# Glass Transition in Powders Determined by Compressional Dynamic Mechanical Analysis

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## ABSTRACT

Rheology holds significant importance in the context of powder handling. In industries ranging from pharmaceuticals and food processing to chemical engineering and metallurgy, the handling of powdered materials is a critical aspect of production. Powder properties such as flowability, cohesion, and compressibility directly impact manufacturing processes and final product quality. Stickiness is important for powder handling as adhesion and cohesion tendencies of powders can significantly impact their flow, compaction, and processing characteristics. In this context, the glass transition temperature (Tg) plays a crucial role. Tg can influence powder stickiness, as it affects particle interaction and molecular mobility within the particles. Above Tg, powders tend to exhibit higher adhesive forces and reduced flowability, potentially leading to issues like caking, bridging, and poor discharge from hoppers.

A new method was developed where Tg of powders can be determined in a simple parallel plate geometry in a rheometer without prior preparation of the powder sample. The method was evaluated and validated using a poly(vinyl alcohol) (PVA) powder and further tested on protein powders of varying handleability. The results were compared to established rheological methods of powder flowability and stability which were found to correlate well with the measured Tg.

## INTRODUCTION

The glass transition temperature has been extensively studied in the context of polymers, glasses, and other amorphous materials, as it significantly affects their mechanical, thermal, and transport properties. Attention has also been directed towards understanding its implications on the bulk behaviour of powders, particularly concerning their tendency to undergo cohesive interactions and exhibit the phenomenon known as "sticking" or "caking"[1]. Sticking occurs when powders adhere to surfaces, leading to challenges in processing, handling, and the overall quality of the final product.

The influence of Tg on the cohesive properties of powders can be attributed to the mobility and adhesion of particles near or above their Tg [2]. At temperatures approaching or exceeding Tg, the amorphous regions within powder particles become more flexible, facilitating the formation of interparticle interaction. This increased mobility enables particles to fuse together upon contact, resulting in agglomeration and cohesive behaviour. Consequently, powders with

Tg values near or below the processing temperature are more prone to sticking, causing operational issues in industrial processes and affecting product quality.

The Tg of powders is mainly determined by differential scanning calorimetry (DSC) and by dynamic mechanical analysis (DMA). Tg can be extracted from the measurements in different ways and for DMA the temperature at the phase angle peak is most commonly used, which is higher than the Tg determined by DSC[3]. DMA is more sensitive to Tg but the particulate nature of powders makes it difficult to apply to existing measuring systems. Compacts, or tablets, of powders have therefore been used in compression or indention mode [4-7], as well as enclosures with powders ("powder pocket" or "powder clamp") deformed in three-point bending [8, 9].

Rheological analysis enables the quantitative assessment of powder flow properties, such as flowability, cohesion, and friction using different specialised measuring systems for conventional rheometers[10, 11]. There are many available methods, empirical or more physical, where the methods used in the present paper determines physical properties such as yield stress and mechanical energy.

The aim of the present study was to develop a method of determining Tg of powders with simple sample handling, and to validate the method. The new method was also applied to biological powders of varying handleability.

## MATERIAL AND METHODS

### Materials

PVA with molecular weight 146-186 kDa was purchased from Sigma Aldrich (363035). Four different pea protein powders were obtained, two concentrates (1 and 2) with protein concentration of 55-60%, and two isolates (1 and 2) with protein concentration of about 85%. The samples were chosen to represent typical food grade powders with different sensitivity to humidity and different degree of flowability.

### Sample preparation

Powders were conditioned in a climate room at 23° and 50% RH. Films were prepared by dissolving the PVA powder in deionized water at 80°C and casting the solution on a Teflon film. The cast solutions were dried to films and conditioned at 23° and 50% RH.

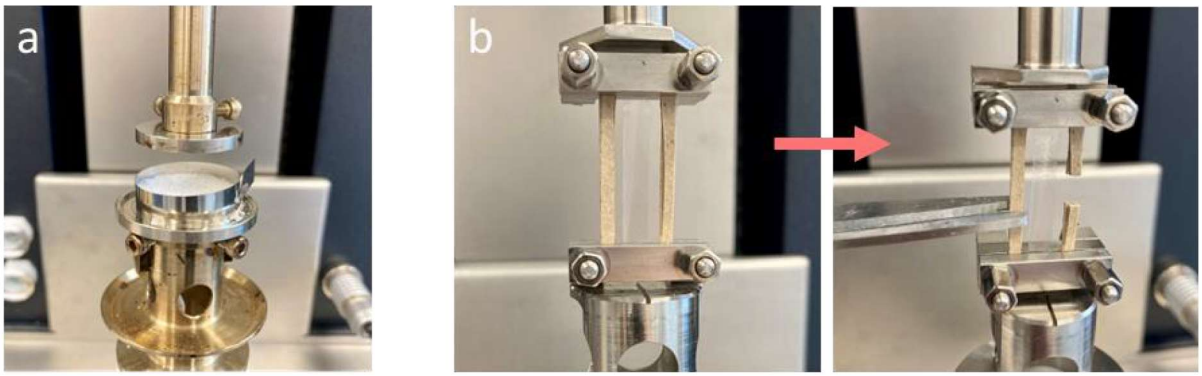


**FIGURE 1**: Experimental setup. a) powder on the bottom plate contained within a melt ring. b) Loading of a film between two clamps using a cardboard frame.

## Dynamic Mechanical Analysis

An HR 30 rheometer (TA Instruments, New Castle, DE, USA) was used for Small Amplitude Oscillatory Compression (SAOC) analysis, equipped with a 25 mm-diameter parallel plate system. Powders were applied on the lower plate surrounded by a melt ring to keep the powder in place as shown in **Fig. 1**. The surface was evened, and the upper plate lowered until contacting the powder. A static compressional stress of 20 kPa was applied throughout the measurement. A harmonic axial compression of strain 0.04% was used to monitor E* during a temperature ramp in the range -40°C to 250°C. The harmonic stress was always kept 25% larger than the static stress.

The same rheometer was used for analysis of films by clamping a 30x4 mm film between two clamps. A static axial tension of 0.3 N was applied and a harmonic strain of 0.1% was used to monitor E* during a temperature ramp in the range -40°C to 250°C. The harmonic stress was always kept 25% larger than the static stress. The film was inserted using a cardboard holder which was cut open when the film was positioned as shown in **Fig. 1**. The film was covered by bearing grease to minimize moisture loss during heating.

The HR 30 rheometer was also equipped with a Powder Rheology Accessory (PRA) which was used to determine shear flow and flowability of powders at 20°C as shown in **Fig. 2**. Both modes consist of two steps where the first conditions the sample. In the powder shear test the second step was a series of determinations of a shear yield stress under stepwise decreasing axial stress which gives a flowability function. A high number of the flowability function indicates that the powder flows easily without sticking.

For flowability determination the second step was a series of rotations down and up through the powder cylinder monitoring torque. The impeller performs a helical path through the powder and the series of steps gives data for an analysis of powder stability. The calculated powder stability index indicates if the powder is affected by the mechanical energy imposed by the impeller. A stability index of 1 indicates a powder which is stable over time when sheared.

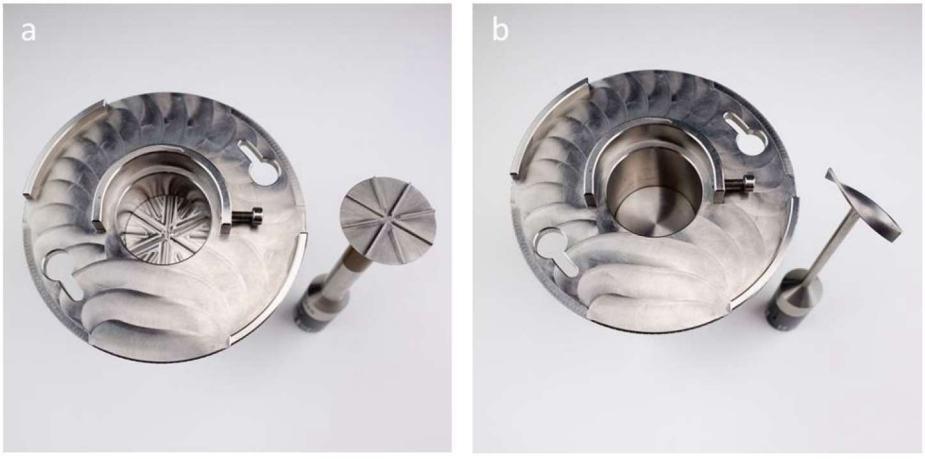


**FIGURE 2**: Experimental setup for powder analysis using PRA. a) Powder shear geometry, and b) Powder flow geometry.

## RESULTS AND DISCUSSION

In previous publications several authors have demonstrated the possibility of determining Tg of powders by either compacting the powders to a tablet or enclosing them in a “powder

pocket" [4, 8, 9]. The current study evaluated the possibility of determining Tg of powders without the compaction step. The powder was applied to a plate and kept in place by a melt ring. The surface was evened, and the upper plate was held in contact with the powder surface by an axial compressional stress. **Fig. 3** shows modulus and phase angle for the PVA powder as compared to a PVA film measured in tensional DMA. The position of the phase angle peaks gives Tg and Tm which correspond well for the powder and film measurements as given in the inset in **Fig. 3** which validates the method. The modulus values differ mainly due to the difficulty in accurately measuring the modulus of a layer of powder particles.

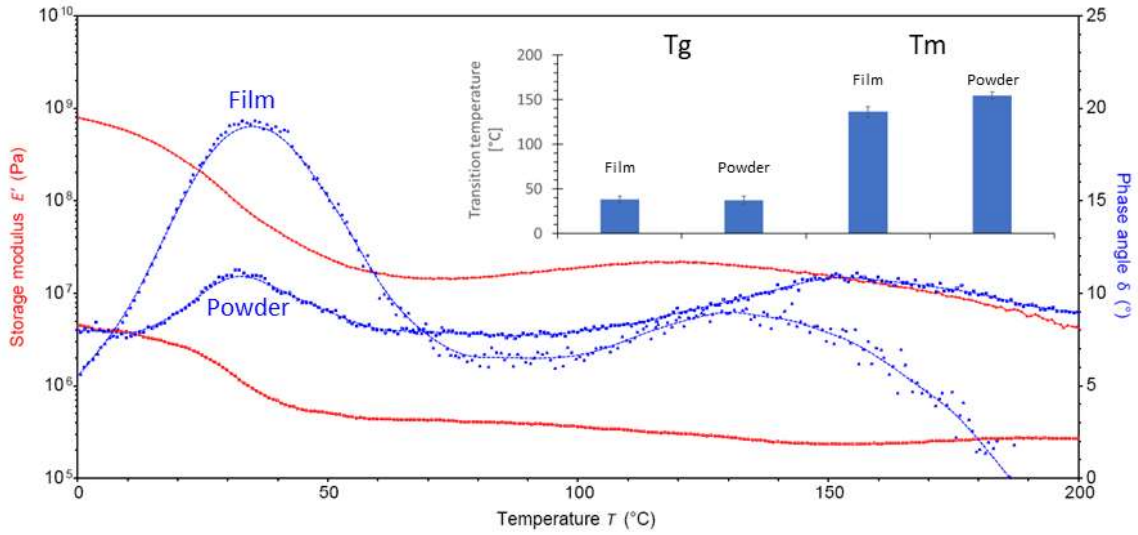


**FIGURE 3**: Example of heating curves of PVA powder as compared to a film. The inset shows the transition temperatures taken from the peaks in the phase angle. Tg=glass transition temperature and Tm= melting temperature. The error bars denote standard deviation.

Four pea protein powders were analysed using compressional DMA as described above, and by powder shear testing and flowability testing using a Powder Rheology Accessory. Some protein powders are known to sticky and difficult to handle, especially concentrates. When feeding them into for example an extruder, bridging and uneven powder flow is common. The isolates are often easier to handle like Isolate 2 but Isolate 1 was included in the study as a representative of an isolate powder with difficult handling.

Stickiness has been correlated to Tg where powders handled at temperatures below Tg flow well and are less sticky due to the powder particles being in their glassy state. There are more factors involved in powder flow such as particle geometry, but **Fig. 4** clearly shows a correlation between Tg and the Flowability function. Isolate 2 which is easy to handle has a Tg well above 20°C and a high Flow function whereas the other protein powders all have Tg below 20°C and lower values of the Flowability function.

The Stability index follows the same trend fairly with being equal to one for Isolate 2, and deviating from one for the other powders. The stability index for Concentrate 1 is still close to 1 indicating that this powder is not strongly affected by flow despite being sticky.

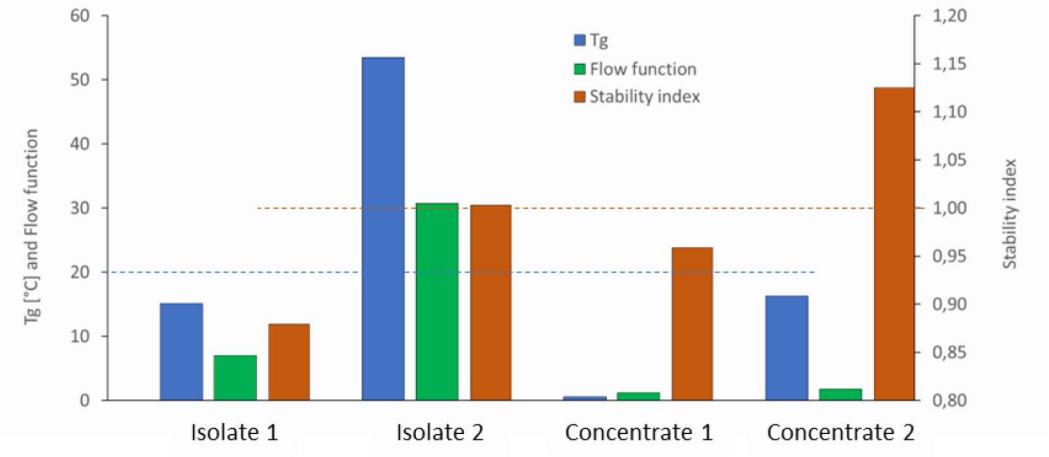


**FIGURE 4**: Comparison of powder data from the different analysis methods. Tg was determined by compressional DMA (first bar, blue), Flow function from Powder Shear Test (second bar, green), and the Stability index from a flowability test (third bar, brown). The dotted lines indicate the temperature of the experiments (20°C, blue line) and a Stability index of 1 (brown line).

## CONCLUSIONS

The new method of measuring Tg of powders was validated and is a fast way of determining Tg and thereby estimating stickiness of powders. It correlates well with results from powder flow which gives further information of powder flow properties.

## ACKNOWLEDGEMENTS

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