in Sweden.

Figure 1. Glass jar containing polymerized HFO-1234yf (?). The foam was formed when a hose from a refrigerant cylinder with R513A was directed into the jar and the cylinder was briefly opened from the liquid side.

To determine what the foam consisted of, we contacted colleagues at the **Department of Chemistry**, specialized in polymers. Polymers are what we commonly refer to as plastics, and the process by which the molecules in the starting material are linked together is called **polymerization**. Our hypothesis was that the refrigerant had polymerized inside the cylinder, or that something in the cylinder triggered polymerization when the refrigerant was released. The polymer chemists agreed that this was a reasonable explanation. In their terminology, HFO-1234yf is “an unsaturated monomer that can be polymerized.”

An initial analysis of the foam from the cylinder has now been carried out, and several conclusions can be drawn.

The analytical method used is **FTIR**, a spectroscopic technique that can identify the molecules and molecular groups present in a sample. At the same time, the analysis also indicates which types of molecules or groups are **not** present. The result is presented as a curve with peaks at certain wavelengths, each peak corresponding to specific chemical bonds.

In brief, the analysis showed that the sample likely contained **carbon–fluorine bonds** and smaller amounts of **carbon–hydrogen bonds**, consistent with HFO-1234yf, but **no carbon–carbon double bonds**, which are present in intact HFO-1234yf. The preliminary conclusion is therefore that the foam consists of **polymerized HFO-1234yf**.

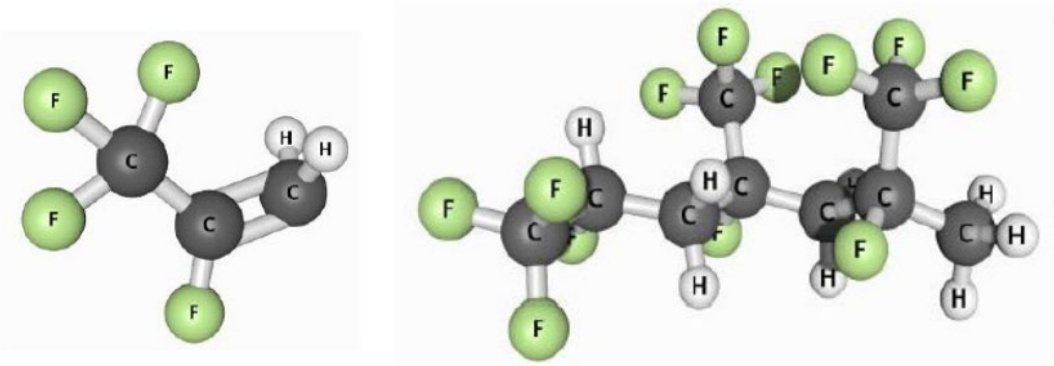

Figure 2. Left: HFO-1234yf. Right: oligomerization of HFO-1234yf – three linked molecules.

That carbon chains with double bonds can undergo polymerization is not surprising. In the early search for new refrigerants to replace CFCs, **HFOs** were also included on the list of possible alternatives. However, they were dismissed at the time because the double bonds were judged to make the molecules **insufficiently stable**.

Later, when HFCs were to be replaced, the focus shifted to molecules with **short atmospheric lifetimes**, and thus **low GWP**. (By tradition, GWP is calculated as the effect on global warming over a period of **100 years**, relative to CO_2. A substance that degrades quickly then obtains a low time-averaged GWP over this period.) HFOs once again became interesting candidates—provided that sufficient stability could be demonstrated. In most cases, this has proven to work. **HFO-1234yf** has been the standard refrigerant in the AC systems of most new passenger cars in Europe for nearly ten years.

However, this is not the first time that problems with polymerization have been reported. The scientific literature contains several articles describing such occurrences and proposing possible explanations. In one paper (Leehey & Kujak, 2023), polymerization in a specific case was likely caused by **peroxide leakage from gasket materials**. Another article reports polymerization occurring during refrigerant tests, without suggesting a cause (McLinden & Perkins, 2023).

More detailed information is provided in a technical bulletin from **Mahle** (Mahle, 2023). There it is stated that the cause is not fully clear, but that **moisture and elevated temperature** are likely triggers for polymerization. The bulletin also notes that the **cylinder valve should be opened carefully** when connecting a manifold, since a rapid pressure rise can induce polymerization. Furthermore, hoses and seals containing **peroxides** should not be used, and refrigerants should be sourced from **reliable suppliers**.

In general, polymerization is most often initiated in the presence of a **catalyst**, i.e., a substance that accelerates a chemical reaction without being consumed. Substances typically used as catalysts in polymer chemistry are not normally present in refrigerant systems or refrigerant cylinders. The causes of polymerization in these cases are therefore not yet fully clarified. Possible candidates include components in the **oil**, substances (such as peroxides) released from **sealing materials** (Leehey & Kujak, 2023), or possibly **moisture alone**.

The reaction does not need to proceed as far as in Figure 1. A smaller number of linked molecules is referred to as **oligomerization** (Figure 2), and such molecular complexes will not evaporate readily; they are likely to accumulate in the **compressor oil**.

It should also be emphasized that polymerization is **not the only chemical reaction** mentioned in the literature for HFOs. The double bond makes these substances inherently unstable, and other reactions may occur as well. These can change the composition of the refrigerant or blend, although they may not be as visually striking as the formation of a solid polymer foam.

Chemours, the manufacturer of **R513A**, has, of course, also investigated compatibility with metals and polymers. The results are available online (Chemours, 2017). There is no mention of polymerization in that document, and the stability in all tests carried out is reported as good. However, it is stated that refrigerant cylinders must **never be exposed to temperatures above 52 °C**.

We will continue to investigate the causes of polymerization of HFO refrigerants and are very interested in receiving any observations from readers where you suspect polymerization, or where the refrigerant has behaved unexpectedly. At the **Department of Energy Technology**, we have access to **gas chromatography**, which is a powerful tool for identifying refrigerants, and we collaborate with the **Department of Chemistry**, from whom we can obtain assistance with further analyses and interpretation of results.

References

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