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Carbohydrate Polymers 56 (2004) 499–503

Carbohydrate Polymers

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Influence of thickness on the mechanical properties for starch films

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Received 16 June 2003; revised 22 December 2003; accepted 31 March 2004

Abstract

The aim of the present study was to investigate some mechanical properties of starch films. Starch is a natural common polymer in nature and the use of natural materials is increasing in the industries. In this study, the mechanical properties of starch plasticized with 30 parts by weight, of glycerol, are investigated. For the mechanical testing films of different thickness were used, the thickness varied between 0.5 and 2.5 mm. T_g was measured with a differential scanning calorimeter and with a dynamical mechanical analysis. The starch films were tested in tension and characterised in terms of stiffness, strength and failure strain. Fracture toughness was measured by single edge notch tests. Both stiffness and strength showed a strong dependence on film thickness, stronger then expected from linear fracture mechanics. This can be due to the different molecule orientation in the films, and due to the crystallinity of the films.

Keywords: Starch films; Mechanical properties; Glass transition temperature

1. Introduction

Naturally occurring fibres like flax and wood fibres can be used as reinforcement in composite materials, replacing glass fibres in less demanding applications. In these applications, it is common to use a synthetic polymer as matrix material. The use of synthetic polymers is dependent on the use of crude oil. Nature is another possible resource for structural polymers. Polymers found in nature are, for example, starch, cellulose, lignin and collagen.

It is expected to be an advantage if a polymer produced by nature could be used as a matrix material. Starch is a possible candidate for a natural matrix material and is commercially available at an industrial scale. Since starch is commercially used as binder in the pulp and paper industry and is a common component in paper coatings.

Starch is a high molecular-weight polymer of anhydroglucose units linked by alpha-D glycoside bonds. The two major polymers in starch are amylose and amylopektin. Amylose is a linear molecule with an extended helical twist. Amylopektin is a branched molecule. Amylose is generally smaller molecules with molecular weight of 1–1.5 million. Amylopektin are by comparison large with a molecular weight of 50–500 million (Zobel, 1990; Maurer Hans, 2001).

Pure starch is a brittle polymer and is, therefore, often plasticized. A common plasticizer is glycerol. Glycerol is compatible with amylose and interferes with the amylose packing (Wurtsburg, 1986). Also, water plays a significant role for the properties of starch. Water is compatible with starch and is an effective plasticizer. With increasing content of water starch shows both an increasing strain at break and stress at break (Hulleman, Janssen, & Feil, 1998; Parker and Ring, 2001). Van Soest and Knooren (1997) showed that material with a higher amount of water crystallizes more rapid than the material with higher overall plasticizer content. The change in water content and crystallinity are affecting the stress–strain properties.

If mechanical tests are performed on starch films, the films can be produced by solution casting. Starch can be heated to 95 °C for 30 min while stirring, the molecules then becomes disentangled and separated from each other in a water solution (Zobel, 1990). The solution is casted and films are formed as the water is removed by drying. The effect of humidity during the formation of the film on the mechanical properties has been investigated. As the humidity is increased from 20 to 90% RH, the modulus measured for the film increased five times. For the films

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0144-8617/$ - see front matter © 2004 Published by Elsevier Ltd.
doi:10.1016/j.carbpol.2004.03.019

tested, the tensile strength was double this while the strain at failure was decreased by half (Rindlav-Westling Stading, Hermansson, & Gatenholm, 1998).

The mechanical properties can be altered by pre-treatment of the starch films. When starch–glycerol was heated, both the tensile strength and strain at failure was altered. If the starch solution is pre-cooked at different temperatures 100, 121 and 180 °C, the elongation at failure decreases from 104 to 5% percent. The tensile strength shows a maximum at 6.0 MPa for 121 °C and decreases both when cooking at 100 and 180 °C (Koskinen, Suortti, Autio, Myllärinen, & Poutanen, 1996). If the material is heated above the glass transition temperature and then cooled again below the glass transition temperature while the molecules are still under stress, the molecules will be oriented which result in a tensile strength that may be five times that of the unoriented material (Brydson, 1995).

From fracture mechanics, it is well known that the measured fracture properties alter with sample thickness (Anderson, 1995). If films are to be used to characterise the properties of starch the influence of film thickness has to be investigated.

In this study, the mechanical properties of starch films of hydroxy propylated native potato starch with glycerol as plasticizer are investigated and the effect of film thickness on measured mechanical properties is studied.

2. Materials and methods

A hydroxy propylated native potato starch is used with glycerol as plasticizer. The starch to this study is supplied by Lyckeby Stärkelsen Research & Technology, Kristianstad, Sweden.

2.1. Film preparation

Mechanical properties are measured on films produced from starch solutions. To produce the films a starch solution, 18 w% starches, was cooked at 95 °C for 30 min while stirring forcefully. Glycerol was added to the starch solution to a ratio of 100:30 by weight. The solution was then poured into petri dishes with a diameter of 110 mm. They were allowed to dry in a constant climate, 50% RH and 23 °C. The drying time differed, the thick films dried slowly, several days to become dry, while the thin films were dry after about 1 day. The thickness of the films varied between 0.3 and 2.6 mm. The film that was used for measuring mechanical properties was held in the constant room before and during the tests.

The glass transition temperature was measured using a differential scanning calorimeter (DSC) (DSC 2920 CE, from TA Instruments) and the T_g was about 38 °C.

2.2. Mechanical analysis

The starch films were cut into bars using a sharp knife to a size of 7 × 70 mm^2 The bars varied in thickness from 0.28 to 2.6 mm. The thickness was measured at six points and the average was used. The sample was tested in tension in 23 °C at 50% RH in the constant room using an Instron 4411. For the test, a gauge length of 50 mm and a crosshead speed of 5 mm/min were used. The samples were tabbed using a soft adhesive tape and data for bars that failed in or close to the grip was excluded.

For the fracture tests, single edge notched samples was used. The bars had the same outer dimensions 7 × 70 mm^2 with notches of about 1 mm. Fracture toughness is measured from stress at failure.

2.3. Results and discussions

The drying rate of the films was measured to confirm that the humidity in the films was constant while doing the mechanical tests. The films were measured on scales and the result is shown in Fig. 1. The moisture contact in the thin film of 0.03 mm was stabilized after 27 h. The moisture content in the thickest film, with a film thickness of 2 mm took 100 h to stabilize.

2.4. Mechanical properties

In Fig. 2, tangent *E*-modulus, E_{tan}, is depicted against varied thickness. The stiffness increases from 20 to 100 MPa as thickness is increased from 0.3 to 1.0 mm. Then as thickness increase further, the stiffness decrease. For a 2.5 mm thick film, the stiffness is about 30 MPa.

In Fig. 3, the ratio between tangent modulus E_{tan} and secant modulus E_{sec} is depicted with film thickness. The constant ratio indicates a linier behaviour.

Variation in degree of molecule stretch is a possible explanation for the variation seen in stiffness with thickness. As water evaporates, the volume decreases and the film shrinks, consequently the film will deform. The rate of deformation will depend on the thickness of the film as

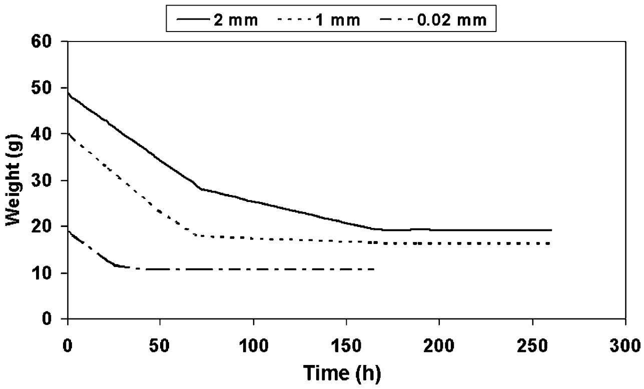

Fig. 1. The time for starch film to dry in a constant room at 23 °C and 50% RH.

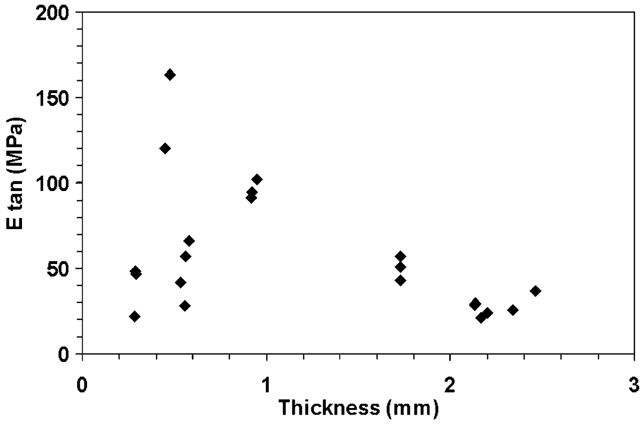

Fig. 2. *E* tan varying with the thickness of the starch film.

the evaporation of water becomes controlled by diffusion for the thicker specimens. Since, the mechanical tests was performed in 23 °C which is below the glass transition temperature of the polymer, the change in crystallinity of the films should not influence in the *E*-modulus.

When thin films are made the water evaporates fast, at room temperature the rate of molecular movement is limited and the molecules in the film do not have time to respond to the shrinking of the film. For the thick films, the water evaporates slowly and the molecules have enough time for relaxation. Since, the thicker films are exposed to a higher degree of water for a longer time the crystallinity in these films are expected to be higher than in the thin films. The same response is observed when drying at different humidity. The relative crystallinity of plasticized starch films increased with increasing air humidity during film formation (Rindlav-Westling et al., 1998). For the films that exhibit the observed increase in stiffness, we may speculate that the drying time is of the same order as the relaxation time providing the possibility for the molecules to stretch in response to the deformation resulting in a stretched molecule orientation in the plane of the film (Brydson, 1995).

In Fig. 4, the strain at failure for the different thickness is depicted. The strain decreases from 100 to 20% as the thickness increases from 0.3 to 2.5 mm.

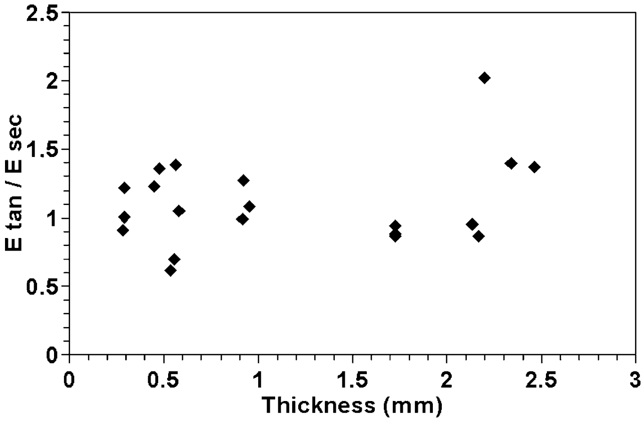

Fig. 3. *E* tan/*E* sec varying with the thickness of starch film.

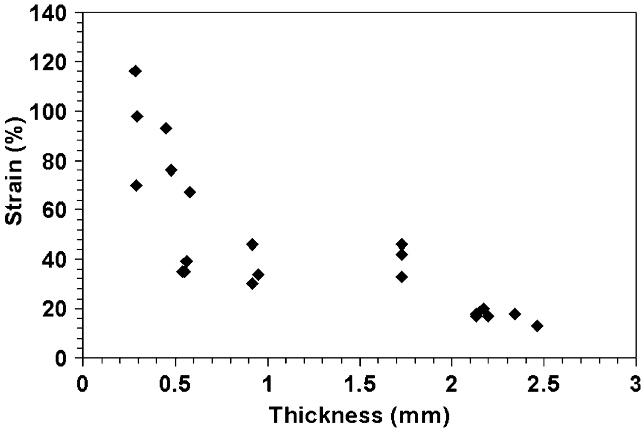

Fig. 4. Strain at break varying with the thickness of the film.

In Fig. 5, the tensile strength changes with thickness for the film. The strength increase from 2 to 4 MPa while thickness increase from 0.3 to 1.0 mm. When the thickness is further increased, the strength decrease from 4 to 1.5 MPa.

If a polymer is stretched at some temperature below its melting point but above its transition temperature, additional crystallization will be induced and the crystalline structure will generally be aligned in the direction of extension. Oriented crystalline filaments are much stronger than the unoriented products. If a sample of an amorphous polymer is heated above its glass temperature and then subjected to a tensile stress, the molecules will tend to align themselves in the direction of the stress. This could lead to a tensile strength which may be five times that of the unoriented material (Brydson, 1995).

Decreasing material volume generally increases the strength since the size of the largest possible flaw or weakness decreases with decreasing thickness. We may expect the sample to behave accordingly. The strain at failure decrease with increasing thickness as expected and is possibly controlled by the increase in flaw size for the thicker samples. This is not reflected in the strength data. The failure stress increase as thickness reduces from 2.5 to 1 mm. For samples thinner than 1 mm, the strength decrease

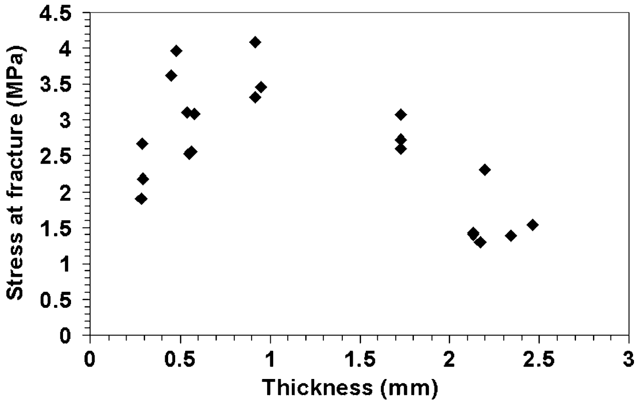

Fig. 5. Stress at fracture varying with the thickness of the starch film.

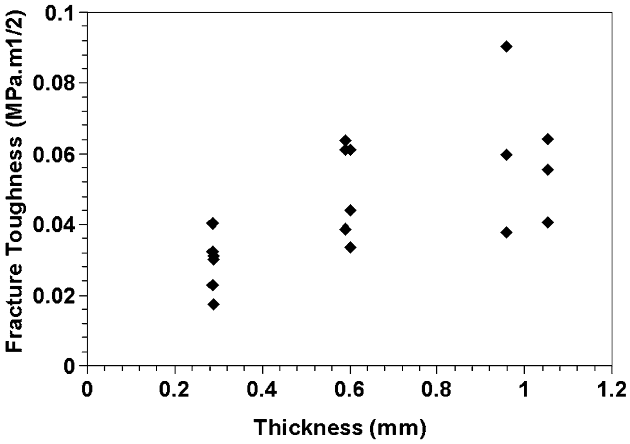

Fig. 6. Fracture toughness is varying with the thickness of the starch film.

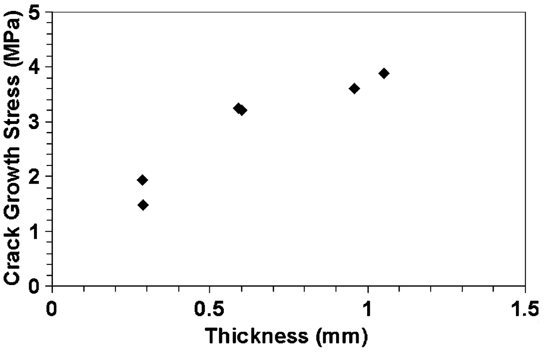

Fig. 8. Crack growth stress is varying with the thickness of the starch film.

with decrease in thickness. The strength decrease from 3.5 to 2 MPa as the thickness is further reduced from 1 mm.

The variation in molecule stretch, expected from the development of stiffness with thickness will influence the stress at failure. As the thickness increase from 1 to 2.5 mm, the stiffness decrease from 80 to 20 MPa, while the strain at failure decrease from 30 to 15%. The decrease in molecular stretch that is expected from the measurements of stiffness is consistent with the observed decrease in strength in the interval.

For samples thinner than 1 mm, the strength is reduced as thickness is decreased. As the strain at failure increases, the measured stiffness decreases. From the stiffness, the degree of molecular stretch is expected to decrease with decreasing thickness. A decreasing molecular stretch is consistent with the observed results.

Similar results are observed as the films are dried at different humidity (Rindlav-Westling et al., 1998). For thin films and for films that has been drying in low air humidity the strain at break is higher then for films that have been drying in high air humidity and thick films.

Measured fracture toughness, K_{Ic} is shown in Fig. 6, K_{Ic} increases from 0.02 to 0.06 MPa as thickness increase from 0.28 to 1 mm. The measured fracture toughness increased with thickness.

From fracture mechanics, this can be expected as the stress state changes with thickness from a plane stress state to a plane strain stress state. Thicker samples should be tested to get adequate data for the material property and to see if the plane strain conditions for measurement of toughness K_{Ic} could be reached (Adams and Wilmington, 1986; Ewalds, 1993) and, consequently, there is little data to be able to say that this is the material property.

The stiffness measured and consequently the expected degree of molecular stretch increase in the interval, as the strain at failure decrease. Films with a low degree of stretch have molecules with the possibility to respond to load by molecular orientation, this tend to relax the stress state at the crack tip, dissipating energy. Especially as the temperature at which the tensile test is performed is close to the glass transition temperature. While a high degree of molecular orientation at the crack tip on the other hand might hinder the initiation of crack propagation. This is reflected in the data by the tensile energy absorption (TEA) that decreases with thickness (Fig. 7) while crack growth stress increase with thickness (Fig. 8).

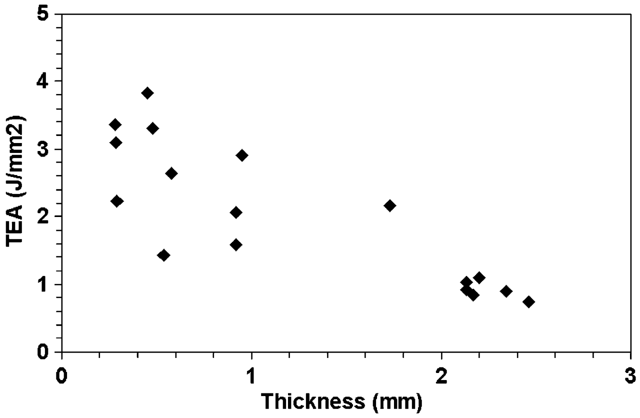

Fig. 7. TEA is varying with the thickness of the starch film.

3. Conclusions

The result from this test shows that if mechanical tests on starch based films should be measured it has to be done with a thickness that is significantly thicker then 2 mm, this to exclude influence of stress state. Also the variations in molecule orientation can be suppressed, as the molecules are likely to relax if given time and dried slowly. In the thin films, the short drying time made the molecules too stretched which could give a tensile strength lower than for thicker films. The films of 2.5 mm hade enough time for the molecules to relax and orient themselves. It was only in the films of 1 mm that the molecules hade induced crystallization caused by some stretch of the molecules.

If the difference in tensile stress shown in this work should depend on the degree of crystallinity, one have to be over T_g in temperature while performing the measurements. Since, T_g for the films was about 38 °C and the temperature in the room about 23 °C the influence in *E*-modulus is low.

Therefore, the drying of the films is a difficult parameter to deal with. It seems like 1 mm thick films drying fast enough to stretch the molecules yet slow enough to prevent molecular relaxation, resulting in molecular orientation. Thin films dry to fast in 23 °C which seems to result in molecular orientation and thick films dry to slow the molecules seems to have time to relax.

Acknowledgements

We would like to thank Lars Järnström for supporting us and the Surface Treatment Programme at Karlstad University for financing. The Surface Treatment Programme is financed by SkFs, Nutek and KK-stiftelsen. And we thank you Mats Stading at Sik in Gothenburg for helping us with the DMTA test.

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