

Determination of the glass transition temperature of powder samples using Dynamic Mechanic Analysis on compacts

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ABSTRACT

Dynamic Mechanic Analysis, DMA, is a sensitive method to determine the glass transition temperature (T_g) of materials. Several different sample geometries such as three point bending, stretched films or compressed cylinders, are commonly used. The T_g of a powder is related to its “sticky point”, i.e. the temperature when the powder particles interact instead of flowing freely. The determination of powder T_g is not straightforward using DMA due to the limiting geometry. Here it is demonstrated that the T_g of powder samples can be effectively and correctly determined by DMA on compacts in compression mode, using a standard wedge shaped probe usually utilized in three point bend analysis. The analysis of compacts holds the benefits of analysing powder samples as received from manufacturers, being relatively robust with regard to deformation as the material becomes rubbery, and enabling easy sample preparation and handling.

INTRODUCTION

The glass transition temperature is a characteristic that is of importance in polymer science and applications^{1, 2}. As the temperature rises above the glass transition temperature of a polymeric material, the

material undergoes a transition from the glassy state, in which the motion of the polymer chains is very limited, to the rubbery state, in which the mobility of the polymer chains is greatly increased^{3, 4}. This increased mobility of the polymer chains is manifested as dramatic changes in material properties; rubbery materials being softer, having a larger viscous character and if purely amorphous deforming irreversibly under an applied force.

Dynamic mechanic analysis is a commonly used and sensitive method to analyse the T_g of polymeric materials^{2, 3}. The T_g is commonly taken as the temperature at which the phase angle has a maximum and the analyses are often performed on film samples. However, this is not always the preparation closest resembling that of the application of the analysed samples. Due to the film preparation the thermal history of the samples could influence the results. Furthermore, for some materials the determination of the T_g as the peak value of the phase angle is not easily performed. This as some samples become very soft as the T_g is approached, those samples then elongate beyond the limits of the instrument or reliable analysis before the phase angle has

reached its maximum. Finally, film samples can not be easily prepared for all materials.

Recognizing the above problems it is realized that in some cases it is beneficial to analyse samples in the powder form. DSC is a common method to analyse the glass transition of powder samples. However, the authors' opinion is that, thermomechanical methods are more sensitive and straight forward. Successful analysis of the glass transition temperature of compacts has been previously performed using oscillatory rheometry^{5, 6} and Mahlin et al.⁷ have reported on the successful DMA analysis of powder using a special sample holder.

The aim of this study was to evaluate if determination of the T_g of powder compacts could be performed using a DMA apparatus, utilizing the standard wedge shaped probe commonly used in three point bend analysis. Some benefits of the method, in addition to being able to use a standard DMA apparatus for determining the T_g of compacts, would be relative insensitivity to geometry and a large exposed area of the samples. This exposed area could be of importance in for example plasticization studies under controlled relative humidity.

MATERIALS AND METHODS

Materials

The samples in this study were prepared from the following materials; Carbopol (971-P NF, Noveon, USA), Ethyl cellulose, EC, (Ethocel N10 CR, Dow Chemical, USA), Hydroxypropyl cellulose, HPC, (HPC LF, Ashland, USA), Hydroxypropyl methylcellulose, HPMC, (HPMC USP 2208, 100cps, Shin-Etsu Chemical Co., Ltd., Japan) and Pemulen (TR-2 NF, Noveon, USA).

Sample preparation

Powder, samples were prepared by compressing about 50 mg of powder to 2.5 mm radius compacts under an applied pressure of 20 MPa using a TA-HDi[®]

(Stable Microsystems, Godalming, United Kingdom).

Film samples to be analysed were prepared from films of EC, HPC and HPMC to a width of 3 or 6 mm using a razor-edged punch.

Dynamic mechanic analysis

DMA measurements were performed using a Rheometrics RSAII (Rheometrics Scientific, Piscataway, NJ, USA) with an external air moisture controlling device⁸. The temperature was calibrated using the well known melting points of Gallium and Indium. The deformation and the force response of the samples were monitored and from those parameters the phase angle δ was calculated.

Powder samples were analysed in strain controlled compression mode utilizing a wedge shaped probe with the setup in Fig. 1. Film samples were analysed in strain controlled stretching mode.

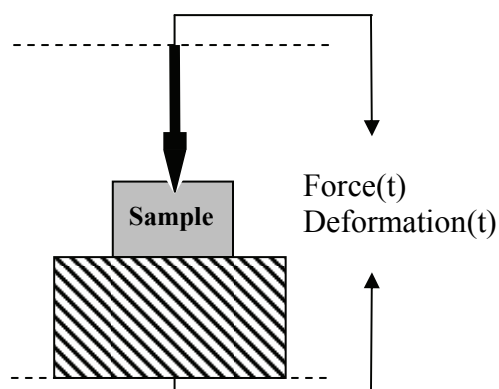


Figure 1. Schematic drawing of the setup for the analysis of compacts.

Determination of T_g was performed by initially keeping the samples at the starting temperature in dry air for 10 minutes. Temperature scans were subsequently performed, increasing the temperature at a rate of 2 °C/ minute for all powder samples and HPMC films, and 5 °C / minute for EC and HPC films. The T_g was determined as

the temperature at which the phase angle had its maximum.

The plasticization by water at different relative humidity, RH, was studied in the RH interval 20-80 % by monitoring the length change and the phase angle at each RH.

RESULTS

Determination of T_g

In order to evaluate how well T_g could be determined using a DMA apparatus in compression mode on compacts, as compared to traditional analysis on films, the analyses of compacts and films from EC, HPC and HPMC were compared.

The analysis of both HPMC films and compacts revealed a clear peak in the phase angle, see Fig. 2 for exemplifying results.

From the peak values the T_g was determined to 191 and 192 °C for compacts and films, respectively. The good agreement between the T_g acquired from analyses of films and compacts have been further validated by the authors in another study on HPMC (submitted manuscript).

For film samples of EC and HPC, no peak in the phase angle was observed before the samples had been deformed beyond the limit of the instrument.

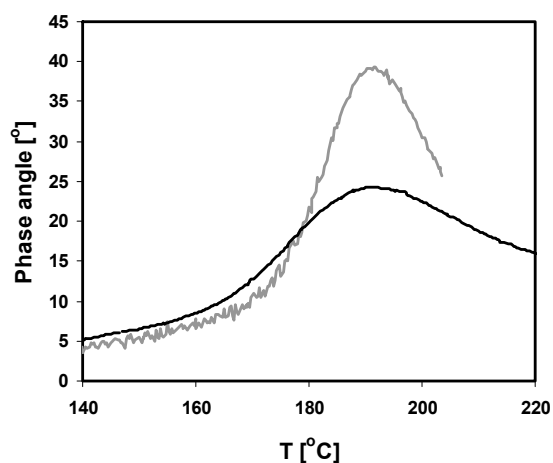


Figure 2. Phase angle as a function of temperature for compact (black) and film (grey) of HPMC.

The analysis of compacts of EC revealed a clear peak in the phase angle. From the peak values a T_g of 146 °C was determined for EC (results not shown). This value is somewhat higher than the T_g commonly reported, being about 130 °C. However, it is known since earlier^{9,10} that T_g values acquired as the maximum of the phase angle during DMA analysis is commonly somewhat higher than T_g values from DSC.

For HPC the analysis of compacts revealed the same continuous increase of the phase angle with increasing temperature and lack of a maximum, as for the analysis of film samples (results not shown). Those results are coherent with previous results on the thermal behaviour of HPC, reported by Kararli et al¹¹.

It is concluded that the determination of T_g of compacts and films give similar results when both are possible, and that in some cases the analysis of compacts is beneficial due to that film samples deform too much prior to the phase angle reaching a maximum.

To illustrate the benefit of the present method in analysing the T_g of materials for which films are not easily formed, Carbopol and Pemulen were chosen. The T_g values for compacts of Carbopol and Pemulen were easily acquired from the maximum of the phase angle, see Fig. 3. The T_g of Carbopol and Pemulen was determined to 140 and 139 °C, respectively.

Gómes Carracedo et al.⁶ have previously determined the T_g of Carbopol compacts of different grades and from different batches using oscillatory rheometry. They reported the main T_g values to be in the range of 135-141 °C, with, most values being in the upper part of the interval. Thus, it can again be concluded that DMA on compacts by the present method is effective and accurate in determining the T_g.

One drawback in relying on the analysis of compacts to determine T_g is that not all powders can be effectively formed into

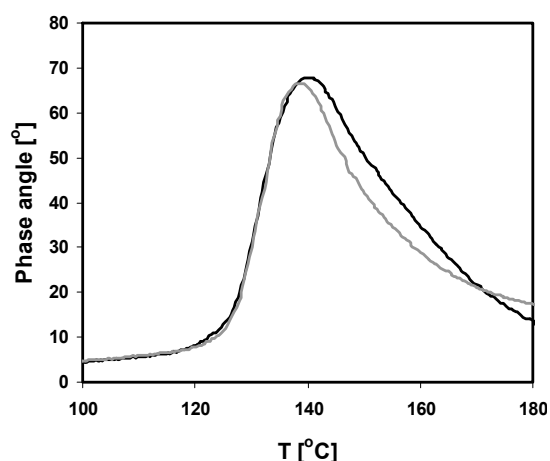


Figure 3. Phase angle as a function of temperature for compact of Carbopol (black) and Pemulen (grey).

compacts. However, it is well known within the pharmaceutical industry that materials which are difficult to form compacts from can be successfully formed into compacts if mixed with another material which has good properties with regard to compact formation. Thus, we propose that even materials that are difficult to form compacts from can be analysed successfully if co-compact with a material with good properties regarding compact formation, and that has significantly higher Tg than the material of interest.

As a proof of concept Carbopol and HPMC powder was mixed in a 1:1 ratio and subsequently analysed. Indeed, as seen in Fig. 4, the Tg of Carbopol, occurring at the lower temperature, can be successfully determined from the maximum of the phase angle.

To summarize, the determination of the Tg of compacts using DMA was highly successful. The Tg values acquired from compacts were comparable to those from films and to those from previous studies. It was also demonstrated that the problem with samples which are difficult to form compacts from could be circumvented by co-compact with a material with good compacting properties and a higher Tg. All of the Tg values from the performed

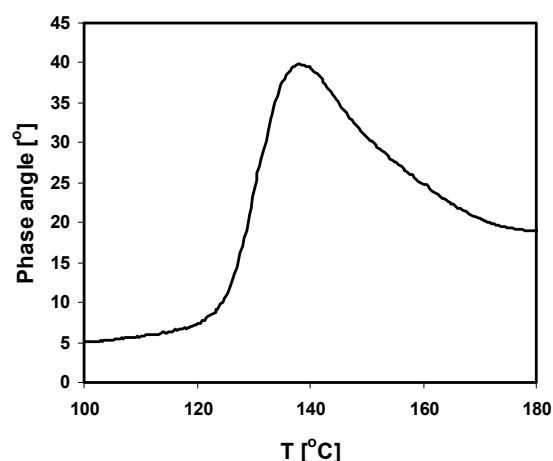


Figure 4. Phase angle as a function of temperature for compact of Carbopol and HPMC in 1:1 ratio.

analyses, determined from the maximum of the phase angle, are summarized in Table 1.

Table 1. Tg values for different materials, in the form of compacts or films.

| Sample | Tg Compacts | Tg Films |
|-------------------|--------------|--------------|
| HPMC | 191.1 ± 0.66 | 192.2 ± 0.49 |
| EC | 146 ± 1.0 | n.d. |
| HPC | n.d. | n.d. |
| Carbopol | 140.4 ± 0.1 | - |
| Pemulen | 139.0 ± 0.25 | - |
| Carbopol:HPM C | 138 | - |

± indicates min/max values (n = 2). n.d.: Not detected, -: Not analysed.

Plasticisation by water vapour

Having established the usefulness of DMA on compacts in determining Tg, it was considered interesting to briefly investigate if the method could also be used to study the plasticisation of compacts by water vapour. In order to do this HPC was analysed both as a film and as a compact in the RH range 20-80 %. For both film and compact the effect of RH was small up to 70 %. At 70 % an obvious increase was seen in the phase angle for the two preparations. Finally, at 80 % RH both samples displayed a large increase in the phase angle, see Fig. 5. Here two remarks needs to be made. First, at 80

% RH the film sample was stretched out beyond the limit of the instrument before the

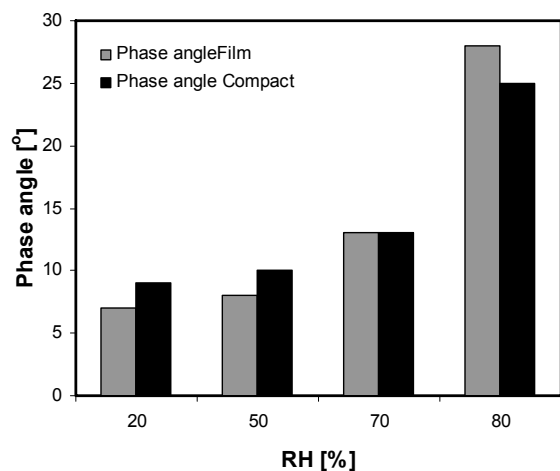


Figure 5. Phase angle at different relative humidity for HPC compact and film sample.

phase angle had reached an equilibrium value. Therefore the phase angle presented for the film at 80% RH is taken as the last measurement within the limits of the instrument. Second, due to the bulky geometry of the compact the time to reach actual equilibrium at each RH is rather long, the values presented in Fig. 5 are not actual equilibrium values, but close enough for a proof of concept. Depending on the nature of the sample, a qualified guess would be that a compact will need about 8 hours to be close to equilibrium with regard to phase angle, when going from a RH at which the sample is in the glassy state to a RH above which the sample is in the rubbery state. However, much shorter time is needed at each RH if the equilibrium condition is relaxed and only an indication of the glass to rubber transition is of interest.

From the investigation of the plasticisation by water vapour it seems as if DMA, using the present setup, can be used to detect the glass to rubber transition when RH is changed. However, the time to reach equilibrium at each RH is rather long and it is probably beneficial to condition the samples prior to analysis. Nonetheless, if the possibility to equilibrate samples prior to

analysis is lacking or if an indication of the RH of interest is needed, the method in question could be useful.

CONCLUSION

In this study we have demonstrated that a DMA instrument, without any special equipment, can be used to determine the glass transition temperature of powder samples in the form of compacts with high precision. Furthermore, the plasticising effect of water vapour can be studied. The results show that DMA can be a good analytical tool, not only in the traditional analysis of films, but also in the analysis of powder samples.

One benefit with the current method over analysis using rheometric instruments is the relative insensitivity to sample geometry. In this study we used disc shaped compacts for simplicity, but analyses could well have been performed on curved surfaces as well.

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