

Supporting Information

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1. Experimental section

1.1 Used equipment and characterization techniques

General. All reagents were obtained from commercial suppliers at least in synthesis purity and used without further purification. The organic solvents utilised as LAG agents were purchased in analysis grade. For all experiments conducted, a MM500 vario mixer mill (*Retsch*) was used. The milling vessels were custom-made from PFA, PP, PE-HD, PE-UHMW, PA6, PA6.6, PA6 GF, PA6.6 GF, PC, POM C, PET, PET GX, PEEK, PEEK GF and PVC. PFA was obtained from *Ammerflon*[®] GmbH, the other materials were obtained from *Technoplast*. The vessels were custom-made from the in-house toolshop through lathe processing. The vessels measure 66.0 mm in length and comprise an outer diameter of 29.8 mm, along with an inner diameter of 19.0 mm. To circumvent severe deformation of the vessel during the milling process, a wall thickness of 5 mm was chosen. The vessels are composed of two equal parts with identical dimensions, connected by a straightforward plug-in mechanism.

High performance liquid chromatography (HPLC) was performed on a shimadzu Nexera LC-40 lite. A Nucleodur C18, 3 μ Reversed phase column from Macherey-Nagel was used as stationary phase. An isocratic solvent mixture of 65 % acetonitrile, as well as 35 % water was used at a flowrate of 0.7 mL/min as mobile phase. The crude product (approx. 4 mg - 5 mg) was dissolved in 3 ml of the acetonitrile/water mixture (65:35) acidified with 5 % acetic acid, filtered through a syringe filter, and subsequently transferred to a HPLC vial.

Nuclear magnetic resonance spectroscopy (NMR). ¹H-NMR spectra were recorded in CDCl₃ on a Bruker Avance III HD spectrometer at 300 MHz. spectra were referenced internally to residual solvent resonances and are reported relative to tetramethylsilane. Chemical shifts are reported in ppm from tetramethylsilane. Data are reported as follows: s = singlet, d = doublet, dd= doublet of doublet, m = multiplet; coupling constants in Hertz.

Inductively coupled plasma atomic emission spectroscopy (ICP-OES) measurements were performed on an ANalytikjena Plasma Quant PQ 9000. The samples were taken out of the vessel immediately after milling. The crude product was dissolved in an acidified mixture of acetonitrile and water (65:35).

Scanning electron microscopy (SEM) measurements were performed on a JEOL JSM IT800SHL with secondary electron detector at 5kV. All samples were applied to a carbon patty. The energy-dispersive X-ray spectra (EDX) were executed by the Oxford Ultim Max with a silicon drift detector at a working distance (WD) of 10 mm.

2. Synthetic procedures

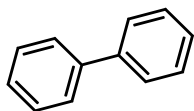
2.1 Direct mechanocatalytical Suzuki coupling

For the standard reaction, phenylboronic acid (122 mg, 1 mmol, 1 eq.), 1 g of potassium carbonate (1 g, 7. mmol, 7.3 eq.), iodobenzene (112 μ l, 1 mmol, 1 eq.), as well as ethanol (199 μ l, η = 0.15, 3.4 mmol, 3.4 eq.) were place in a 19 ml vessel made of different materials studied in this work. Before the reaction mixture was added, a palladium ball with an approximate diameter of 10 mm was placed inside the milling jar. The sealed reaction vessel was shaken for 15 minutes at 35 Hz in a MM500 mixer mill by *Retsch*. The crude product was dissolved in water and ethyl acetate and the water phase was extracted with ethyl acetate (2x20 ml). The organic phase was dried using MgSO₄ and the solvent was removed under vacuum. The Product was quantified via HPLC.

2.2 Acid catalysed Acetalisation

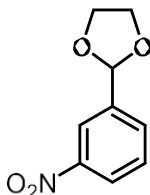
For the reaction, 1g of potassium sulfate (5.7 mmol, 5.7 eq.), 3-Nitrobenzaldehyde (151 mg, 1 mmol, 1 eq.), ethylene glycol (62 mg, 1 mmol, 1 eq.) and para-toluol sulfonic acid (150 mg, 0.8 mmol, 0.8 eq.) were placed in a 19 ml vessel made of the different materials studied in this work. Before the reaction mixture was added, a steel ball with a diameter of 10 mm was added. The sealed reaction vessel was milled for 1.5 hours at a frequency of 35 Hz. The crude product was dissolved in water and ethyl acetate and the water phase was extracted with ethyl acetate (2x20 ml). The organic phase was dried using MgSO₄ and the solvent was removed under vacuum. The product was quantified via NMR with dibromoethane as external standard.

2.3 Product characterization



Biphenyl

^1H NMR (400 MHz, Methylene Chloride- d_2) δ 7.63 – 7.59 (m, 4H), 7.45 (dd, J = 8.4, 6.9 Hz, 4H), 7.38 – 7.33 (m, 2H).



2-(3-nitrophenyl)-1,3-dioxolane

^1H NMR (400 MHz, Chloroform- d) δ 4.05-4.18 (m, 4H), 5.90 (s, 1H), 7.54-7.60 (m, 1H), 7.79-7.83 (m, 1H), 8.20-8.25 (m, 1H), 8.35-8.37 (m, 1H).

3. Stability tests under milling conditions

3.1 Pre-milling

To remove remaining shavings from the manufacturing process and ensure a smooth surface, the vessels have been pre-milled in a MM500 at 35 Hz for one hour using potassium carbonate (1 g, 5.7 mmol) and ethanol (200 μl , 3.4 mmol). Materials with low resistance against bases were milled with NaCl (1 g, 7.2 mmol) and ethanol (200 μl , 3.4 mmol). After this procedure, the PC and PC GF vessel were damaged, therefore these vessels were excluded from the study.

3.2 Long term stability

To examine the long-term stability of the vessels tested, they were milled for 12 hours at a milling frequency of 35 Hz with one steel ball, as well as K_2CO_3 (1.12 g, 8.76 mmol) and ethanol (311 μl , 3.3 mmol). To quantify the abrasion approximately, the mixture was suspended in water and filtered. The remaining polymer residues were weighed after 24-48 hours of drying at 80°C.

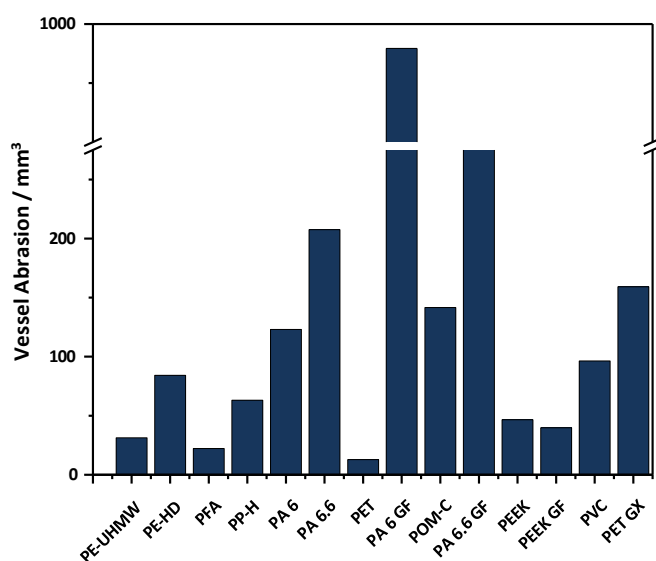


Figure S 1: Results of the gravimetric analysis of the polymer vessel abrasion. All experiments were performed in a MM500 mixer mill for 12 hours at a frequency of 35 Hz with a Pd ball, as well as K_2CO_3 (1.12 g, 8.76 mmol) and ethanol (311 μl ,

3.3 mmol). The raw mixture was suspended in water and the insoluble residue was filtered and dried in an oven at 80°C for 24 h – 48 h.

After this procedure, PET displayed extensive damage (Figure S) after prolonged reaction times. This is likely to be caused by the high hydrolysis sensitivity of the material and the alkaline conditions applied during milling. After repeating this experiment using sodium chloride instead of potassium carbonate, PET proved satisfactory durability, showing that basic bulk materials should only be used short-term, to ensure sufficient stability. In case of the PEEK vessel, metal particles of the ball material used were incorporated into the vessel ends during the milling process (Figure S). Hence, the possibility of contamination and the occurrence of side reactions in subsequent experiments should be contemplated.

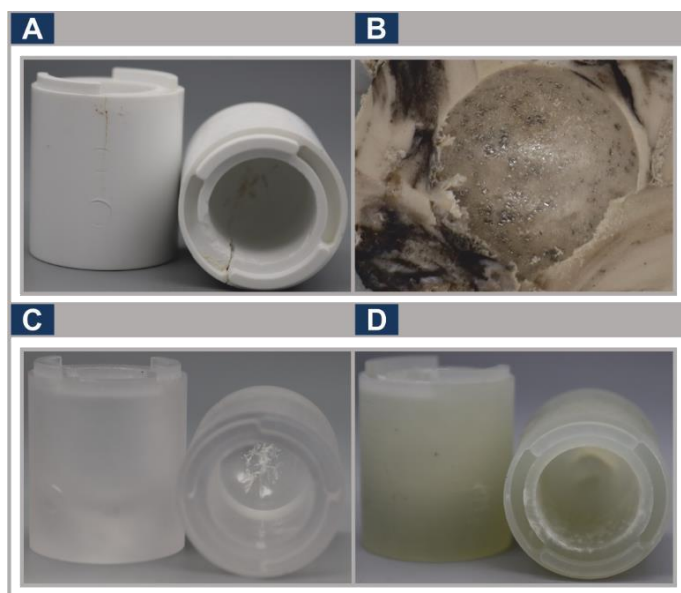


Figure S 2: A) shows a broken PET vessel after 12 hours of milling at 35 Hz. B) demonstrates the vessel end of a PEEK vessel with steel fragments integrated into the material after 12 h of milling at 35 Hz. C) shows a PC vessel, which was damaged during pre-milling and D) shows a PC GF vessel which exhibits damage after pre-milling.

4. Chemical resistance

Data about the chemical resistances of the tested polymers were obtained from different sources, as there is no information on the manufacturer's datasheets.

Chemical resistance													
Polymer	Alcohols	Ether	Aldehydes	Ester	Aliph. HC	Arom. HC	Halog. HC	Ketones	Bases (W)	Bases (S)	Acids (W)	Acids (S)	Acids Ox.
PFA ⁽¹⁾	+	+	+	+	+	+	+	+	+	+	+	+	+
PP ⁽¹⁾	+	0	+	0	+	0	0	0	+	+	+	+	-
PE-HD ⁽¹⁾	+	0	+	0	+	+	0	0	+	+	+	+	-
PE-UHMW ⁽²⁾	+	0	+	0	+	0	-	+	+	+	+	+	0
PA6 ⁽³⁾	+	+	+	+	+	+	-	+	0	+	-	0	-
PA66 ⁽⁴⁾	+	+	+	+	+	+	-	+	0	+	-	0	-
PA6GF ^(4,5)	+	+	+	+	+	+	-	+	0	+	-	0	-
PA66GF ⁽⁵⁾	+	+	+	+	+	+	-	+	0	+	-	0	-
PC ^(1,6)	+	-	0	-	0	-	-	-	-	-	-	0	-
PC GF ⁽¹⁾	+	-	0	-	0	-	-	-	-	-	-	0	-
POM C ⁽¹⁾	+	+	0	-	+	+	+	+	+	+	-	-	-
PET ⁽⁷⁾	+	+	+	+	+	0	+	0	-	0	+	+	-
PET GX ⁽⁸⁾	+	-	-	-	+	-	-	-	-	-	+	-	+
PEEK ⁽⁹⁾	+	+	-	+	+	+	-	+	+	+	+	+	-
PEEK GF ⁽¹⁰⁾	+	+	/	+	+	+	-	+	+	+	+	+	-
PVC ⁽¹⁾	+	-	-	-	+	-	-	-	+	+	-	+	-

Figure S 3: Table of chemical resistance of the 16 different polymers used. Green (+) indicates excellent chemical resistance of the material, while yellow (0) is representing partial resistance. Red boxes (-) demonstrate poor resistance of the material regarding the substance group stated. Data for PFA¹, PP¹, PE-HD¹, PE-UHMW², PA6³, PA66⁴, PA6 GF^{4,5}, PA66 GF⁴, PC^{1,6}, PC GF¹, POM-C¹, PET⁷, PET GX⁸, PEEK⁹, PEEK GF¹⁰ and PVC¹ were obtained from various sources.

Standard tests are usually carried out in a standard atmosphere at 23 °C/50 % relative humidity in accordance with DIN 50014. Resistance is tested by exposure for a certain time interval while examining whether the material swells or softens.¹¹

5. Material properties

The material properties have been obtained from the technical data sheets, which were received from the manufacturers *Technoplast* and *Ammerflon*[®] GmbH on request. For this study, the maximum working temperatures (long-term), the densities, as well as the ball indentation hardness values were used. The prices for the polymers are corresponding to the purchase prices in 2023. The glass transition temperatures are available in the datasheets of PA66, PA66 GF, PC, PC GF and PEEK GF. For PE-UHMW¹², PA6¹³, PA6 GF¹⁴, POM-C¹⁵, PVC¹⁶, PP¹⁷, PE-HD¹⁷, PEEK¹⁷, PET¹⁸, PET GX¹⁹ and PFA²⁰ values were obtained from various sources.

4. Temperature stability

6.1 Experimental procedure

The information regarding the temperature stability of the different thermoplastics served as rough guidelines, as the durability can be reduced under simultaneous mechanical stress. This is due to these values being solely derived from the manufacturers own empirical knowledge. The maximum working temperature values were obtained while exposing the materials to warm air, without additional mechanical stress. Testing of the vessel stability under heated milling conditions was performed in a MM400 mixer mill by *Retsch* at a milling frequency of 30 Hz. The vessels were filled with K₂SO₄ (1 g, 5.7 mmol) and ethanol (200 µl, 3.4 mmol). For the high-performance polymers, heptanol (200 µl, 1.4 mmol) was used instead of ethanol, as higher temperatures were chosen. For temperatures over the boiling point of heptanol, no solvent was used. The vessels were heated in a custom-made heating set-up equipped with two heating jackets and a temperature controller (Figure S3). For testing the vessel stability under heating with simultaneous mechanical impact, the temperature was increased in steps of 5°C, starting at temperatures significantly lower than the maximum working temperature. During the heating periods, the mill was not running, whereas the vessels were milled at 30 Hz for 5 minutes, as soon as the temperatures stabilized. This was repeated until the desired temperature was reached. For PET and PVC, the temperature could be increased up to the maximum working temperature given by the vendor, while milling at 30 Hz for additional 15 minutes. For the glass fiber reinforced polyamides, there was damage observable after milling at the maximum working temperature for 15 minutes, as polymer pieces were breaking out of the vessel ends. Heating up to a temperature 10°C lower than their maximum, long-term application temperature given from the manufacturers was, however, applicable for all standard and construction thermoplastics. In case of PEEK, heating up to 240°C was possible without damaging the vessel. PFA, however, was melting at this temperature. Furthermore, there was a smell of burnt plastic noticeable when the temperature was increased to 160°C. This smell was getting stronger as the temperature was increased further. Due to insufficient ventilation, and therefore for safety reasons, the test was aborted at a temperature of 230°C. It has to be noted, however, that this vessel has been used frequently at a temperature of 150°C in other studies.

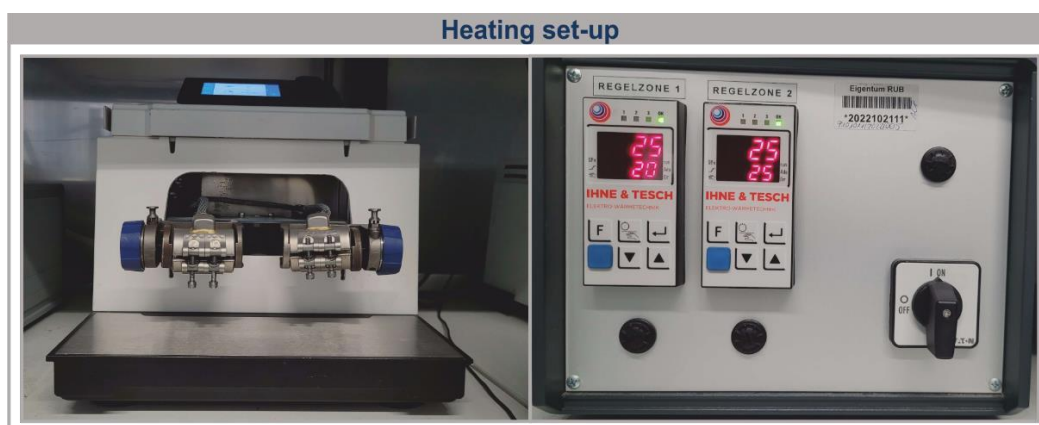


Figure S 4: The MM400 mixer mill by *Retsch*, which is equipped with two heating jackets (left) and attached to a temperature controller (right). Both heating jackets can be heated independently.

6.2 Vessels before and after heating

To document the vessel damage after the heating periods, pictures have been made before and after. Figure S4 shows the vessels before and after heating 10°C lower as their maximum working temperature. In the beginning, PVC and PP have been heated to their maximum working temperature, however, in case of PA6GF there were polymer fragments were breaking out of the vessel ends. Afterwards, the other polymers have been heated up to a temperature 10°C lower than their maximum working temperature.



Figure S 5: Vessels before and after heating 10 °C lower than their maximum working temperature. In case of PEEK, PEEK GF and PFA, these were not heated up to his temperature, but it was limited to 240°C.

6. PXR D spectra

To investigate, whether the materials tested are suitable for in-situ PXR D measurements, reference spectra of certain materials were measured. Therefore, it is possible to make predictions on whether reflections may interfere with the substances measured in in-situ monitoring experiments. The reference spectra of PFA, POM C, PA6, PE-HD, as well as PEEK have been measured at the DESY, Hamburg. Therefore, the vessels could be measured directly in the in-situ set-up. The other materials, however, were measured on a regular PXR D, and material had to be abraded from the vessels to be

able to measure the reference spectra. PA6 GF, PA66 GF, as well as PEEK GF were not measured, as further reflections are not expected from the amorphous glass fibres. As with this method, the resulting sample consists of larger polymer pieces, and because of the lower energy X-rays, the measurement time was prolonged to in-situ PXRD cannot be performed in a regular laboratory setting, further testing needs to be done in the future at the DESY in Hamburg.

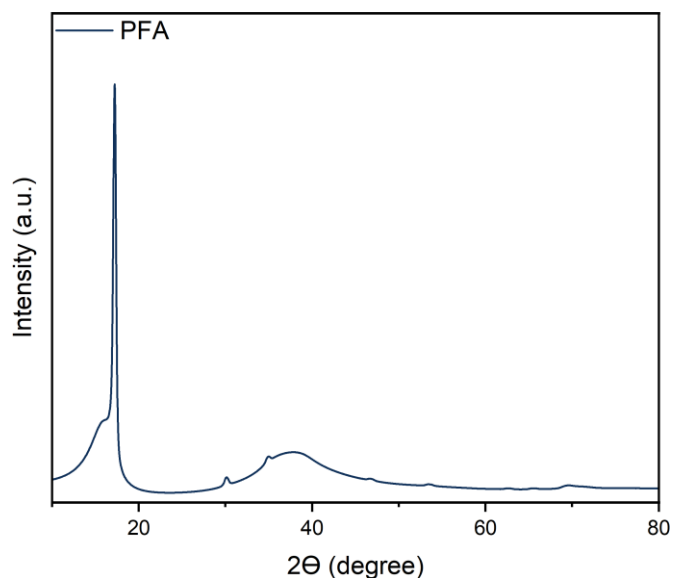


Figure S 6: Reference PXRD spectrum of PFA, which has already been used successfully in in-situ monitoring experiments, as it only has one distinct reflection at approximately 17°.

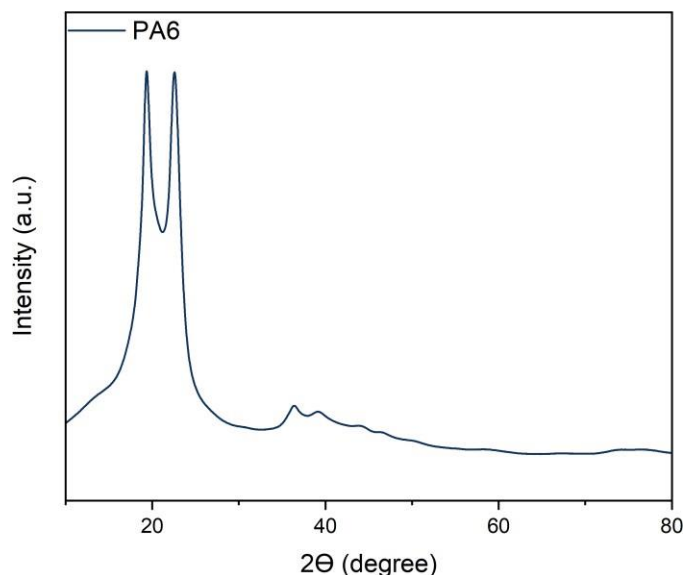


Figure S 7: Reference PXRD spectrum of PA6. There are two distinct reflections visible at approx. 19.4° and 22.6°, therefore this material could be appropriate for in-situ measuring, if these do not interfere with the reflections of the measured sample. Further testing needs to be done to investigate whether this material can be used for in-situ PXRD measurements.

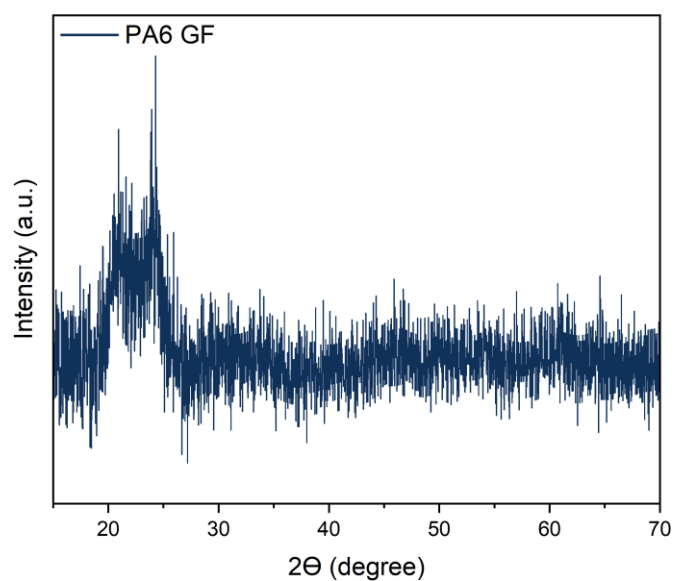


Figure S 8: Reference PXRD spectrum of PA6 GF. There are two reflections visible between approx. 19.4° and 22.6°, therefore this material could be appropriate for in-situ measuring, if these do not interfere with the reflections of the measured sample. Further testing needs to be done to investigate whether this material can be used for in-situ PXRD measurements.

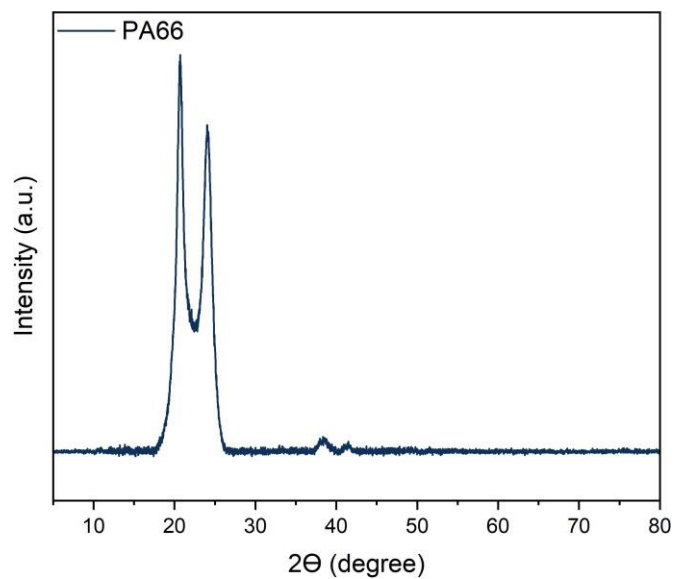


Figure S 9: Reference PXRD spectrum of PA66. There are two distinct reflections visible at approx. 20.7° and 24.1°, therefore this material could be appropriate for in-situ measuring, if these do not interfere with the reflections of the measured sample. Further testing needs to be done to investigate whether this material can be used for in-situ PXRD measurements.

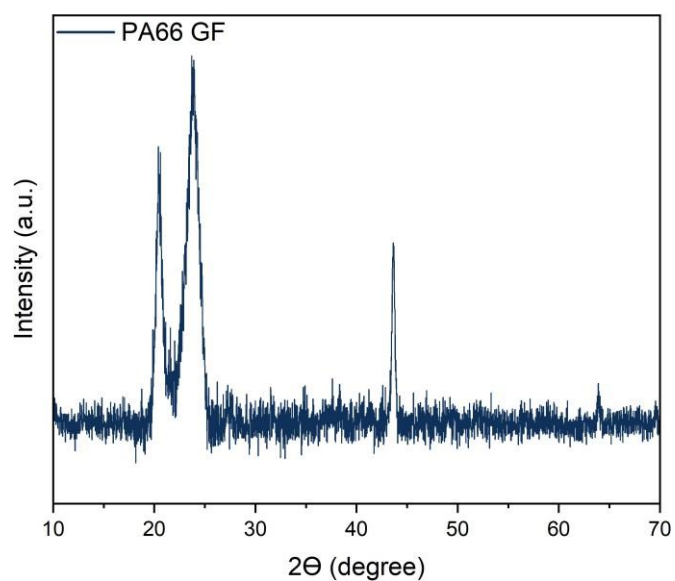


Figure S 10: Reference PXRD spectrum of PA66 GF. There are two distinct reflections visible at approx. 20.7° and 24.1° , as well as one at approx. 44° , therefore this material could be appropriate for in-situ measuring, if these do not interfere with the reflections of the measured sample. Further testing needs to be done to investigate whether this material can be used for in-situ PXRD measurements.

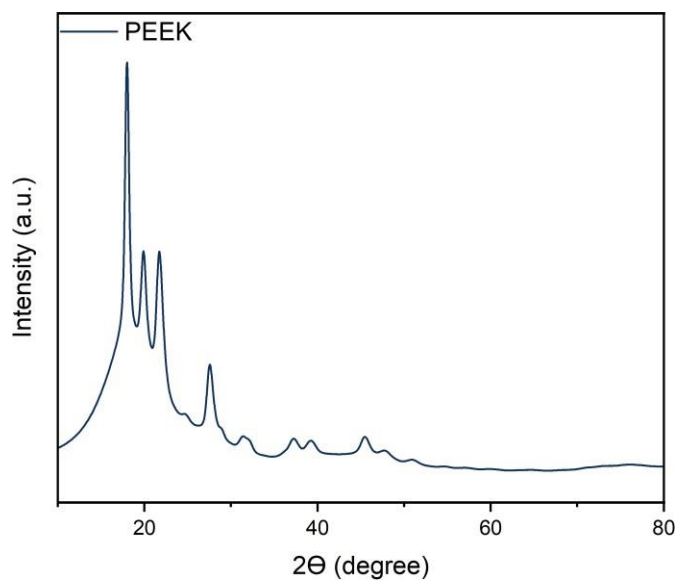


Figure S 11: Reference PXRD spectrum of PEEK. This material shows several intense reflections ranging from 18° to 26.6° , as well as slightly less intense reflections up to 45.4° . As these can potentially interfere with the reflections of the substances measured, it is potentially only applicable for certain reactions.

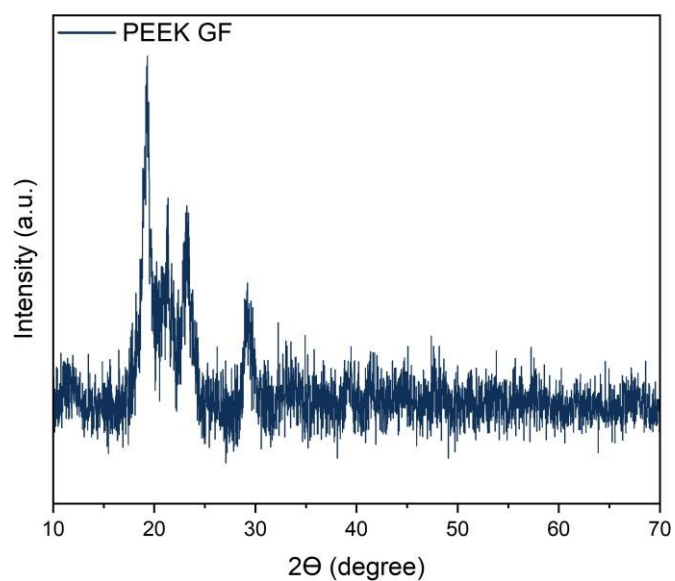


Figure S 12: Reference PXRD spectrum of PEEK GF. This material, just like the non-glass fibre reinforced counterpart, shows several reflections ranging from 18° to 26.6°. As these can potentially interfere with the reflections of the substances measured, it is potentially only applicable for certain reactions.

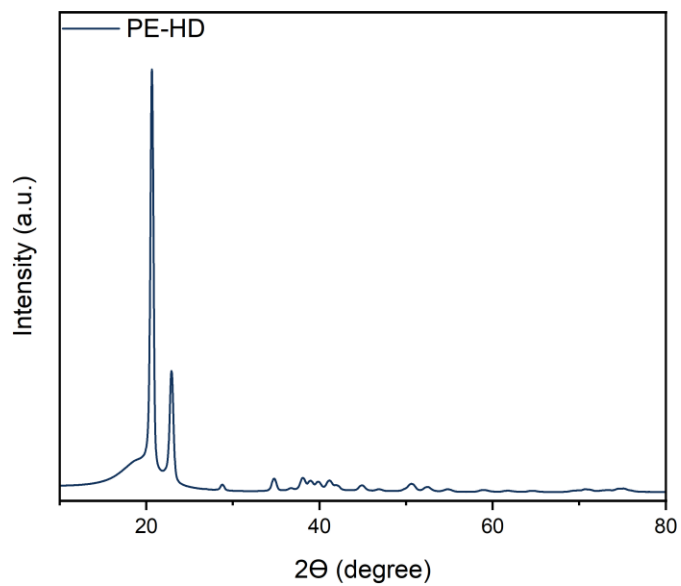


Figure S 13: Reference spectrum of PE-HD. There are two distinct reflections at 20.6° and 22.9° observable, as well as reflections with low intensity ranging from 28.8° to 52.7°.

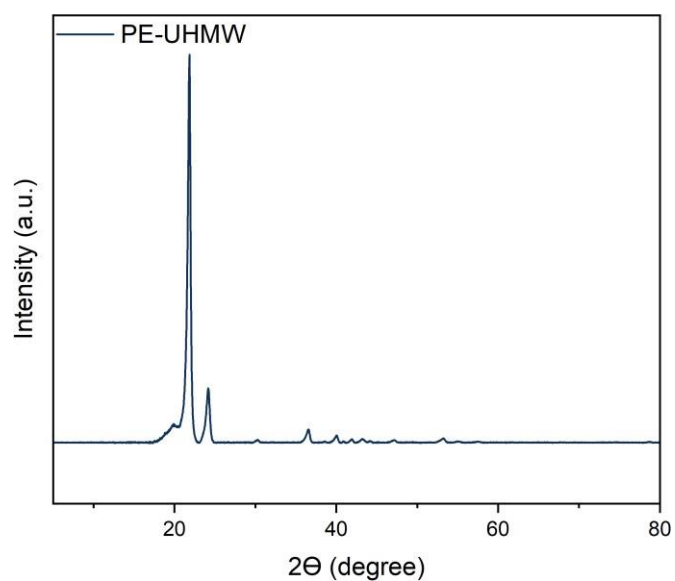


Figure S 14: Reference spectrum of PE-UHMW. There are two distinct reflections at 21.8° and 24.2° observable, as well as reflections with low intensity ranging from 30° to 53°.

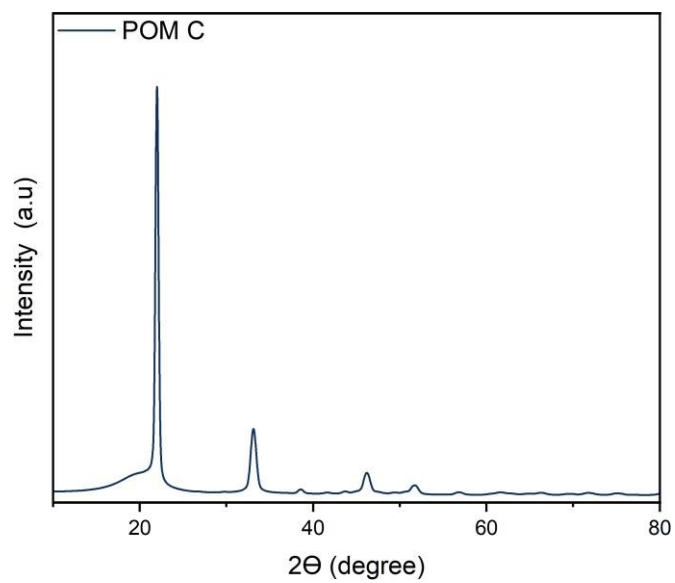


Figure S 15: Reference spectrum of POM C. There are reflections observable at 22°, 33° and 46.1°, whereas the reflection at 22° is the most intense. It needs to be further investigated, however, if this could be a suitable vessel material for certain applications.

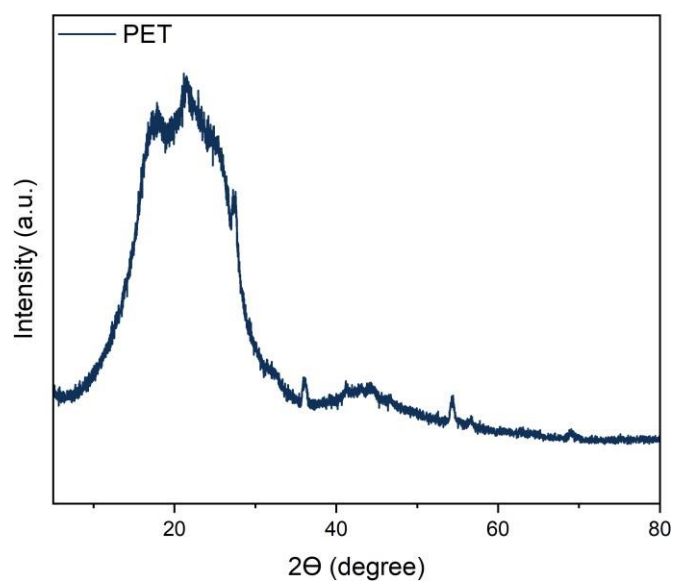


Figure S 16: Reference spectrum of PET. One reflection between 10° and 35° is observable. For certain applications, this material can potentially be used.

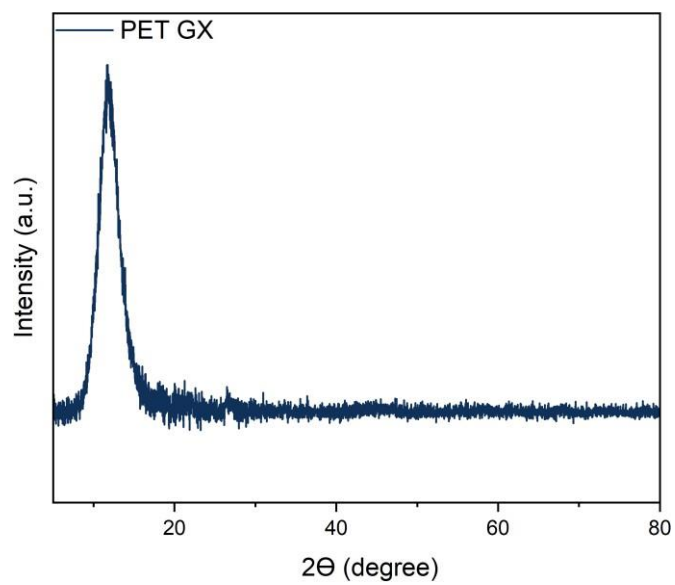


Figure S 17: Reference spectrum of PET GX. One reflection is measurable between 10° and 20°, otherwise this is a promising candidate for in-situ PXRD measurements. Further tests need to be conducted at the DESY, Hamburg.

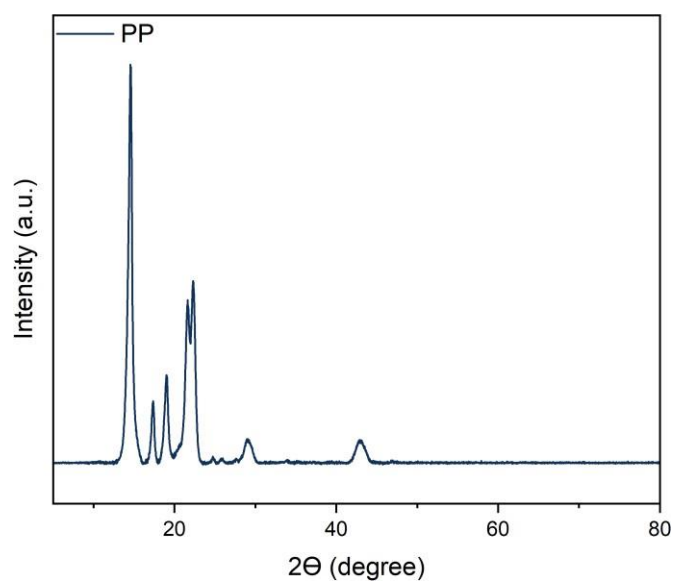


Figure S 18: Reference spectrum of PP. There are reflections observable between 10° and 30° as well as one at 42° . It needs to be further investigated, however, if this could be a suitable vessel material for certain applications.

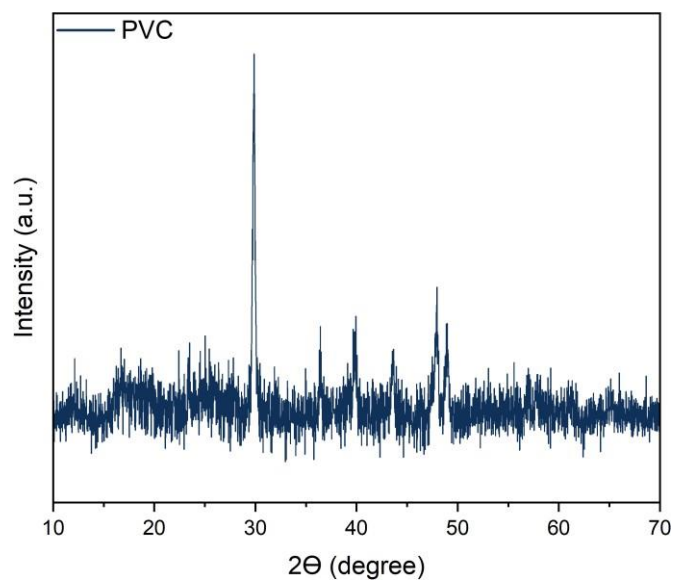


Figure S 19: Reference spectrum of PVC. The reflections detected are caused by an additive, as PVC itself is an amorphous polymer.

7. Raman spectra

To investigate whether the materials tested are suitable for in-situ investigations, reference spectra were obtained using a 785 nm laser by *Renishaw*. All measurements were conducted under the microscope using a 50x lens. Additionally, the raw reaction mixture of a Sonogashira coupling of Iodobenzene and phenylacetylene has been measured underneath the plates, to examine whether the materials are suitable for measuring substances in-situ. All tested materials show signals in the range of approximately 700 cm^{-1} to 1750 cm^{-1} , as well as 2750 cm^{-1} to 3000 cm^{-1} . Polypropylene additionally exhibits signals between 100 cm^{-1} and approx. 600 cm^{-1} . Generally, these could potentially interfere with a huge number of signals of substances to be measured.

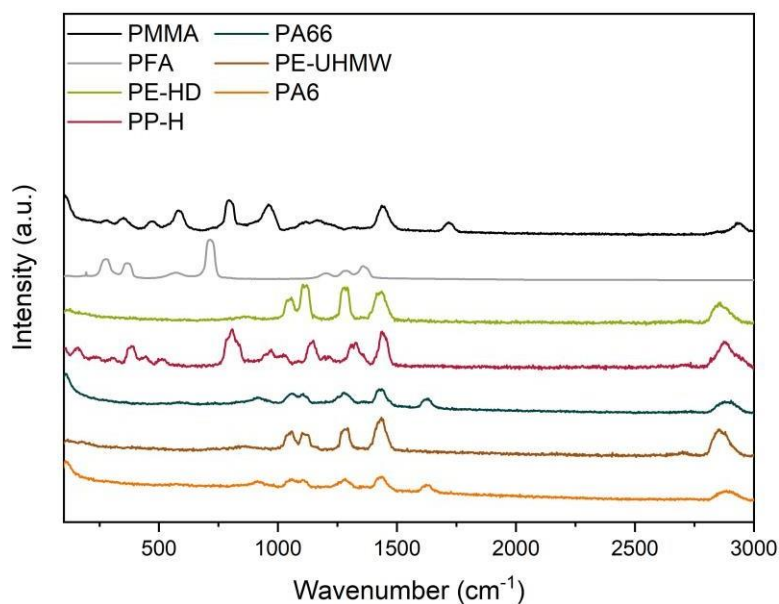


Figure S 20: Reference spectra of PE-HD, PP, PA66, PA6 and PE-UHMW. Plates with a thickness of 2 mm were prepared and measured under a Raman microscope using a 785 nm Laser by *Renishaw*. The tested materials do not exhibit signals between approximately 1750 cm^{-1} and 2750 cm^{-1} .

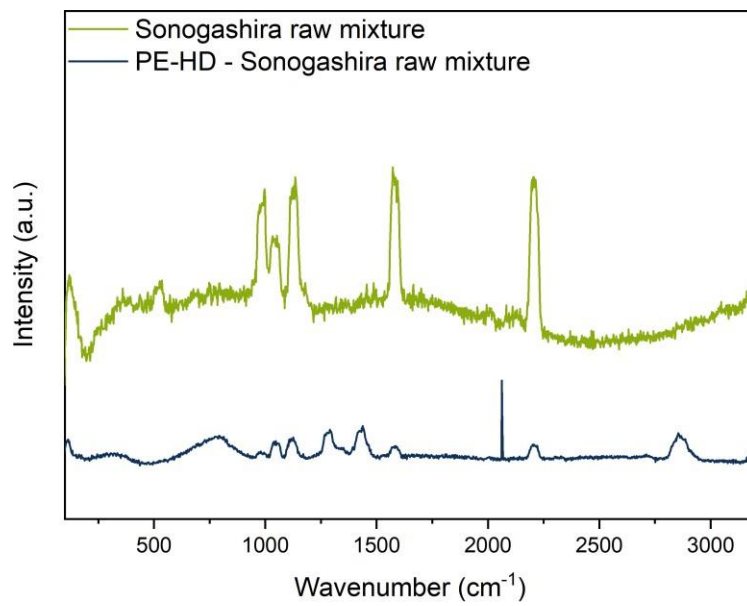


Figure S 21: measured Sonogashira raw mixture as reference, as well as measured underneath a PE-HD plate with a thickness of 2 mm.

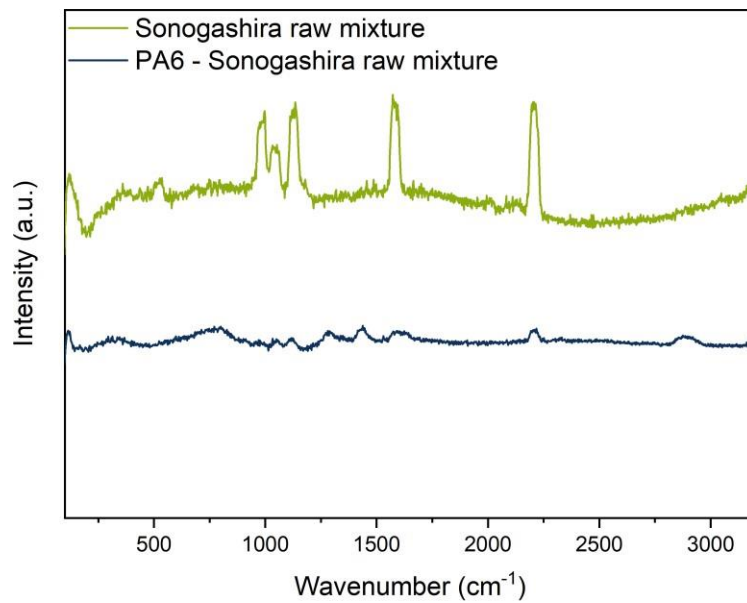


Figure S 22: Measured raw mixture of a Sonogashira coupling measured under a Raman microscope, as well as the raw mixture measured below a PA6 plate with a thickness of 2 mm.

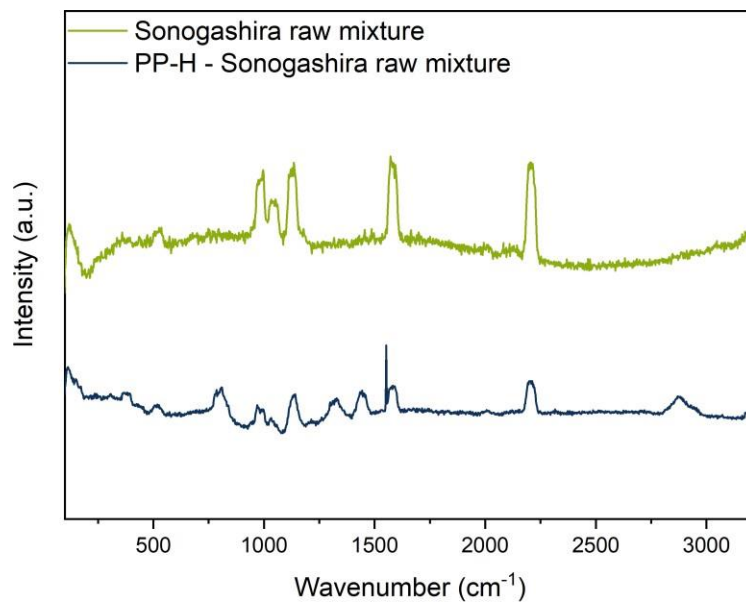


Figure S 23: Measured raw mixture of a Sonogashira coupling measured under a Raman microscope, as well as the raw mixture measured below a PP-H plate with a thickness of 2 mm.

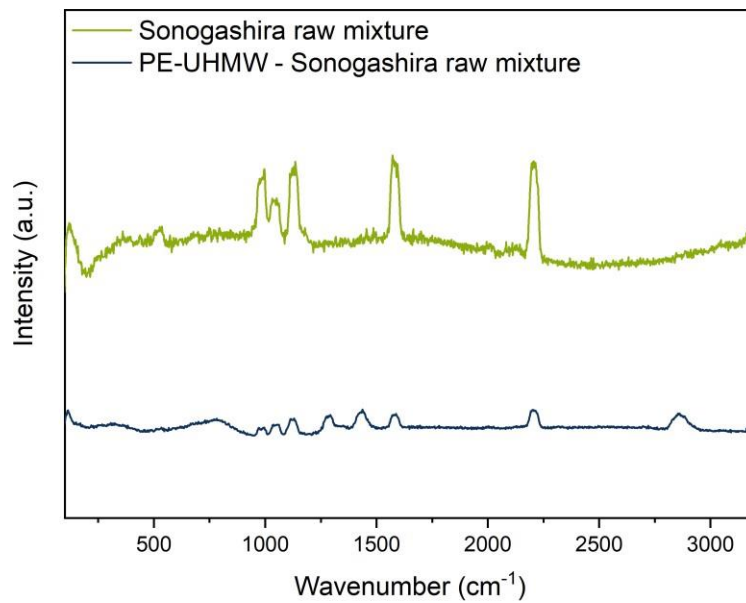


Figure S 24: Measured raw mixture of a Sonogashira coupling measured under a Raman microscope, as well as the raw mixture measured below a PE-UHMW plate with a thickness of 2 mm.

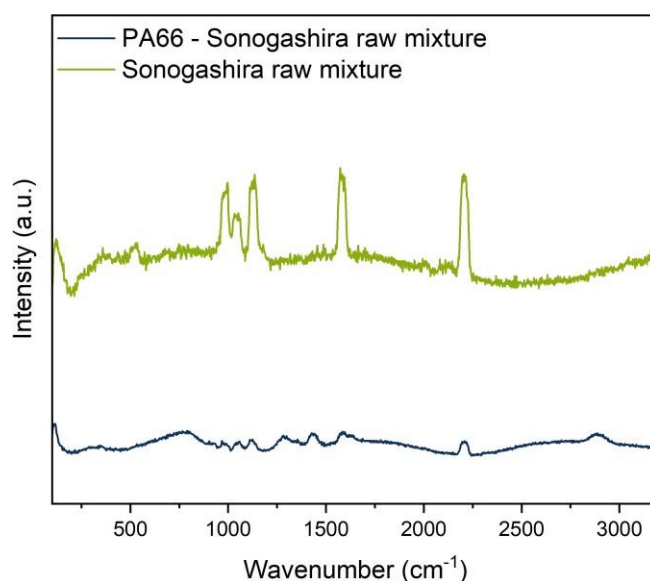


Figure S 25: Measured raw mixture of a Sonogashira coupling measured under a Raman microscope, as well as the raw mixture measured below a PA66 plate with a thickness of 2 mm.

8. Material performance regarding the Suzuki coupling

To further investigate the material performance, the Suzuki coupling of iodobenzene and phenylboronic acid has been conducted. All reactions have been conducted in a MM500 by *Retsch* at 35 Hz for 15 minutes using one 10 mm palladium ball. The yields obtained are shown in Figure S 26.

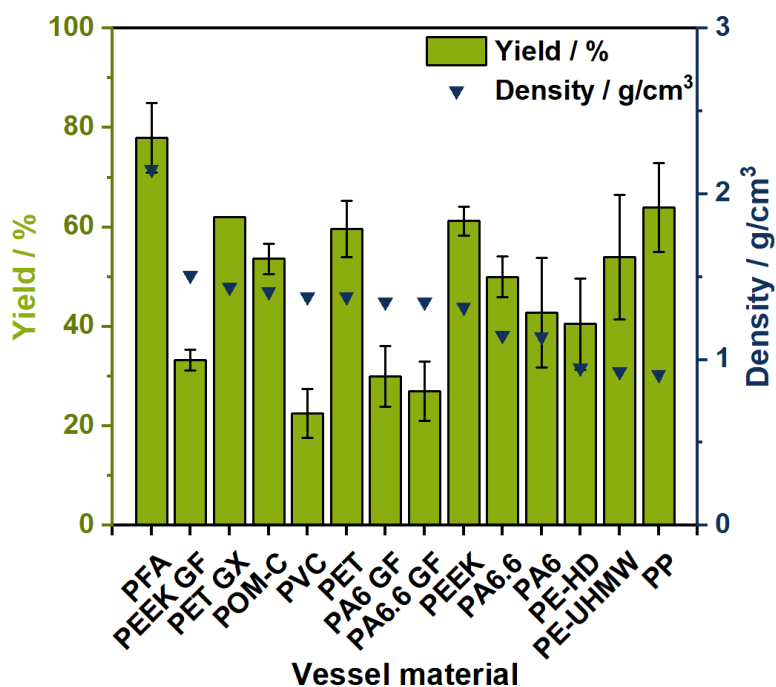


Figure S 26: Yields of the Suzuki coupling of iodobenzene and phenylboronic acid for the different polymers tested, as well as their respective densities. All reactions have been repeated 3 times to ensure reproducibility.

