Dynamic Mechanical Analysis of Biopolymer Films

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ABSTRACT

Dynamic Mechanical Analysis, DMA, was used to measure the mechanical properties of biopolymer films at varying temperature and relative humidity. Biopolymer films are sensitive to an increase in surrounding humidity since it leads to an increased water content and thus a plasticization. This seriously effects the possibility to measure thermal mechanical properties and requires thorough control of environmental conditions.

INTRODUCTION

There is an increased interest in the utilisation of renewable resources for the preparation of disposable, biodegradable materials such as food packagings. Biopolymers are studied with the goal of producing degradable barrier films for such applications. Films from starch and many other biopolymers are excellent oxygen barriers and could *e.g.* replace aluminium and plastic films in some applications[1, 2].

Several studies have been made on starch based films cast from a solution or gel. As early as in the 1950s, self-supporting amylose films were prepared and evaluated with regard to their mechanical fracture properties[3]. The mechanical properties of cast films has also been studied by Dynamic Mechanical Analysis (DMA)[4-7]. Mechanical properties of films are crucial for most applications. When measuring the mechanical properties of a biopolymer film, a thorough control over environmental conditions has to be maintained. A small change in water content influences the material properties and various experimental techniques has been used[6, 8]. A comparison of different techniques will be presented in this paper and their influence on the results of DMA measurements of starch based films will be shown.

MATERIALS AND METHODS

Materials

Amylose (104561, batch 209861511) from potato was purchased from Merck (Darmstadt, Germany). Amylopectin was kindly supplied by Lyckeby Stärkelsen (Kristianstad, Sweden) in the form of granular amylopectin potato-starch. This potato was developed by Lyckeby Stärkelsen and Svalöv Weibull (Svalöf, Sweden) using genetic engineering to suppress amylose synthesis[9]. A hydrophobic grease (Stabox 9415) to cover the films during measurements was kindly supplied by AB Axel Christiernsen (Nol, Sweden).

Film preparation

5 %w/w amylose or 3 %w/w amylopectin was dispersed in distilled water, degassed and heated to 150 °C and 90 °C respectively. Glycerol was then added to the hot solutions

(40% glycerol/polymer) as a plasticizer. The solutions were poured on a PVC dish and allowed to gel at 23 °C.

The dishes were then dried at a constant relative air humidity at 23 °C for three days. The films were peeled off and reconditioned for at least two days at 50 %RH before measurements. The thickness of the films was measured using a digital indicator and found to be 70-100 μm.

Dynamic Mechanical Analysis

Dynamic Mechanical Analysis of the films was performed in tension in a Rheometrics RSA-II (Rheometrics Scientific, Piscataway, NJ, USA). A rectangular film strip 4x30 mm was clamped in the instrument and a sinusoidal, deformation was applied on top of a static deformation, the sum of these being non-destructive. The resulting force and phase shift δ to the applied deformation was recorded and the complex tensile modulus E^* was calculated.

The sample was enclosed in an air convection oven with circulating dry air. The instrument was also equipped with humidity control system designed in house. The system consists of a relative humidity (RH) sensor in the oven which sends a signal to a PID-regulator. The regulator controls an electric valve which mixes a dry and a humid air stream to set the relative humidity.

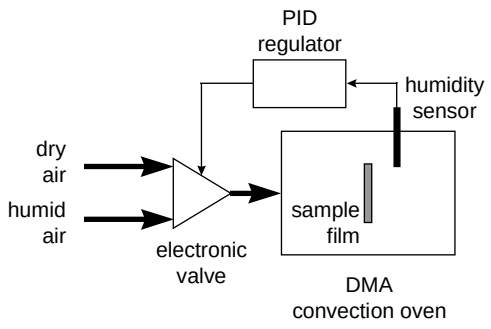

Figure 1. Sketch of the humidity control system.

The films were stored in 50% RH and then transferred to the instrument and again conditioned at 50% RH before measurements. The **humidity scans** were then performed by stepwise changing RH in steps of 10% up to 90% RH and then down. The **temperature scans** were performed after the initial conditioning at 50% RH by first covering the film with a the hydrophobic grease to prevent evaporation. The instrument was then set to temperature mode and the temperature was directly lowered to -80 °C and then raised from -80 °C at 1 °C/minute. The applied static force and dynamic strain were automatically controlled during the measurement within the intervals [0.15, 1.5N] and [0.01, 0.1] respectively, to apply as low deformation as possible without getting below the resolution of 0.1N. The applied strain was well within the linear region all through the measurements.

RESULTS AND DISCUSSION

The temperature in the DMA instrument is controlled by an air convection oven with a dry air flow that rapidly decreases the moisture content of the films which in turn changes the material properties. The moisture loss must therefore be avoided by e.g. encapsulating the film with a thin plastic film or by sealing it in grease. If a plastic film is used it will contribute to the modulus and it is difficult to get it tight enough to totally avoid evaporation. Sealing the film with grease contributes less to the modulus and gives a tight encapsulation. The moisture loss below 0 °C is comparably slow and fairly accurate measurements can be performed without any encapsulation of the film.

Fig. 2 shows a temperature scan of a plasticized amylose film covered with grease. The length of the film increased when the temperature was increased from

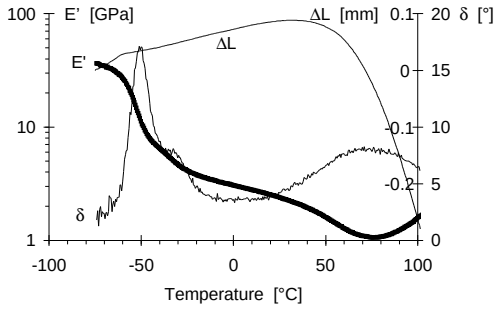

Figure 2. Storage modulus E', phase angle δ, and length increase ΔL of a grease-covered plasticized amylose film.

-75 °C up to 40 °C due to thermal expansion of the film.

The length decrease over 40 °C was caused by moisture loss and the onset of the length decrease can therefore be used as a measure of the maximum temperature where reliable data can be measured.

The onset depends on how well the grease covers the film and also on the material itself. Films of *e.g.* whey protein loses less moisture and can therefore be tested at higher temperatures.

At -50 °C crystallisation in the grease occurred which interfered with the measurements and gave a peak in the phase angle. The temperature scans are therefore limited to the temperatures higher than interval -30 ° at the present conditions.

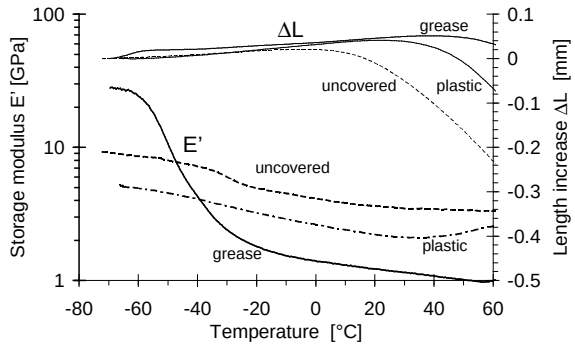

Figure 3. Storage modulus E' and length increase ΔL of plasticized amylose films covered with grease, covered with plastic film and uncovered.

Storage modulus, phase angle and length increase of three plasticized amylose films are shown in Fig. 3. For the uncovered film there was a normal length increase up to around 0 °C whereas the plastic and grease covered films had a normal length increase up 10 °C and 50 °C respectively. The uncovered film had a higher modulus at sub-zero temperatures than the plastic-covered film, probably due to some moisture evaporation from the uncovered film. The high E' for the grease-covered film below -40 °C was mainly due to the crystallisation of the grease. Taking all these factors into account, a "true" E' vs. temperature curve should lie between the uncovered and plastic curves at temperatures below -40 °C and then follow the grease curve at higher temperatures. The upper temperature limit using grease is 60 °C. The measurable temperature range can be extended by using different types of grease, which will be further studied.

An alternative to the temperature scan is a humidity scan as shown in Fig. 4. When the relative humidity surrounding the films is increased the water content of the films increases. Water acts as a plasticizer and an increase in surrounding RH therefore plasticizes the films from the glassy state into the rubbery state[7]. Fig. 4 shows the difference between plasticized amylose and

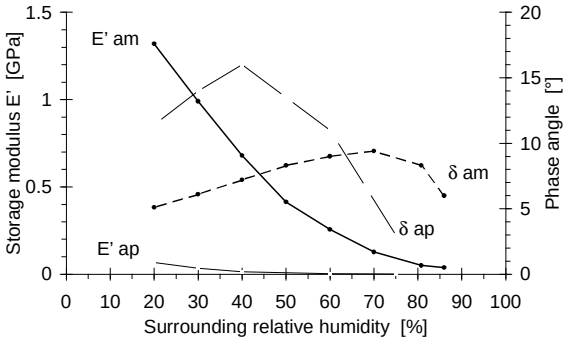

Figure 4. Storage modulus E' and phase angle δ of a plasticized amylose (am) and amylopectin (ap) films at 25 °C.

amylopectin films. It can be seen that the amylopectin film had lower storage modulus than the amylopectin films and that the transition occurred at higher surrounding RH for the amylose film. Practically this means that the amylose films are stronger and less sensitive to humidity. It also means that the glass transition temperature, T_g, should be above 25 °C for the amylose film and below 25 °C for the amylopectin film, at 50% RH [7].

CONCLUSIONS

Dynamic Mechanical Analysis is a useful method for studying the mechanical properties and transitions in biopolymer films. The experimental conditions during the measurement are crucial for the measured material properties. By covering the films with a hydrophobic grease, moisture loss can be avoided and the true material properties can be assessed.

ACKNOWLEDGEMENTS

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