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Properties of a plasticised starch blend – Part 2: Influence of strain rate, temperature and moisture on the tensile yield behaviour

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ABSTRACT

The tensile yield behaviour of a commercial plasticised starch/high molecular weight polyol blend has been studied. The effects of moisture content, strain rate and temperature were investigated and related to dynamic mechanical measurements in order to seek some molecular understanding of the yield behaviour. Dynamic mechanical thermal analysis revealed the presence of two relaxations associated with the glass transition of each phase of the blend. The effect of moisture could be explained by a 'time-moisture' superposition demonstrating that the effect of the water content was analogous to the effect of temperature. The variation in the yield stress with strain rate and temperature was described accurately by a two-process Eyring's model. The process, which dominates the deformation behaviour at low strain rates and/or high temperatures correlated well with the relaxation of the plasticised starch-rich phase, while the second process involved at higher strain rates and/or lower temperatures could be associated with the relaxation of the polyol-rich phase.

1. Introduction

Over the past decade, starch, composed of amylose and amylopectin polysaccharides, has received considerable interest as a possible alternative to replace oil-based plastics due to its renewability, biodegradability, and low cost (Röper & Koch, 1990). Several authors (Doane, 1992; Swanson, Shogren, Fanta, & Imam, 1993; Tomka, 1991) have shown the possibility of converting native starch into thermoplastic material through disruption of its granular structure in the presence of plasticisers (e.g. water, polyols) by applying thermo-mechanical energy. Plasticised starch (PlS), also called thermoplastic starch, is processable using conventional plastic processing techniques, such as extrusion and injection-moulding. Unfortunately, the development of PlS-based products has been strongly impeded by their limited mechanical performance generally attributed to the highly branched structure of amylopectin, along with their intrinsic hydrophilicity. To increase the level of mechanical stability and performance and improve water resistance, one of the strategies has been to blend PlS with other polymers (Avérous, 2004).

As a hygroscopic material, PlS can absorb varying amounts of moisture under different relative humidity environments. It is well known that absorbed moisture affects the physical properties of polymers and in some cases, moisture can have a major effect on their mechanical properties if the adsorbed moisture acts as a plasticiser to lower the glass transition temperature. Emri and Pavsek (1992) studied poly(vinyl acetate) for which water is a plasticiser and have shown that the effect of moisture content was analogous to the effect of temperature and can be described using similar mathematical functions.

Polymers show a yield point usually corresponding to the maximum load in the load-extension curve of a tensile test (Ward & Hadley, 1993). Generally, the yield stress of a viscoelastic polymer increases with increasing strain rate and pressure but decreases with increasing temperature. Many models have been proposed to describe the yielding process (Argon, 1973; Bowden & Raha, 1974; Robertson, 1966). The yielding process of a polymer is usually regarded as a momentary condition of pure viscous flow, because it denotes the point at which the change of stress with strain is zero for a given strain rate. It is thus considered to be a thermally activated rate process involving inter- and intra-molecular motions. Eyring's viscosity theory has been successfully used in this case to describe the tensile yielding process of solid polymers although it was first developed for shear-induced viscous liquid flow (Eyring, 1936).

Although development of PlS-based plastics requires a full understanding of their performance and how this is related to their structure, there has been little systematic work in the literature detailing exclusively the influence of moisture content on their mechanical properties in relation to their morphology and thermal properties. In a previous study we reported the influence of moisture content on the tensile and fracture properties of a commercial grade of a plasticised starch-based plastic (Chaléat, Halley, & Truss, 2008). In the present work, the yield behaviour of the same material is studied using dynamic mechanical thermal analysis (DMTA)

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and tensile experiments. The study focuses on the influence of temperature, strain rate and moisture content in order to seek some molecular understanding of the yield behaviour. The Eyring's theory is used to model the tensile yield behaviour.

2. Experimental

2.1. Materials and processing

Experiments were conducted on a commercial PlS/polyol grade, Plantic® R1, supplied from Plantic Technologies Ltd. (Melbourne, Australia) in the form of pellets. It consists of a chemically modified high amylose maize starch to which a small amount (less than 10%) of a water-soluble high molecular weight polyol was added in accordance with the patents (Buehler, Casanova, Ernst, & Schultze, 1994a, 1994b). This material was extruded using water as the plasticiser.

Pellets of this material were compression-moulded into sheets at 125 °C for 5 min under a pressure of 7.5 to 9 MPa and then rapidly cooled. Specimens for subsequent mechanical characterisation were cut out from several compression-moulded sheets.

2.2. Conditioning

Because starch-based plastics absorb and desorb water, special care was taken to condition the samples at 20 ± 1 °C until equilibrium in constant equilibrium relative humidity (ERH) environments maintained by saturated salts solutions. The salts used (with their corresponding ERH at 20 °C) were CH_3COOK (23%), K_2CO_3 (43%), $Mg(NO_3)_2$ (54%), KI (70%) and $(NH_4)_2SO_4$ (81%) (Greenspan, 1977). Samples were considered to reach equilibrium after 14 days of conditioning.

The equilibrium moisture content (MC) of this material at each of these ERH was measured previously gravimetrically (Chaléat et al., 2008) and is detailed in Table 1.

2.3. Dynamic mechanical thermal analysis

Dynamic mechanical thermal measurements were performed on a DMTA IV from Rheometrics Scientific using rectangular-shaped specimens ($25 \times 9 \times 1.3$ mm^3) cut out from the compression-moulded sheets and conditioned for 14 days at 20 °C in different constant ERH environments (as described previously). Samples were tested in dual cantilever bending mode (span length of 14 mm) at a strain rate of 0.05% and a frequency of 1 Hz. The range of temperature scanned was approximately from −50 to 150 °C at a heating rate of 2 °C/min. Samples were coated with petroleum jelly to avoid water evaporation during testing.

2.4. Tensile testing

Dumbbell-shaped specimens, approximately 1.5 mm thick, punched using an ASTM D-638-M-3 die (ASTM Standard D 638M, 1996) were conditioned for 14 days at 20 °C in the different constant ERH environments as described in Section 2.2. An Instron 4505 tensile testing machine equipped with a temperature controlled chamber and a 10-mm gage length extensometer for accurate monitoring of the tensile strain was used.

Specimens equilibrated at 54 and 81% ERH were tested at 23 and 50 °C at crosshead speeds ranging from 0.05 to 50 mm min^{-1}, which are equivalent to strain rates of 5.5×10^{-5} to 5.5×10^{-2} s^{-1}. Samples equilibrated at 23, 43 and 70% ERH were tested only at 23 °C at strain rates ranging from 5.5×10^{-4} to 5.5×10^{-2} s^{-1}.

The yield stress, σ_y, was determined as the stress at an arbitrary plastic strain of 1% (offset yield stress) due to the lack of a clearly defined yield point. Testing was performed on a minimum of five replicates for each condition. Specimens tested at 50 °C or at slow strain rate were covered with petroleum jelly since the tests last for a longer time under these conditions and water loss could affect the reproducibility of the results.

Table 1
Equilibrium moisture content and temperatures of the α-relaxation associated with the glass transition of each phase (after conditioning at different ERH)

ERH (%)	MC[a] (%)	$T_{\alpha(\mathrm{Polyol})}$[b] (°C)	$T_{\alpha(\mathrm{PIS})}$[b] (°C)
23	6.5 ± 0.3	53	144
43	9.5 ± 0.8	–	–
54	11.4 ± 0.7	27	89
70	12.3 ± 0.3	–	–
81	14.9 ± 0.2	2	45

[a] Data taken from Chaléat et al. (2008) with their 95% confidence limits.

[b] T_α determined as E'' peak.

3. Results and discussion

3.1. Dynamic mechanical thermal analysis

In Fig. 1a, the temperature dependence of the storage and loss modulus, E' and E'', respectively, are presented for Plantic® R1 stored at 23%, 54% and 81% ERH, which correspond to an equilibrium MC of 6.5%, 11.4% and 14.9%, respectively (Chaléat et al., 2008). For each MC investigated, the shape of the E'' curve clearly reveals two distinct peaks.

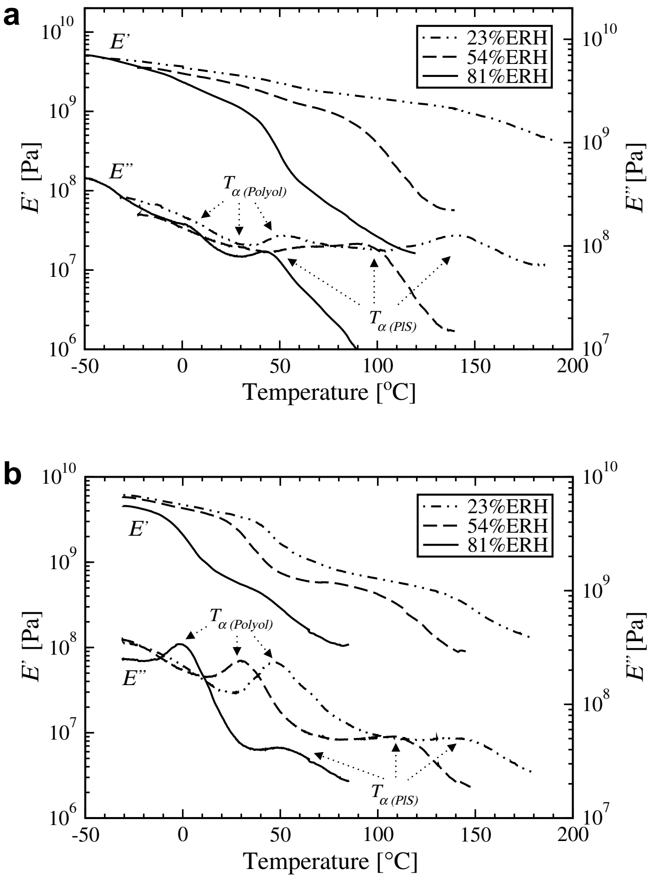

Fig. 1. Storage modulus, E' and loss modulus, E'' curves for the studied commercial PIS/polyol blend (Plantic® R1) (a) and a 50:50 PlS/polyol blend (b) obtained at 23%, 54% and 81% ERH.

To establish whether these two peaks could be related to the components of the blend (PlS and polyol), a material was prepared with a much higher content of polyol (50:50 starch to polyol ratio) in a laboratory extruder from the same raw materials. By comparing the DMTA thermogram of Plantic® R1 to the one obtained for the 50:50 blend displayed in Fig. 1b, it is clear that the two distinct peaks could be related to α-relaxations of the components of the blend. This suggests a two-phase system. The lower temperature relaxation could be attributed to the high molecular weight polyol-rich phase ($T_{\alpha(\mathrm{Polyol})}$) while the PlS-rich phase was associated with the higher temperature E'' peak ($T_{\alpha(\mathrm{PlS})}$). Lower relaxation amplitude was obtained for the polyol phase of the commercial PlS/polyol blend simply because small proportions of polyol were used (less than 10%).

The effect of an increase in MC is clearly visible as a shift in the relaxation temperatures, which can be associated with the glass transition temperatures (T_g) of each phase. For the Plantic® R1 material conditioned at different ERH, $T_{\alpha(\mathrm{Polyol})}$ and $T_{\alpha(\mathrm{PlS})}$ with their respective MC are summarised in Table 1. Water acts as a plasticiser for each of the phases of this blend lowering $T_{\alpha(\mathrm{PlS})}$ from approximatively 144 to 45 °C and $T_{\alpha(\mathrm{Polyol})}$ from 53 to 1 °C when the blend overall MC varied from 6.5% to 14.9%. Although the drop of $T_{\alpha(\mathrm{Polyol})}$ was small compared to $T_{\alpha(\mathrm{PlS})}$, it has been shown to dramatically alter the room temperature toughness properties (Chaléat et al., 2008).

3.2. Tensile behaviour

Fig. 2a and Fig. 2b show, respectively, the stress–strain curves obtained at 23 °C at a strain rate of $5.5 \times 10^{-3}\ \mathrm{s}^{-1}$ for several MC and the stress–strain curves obtained for a MC of 11.4% at different strain rates and testing temperatures. As expected it was observed that the overall stress level increased with decreasing MC, decreasing temperature and increasing strain rate. At low MC, low temperature and high strain rates, failure occurred before or shortly after the sample yielded. As the MC and testing temperature increased, the Plantic® R1 material displayed more ductility. In the absence of a clearly defined yield point, the analysis of the yield behaviour was therefore based on an offset yield stress calculated at a strain of 1%.

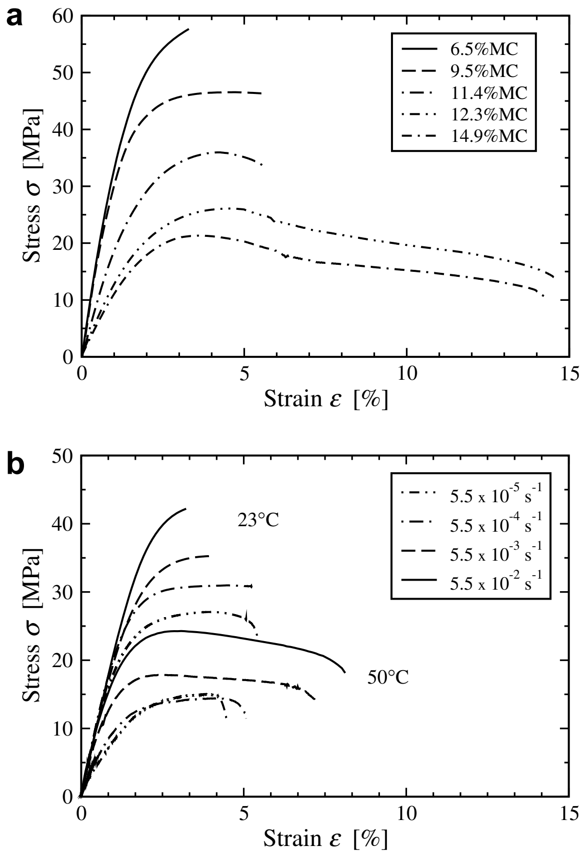

Fig. 2. Stress–strain curves: (a) obtained at 23 °C at a strain rate of $5.5 \times 10^{-3}\ \mathrm{s}^{-1}$ for the Plantic® R1 material equilibrated at different MC, and (b) obtained at strain rates ranging from 5.5×10^{-5} to $5.5 \times 10^{-2}\ \mathrm{s}^{-1}$ at 23 and 50 °C for the Plantic® R1 material at a MC of 11.4%.

It should be noted that as an extensometer was used during testing, the measurement of the strain at break was affected (especially at high temperature and low strain rates) due to the formation of a notch on the extensometer blades.

3.3. Yielding behaviour

For many polymers (Bauwens-Crowet, 1973; Bauwens-Crowet, Bauwens, & Homès, 1969; Foot, Truss, Ward, & Duckett, 1987; Liu & Truss, 1994; Roetling, 1965; Truss, Clarke, Duckett, & Ward, 1984), variation in yield stress, σ_y, with temperature, T, and strain rate, $\dot{\varepsilon}$, can be described as a thermally activated rate process following the formalism developed by Eyring and coworkers (Eyring, 1936; Halsey, White, & Eyring, 1945). The Eyring's theory gives the following relationship between strain rate, $\dot{\varepsilon}$ and yield stress (usually tensile or compressive), σ_y:

$$\dot{\varepsilon} = \dot{\varepsilon}_0 \exp\left(-\frac{\Delta H}{RT}\right) \sinh\left(\frac{\upsilon\sigma_y}{RT}\right), \tag{1}$$

where $\dot{\varepsilon}_0$ is the constant pre-exponential factor, R the gas constant, ΔH the activation energy (in J mol^{-1}), and υ is the activation volume. This gives the yield stress as:

$$\frac{\sigma_y}{T} = \frac{R}{\upsilon}\sinh^{-1}\left[\frac{\dot{\varepsilon}}{\dot{\varepsilon}_0}\exp\left(\frac{\Delta H}{RT}\right)\right], \tag{2}$$

which for high values of stress reduces to:

$$\frac{\sigma_y}{T} = \frac{R}{\upsilon}\left(\frac{\Delta H}{RT} + \ln\frac{2\dot{\varepsilon}}{\dot{\varepsilon}_0}\right). \tag{3}$$

To adequately describe the yielding process over a large range of temperatures and strain rates, Ree and Eyring (1955) have modified Eq. (2) to allow multiple processes to be involved. Frequently, two-process yielding have been required to describe solid polymers with $\sigma_y = \sigma_1 + \sigma_2$, where σ_1 and σ_2 are the stresses associated with Process 1 and Process 2, respectively. σ_1 is expressed as Eq. (3), where $\sigma_y \approx \sigma_1$ at low strain rate and high temperature. σ_2 is expressed in terms of Eq. (2), which is added to the stress of Process 1, to adequately describe yielding at high strain rate and low temperature. That is:

$$\frac{\sigma_y}{T} = \frac{R}{\upsilon_1}\left(\frac{\Delta H_1}{RT} + \ln\frac{2\dot{\varepsilon}}{\dot{\varepsilon}_{01}}\right) + \frac{R}{\upsilon_2}\sinh^{-1}\left(\frac{\dot{\varepsilon}}{\dot{\varepsilon}_{02}}\exp\left(\frac{\Delta H_2}{RT}\right)\right). \tag{4}$$

Eq. (4) has been shown to agree well with experimental data for a number of polymers (Bauwens-Crowet et al., 1969; Foot et al., 1987; Liu & Truss, 1994). According to Eq. (4), the diagram of σ_y/T versus $\ln\dot{\varepsilon}$ can be divided into two regions: Region 1, at high temperatures and low strain rates, where Process 1 predominates and Region 2, at low temperatures and high strain rates where Process 2 is activated. The transition boundary between these two regions can be expressed as a function of strain rate (Liu & Truss, 1994):

$$\frac{\sigma_{y_c}}{T} = \frac{R}{\upsilon_1}\left(\ln\frac{2\dot{\varepsilon}}{\dot{\varepsilon}_{01}} - \frac{\Delta H_1}{\Delta H_2}\ln\frac{\sqrt{3}\dot{\varepsilon}}{\dot{\varepsilon}_{02}}\right) + \frac{R}{\upsilon_2}\ln\sqrt{3}, \tag{5}$$

where σ_{y_c} is the critical yield stress at the transition boundary. It is useful for predicting the yielding behaviour of polymers.

The strain rate dependence of the yield stress at 23 and 50 °C is presented, respectively, in Fig. 3a and Fig. 3b for several MC. Temperature-normalised yield stress versus $\ln \dot{\varepsilon}$ shows a series of parallel straight lines at 23 °C for MC between 6.5% and 11.4%. At higher MC, a change of slope can be observed. At 50 °C, σ_y/T against $\ln \dot{\varepsilon}$ also reveals two distinct slopes for the two MC tested. Therefore it appears that the Plantic® R1 material displayed specific contributions from two molecular processes as two different slopes were observed. At low strain rate, high temperature and high MC, the deformation is governed by a single process. With increasing strain rate and decreasing temperature and MC, a second process starts to contribute to the stress level.

In polymers where water acts as a plasticiser lowering the T_g, several studies (Emri & Pavsek, 1992; Govaert, de Vries, Fennis, Nijenhuis, & Keustermans, 2000; St. Lawrence, Willett, & Carriere, 2001) have shown that the variation of MC in amorphous polymers have an analogous effect to the variation of temperature. It is clear from Fig. 3 that an increase in MC reduced the yield stress over the strain rate range covered and it seems that equivalent yield stress values at higher MC have been shifted to higher strain rates. The shift is in accordance with the reduction in the T_g with an increase in the MC as observed in the DMTA experiments (Fig. 1 and Table 1). It is indeed comparable to the effect of increasing the temperature on the tensile properties of amorphous polymers.

Emri and Pavsek (1992) created a master curve for the shear compliance of poly(vinyl acetate) by shifting data from different moisture levels to a common reference point by applying the so-called 'time-moisture' superposition principle, which is using a similar equation to the Williams–Landel–Ferry (WLF) equation (Ferry, 1980; Williams, Landel, & Ferry, 1955):

$$\log a_c = \frac{-B_1(c - c_0)}{(B_2 + c - c_0)}, \qquad (6)$$

where B_1 and B_2 are constants, c_0 is a reference MC, c an arbitrary MC, and a_c the shift factor. Therefore, at a constant temperature T, the yield stress to temperature ratio, σ_y/T at a specific MC, c can be obtained at another MC, c_0, which is chosen as reference, simply by multiplying the time scale with a corresponding shift factor, a_c. This can be expressed as:

$$\frac{\sigma_y}{T}(\dot{\varepsilon}, c_0) = \frac{\sigma_y}{T}(\dot{\varepsilon}\, a_c, c). \qquad (7)$$

By applying this 'time-moisture' superposition principle, data from Fig. 3(a) and (b) obtained at different MC were shifted with regard to the curve at 11.4% of MC for each testing temperature.

The master curves created at 23 and 50 °C using a reference MC of 11.4% are displayed in Fig. 4. The corresponding shift coefficients for the 23 °C master curve are given in Fig. 5. The curve obtained at 50 °C for a MC of 14.9% (Fig. 3b) was shifted with the same shift coefficient as the one obtained at 23 °C with an identical MC since the equivalence between time and MC was assumed to be the same

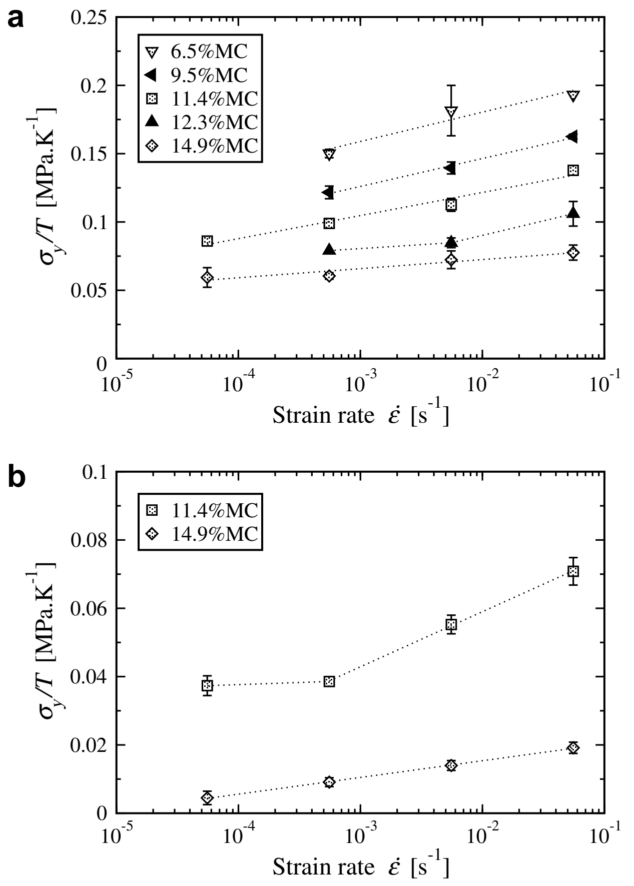

Fig. 3. Strain rate dependence of the yield stress to temperature ratio at 23 °C (a) and 50 °C (b) for several MC. Line segments have been drawn to show the approximate behaviour.

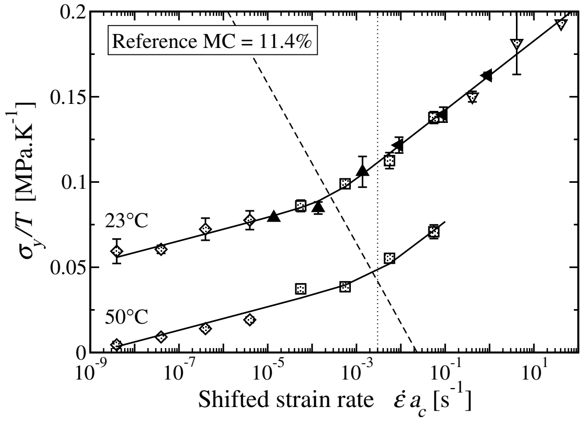

Fig. 4. Master curves of the yield stress to temperature ratio versus the shifted strain rate, obtained at 23 and 50 °C, for a reference MC of 11.4%. Curves were calculated from Eq. (4) with best fit parameters listed in Table 2. The transition boundary from Process 1-dominated yielding to Process 2-activated yielding based on Eq. (5) is indicated by a dashed line. The dotted line shows the equivalent strain rate of the DMTA experiments. (*Note.* The symbol code was kept the same as in Fig. 3).

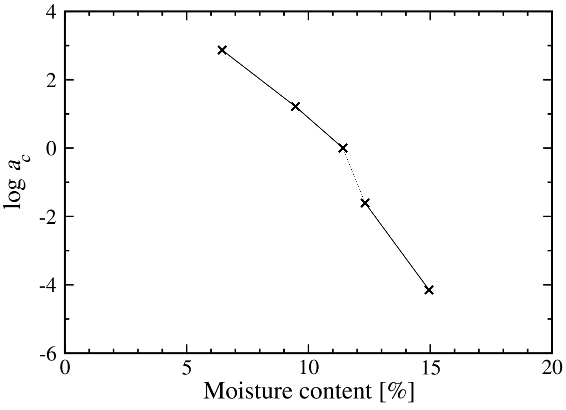

Fig. 5. Dependence of the shift factor, a_c on moisture content.

Table 2
Best fit parameters for Eq. (4) of the Eyring's model

	Process 1	Process 2
υ (nm^3)	4.64	2.73
ΔH (kJ mol^{-1})	518	66.2
$\ln \dot{\varepsilon}_0$	173	19.1

at different testing temperatures for an identical MC. The evaluation of the WLF constants has not been possible due to insufficient data points.

Shifted data were well described by the Eyring's theory for two-process yielding (Eq. (4)). The results of the curve-fitting are plotted with solid lines in Fig. 4 and the Eyring parameters obtained for each of the processes are listed in Table 2. σ_{y_c}/T giving the transition from Region 1 to Region 2 was calculated with Eq. (5) using the data listed in Table 2 and is shown in Fig. 4 as a dashed line. It is worth noting that shifting the experimental data obtained at different levels of MC allows the yield stress to be described over a broader range (10 decades) of strain rate. In comparison, the experimental data at different level of MC were limited to 3 decades.

The Plantic® R1 material displayed specific contributions from two molecular processes. These processes activated during the deformation could be related to the relaxations observed in the linear viscoelastic behaviour of the material during the DMTA experiments (Fig. 1). At 23 °C for a MC of 11.4%, the PlS blend is below $T_{\alpha(\mathrm{PlS})}$ and $T_{\alpha(\mathrm{Polyol})}$, and therefore the yield stress would have contributions from both relaxation processes. This corresponds to the higher slope in the 23 °C master curve in Fig. 4. The strain rate of $3 \times 10^{-3}\ \mathrm{s}^{-1}$ (dotted line) was the approximate equivalent strain rate of the DMTA experiments. At 50 °C, the blend material was above $T_{\alpha(\mathrm{Polyol})}$ but below $T_{\alpha(\mathrm{PlS})}$, resulting in only the later relaxation process contributing to the yield stress. This also correlates well with the 50 °C master curve where the change in slope occurred at a strain rate of approximately $3 \times 10^{-3}\ \mathrm{s}^{-1}$.

At relatively high temperature and/or low strain rate the deformation behaviour is dominated by the relaxation due to the PlS-rich phase. This process is 'slow' and thus, is the predominant mechanism in long-term loading, like creep. At lower temperature and/or higher strain rate, the relaxation due to the polyol-rich phase also becomes involved in the deformation as the time scale of the loading reaches the time scale order for this molecular relaxation process. As this process is 'faster', it will be of particular importance in the short-term mechanical behaviour. Another result of this investigation is that the rate dependence of the yield stress with strain rate is not pronounced at high MC and/or high temperature when only the relaxation process of the PlS-rich phase is involved. At lower MC and/or lower temperatures, the yield stress will increase much faster as a function of strain rate with the contribution of the second process due to the relaxation of the polyol-rich phase.

It is difficult to compare the measured activation energies and activation volumes obtained here with actual physical processes occurring in the blend since there is little data available in the literature on the yielding phenomena in plasticised starch. The activation energy for Process 1 is quite high while the activation energy for Process 2 is similar to those obtained in other polymers for high temperature low rate testing regimes (Bauwens-Crowet et al., 1969; Foot et al., 1987), which have been related to sub-T_g relaxations in the polymer. The previous analysis has shown that the change in slope of the temperature-normalised yield stress with temperature correlates with $T_{\alpha(\mathrm{Polyol})}$ and it would be logical to relate the activation energy for yield found here to this. However, the activation energy for the T_g of polyol is not available. Alternatively, the activation energy for Process 1 is of the order of the dissociation energy of covalent bonds (300–500 kJ mol^{-1} for C–C or C–O). Gedde (1995) gave the dissociation energy of hydrogen bonds as 10 to 50 kJ mol^{-1}, which is similar to the activation energy for Process 2. Relative movement of molecular chains in this material might be expected to require the breakage of hydrogen bonds. However, although there may be some correlation in the magnitude of the yielding activation energies with these molecular processes, associating these to the molecular processes occurring in yielding of this PlS/high molecular weight polyol blend must remain speculative at this stage.

4. Conclusions

Dynamic mechanical thermal analysis of a plasticised starch/high molecular weight polyol blend reveals the existence of two relaxations associated with the glass transition of each component of the blend, suggesting the occurrence of a two-phase system.

The effect of increasing moisture content on the tensile yield stress was found to be similar to the effect of increasing temperature, and could be modelled by a 'time-moisture' superposition using a similar equation to the WLF equation. Over the range of shifted strain rates and temperatures covered in this study, the tensile yield behaviour of this blend was shown to follow a two-process Eyring's model. The ability of this theory to describe the experimental data illustrates the equivalence between temperature and moisture content. It was found that the process, which dominated the deformation behaviour at high temperatures and/or low strain rates correlated well with the relaxation of the plasticised starch-rich phase while the second process that starts contributing at higher strain rates and/or lower temperatures could be associated with the relaxation of the polyol-rich phase.

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