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On the yield stress of frozen sucrose solutions

X. XU, G. JERONIMIDIS, A. G. ATKINS
Department of Engineering, The University of Reading, Whiteknights, Reading, RG6 6AY, UK
E-mail: x.xu@reading.ac.uk

P. A. TRUSTY
Unilever Research, Colworth Laboratory, Sharnbrook, Bedford, MK44 1LQ, UK

Measurement or prediction of the mechanical and fracture properties of foods is very important in the design, operation and optimization of processes, as well as for the control of quality of food products. This paper describes the measurement of yield stress of frozen sucrose solutions under indentation tests using a spherical indenter. Effects of composition, temperature and strain rate on yield stress of frozen sucrose solutions have also been investigated.

1. Introduction

The study of the large deformation mechanical properties of solid foods is an important aspect in the food science, engineering and technology. This is because the yielding and fracture behaviour of food products heavily affects processing, storage, transportation and the texture of final products. A number of reports about the measurement and prediction of the mechanical and fracture properties of various foods have been published. These have dealt with meat [1, 2], sea food [3], dairy products [4–7], starchy food [8–10], fruit and vegetable [11–13]. The mechanical and fracture properties of solid foods have been given increasing attention by researchers as it is thought that they are important mark of food quality.

Sugar containing foods are important part in people's life. Understanding the physical processes that occur, and the state of the nonequilibrium phases that are produced during the freezing of saccharide solutions, has fascinated research scientists for many years [14]. The thermal changes in frozen aqueous sucrose solutions have been extensively studied by several researchers [14–17] and it is now better understood how phase and glass transitions phenomena occur (or not) during freezing and thawing. There have been a few studies in the literature concerned exclusively with the dynamic thermo-mechanical properties of sucrose solutions at small deformation [18–20], but nothing on large strain flow or fracture behaviour which are much more likely to control sensory perception.

Yield stress is an important factor when considering the mechanical and fracture behaviour of frozen sucrose solutions under loading. It dominates the transition of flow and fracture of materials together with Young's modulus, fracture toughness and geometry of specimen tested. The components in frozen sucrose solutions are ice crystals and unfrozen matrix. The properties of both are related to the strain rate and temperature. The purpose of the present study was to determine the yield stress of frozen sucrose solutions at various different temperature and strain rate and investigate the relationship between yield stress of frozen sucrose solutions, temperature and strain rate.

2. Dependence of yield stress on strain rate and temperature

At high temperatures ($>0.5T_\mathrm{m}$, where T_m is the melting point of material on the absolute scale), stresses imposed on specimen components produce a continuously increasing strain and result in a phenomenon known as creep. For many materials the deformation obey the familiar power law of steady-state creep [21–24]:

$$\dot{\varepsilon}_\mathrm{st} = B\sigma^m \exp\left(\frac{-Q}{RT}\right) \tag{1}$$

where $\dot{\varepsilon}_\mathrm{st}$ is the steady-state creep strain rate, σ is stress, Q is an activation energy; T is the temperature; R is gas constant, B and m are constants.

Hawkers and Mellor [25] found that there is a direct relation between creep and yielding of ice and the relationships of Equation 1 could be used to describe the dependence of yield stress on strain-rate and temperature. This is not surprising if the connection between creep properties and hardness, on the one hand, and between hardness and yield stress, on the other, are considered. Early in the 1950's, Glen [26] showed that the steady-state creep strain rate exponent m and the activation energy Q in Equation 1 can be derived from hardness tests. The agreement of dependence of yield stress or hardness on strain-rate and temperature with properties of power law steady-state creep has also been confirmed by the works of Barnes *et al.* [27], Gold [28] and many other researchers in their studies on ice [23].

Atkins *et al.* [29] have linked hardness behaviour with creep properties by assuming that the rate determining process is the diffusion of the hemispherical elastic/plastic boundary surrounding the indenter into the undeformed material ahead. In this way they obtained the relationship:

$$H = (\text{constant})\left(\frac{1}{t}\right)^{1/m} \exp\left(\frac{Q}{mRT}\right) \tag{2}$$

where H is the hardness and t is the time for which the load is applied. It can be seen that Equation 2 is analogous to the rearranged form of Equation 1. Generally, yield stress and hardness are related [30] by

$$\sigma_y = \frac{H}{C} \tag{3}$$

where C is a constraint factor, which depends principally on the geometry of the indenter. Therefore, the dependence of yield stress on strain-rate and temperature can be expressed as

$$\sigma_y = A\dot{\varepsilon}^{1/m} \exp\left(\frac{Q}{mRT}\right) \tag{4}$$

where A is a constant. It is expected that the equation holds for the plastic deformation processes which occur in pure polycrystalline ice and frozen sucrose solutions.

3. Materials and method

Two different frozen-sucrose-solutions, with concentration of sucrose by mass fraction of 7% and 19%, respectively, and pure polycrystalline ice were tested. The solutions of sucrose were mixed using tap water. As frozen sucrose solutions and pure polycrystalline ice are very sensitive to temperature, microstructure, etc., any variation of the cooling conditions will markedly change their structure and properties. In attempting to achieve a uniform and fine crystal structure, a special method for preparation of specimens was developed. The pre-frozen blocks of sucrose solutions and pure water were finely comminuted using a food mixer blender with metal blades and the achieved diameter of the fragments was in the range of 0.1–0.5 mm. Then the fragments were made into a poultice by adding a little identical concentrated solution and poured into mould boxes made of cardboard (100 mm × 100 mm × 50 mm). The samples were then put into a freezer (at about −20°C) over 24 hours. Before testing, the cardboard was peeled off and the samples were kept in the thermal cabinet for 30–45 minutes at the testing temperature to equilibrate.

The tests have been carried out in the temperature range from −20°C to −40°C and in the range of crosshead speed from 0.05 mm/min to 100 mm/min, using an Instron Tensile Testing Machine. The temperature was controlled using a thermal cabinet and the coolant used was liquid CO_2. A spherical indenter of 10 mm diameter was pushed into a block of sample material at a given crosshead speed, and the load-displacement curve was recorded. A typical load-displacement curve for frozen sucrose solutions and pure polycrystalline ice in an indentation experiment is shown in Fig. 1. The mean pressure between the surface of the indenter and the indentation is equal to the ratio of the load to the projected area of the indentation. This quantity is referred to as the Meyer hardness [30].

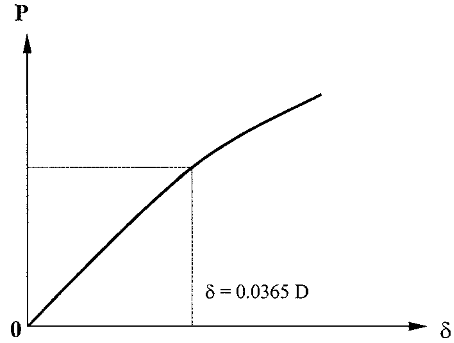

Figure 1 Typical load-displacement curve of frozen sucrose solutions and pure polycrystalline ice under indentation tests.

$$H = \frac{P}{\pi\delta(D-\delta)} \tag{5}$$

where H is Meyer hardness, P the applied load, D the diameter of indenter and δ the depth of the indentation. In testing conventional engineering materials, it is customary to use indentations with diameters ranging between $0.25D$ and $0.5D$ [30–32]. The average of these is $0.375D$, which corresponds with a value of $\delta \cong 0.0365D$. For spherical indenters, the value of C in Equation 3 is 2.8–2.9.

The average strain of the non-uniform deformation field beneath the indentation is dependent on the 'shape factor' d/D [30], namely,

$$\varepsilon \approx 0.20(d/D) \tag{6}$$

where d is the diameter of the indentation, given by $2\sqrt{\delta(D-\delta)}$. If the crosshead speed is $\dot{\delta}$ and loading time is t, the depth of the indentation will be $\delta = \dot{\delta}t$. Therefore, the strain rate can be written as follows:

$$\dot{\varepsilon} = \frac{\mathrm{d}\varepsilon}{\mathrm{d}t} = \frac{0.2(D-2\delta)}{D\sqrt{\delta(D-\delta)}}\dot{\delta} \tag{7}$$

To calculate the value of hardness and the yield stress, a value of $\delta = 0.0365D$ was chosen, so that

$$\dot{\varepsilon} = 0.9886\,\dot{\delta}/D \tag{8}$$

4. Results and discussion

Using Equations 3, 5 and 8, the yield stresses of pure polycrystalline ice, 7% sucrose solution and 19% sucrose solution, at the different temperatures and at the different strain rates, have been determined. The results are shown in Figs 2–4. For all tested samples, the yield stress increases with decreasing temperature, and also increases initially with increasing strain rate before reaching a peak. At this critical strain rate the yield stress reaches a maximum and then decreases with increasing strain rate. Also, the strain rate corresponding to the maximum yield stress varies with the composition of samples and testing temperature. The magnitude of yield stress is strongly dependent on the sucrose concentration, which must be related to the amount and size of ice crystals in the samples. The higher the content

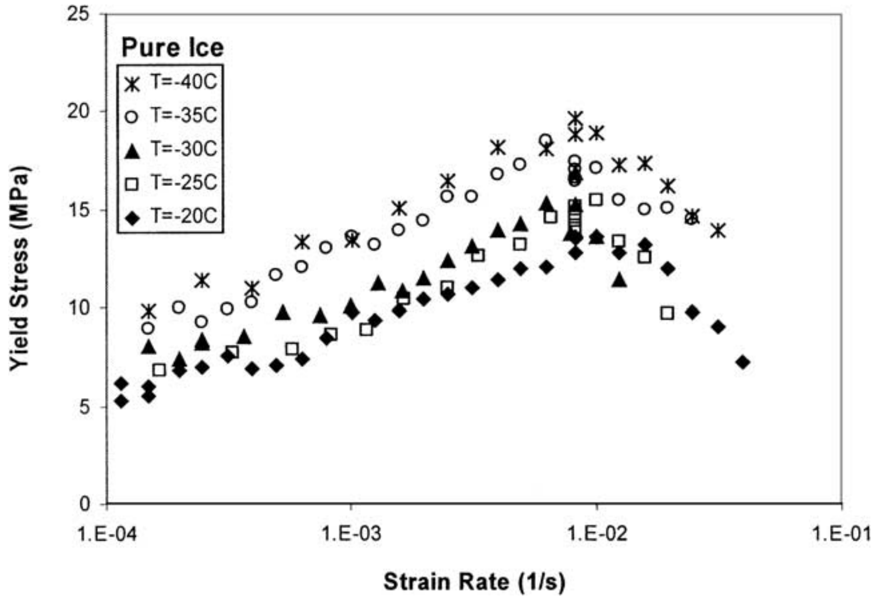

Figure 2 Yield stress of pure polycrystalline ice at various temperatures and strain states.

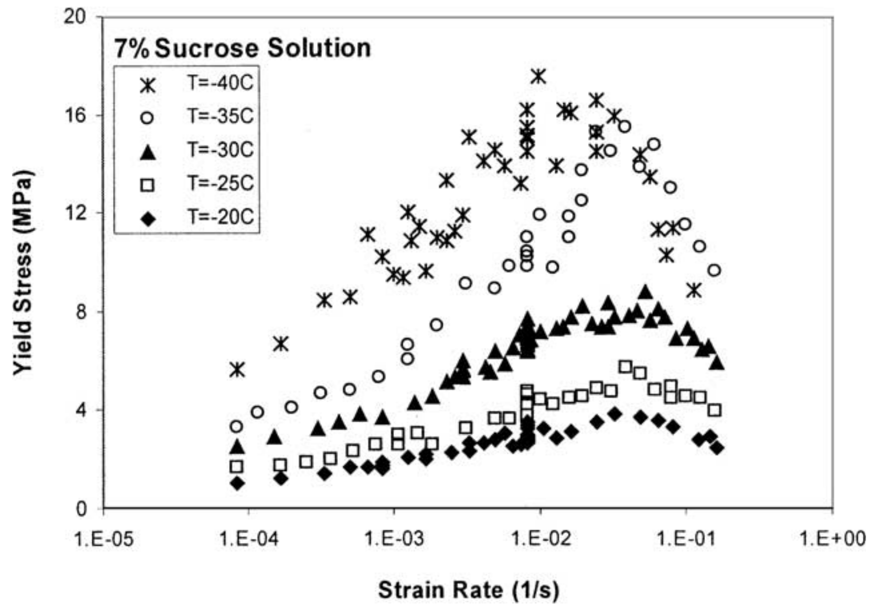

Figure 3 Yield stress of 7% sucrose solution at various temperatures and strain rates.

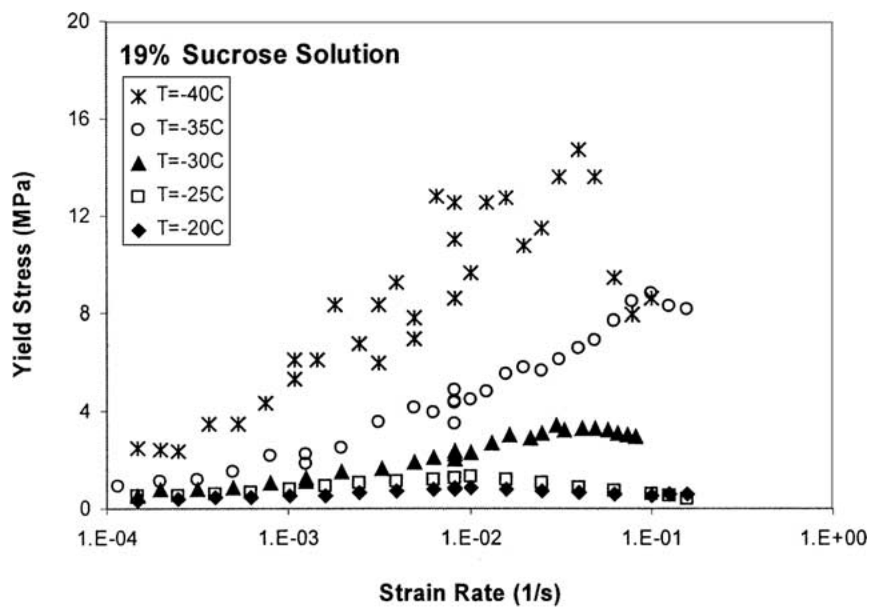

Figure 4 Yield stress of 19% sucrose solution at various temperatures and strain rates.

of sucrose, the lower the amount of ice crystals and the finer the crystal size, resulting in lower yield stresses.

Depending on the loading condition, ice exhibits two types of behaviour: ductile when loaded slowly and brittle when loaded rapidly [33]. During compression tests the transition from ductile yielding to brittle fracture occurs at a strain rate of $10^{-2}\,s^{-1}$ in the temperature range between $-20°C$ and $-40°C$ [25, 33–35]. Ductile behaviour of ice is controlled by the glide and climb of basal dislocations and by dynamic recrystallization; whereas the growth and interaction of propagating cracks control brittle behaviour. On loading, cracks will first nucleate within virgin material at stress around 1.2 MPa for ice [28]. At the lower strain rates, the cracks do not propagate; instead, new cracks formed as the load increased, and the ice exhibits ductile behaviour. At a higher rate, the cracks do propagate and the ice is brittle. The transition results from a competition between stress buildup and stress relaxation near the crack tips. Stress buildup dominates at higher loading rates: the stress intensity factor eventually reaches the critical level at which point the cracks grow and interact and brittle failure ensues. Relaxation dominates at lower loading rates, leading to crack blunting and to ductile behaviour.

The results presented here showed that the critical strain rate for pure polycrystalline ice lies between $0.6–1.3 \times 10^{-2}\,s^{-1}$ under indentation tests. It is believed that this critical strain rate corresponds to the ductile-brittle transition strain rate. During an indentation process, the specimen is not loaded uniformly and the stress varies spatially and temporally. In fact, as soon as the indenter is pushed into the specimen, the mean pressure between the surface of the indenter and the indentation increases very quickly and reaches a large value immediately. The magnitude of this initial mean pressure, of course, is dependent upon the resistance of specimen to the indenter. With the increase of the indentation depth, the mean pressure increases. Because of the large shear stress due to the stresses which develop sharply within the contact zone, microcracks are generated. The growth and interaction of microcracks is a very complicated process. Under lower strain rates, the microcracks continue to nucleate as the stress increases, but do not propagate until the failure strain is reached. At the critical strain rate the cracks begin to propagate and then the transition from ductile to brittle behaviour occurs.

The values of the ductile-brittle transition strain rate for pure polycrystalline ice and frozen sucrose solutions during indentation tests at the different temperature are shown in Fig. 5 and summarised in Table I. Obviously, the ductile-brittle transition strain rate of the frozen sucrose solutions varies with the variation of composition and temperature. The dependence of the transition from ductile to brittle behaviour of frozen sucrose solutions on the strain rate can be also explained in terms of the mechanism of cracks propagating or blunting as discussed above. The properties and the amount of matrix around ice crystals in frozen sucrose solutions plays an important role on the establishment of this transition mechanism. It has been noted that the property of the matrix (essentially, viscosity) is related to the temperature and independent on the initial sucrose concentration; the amount of matrix is strongly affected by the initial sucrose concentration and slightly by the temperature [36]. The amount and viscosity of matrix in the frozen sucrose solutions investigated can be calculated from results in the literatures [15, 37]. The details of the calculations have been given by Xu [36] and the results obtained are shown in Figs 6 and 7.

TABLE I Temperature-dependent critical strain rate of pure polycrystalline ice and frozen sucrose solutions in the indentation tests (Unit: s^{-1})

Temperature	Pure ice	7% Sucrose solution	19% Sucrose solution
$-20°C$	1.3×10^{-2}	3.3×10^{-2}	1.0×10^{-2}
$-25°C$	1.0×10^{-2}	4.0×10^{-2}	1.0×10^{-2}
$-30°C$	0.8×10^{-2}	5.3×10^{-2}	3.0×10^{-2}
$-35°C$	0.6×10^{-2}	4.0×10^{-2}	10.1×10^{-2}
$-40°C$	0.8×10^{-2}	1.7×10^{-2}	3.1×10^{-2}

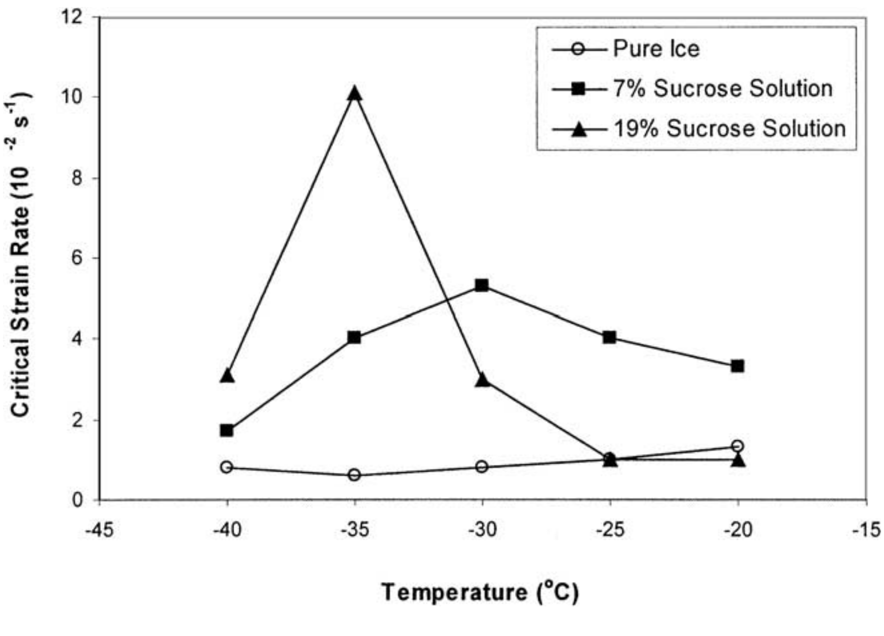

Figure 5 Critical strain rates of pure polycrystalline ice and frozen sucrose solutions as a function of temperature.

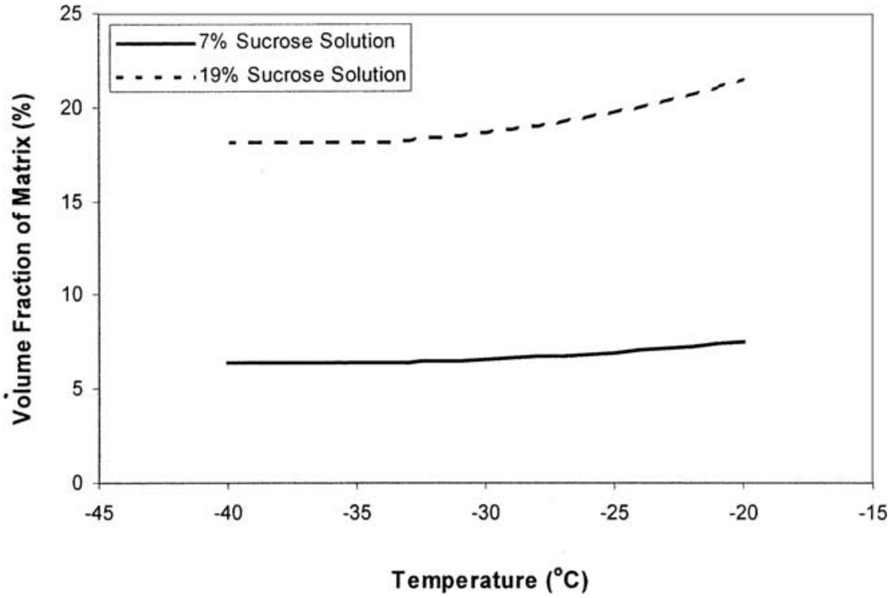

Figure 6 Volume fraction of matrix in frozen sucrose solutions as a function of temperature.

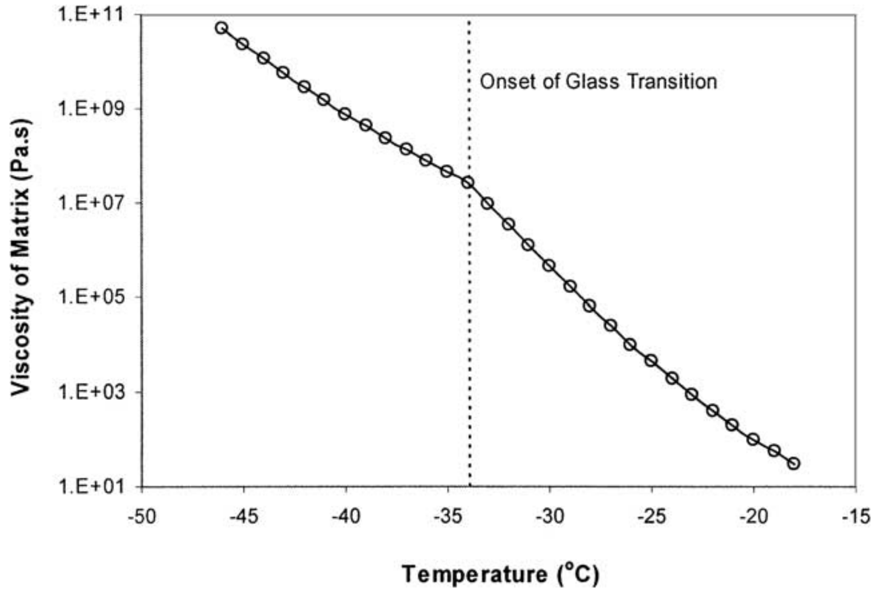

Figure 7 Viscosity of matrix in frozen sucrose solutions as a function of temperature.

At temperatures of −20°C and −25°C, the viscosity of the matrix is extremely low so that the sliding between the ice crystals occurs readily when the specimen is stressed, and the critical sliding distance is reached quickly. The observation of the lower transition strain rate in this temperature range is good evidence of this phenomenon. At a temperature of −30°C, because of the increased viscosity of the matrix, the bearing capacity of the sample increases and the transition strain rate increases. Since the volume fraction of matrix in 19% sucrose solution is greater than that in 7% sucrose solution, the shear resistance of 19% sucrose solution is less than that of 7% sucrose solution (assuming that the ice crystals is uniformly covered by matrix, therefore, the thickness of matrix film in 19% sucrose solution must be greater than that in 7% sucrose solution). Therefore, above −30°C, the transition strain rates of 7% sucrose solution are greater than those of 19% sucrose solution. There is a glass transition for sucrose solutions in the temperature between −34°C to −46°C and it is time-dependent [15]. At temperatures of −35°C and −40°C, a partial glass phase exists and correspondingly, it increases the deformation resistance of the matrix and reduces the transition strain rate. Also, owing to the fact the amount of matrix in 19% sucrose solution is more than that in 7% sucrose solution, the time needed for glass transition of matrix in 19% sucrose solution may be longer than that in 7% sucrose solution. As a result, under same conditions (such as cooling temperature and cooling time), the maximum transition strain rate of 19% sucrose solution occurs at −35°C while the maximum transition strain rate of 7% sucrose solution occurs at −30°C (see Fig. 5).

Clearly, when the applied strain rate exceeds the transition strain rate, the indentation process is dominated by crack propagation, which is, of course, unstable. Therefore, the dependence of yield stress on strain rate and temperature in Equation 4 is only valid in the range of the applied strain rate less than the transition one. By plotting the logarithm of the yield stress against l/T for same strain rate, the values of the Q/m and the constant A may be obtained. Similarly from the variation

TABLE II Values of the parameters in Equation 4 for pure polycrystalline ice and frozen sucrose solutions

	Pure ice	7% Sucrose solution	19% Sucrose solution
A (MPa $s^{1/m}$)	2.40×10^{-1}	2.15×10^{-8}	3.10×10^{-13}
m	5.25	4.67	4.47/2.82*
Q (kJ/mol)	54	195	224/147*

Note: $^*m = 4.47$ and $Q = 224$ kJ/mol. for the higher temperatures of −20°C and −25°C; $m = 2.82$ and $Q = 147$ kJ/mol. for the lower temperatures of −30°C, −35°C and −40°C, respectively.

TABLE III Values of m and Q obtained from stress relaxation experiments for pure polycrystalline ice and frozen sucrose solutions

	Pure ice	7% Sucrose solution	19% Sucrose solution
m	4.1–5.3	3.0–3.6	2.4–3.5
Q (kJ/mol)	93	124	138

of the yield stress with strain rate at a constant temperature the value of m can be found. This type of analysis has been employed on indentation tests by Atkins [38] for metals, by Glen [26] and Barnes *et al*. [27] for ice. Present results for pure polycrystalline ice and frozen sucrose solutions are shown in Table II.

The stress exponent m of 5.25 in our experiments for pure polycrystalline ice is greater than that of 4.4 from Barnes *et al*. [27]. The stress exponent, m, for 7% sucrose solution is 4.67, while the 19% sucrose solution has two different values of m, 4.47 at the higher temperatures of −20°C and −25°C and 2.82 at the lower temperatures of −30°C, −35°C and −40°C, respectively. These variations are perhaps related to the magnitude of internal stress in the samples. Duval *et al*. [39] noted that on loading, an increasingly nonuniform state of internal stress, with a wavelength about equal to the grain size, develops with strain around the grains due to the anisotropy of ice. Its average is always equal to the applied stress, but the peaks can be many times larger. At a given temperature and a given strain rate, pure polycrystalline ice has the greatest yield stress, followed by 7% sucrose solution and 19% sucrose solution. This means that, under the same conditions of temperature and strain rate, the stress applied in the specimen of pure polycrystalline ice is greater than that in the specimen of 7% sucrose solution, while the stress applied in the specimen of 7% sucrose solution is greater than that in the specimen of 19% sucrose solution. Correspondingly, the ranking of values of m, from greatest to smallest, are pure polycrystalline ice, 7% sucrose solution, and 19% sucrose solution due to the magnitude of yield stress i.e., to the phase volume of ice crystals present.

The activation energy for pure polycrystalline ice obtained in this work is 54 kJ/mol, which is less than the value of 72 kJ/mol obtained by Barnes *et al*. [27] from hardness tests, but still lies in the range of 40–140 kJ/mol that has been obtained from many creep experiments [23, 40, 41]. The value of Q of 7% sucrose solution is equal to 195 kJ/mol. For 19% sucrose solution, there are also two different values of activation energy, 224 kJ/mol. At the higher temperatures of −20°C and −25°C, and 147 kJ/mol. At the lower temperatures of −30°C, −35°C and −40°C, respectively. These indicate that different mechanisms dominate the deformation process of 19% sucrose solution in the different temperature ranges. The values of m and Q of pure polycrystalline ice and both sucrose solutions have been also determined by Xu [36] in terms of stress relaxation experiments. The differences between the data obtained by indentation tests (Table II) and those by stress relaxation tests (Table III) may be dependent on the stress level and the change of the structure.

As mentioned before, pure polycrystalline ice has the lowest critical transition strain rate so that it may have more microcracks underneath the indenter than the others. During stress relaxation, owing to the stress drop off, recrystallization and growth of ice crystals may occur, thus result in the increase of activation energy. For frozen sucrose solutions, the flow of matrix should strongly affect their creep behaviour. This is why the activation energies of sucrose solutions obtained by indentation tests are greater than those by stress relaxation tests, while for pure polycrystalline ice it is the opposite. The data obtained show that the activation energy is related to the interaction of matrix and ice crystals at the boundaries. The effect of the matrix on the loading and stress relaxation processes of frozen sucrose solutions depends on whether it is extruded or not. When the temperature is higher than the glass transition temperature of the matrix, the deformation of the system is significantly determined by the flow of matrix. The strain of ice crystals (elastic, plastic and creep) just contributes a little. The greater the sucrose contents the more the amount of matrix, the greater the activation energy. As can be seen from Fig. 6, the amount of matrix in 7% sucrose solution is less and therefore, the variations of stress exponent and activation energy with temperature are not apparent. The amount of matrix and its change with temperature in 19% sucrose solution are obviously large so that at the higher temperatures, the matrix can be easily extruded during loading and the ice crystals readily touch each other in the stress direction. Thus, the direct contact of ice crystals keeps the stress exponent at a higher value and the flow of matrix makes the greater contribution to the activation energy. At temperatures lower than the glass transition temperature of the matrix, the movements of the matrix are restricted due to the existence of a glass phase. During loading, the matrix may be still remain between the ice crystals in the stress direction, reducing the magnitude of m although the internal stress rises. The decrease of the matrix flow accompanies the decrease of activation energy. For an identical material, the internal stress in the specimen during loading is greater than that during stress relaxation. Therefore, the values of m obtained by indentation tests are somewhat greater than those by stress relaxation tests for all samples.

Substituting the results of Table II into the Equation 4, the calculated yield stresses for all samples agree with the measured yield stress very well (Figs 8–13). These indicate that, for pure polycrystalline ice and frozen sucrose, the dependence of yield stress of on strain rate and temperature can be reasonably predicted by means of Equation 4.

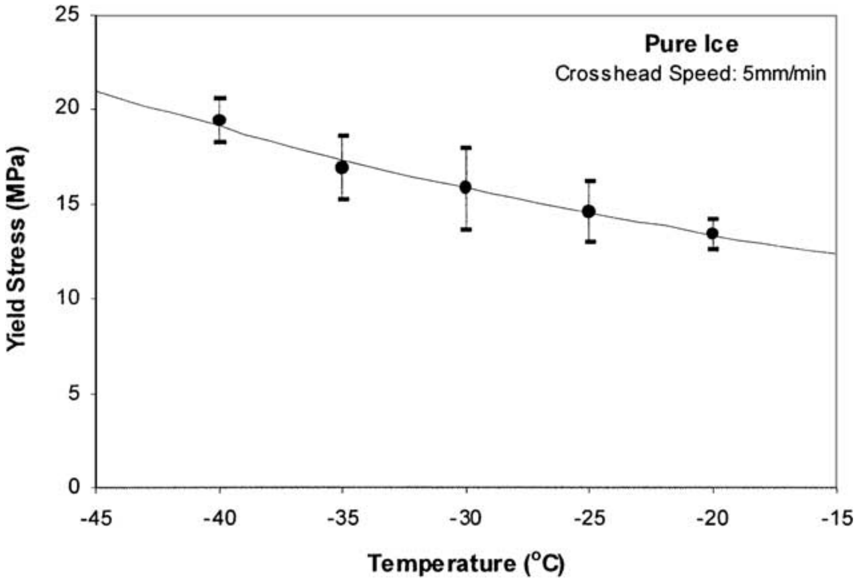

Figure 8 Yield stress of pure polycrystalline ice as a function of temperature.

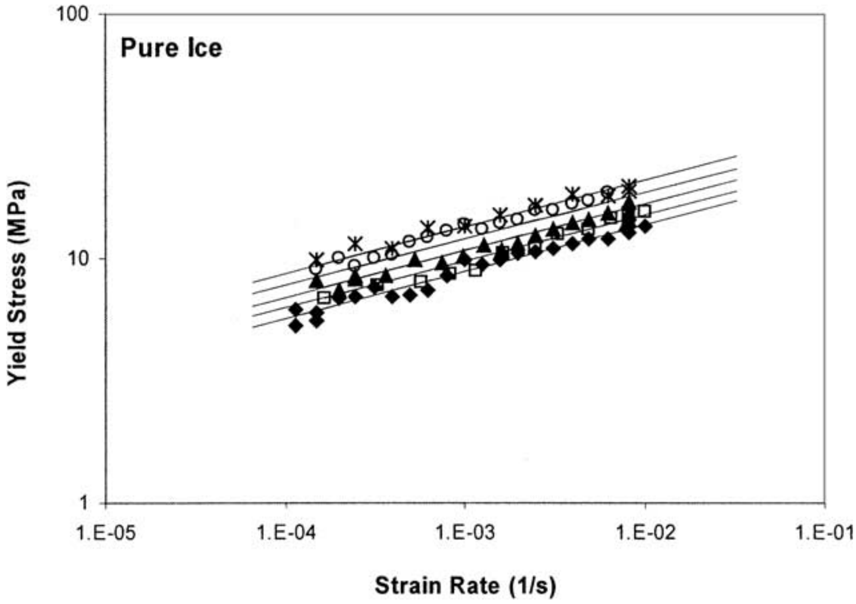

Figure 9 Yield stress of pure polycrystalline ice as a function of strain rate.

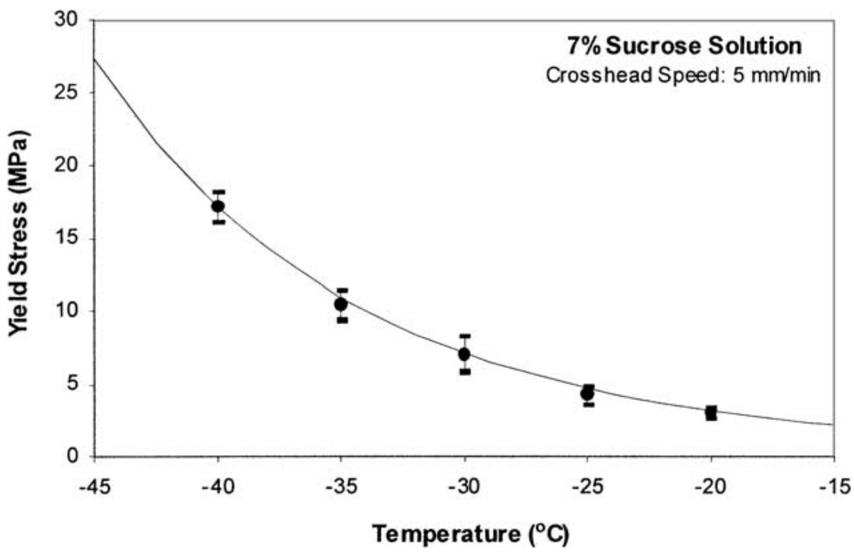

Figure 10 Yield stress of 7% sucrose solution as a function of temperature.

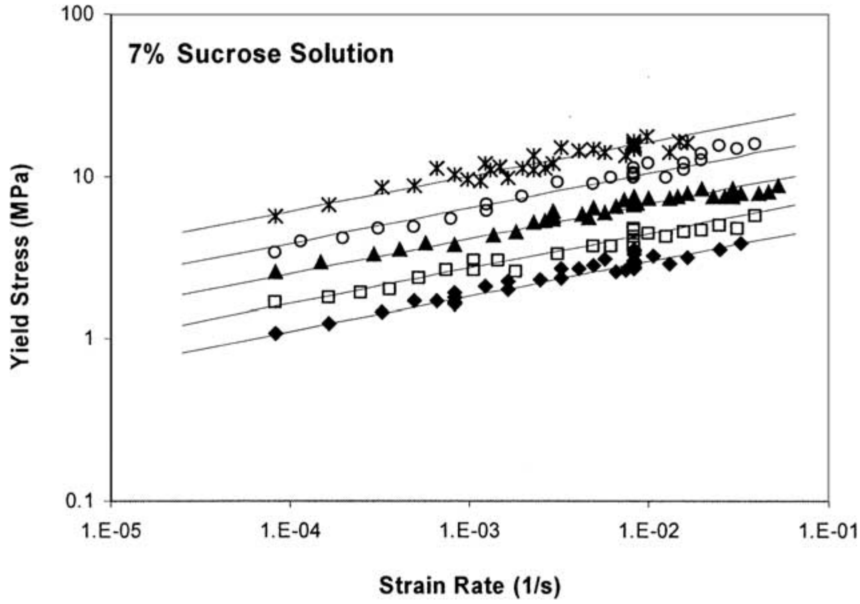

Figure 11 Yield stress of 7% sucrose solution as a function of strain rate.

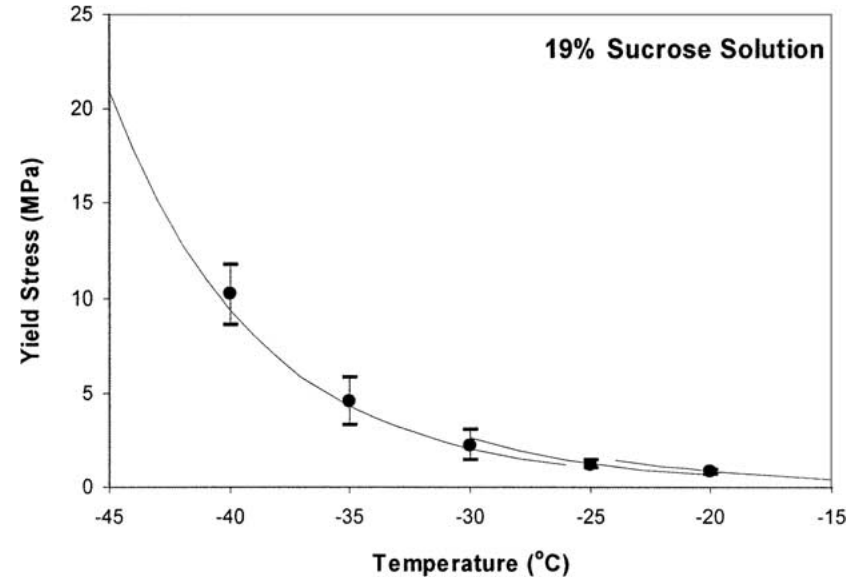

Figure 12 Yield stress of 19% sucrose solution as a function of temperature.

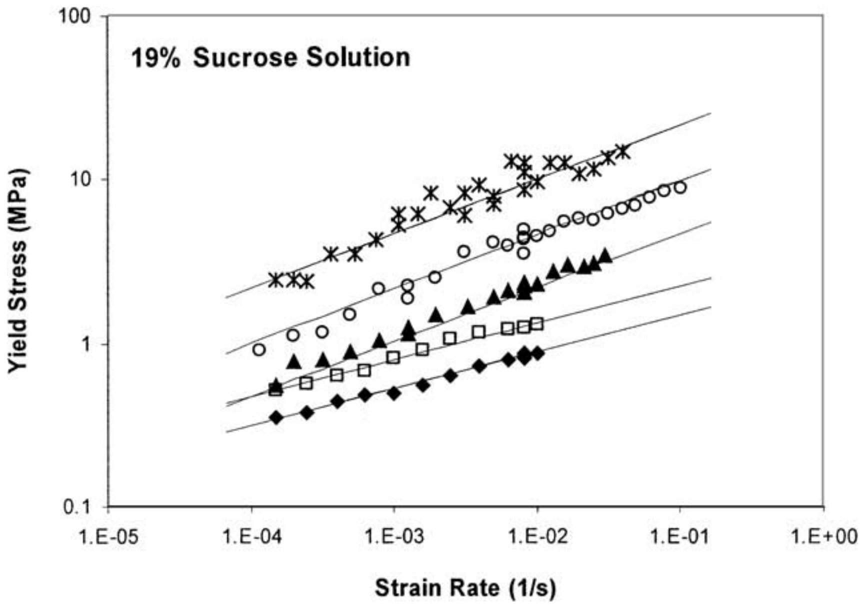

Figure 13 Yield stress of 19% sucrose solution as a function of strain rate.

5. Conclusions

The yield stress of frozen sucrose solutions and in particular, the effects of composition, strain rate and temperature have been investigated systematically. The conclusions are given below: (1) in the temperature range -20°C to -40°C there is a transition from ductile yield to brittle fracture under indentation tests. The transition strain rate varies with temperature and depends on the amount and properties of matrix, in other words, the composition of the sample; (2) when the applied strain rate is less than the transition strain rate, the yield stress of sucrose solutions increases with decreasing temperature, and also increases with increasing strain rate. The dependence of yield stress, of frozen sucrose solutions on strain rate and temperature can be described by means of the rearrangement of the power law equation of steady-state creep. The steady-state creep parameters of sucrose solutions vary with the composition and the temperature range.

Acknowledgements

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