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PROOF-OF-CONCEPT EXPERIMENT REPORT

TEMPERATURE STABILITY OF RAW MATERIALS AND DENTAL POLYMERS

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Proof-of-Concept experiment details

Received sample: Three Polirepair S powder samples, three Polirepair S liquid samples, two Polirepair S polymerized dental plates

Description by customer: The provided samples have been incubated at different temperatures as indicated in the table below.

Table 1. Incubation temperatures for the eight samples investigated in the current study.

No.	Sample name	Temp.	Lot, date of production	Duration of temp. exposure
1.	Polirepar S – powder	S.T.	#313, nov.2019	/
2.	Polirepar S – powder	54°C	#313, nov.2019	18 days
3.	Polirepar S – powder	-23°C	#313, nov.2019	18 days
4.	Polirepar S – liquid	S.T.	#10, jun.2020	/
5.	Polirepar S – liquid	40°C	#10, jun.2020	18 days
6.	Polirepar S – liquid	-23°C	#10, jun.2020	18 days
7.	Polirepar S polymerized plate	S.T.	Polymerized from materials No. 1 and 4 in this table	/
8.	Polirepar S polymerized plate	54°C	Polymerized from materials No. 2 and 4 in this table	/

Planned analysis:

Fourier transform infrared spectroscopy and thermogravimetric analysis were used on all starting materials (samples No. 1 – 6), powder X-ray diffraction was used on samples No. 1 – 3, electron microscopy was performed on the polymerized plates No. 7 and 8.

Sample preparation: All samples were used as provided. For the SEM measurement, the sample surface has been coated with 8 nm of Au.

Measurement author, dates and place: Electron microscopy was performed by Dr. Blaž Belec and all other experiments were performed by Dr. Tina Škorjanc in February and March 2021. The current report was reviewed by Prof. Mattia Fanetti and Prof. Matjaž Valant.

Observation conditions:

SEM Imaging: beam energy 15 KeV; secondary electron detector.

Thermogravimetric analysis (TGA): ramp 10 °C per minute, up to 1000 °C (powder samples), or 250 °C (liquid samples).

Fourier-transform infrared spectroscopy (FT-IR): range 450 – 4000 cm^{-1}, all measurements performed in the Attenuated Total Reflection (ATR) mode.

Powder X-ray diffraction (PXRD): 600 W, 30 kV, 15 mA, range 8°- 80°.

Main aim of the experiment: to test TGA, FT-IR, PXRD and SEM in investigating the effect of incubation temperature on the chemical, thermal, and structural stability, and to evaluate changes in the morphology of the polymerized dental products.

Results

In the current proof-of-concept study, a total of eight samples prepared and delivered were analyzed. Six of the samples represented the Polirepair S starting materials used in the synthesis of the dental plates. Three Polirepair S samples were in the solid powder form, three Polirepair S samples were in the liquid form and all of them had previously been exposed to various temperatures as indicated in Table 1. These six samples were evaluated for thermal stability through thermogravimetric analysis (TGA), chemical stability through Fourier-transform infrared spectroscopy (FT-IR), and structural stability through powder X-ray diffractions (PXRD) studies.

The results of the TGA measurements are shown in Figures 1 and 2 for the solid and liquid samples, respectively. The Polirepair S powder materials exhibit similar thermal stabilities, which indicated that the exposures to elevated (54 °C) and low (-23 °C) temperatures for 18 days did not significantly influence the thermal stability of the material. It may be possible to detect changes in this parameter if the exposure is prolonged, or if more extreme temperatures are investigated. The Polirepair S liquid sample is highly volatile, as noted by naked eye as well as by the shape of the TGA curves in Figure 2. Due to the lack of the initial plateau and a sharp drop in the % weight loss at the very beginning of the curve, a comparison between the three curves might be biased. We presume that this shape of the curves is related to the high volatility of the sample, which starts to evaporate rapidly even at room temperature. Therefore, the physical nature of these samples prevents the use of TGA as a suitable method of stability evaluation.

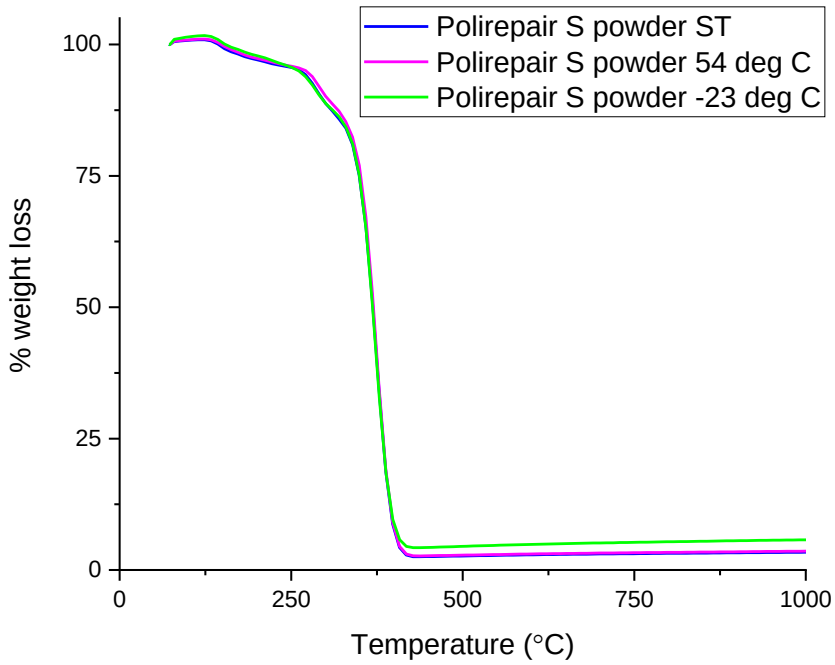

Figure 1. Thermogravimetric analysis of the Polirepair S powder samples.

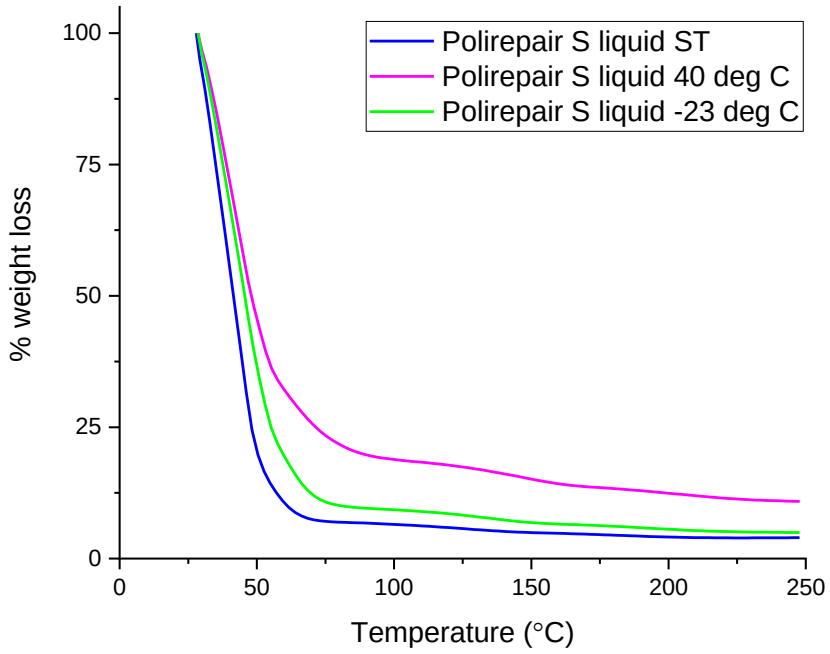

Figure 2. Thermogravimetric analysis of the Polirepair S liquid samples.

FT-IR measurements were conducted on all three powder and liquid samples of Polirepair S in order to understand any changes to the chemical bonding and functionalities in the samples induced by elevated or decreased temperature. Figures 3 (powder samples) and 4 (liquid samples) indicate a near-perfect overlap of the spectra regardless of the temperature. This strongly suggests that the temperature changes to which the samples were exposed did not induce alternations in the chemical structure of the materials.

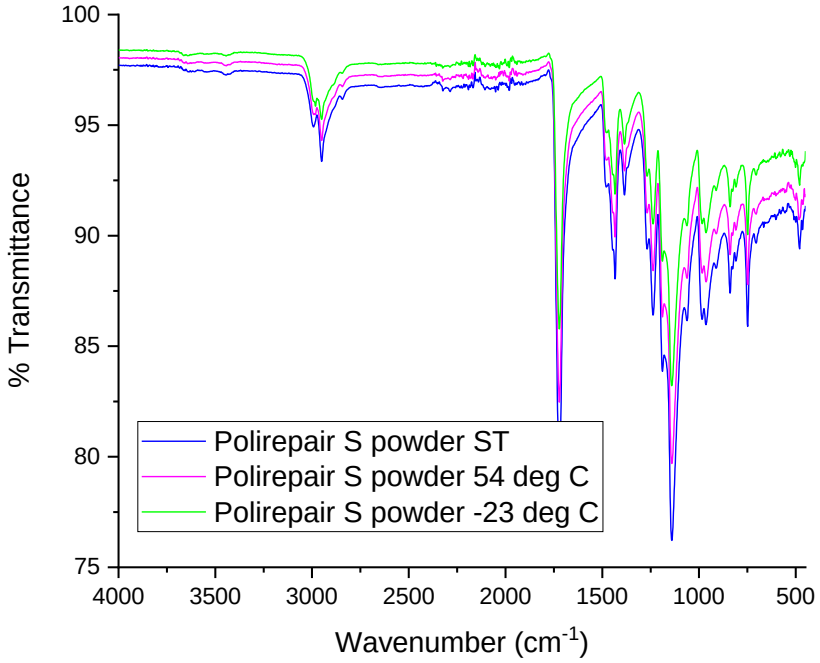

Figure 3. FT-IR spectrum of the solid Polirepair S powder samples.

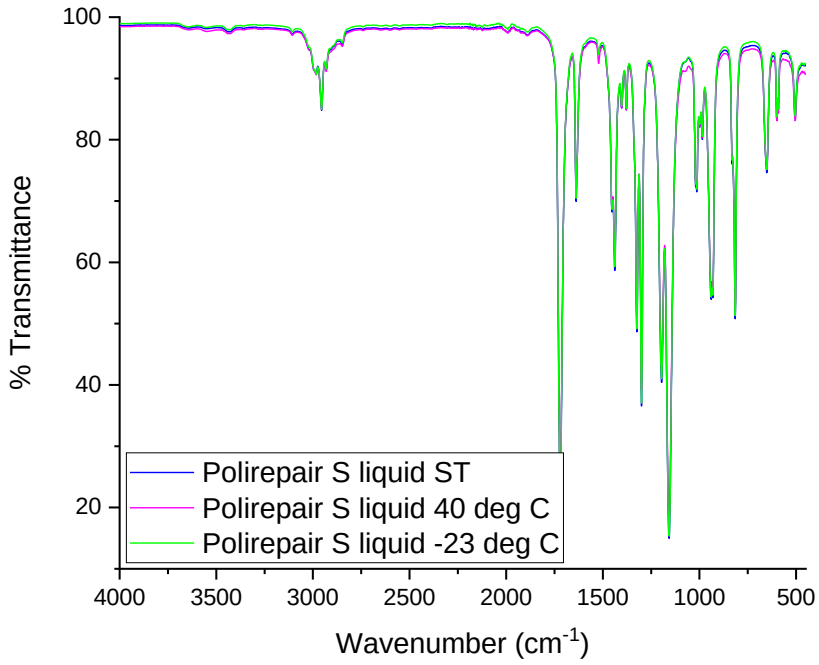

Figure 4. FT-IR spectrum of the Polirepair S liquid samples.

In order to investigate changes in the structural order of the powder Polirepair S samples, we measured the PXRD patterns of the three samples exposed to various temperatures. The data shown in Figure 5 below indicate the presence of three broad peaks in all three samples. The broadness of the signals is indicative of low crystallinity within the sample. The peaks occur at

~13°, ~29°, and ~43°. The ratios of peak intensities are similar in all three samples and so are the positions of peaks. This indicates that little changes occur in the order within the material in response to the 18-day exposure to 54 °C or -23°C.

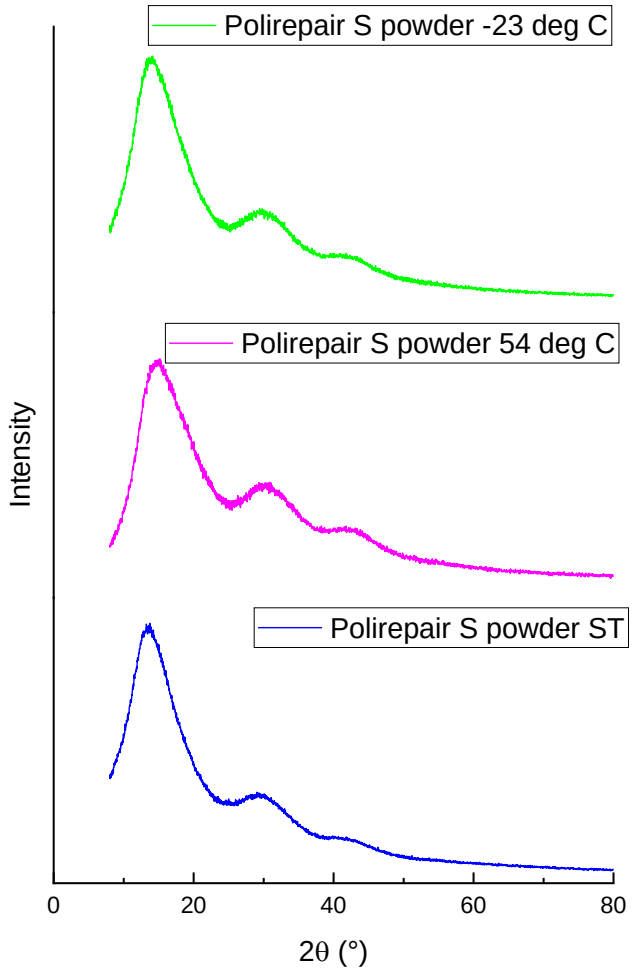

Figure 5. PXRD patterns of the solid Polirepair S samples.

In addition to investigating the physical properties of the Polirepair S powder and liquid starting materials, we also studied the polymerized plate product by scanning electron microscopy (SEM). Using this advanced analytical method, we aimed to observe any morphological changes of the solid product that is produced from raw materials incubated at room temperature (sample No. 7) or at increased temperatures (sample No 8). For the analysis, a small square of the material (2 by 2 cm) was broken from the larger plate provided by the industrial partner.

Image 6 represents sample No. 7 in Table 1. Its surface is relatively smooth (Figure 6a). Occasional rough spots are noted as indicated in Figure 6b and enlarged in Figure 6c. The spherical spots marked with arrows in Figure 6d are also interesting. These marks probably originate from the plate preparation process, where trapped air bubbles pop and leave behinds these patterns.

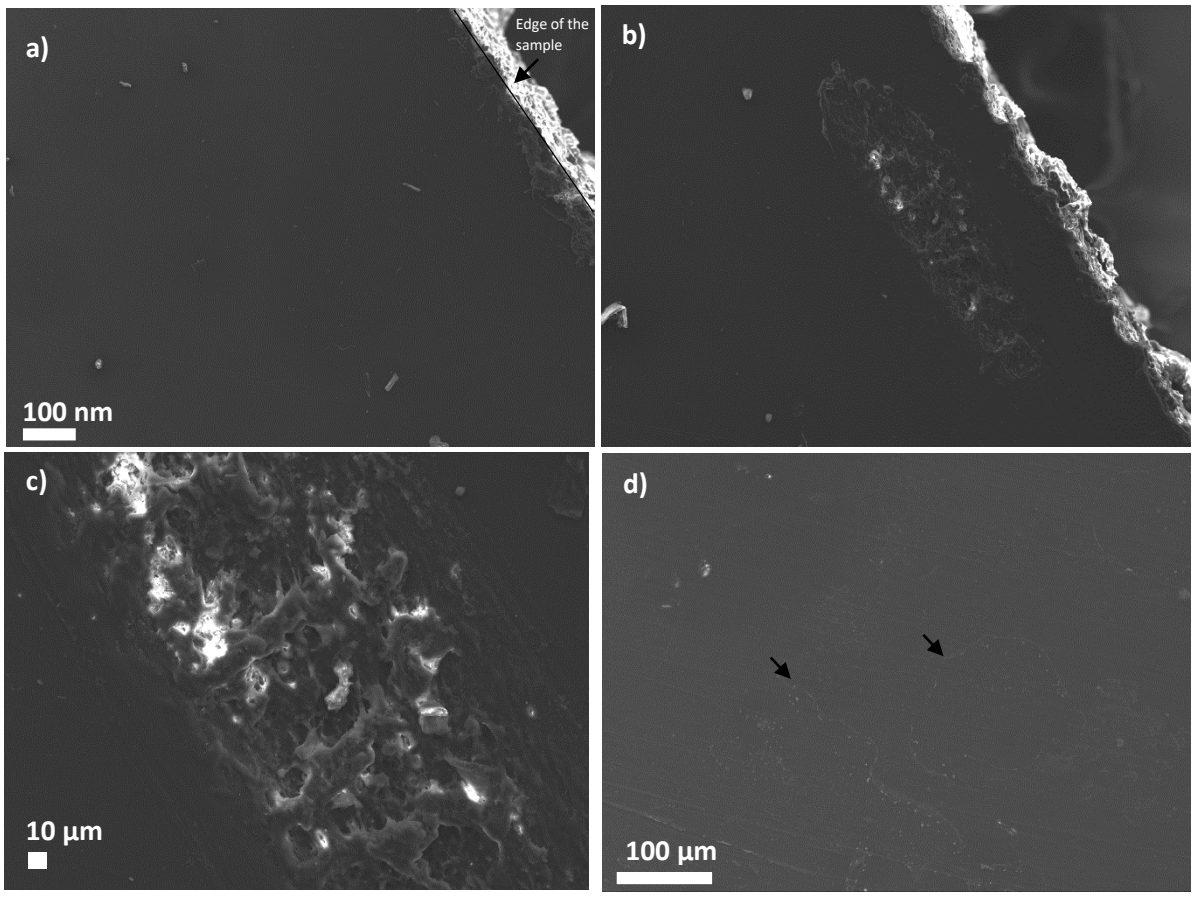

Figure 6. SEM images of the Polirepair S sample kept at room temperature.

Figure 7 represents sample No. 8 that was produced from the powder Polirepair S incubated at 54 °C for 18 days and liquid Polirepair S incubated at room temperature for the same duration. The sample exhibits two types of surface features. As shown in Figure 7a, some areas of the surface appear smooth. The sample areas shown in Figure 7b and 7c, however, exhibit a different morphology than the original sample in Figure 6. Here, surface roughness in the form of 10-50 µm large islands can be observed. Most of these features display the shape of a crater, resembling the evaporation and popping of a solvent or air bubble.

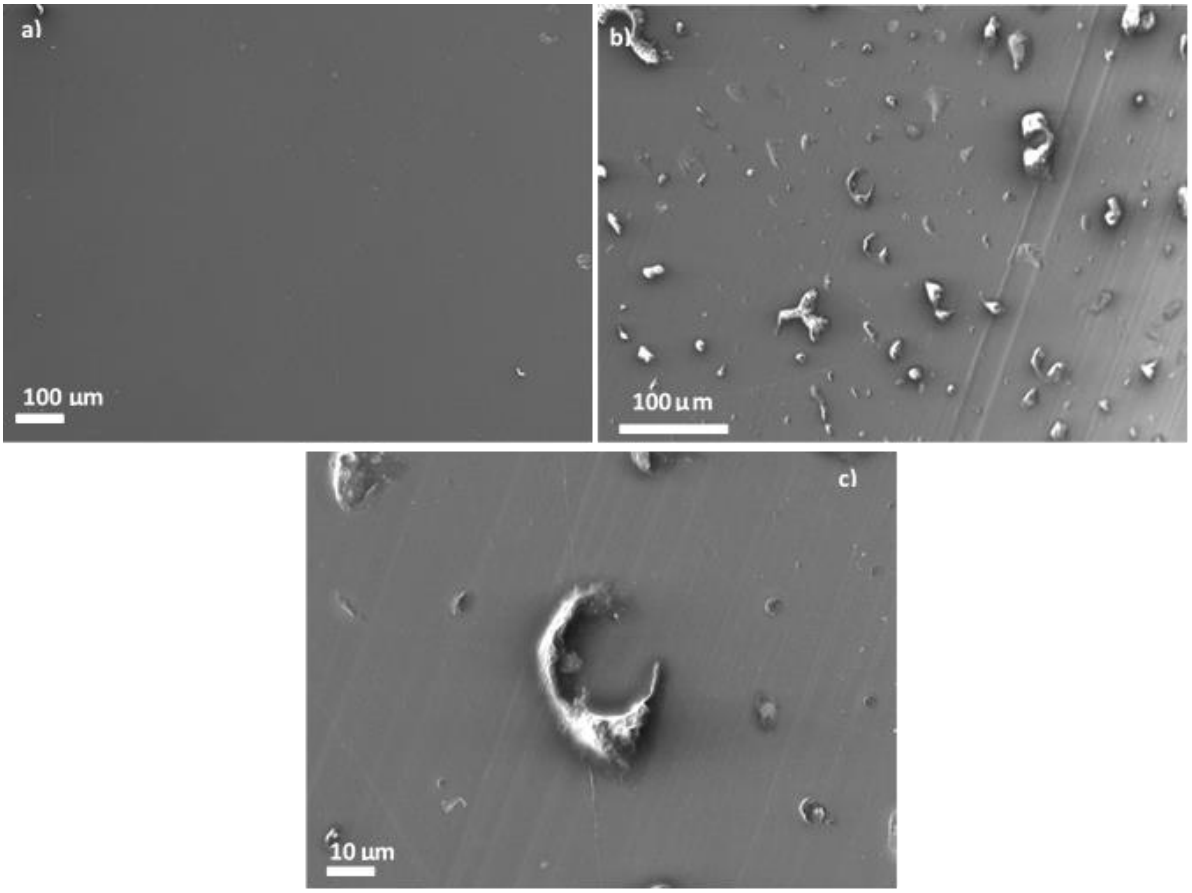

Figure *7.* SEM images of the Polirepair S sample incubated at 60 °C.

In conclusion, we note that exposure to -23 °C and 40/54 °C does not significantly change the thermal stability, the order within the structure of the material, or the chemical composition of the Polirepair S samples. The SEM analysis in particular, was demonstrated to be a powerful technique to analyze the final polymerized products. Microscopic morphological changes that cannot be studied with any other technique can negatively affect the mechanical properties of the produced materials. It may be useful to investigate the morphology of the exact same polymerized plate in different conditions rather than using a different plate for each treatment.

This proof-of-concept evaluation looked at the temperature as a potential source of chemical and physical changes to the material. It would, however, make sense to also investigate the effect of other parameters to which these dental products might be exposed. We suggest evaluating pH and mechanical force as two potential, highly relevant parameters to be studied. Ingested food is characterized by a range of pH values, and the force exerted by the teeth during chewing might cause mechanical damage that can be observed qualitatively with electron microscopy and quantitatively with mechanical testing instrumentation.

This report has been written by Dr. Tina Škorjanc

Date: 26 March 2021