

GLASS-RUBBER TRANSITION IN STARCH-SORBITOL FILM

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Abstract. Rheological behaviour of wheat starch-sorbitol films, obtained by the casting/evaporation method from solution has been studied by the dynamic mechanical-thermal analysis (DMTA). The dispersion curves of the storage and loss moduli have revealed characteristic sharply outlined glass transition in the temperature range of 270-300 K, with transition point T_g changing depending on the drying conditions and frequency of the tensile stress applied. The method of data transformation based on the theory of Williams-Landel-Ferry involving the frequency shift to superimpose the time-temperature dependence of viscoelastic properties has been used to produce a master curve for the starch-sorbitol film.

Key words: starch film, sorbitol, DMTA, glass transition, WLF equation

INTRODUCTION

Extensive research has been carried out on biopolymers in the aspect of their application as recycling materials. Recently, the idea of utilisation of starch and its polymer components, amylose and amylopectin, to produce biodegradable packaging materials and edible coatings has been intensely developed [7]. Starch is a commercially easily available, inexpensive, partly crystalline biopolymer of thermoplastic behaviour suitable for process engineering (extrusion, thermal moulding). It undergoes physical changes governed by nonequilibrium phenomena that affect deterioration and shelf-life of starch products. The incorporation of starch into commodity plastics has generated world-wide growing interest in the use of starch for enhancement of biodegradability of plastic material. The mechanical properties of starch-based films are indicative of a vitreous material with glass transition temperature T_g , and classical viscoelastic properties. As with classically produced synthetic polymers, the glass transition temperature of amorphous starch is controlled by adding a plasticizer. The purpose of the study

was to check the viscoelastic behaviour and molecular dynamics of glass transition in starch film with the addition of sorbitol as a plasticizer.

THEORY

Glass transition theory has been widely studied in polymer science. The glass transition of an amorphous polymer is that from a vitreous to a rubbery state. The molecular structures are different in both domains. The importance of the study of glass transition temperature T_g has been demonstrated for many food products such as cookies or snacks in which the preservation of crispness is important. The T_g is defined as the temperature at which an amorphous, glassy material softens (becomes rubbery or viscous) due to the onset of long-range coordinated molecular motion. The glass transition temperature can be estimated by different techniques, such as nuclear magnetic resonance, differential scanning calorimetry, DMTA [9]. The Williams-Landel-Ferry equation describes the kinetic nature of the glass-rubber transition and has been shown to be applicable to any glass-forming polymer, oligomer and monomer [1,2]. The rate of the mechanical relaxation processes as a function of temperature and frequency is expressed by the equation:

$$-\log a_T = \frac{c_1(T - T_g)}{c_2 + (T - T_g)} \quad (1)$$

where a_T is the shift factor, c_1 and c_2 – coefficients describing the temperature dependence of the relaxation process at temperatures above the reference one. For an undiluted polymer, when T_g is used as the reference temperature, c_1 is proportional to the inverse of free volume of the system at T_g , while c_2 is the ratio of the free volume at T_g to the expansion coefficient of the free volume. The expansion coefficient of the free volume is a constant that describes the linear dependence of this volume on ΔT above T_g , due to thermal expansion (i.e. the difference between the volumes of the rubbery liquid and glassy solid state). Both c_1 and c_2 are material specific constants for an undiluted polymer, but they vary with the polymer composition in the presence of a solvent, such as water [2].

It is possible to interrelate the frequency and the temperature dependencies of the viscoelastic properties of polymers [2]. Thus, the two curves of viscoelastic properties as functions of frequency in a certain range of frequencies, at different temperatures, can be superimposed by keeping one end fixed and shifting the other horizontally and parallel to the log frequency axis [2,4,5]. The shift factor required to superimpose the two curves is the displacement along the frequency axis, which is a function of temperature only and is related to the WLF equation.

This approach was used in this work to determine the activation energy for the phase transition in starch-sorbitol films subjected to temperature changes.

MATERIAL AND METHODS

Starch-sorbitol film preparation

Unmodified wheat starch (Sigma – Aldrich, Germany) was used. The starch-sorbitol films were prepared from the paste by the casting/solvent evaporation method. The first step was the dissolution of 5g of starch in 200 ml of 2% sorbitol solution. The mixture was heated on a magnetic stirrer to the boiling point and stirred for 2 hours to obtain a completely homogenous solution. D-Sorbitol (Sigma – Aldrich, Germany) was used as a plasticizer, and purified bidistilled water as a solvent.

Well-mixed solutions were then immediately cast onto poly(tetrafluoroethylene) plane moulds, and air dried to constant weight at two different temperatures. Some samples were dried at room temperature, 295 K, and others in a thermostated chamber at 309 K. After removing the films from the support, they were stored in closed separate polyvinyl bags for 15 days before testing. The thickness of the dried films was measured by a micrometer and ranged from 0.13 to 0.16 mm.

The moisture content in the film was determined by drying the samples to the constant weight at 371 K. Each test was repeated at least 3 times. The average value of moisture content in all the samples was 6 ± 1 (%/d.b).

DMTA measurements

The thermomechanical measurements of starch-sorbitol films were performed on a DMA 242 apparatus (Netzsch, Germany). Small pieces of the size of 5x10 mm, cut out of the centre of the sample, were subjected to dual cantilever bending. The frequency of the vibration of the force applied was set at 1, 2, 5, 10 and 20 Hz. The heating rate was 3 K/min and the maximum force 1 N. The components of the complex elasticity modulus, storage modulus E' and loss modulus, E'' were measured for the samples in a wide temperature range from 123 to 473 K in helium atmosphere.

RESULTS AND DISCUSSION

The rheological properties of the films, obtained by air drying of the starch paste with sorbitol, were measured by DMTA in large ranges of temperatures and frequencies of the dynamic force applied. The long time natural drying process of the starch paste on the Teflon mould resulted in the product showing interesting

mechanical properties. Figure 1 presents exemplary dispersion curves of temperature dependencies of the components of the elasticity modulus: storage E' and loss modulus E'' , obtained for the starch-sorbitol film dried in a thermostated chamber at 309 K. The frequencies of the perturbing force were chosen to be 1, 5, 10 and 20 Hz. The changes in the viscoelastic functions vs temperature occur in a wide range from 123 to 473 K, however, they are the most pronounced in the region of the transition from the rubbery to glassy state. All the temperature runs evidence the occurrence of such a transformation in the temperature range of 270-300 K.

With increasing frequency, the viscoelastic functions shift on the temperature scale towards higher temperatures. The storage modulus E' is a measure of the storage elastic energy accumulated in the bonds of the polymer chains subjected to elastic stress. At the glass-rubber transition, the value of E' drops by about three orders of magnitude, which is characteristic of conformational transformations of this type in polymer systems [2]. Starch-sorbitol film is a rheologically modified system which shows areas of different molecular mobility, determined by the presence of sorbitol molecules, water and polymer chains. The mobility of the most mobile parts of starch is reduced by the addition of sorbitol, which has been observed in NMR relaxation [3]. The study of the plasticizing effect of sorbitol on starch films for different sorbitol contents has revealed that at high concentrations the sorbitol-sorbitol and starch-sorbitol interactions increase and enhance the system's mobility observed at a macroscopic level. Because of that the glass transition of starch was observed at room temperature for the sorbitol content of 27% [3]. The low molecular weight compounds decrease the glass transition temperature of the polymer [2,8]. In our samples the mass fraction of sorbitol was very high relative to starch. The presence of the polymer plasticizer in the starch film reduced the glass transition temperature T_g determined from the loss tangent maximum $\tan \delta = E''/E'$ by about 200 K relative to that of dry starch being 513-523 K [7]. The effect of the drying temperature on the starch-sorbitol film was insignificant. In the films dried in higher temperature, e.g. at 309 K, a slight decrease in T_g was noted on the basis of the loss tangent values (Fig. 2), and the loss tangent increased for all the frequencies applied. These effects evidenced the influence of the evaporation conditions on the starch structure formation accelerated by higher drying temperature. In higher drying temperatures the starch crystallisation process was less effective than when the starch-sorbitol mixture was dried at room temperature. Higher mechanical energy loss observed in starch films prepared in 309 K was accompanied by a significant decrease in the storage modulus E' .

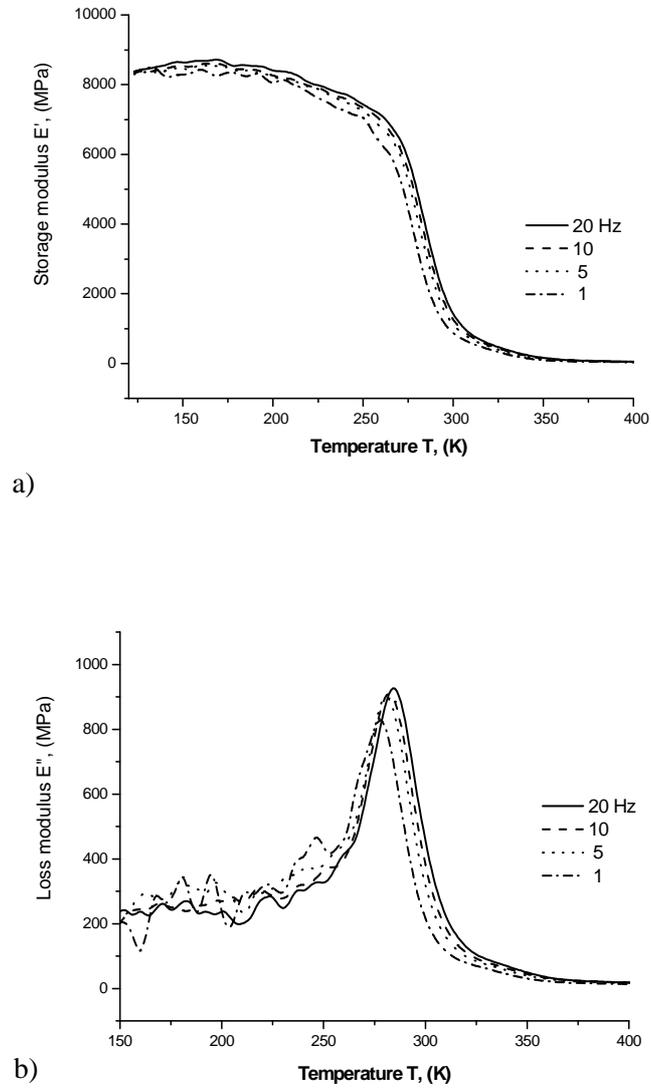


Fig. 1. Temperature dependencies of the elasticity modulus on: storage modulus E' (a), loss modulus E'' (b) in starch-sorbitol film, obtained for the mixture subjected to air drying at 309 K

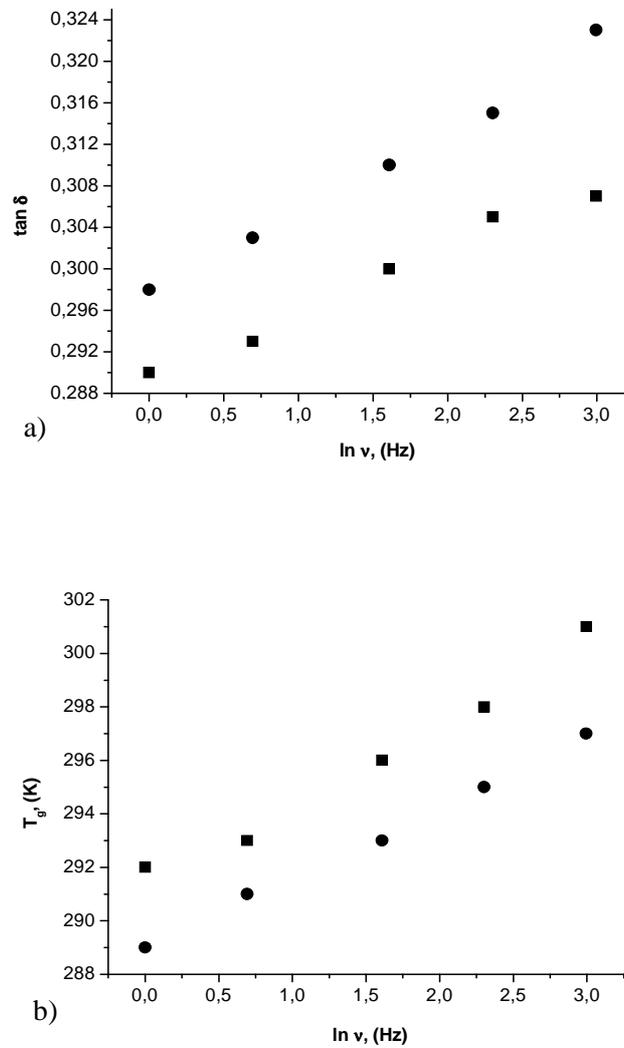


Fig. 2. Frequency changes of $\tan \delta$ (a) and T_g (b) in DMTA measurements of starch-sorbitol films subjected to drying at room temperature (■) and at 309 K (●)

In the production of thermoplastic starches, plasticizers are expected to reduce the number of intermolecular hydrogen bonds and to stabilise the properties of the product [6,7]. This role is played by sorbitol in the presence of water. Strong interactions between the hydroxyl groups of polymer chains of the starch and

sorbitol, in high concentrations acting as a good plasticizer [3], reduce the starch ability to format helices, which can be detected on the basis of the viscoelastic behaviour of starch-sorbitol films.

Significant differences in the temperature dependencies of the viscoelastic functions for the films studied at the rubber-glass transition recorded for the frequency varying from 1 to 20 Hz, permitted the use of the method of reduced variables [2,4,5]. In order to do this, the logarithmic plots of the elasticity modulus components E' and E'' of the starch films studied were made for a few temperatures in the region of the glass-rubber transition. One of the plots, made for the storage modulus E' in the temperature range 278-328 K obtained on the basis of the shift of the temperature dependencies of the viscoelastic functions with respect to the function $E'(T)$ for 303 K, is shown in Figure 3. On the basis of the above plots, the values of the logarithmic shift factor a_T were obtained. As follows from the WLF theory, the shift factor required to superimpose the two curves being the displacement $\log \omega_s - \log \omega$ along the frequency axis is a function of temperature only and is defined as

$$\log a_T = \log \omega_s - \log \omega = \log(\omega_s/\omega) \quad (2)$$

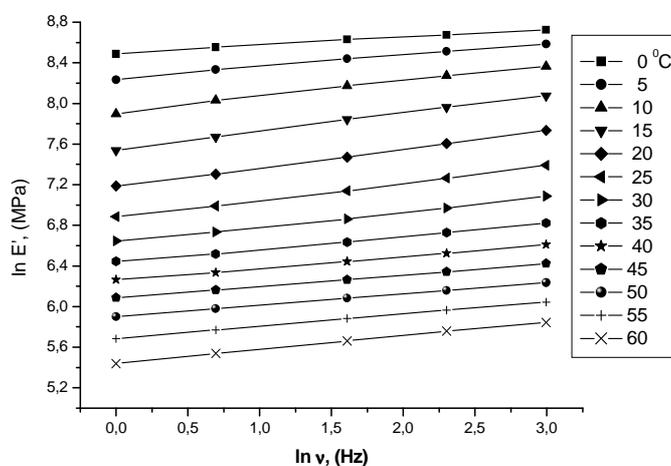


Fig. 3. Log-log plot of the storage modulus E' of the wheat starch-sorbitol cast film at the transition from the glassy to rubbery state as a function of frequency for 13 values of temperature

From the results of the superimposition of the time-temperature curves, the Williams-Landel-Ferry master curve was successfully produced for the storage modulus of the starch-sorbitol film presented in Figure 4.

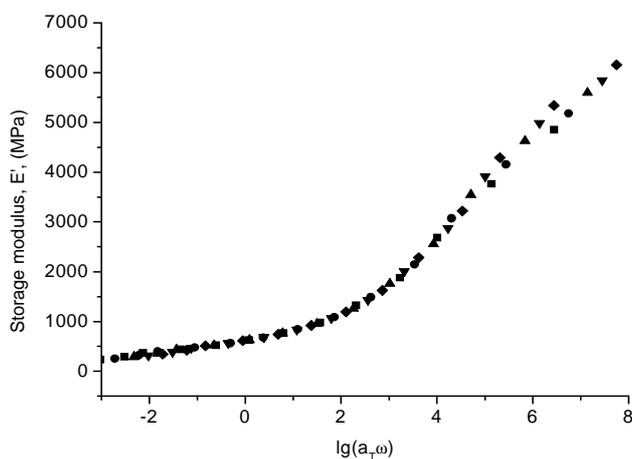


Fig. 4. The WLF master curve, in reduced variables, generated from the storage modulus E' for wheat starch-sorbitol cast films, scaled at 303 K

CONCLUSIONS

The cast film made of starch-sorbitol mixture shows a clear glass-rubber transition in the range 270-300 K, related with the presence of the polymer complexes with sorbitol. The transition temperature T_g of starch mixtures with sorbitol depends on the temperature of the film drying and the frequency of vibrations applied, which indicates a strong effect of sorbitol on the starch film structure formation. The presence of sorbitol in the starch paste inhibits the process of helices formation by the polymer chains, consequently the glass-rubber transition T_g of the starch-sorbitol film is nearly 220 degrees lower than that of dry starch.

The method of superimposition of the time-temperature curves applied to the starch-sorbitol films permitted prediction of the viscoelastic behaviour of the material over the frequency range of about ten logarithmic decades greater than that used in the experiment.

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PRZEJŚCIE ZE STANU SZKLISTEGO W STAN WYSOKOELASTYCZNY W FILMACH SKROBI Z SORBITOLEM

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Streszczenie. Własności reologiczne filmów skrobi pszenicy z sorbitolem, jako plastyfikatorem, otrzymywanych w wyniku suszenia konwekcyjnego z roztworu, poddane zostały badaniom za pomocą mechaniczno-dynamicznej analizy termicznej (DMTA). Krzywe dyspersji składowych zespolonego modułu sprężystości: modułu zachowawczego, E' i modułu strat, E'' ujawniły charakterystyczne przejście szkliste w obszarze temperatur 270-300 K, z maksimum temperaturowym T_g zależnym zarówno od warunków suszenia folii, jak i częstotliwości przyłożonej siły zaburzającej. Stosując metodę zmiennych zredukowanych, opisaną przez Williamsa-Landela-Ferry'ego, wyznaczono, w wyniku transformacji danych ze strefy przejścia rozszklenia, krzywą wzorcową, przedstawiającą przebieg zmienności modułu zachowawczego E' w 10-krotnie powiększonym obszarze dyspersji w stosunku do zastosowanego.

Słowa kluczowe: film skrobiowy, sorbitol, DMTA, przejście: stan szklisty – stan wysokoelastyczny, równanie WLF