Scientific and technical information on the manufacture, placing on the market and use of per- and polyfluoroalkyl substances (PFAS)

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Authors:
Dr. Matthias Weller[1], Director Technical Product Management Research NMR&EPR
Dr. Peter Ullmann[2], Director Technical Product Management MRI
Dr. Rainer Kuemmerle, Product Manager and Head of NMR Application Sciences
Dr. Matteo Alessandrini[1], Technical Director Magnets
Beat Grossniklaus[1], Technical Director Probes
Dr. Daniel Guy Baumann[1], Head of Mechanical Engineering Probes
Dr. Andreas Kraus, Materials Engineer NMR Magnets
Dr. Martin Wootli, Materials Engineer NMR Probes
Cengiz Cetrefli[1], Head of Mechanical Engineering Magnets
Markus Streckfuss[2], Head of Mechanical Engineering
Dr. Alexander Krieg[1], Head of Quality, Regulatory Affairs and Environmental Health & Safety

1) Bruker Switzerland AG, 8117 Fällanden, Switzerland
2) Bruker BioSpin GmbH, 76275 Ettligen, Germany

1. Terms

NMR	Nuclear magnetic resonance spectroscopy
MRI	Magnetic resonance imaging
EPR	Electron paramagnetic resonance
PET	Positron emission tomography
MPI	Magnetic particle imaging
CT, uCT	Computed tomography (micro computed tomography)
SPECT	Single photon emission computed tomography
PTFE	Polytetrafluoroethylene
PFAS	Per- and polyfluoroalkyl substances

2. Introduction

As a manufacturer of magnetic resonance instruments (NMR, EPR, preclinical MRI) and other devices in the pre-clinicial imaging market (uCT, PET, CT, MPI, SPECT), Bruker BioSpin is relying on PFAS materials or materials containing PFAS for many different reasons. However, the amount of materials Bruker BioSpin brings into the market is – based on a very rough, unaudited estimate - of the order of 1 t – 10 t per year. Most of these materials are not consumed during instrument use and – if customers follow the instruction to let Bruker BioSpin take old instruments out of operation and recycle the components – do not get into the environment and can be disposed in agreement with laws and regulations.

The use of PFAS materials in the instruments manufactured by Bruker BioSpin is critical because of several reasons:

- The NMR method is based on the detection of nuclear spins in liquid and solid materials. The atom ^{1}H (Hydrogen Atom, containing 1 proton) contains the most important nuclei that is detected by a broad range of applications in NMR and MRI. Most synthetic materials contain Hydrogen and thus they cannot be used close (few centimeters) to the detection volume, otherwise there is a strong background signal pick up, which diminishes or even masks the spectroscopical results. On the other hand, leaving away synthetic materials as good electrical isolators is not an option, as the NMR involves high power radio frequency (rf) pulses and for example arcing would make impossible proper nuclear spin system excitations, which is a basic element of the method. Therefore, PTFE is an exclusive material, as it a) does not contain Hydrogen (^1H), b) its electrical isolation properties are outstanding and can deliver enough performance within the limited space.

- Another aspect of magnetic resonance is the need for very large magnetic fields. For this, superconductive solenoid coils are used, which carry approx. 100 - 300 A current. To be in the superconductive state, these coils are operated at cryogenic temperatures down to approx. 2 K. At these temperatures, PTFE materials have extraordinary mechanical, thermal and electrical properties. In general, PFAS are used in low to ultra-low temperature applications to exploit these.

- There are processes in production at Bruker BioSpin, which rely on very relevant properties of PTFE: a) resistance against acids b) temperature resistance between above 200°C and useful as a solid below the melting point and c) the chemical robustness and d) anti-stick properties.

- Further properties of PTFE are very performant and exceptional, especially as they are combined in one material: relatively high density for a synthetic material, mechanical robustness, chemical robustness, thermal robustness, electrical isolation, low dielectric constant, sealing capabilities, thermal expansion coefficient and the dependence of those quantities on temperature in the range between ultra-low temperatures (-271 °C) to approx. 300°C.

In the following chapters, a few examples are listed to show the need for exception to use PFAS in the products mentioned, as long as there are no alternatives available on the market that combine similarly these properties. There are more cases in the Bruker BioSpin product portfolio where PFAS materials are difficult or even impossible to be replaced with state-of-the-art technologies.

We are searching for alternative substances, however due to the specific physical and chemical properties of PFAS, PFAS cannot be replaced in the near future for our niche applications.

3. Example 1: Use of fluorinated materials in NMR probes and their accessories

The design of NMR probes (RT & Cryo) and their accessories (e.g. spinners, components like spacers and seals of the Cryo Cooling Unit) requires insulating materials with the excellent properties in various positions. The relevant properties are listed below:

a.) Absence of background signal caused by absence of hydrogen atoms
b.) High dielectric strength
c.) Low dielectric constant
d.) Low dielectric loss
e.) Wide application temperature range (e.g. cryogenic applications)
f.) Certain mechanical toughness (absorbs mechanical tolerances)
g.) Tribological behavior (low friction), also in the form of blended polymers (e.g. PEEK/PTFE)

For this, the materials of choice are fluorinated polymers. Either they are used as a dielectric material in cables, trimmers and resonators or simply as an insulation aid, especially for cryogenic NMR probes in the form of foils or flexible bands.

High performance RF (radio frequency) cables are bought as standard products from multiple providers. If the industry will switch to protonated insulation materials, we are forced to take over the change. This leads to higher proton background signals and reduces performance.

Replacing PTFE in several very specific components (insulation of cables and networks) by materials with protons are a serious problem, since they are close to the detection space and will generate a huge proton background that will turn the method unusable.

4. Example 2: Use of fluorinated materials for jigs and other auxiliary equipment

The necessity of using fluorinated polymers in operating and auxiliary equipment also results from its excellent properties:

a.) High dielectric strength
b.) Low dielectric constant
c.) Low dielectric loss
d.) Wide application temperature range
e.) Certain mechanical toughness (absorbs mechanical tolerances, small air gaps)
f.) Tribological behaviour (low friction)
g.) Poor wetting
h.) High specific weight

For these tools, the materials of choice are fluorinated polymers.

5. Example 3: Use of fluorinated liquids for vapour phase soldering

One family of NMR coils is manufactured using vapour phase soldering. Only the combination of the following properties of the soldering medium allows successful manufacturing:

a.) High and defined boiling point, no thermal over-shooting.
b.) High specific weight (displacement of oxygen)
c.) High heat transfer
d.) Low consumption, high yield
e.) High chemical and thermal stability
f.) Transparency

The fluorinated liquids do not remain in the product and are only used during the fabrication process.

6. Example 4: Use of fluorinated materials in NMR magnets

The manufacturing of superconducting NMR magnets needs fluorinated polymers in various positions with three main requirements:

a.) Cryogenic and high temperature resistance and toughness
b.) Chemical resistance
c.) Sealing material at cryogenic temperature

NMR magnets are based on superconducting solenoids and need to be cooled at cryogenic temperature below 4.2 K. The electrical insulation of cables is made of PTFE to avoid cracking caused by thermal cycling.
Production tools made of PTFE are used where high temperature resistance is required (for example tools for soldering). For chemical etching of superconductor single and multifilament wires, fluorinated polymers

are used because of their high chemical resistance against acids. These tools are not part of the product, but needed in the fabrication process.
Favorable low temperature mechanical properties are ideal for using seals from PTFE. Special sealing solutions are based on the thermal shrinkage of PTFE.

7. Example 5: Use of fluorinated materials in solids NMR, EPR and preclinical MRI Sensoric Probes

The fabrication of solids NMR, EPR and preclinical MRI sensing probes for spectroscopy and imaging requires fluorinated polymers. At different points of the measurement chain, the known benefits from the specific properties have been successfully used for decades at Bruker. Through these materials Bruker BioSpin can offer some of the products on the market at all. The measuring instruments are extremely sensitive, that substance analyses are obtained on the atomic and molecular level and any material surrounding the samples may cause background signals, if the materials are not chosen accordingly. The use of PFAS is of paramount importance because of the following points:

a) Background signal free measurement in spectroscopy (avoid using protons) is a basic requirement for error free measurement in solids-NMR, EPR and special MRI applications (Imaging). Background signal overlays the desired measurement signal and can only be compensated under some conditions, which in turn leads to losses in the signal-to-noise ratio, which is one of the dominating performance parameters in the techniques.
b) Advantages in the subtractive manufacturing process of the individual parts/ Geometric stability in the product (wear resistance)
c) High resistance to chemicals bases, alkali and solvents
d) Very wide range of applications due to temperature resistance (up to approx. 200°C)
e) Dielectric properties, which is why PTFE is often used as a dielectric in variable capacitors/trim capacitors; the low loss angle (tan d) in the high-frequency range is also helpful here. Therefore, PTFE is also often used for electrical insulation.
f) Favourable mechanical properties at low temperatures are ideal for the use of seals made of PTFE. Special sealing solutions are based on the thermal shrinkage of PTFE.
g) In addition to PTFE, PCTFE (brand name Kel-F®) is also used in MAS (Magic Angle Spinning) probes. Especially as a material for rotor caps, PCTFE is common here because it combines good mechanical properties with the above-mentioned absence of protons. A rotor cap is naturally located very close to the sample volume and thus in the sensitive area of the coil, here the interfering influence by background signal would be particularly large.