Cold Chocolate under stress

An alternative approach to study high-rate behaviour in polymers

Rhiannon Heard

Quasi-static loading of polymers has many industrial applications with this study focussing on the confectionary market. This research investigates quasi-static loading of polymers in the Environmental Scanning Electron Microscope (ESEM) in an attempt to characterise the high rate behaviour of Lindt 85% chocolate. It combines the techniques of the Brazilian Disk Tensile Test with the ESEM at a range of temperatures in order to identify the optimal conditions for preventing chocolate from fracturing during transport and storage.

Introduction

The chocolate industry has rapidly developed over time with each Brit eating approximately 9.5 kg per year [EAUK, 2017]. However, there are still difficulties with transport where consumers often receive fat and sugar bloom as well as broken chocolate. Hence, the use of an advanced imagery technique such as Environmental Scanning Electron Microscopy (ESEM) in examination of chocolate on a microscopic level may facilitate a clearer understanding of the structure-property-composition relationship of chocolate and thus identify the ideal environmental conditions for transportation that prevent breakage and optimise strength.

The principle of ESEM utilises a multiple aperture graduated vacuum system, which allows specimen imaging to occur under water vapour or other auxiliary gases, including nitrogen or nitrous oxide [Meredith, P, Donald, A. M, 1996]. ESEM uses a system of differential pumping to enable the chamber to be held at varying pressures between 1 and 10 Torr, whilst the gun and column pressure remains at 7.5×10^{-7} Torr [Dragnevski, K.I, 2012]. Samples can be imaged in their natural state by using a correct pump down procedure [Cameron, R. E, Donald, A.M, 1994] and by controlling the temperature of the specimen using a Peltier cooling module, thus preventing dehydration. This procedure was utilised in order to minimise charging and avoid the need for extensive sample preparation (gold coating), which would most likely be broken during the tension experiment and hence prove difficult to image under SEM alone. It also ensures the data collected relates to the properties of the specimen only and is not impacted by the sample preparation process such as the gold coating required to enable it to be imaged under standard high vacuum SEM.

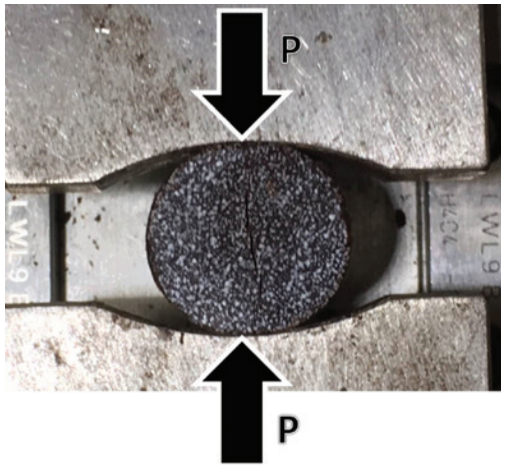

Figure 1. Brazilian Disk Test Specimen geometry superimposed on the 14 mm diameter disk shaped specimen after test with white silica paint pattern to enable tracking to occur, the crack can be seen clearly on the DIC (Figure 5b).

In order to supplement the ESEM and tensile strength data, Differential Scanning Calorimetry (DSC) was used to identify the melting temperature and any other transformations within the studied system [EAG Laboratories, 2016]. DSC was further utilised to identify temperatures that caused a noticeable change in heat flow (either endothermic or exothermic) and hence suggested a transition occurred in the physical structure of the specimen. These values provided a basis for the choice of temperatures at which to investigate the tensile strength.

A heat flux DSC comprises of a thermal cell with a sensor that registers the temperature difference between the sample-filled pan and the empty (air-filled) reference pan. As the sample changes due to thermal processes the DSC plot shows an increase or decrease in heat flow, suggesting an endothermic or exothermic process is occurring [EAG Laboratories, 2016]. This can then be used to identify when the sample is undergoing a change of state, for example melting, which further enhances the understanding of the specimen's thermodynamic properties.

The samples being investigated were made from Lindt Chocolate which contains 85% cocoa mass and 15% demerara sugar. Hence, its properties not only depend on the ingredients, but perhaps more importantly the interactions between them. Initial studies examining the properties of chocolate using x-ray diffraction suggest that it is mostly an amorphous polymer with some crystalline features [Brooker, B.E, 1990]. Given most chocolatiers use sugar in its crystalline form rather than amorphous to avoid water absorption [Beckett, S.T, 1995] and as sugar is one of the three ingredients of dark chocolate this is unsurprising. However, further research on a microscopic level is required to fully appreciate how the different ingredients interact and are effected by impact loading. Understanding the effects of impact loading is vital in the transportation of chocolate as boxes of chocolate may be dropped from a height leading to fracture. The severity of the fracture is particularly effected by different environmental conditions, such as temperature and pressure, which chocolate may be exposed to.

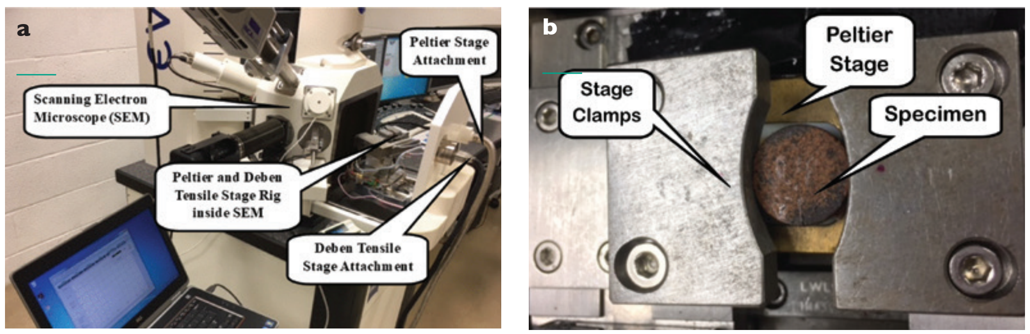

Figure 2. a) Rig set up within the ESEM. b) Deben Stage containing specimen and Peltier stage.

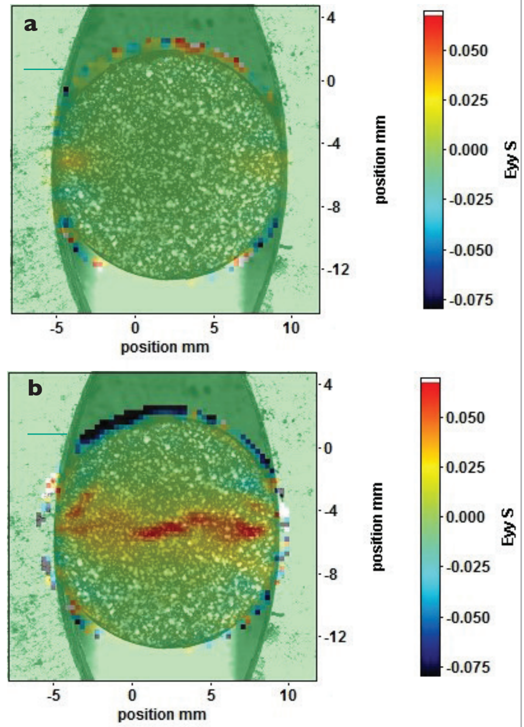

Figure 3. Brazilian Disk Test displacement image. a) The point load with strain concentrations are shown in yellow; this is before failure at 120s. b) The maximum displacement propagating from the centre as specimen fails at 540s in red.

2 Materials and Methodology

2.1 Materials

The circular specimens (14 mm diameter) used for the Brazilian Disk Test were made from Lindt Chocolate, which contains 85% cocoa mass (cocoa powder and cocoa butter), with the remaining 15% Demerara sugar [Lindt, 2015]. The only other ingredient listed was vanilla extract, which is considered negligible by most chocolatiers [Beckett, S.T, 1995]. The same chocolate was used for the DSC tests.

A number of experiments were conducted on the chocolate in order to facilitate understanding of its behaviour at "extreme temperatures" ranging from 25 to -20 °C. These are detailed below.

2.2 Differential Scanning Calorimetry (DSC) Testing

The TA Instruments DSC Q2000 was used to carry out testing; two Tzero low mass aluminium pans and corresponding lids of size weighing approximately 27 mg and containing a specimen of less than 10 mg were deposited. Three specimens were tested of sample size 8.05 mg, 8.56 mg and 7.52 mg respecctively. The specimens were sealed between the pan and lid and were placed in the DSC with an empty (air-filled) pan and lid for reference. The DSC was then set to the automatic ramp setting to gradually increase the temperature by 5 °C per minute from -5 °C to 45 °C. The Heat flow was then measured and recorded to identify the melting temperature. Modulated DSC was also used in order to identify any other transformations within the studied system. In modulated DSC the same

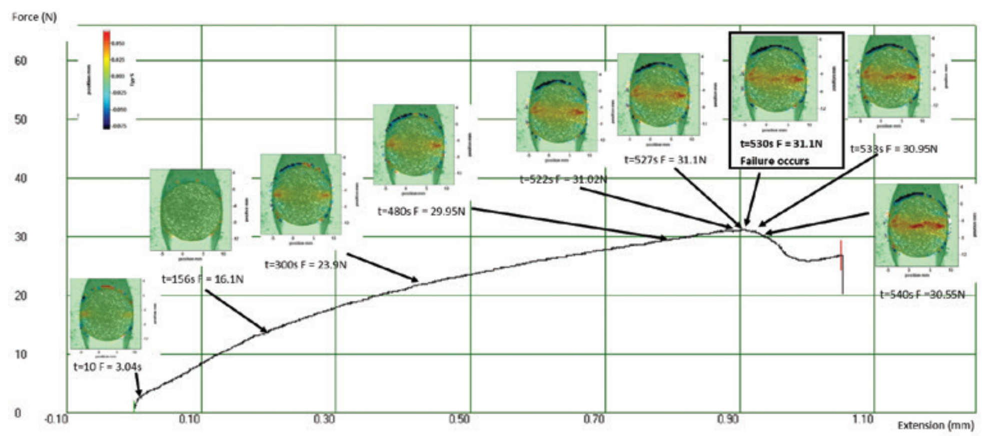

Figure 4. Brazilian Disk Test Force vs Displacement plot with images showing the concentration of strain across the centre.

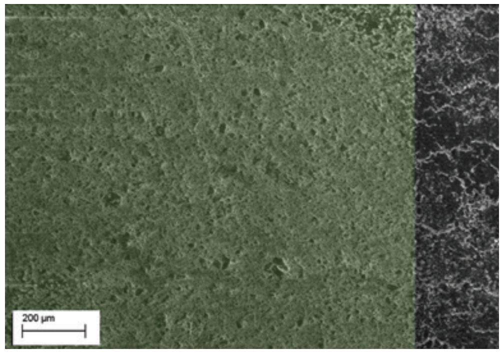

Figure 5. Brazilian Disk Test ESEM image showing the densification of the specimen along the centre where tension occurs. The densification is highlighted in green.

method was applied to the sample but, reverse heat flow was plotted against temperature and the temperature increased in cycles rather than a simple linear fashion.

2.3 Brazilian Disk Test

The Brazilian Disk Test was employed to simulate quasi-static tensile loading due to the relatively brittle nature of the chocolate specimen, which was machined into a 14 mm diameter disk; 5 mm thick. The test was first developed for analysis of concrete by Carneiro and Barcellos in 1953 [Carneiro, F.F.L and Barcellos, A, 1953] and its principle is shown in Figure 1.

The test was conducted on a 5 kN Deben tensile stage equipped with a Peltier cooling module, within the chamber of a Carl Zeiss EVO L515 ESEM, (as in Figure 2). The specimens were tested at a range of temperatures in order to simulate the different environments that chocolate may undergo quasi-static loading in. The rig was connected to the Deben Software to facilitate the recording of the displacement and force applied in compression which simulates a tensile force at the centre of the disk specimen. This was plotted on a graph highlighting the specimen breaking point and hence the maximum force (P/N). Subsequently, these results were used to calculate the maximum tensile strength from the equation below; where the contact half width (b = 3 mm) for all specimens, disk thickness (t = 5 mm) and the disk diameter (D =2R = 14 mm).

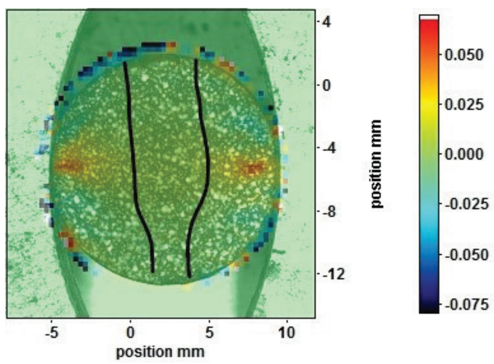

Figure 6. Validated DIC Brazilian Disk Test image showing the densification of the specimen along the centre where tension occurs as outlined in black.

$$\sigma_{Tensile} = (1-\frac{b}{R})^2 \frac{2P}{\pi D t}$$

Tests were carried out at a range of temperatures listed below, simulating different conditions:

- 25 °C (Tropical Weather)
- 20 °C (Recommended storage)
- 10 °C (see DSC reverse heat flow plot in section 3.2)
- 3 °C (Fridge temperature)
- -3 °C (initial freezer temperature)
- -20 °C (freezer temperature)

In order to achieve these, testing was carried out in a controlled environment where all specimens were cooled or heated from 20 °C, which is the recommended chocolate storage temperature. The specimens were cooled on the Peltier cooling module for up to two hours depending on the temperature required. Then the specimen was carefully clamped between the jaws and put under slight compression. The jaws themselves had also been cooled during this time. The motor was run in compression in order to generate a tensile stress in the centre of the chocolate specimen until fracture occurred along the central line. The tensile testing was carried out in-situ, so that the crack propagation could be viewed on a micro-level. The set-up also enabled the videoing of the crack propagation from inside the ESEM chamber.

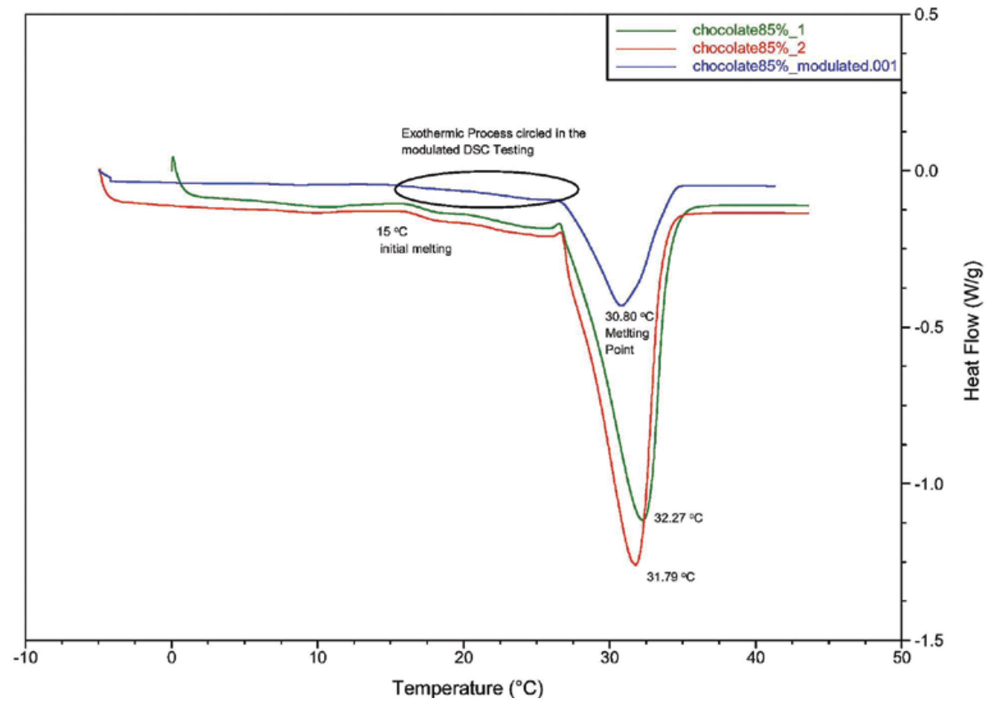

Figure 7. DSC Heat Flow vs Temperature plot, showing the initial melting of one of the ingredients (most likely the cocoa butter, given the other main ingredients are cocoa mass and sugar with higher melting temperatures). Plot shows all three tests carried out, two using standard DSC mode and a a steady increment in temperature (red and green) and one using modulated DSC. The modulated graph highlights an exothermic process occurring in the area circled, indicating crystallisation.

2.4 Digital Image Correlation (DIC)

The Brazilian Disk test was also combined with DIC at room temperature (20 °C) in order to validate the in-situ tensile test results. Firstly the rig was set up using a Point Grey Camera with a 200 mm lens and the 5 kN tensile (Deben) stage for the Brazilian Disk test. Due to the relative smoothness of the chocolate surface the specimen was coated in a white silica based paint, which produced a speckled pattern across the tablet, shown in Figure 1. This enabled the tablet's movements to be tracked at a rate of one frame per second by the camera rigged directly above the sample and then the DaVis 8.3.0 software was able to use the data obtained to generate graphical displacement plots.

3. Results and Discussion

3.1 Tensile Strength Effects

The use of the Brazilian Disk Test inside the ESEM facilitated the collection of both qualitative and quantitative data for the tensile strength of chocolate under quasi-static loading. The real-time force vs extension graph, shown in Figure 4 indicates that the chocolate exhibits polymer-like properties where initially it experiences reversible visco-elastic deformation and then becomes irreversible [Swallowe, G.M, 1999]. Eventually, the chocolate yields causing a crack to propagate from the central point as is expected in the Brazilian Disk test but this doesn't completely crack the disk in half as shown by the ESEM images. Thus, after decreasing in force, the force begins to increase until complete rupture at the second peak, which is consistently lower than the first peak.

The DIC testing demonstrates the effectiveness of the test with Figure 3a illustrating a point load being applied to the disk before failure, as well as the effect of fracture in Figure 3b. It also enabled the graph, shown in Figure 4, to be plotted with the appropriate images superimposed on the graph. This demonstrated the exact point the crack propagated (in both space and time), initially from the centre.

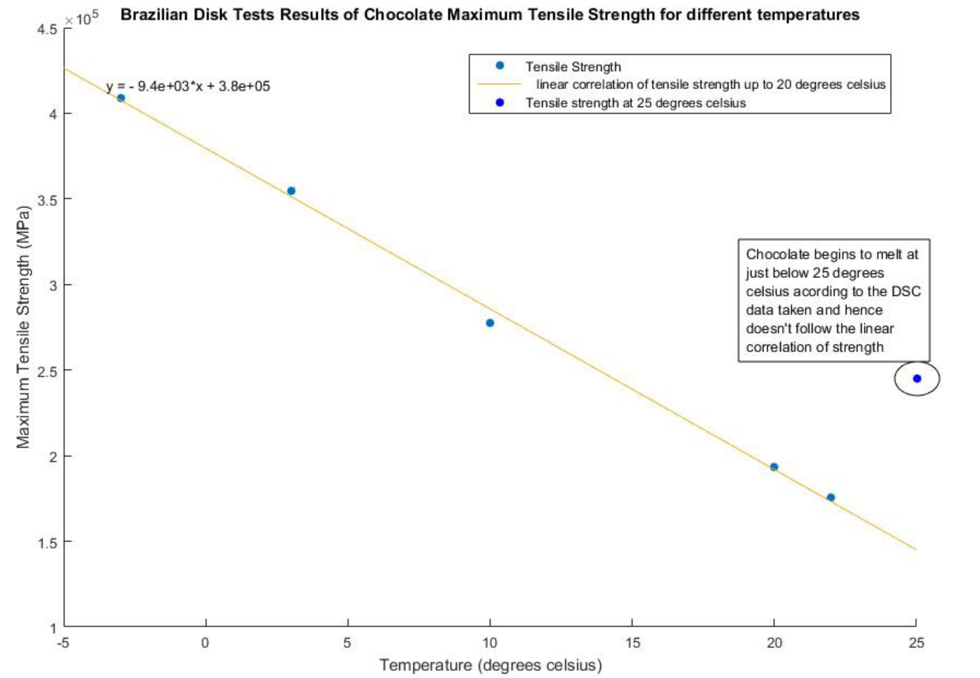

Figure 10. Tensile Strength vs Temperature for Brazilian Disk Test of Chocolate showing linear correlation.

During the tensile test the ESEM images revealed that some compression and densification was occurring in the centre of the disk. This indicated a larger force concentration in this area and hence led to a differential in the surface properties in this area across the specimen, as shown in Figure **5.** The DIC displacement images were able to verify this by highlighting a central point where a high level of displacement occurred as shown in Figure **6.**

3.2 DSC Results

The melting temperature was measured using DSC and was found to be an average of 31.6 °C over the three tests, which are depicted in Figure 7. The initial melting, seen in the graph at 15 °C is attributed to the cocoa butter, which is not 100% solid until -10 °C [Beckett, S.T, 1995], [Hitachi High-Tech, 2008]. The DSC also indicated temperatures to identify how the different levels of solid cocoa butter affected the strength of the chocolate. Furthermore modulated DSC testing indicated that the chocolate has a degree of crystallinity [da Silva, T.L.T et al, 2017], shown in Figure 7, where a step down in the reverse heat flow suggested an exothermic reaction is occurring most likely attributed to crystallisation. However, when the reverse heat flow was examined it did not show a clear glass transition temperature. This is a common occurrence when evaluating the glass transition temperature of semi-crystalline polymers [AZO Materials, 2001] and hence suggests that chocolate exhibits semi-crystalline behaviour. Moreover, since most chocolatiers state to use sugar in its crystalline form rather than amorphous [Beckett, S.T, 1995] and as sugar is one of the three ingredients of dark chocolate; this further strengthens the idea that chocolate will have a crystalline aspect.

3.3 Temperature vs Tensile Strength

The Brazilian Disk results produced a negative linear correlation below 20 °C with a decrease in temperature resulting in an increased strength, as shown in Figure 10. This is similar to the behaviour of polymers such as Pa 12-based semi-crystalline polymer and PETP which both increase in strength with decreasing temperature [AZO Materials, 2001], [Vettegren, V.I et al, 2005]. The only exception occurred at 25°C; this is attributed to the initial melting stages of the specimen (supported by the DSC results), which causes a reduction in brittleness, which itself is reducing the effectiveness of the Brazilian Disk test. It can also be suggested that the linear correlation is due to the solidification of the cocoa butter over time from room temperature of 20 °C with the liquid to solid transition leading to an increase in strength of the chocolate and hence the higher tensile stresses seen at lower temperatures. Once the cocoa butter has reached a 100% solid form it is thought to crystallise. This is considered as the cocoa butter has already reached solid form at -10 °C and hence may undergo further crystallisation. This is supported by the ESEM images where at room temperature the chocolate structure is polymer-like with no obvious structure as shown in Figure 11a, but at -20 °C some crystallisation is visible (Figure 11b).

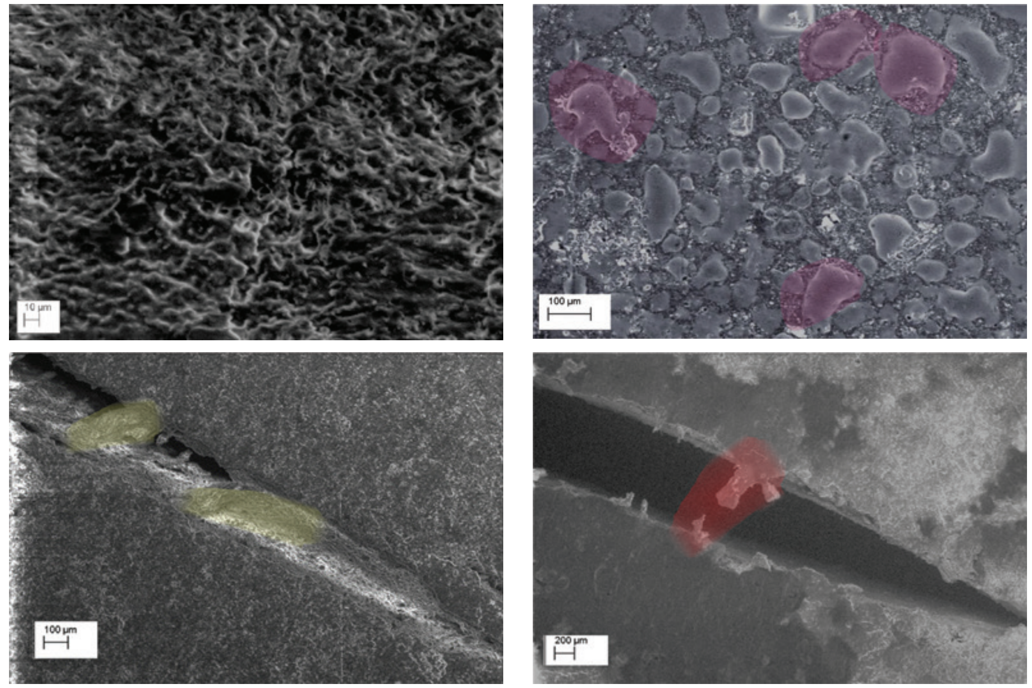

Figure 11. ESEM image of Chocolate at various temperatures. a) Room temperature ESEM image showing a typical 'messy' polymer structure. b) Chocolate at -20 °C showing a semi-crystalline structure with some uniform shaping contrasting to the polymer-like structure. c) Crack at 10 °C depicting crazing (highlighted in yellow). Crack at 10 °C depicting crazing (highlighted in yellow). d) Crack at -20 °C showing a clean break with minimal crazing (highlighted in red).

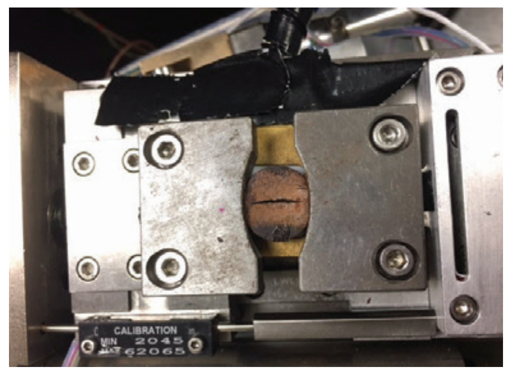

Figure 12. Brazilian Disk test chocolate specimen after cooling and cracking at -20 °C shows some discolouration.

The ESEM images also depicted crazing across the cracks, as highlighted in Figure 11c, for all Brazilian Disk tests except -20 °C. Crazing is a common phenomenon; polymers at temperatures above 80% of the glass transition temperature [Swallowe, G.M, 1999] and is associated with increased strength as it prevents complete breakage across the crack. This is due to fibrils in the chocolate being drawn out, as the chocolate yields in tension. The reason for the exception to this at -20 °C, which breaks cleanly through (Figure 11d), is possibly due to crystallisation occurring.

Furthermore, once the disk at -20 °C had undergone cooling it showed signs of discolouration due to the decrease in temperature suggesting a physical change had likely occurred as shown in Figure 12**.** In contrast the rest of the other specimens showed no noticeable change in colour after cooling. This suggests that a fundamental change occurs between -3 °C and -20 °C that greatly impacts the chocolates properties.

Other data gained from the ESEM included the propagated crack size, where the maximum and minimum width doesn't appear to be temperature dependent on a macro scale. The cracks had a maximum width of around 0.4 mm and a minimum width of 0.03 mm. It also evidenced that the cracks do not completely propagate across the length of the specimen despite appearing to do so to the naked eye; this is likely due to the plastic deformation and minor end crushing that occurs during the test.

The ESEM part of the testing procedure was vital in validating the results and ensuring the crack was propagating from the centre of the disk. It also facilitated the environment to reach the colder temperature of -20 °C, which was key to exploring the extent of crystallinity in chocolate and hence how it behaves under quasi-static loading.

4. Conclusions

The results indicate that the tensile strength of the chocolate increases as the temperature decreases. However, the ideal transport temperature to prevent breakage must be balanced with the impact on taste and texture where the surface is glossy [Machalkova, L et al, 2014]. Therefore a suitable range would be between -3 °C and no lower than -20 °C given there is minimal difference in ESEM images at -3 °C and room temperature (room temperature being the ideal storage temperature [Lindt, 2015]), but a clear difference at -20 °C. Hence, it is likely the chocolate will be able to return to its ideal structure, polymorph form V [Machalkova, L et al, 2014] at -3 °C, but possibly not at colder temperatures due to the visible change in surface properties shown in the -20 °C ESEM images. Thus, further research into the heating of chocolate from 'extreme' temperatures, such as -20 °C, may further enhance the understanding of the optimal transportation conditions to prevent breakage from impact loading whilst preserving the chocolate's ideal taste and texture.

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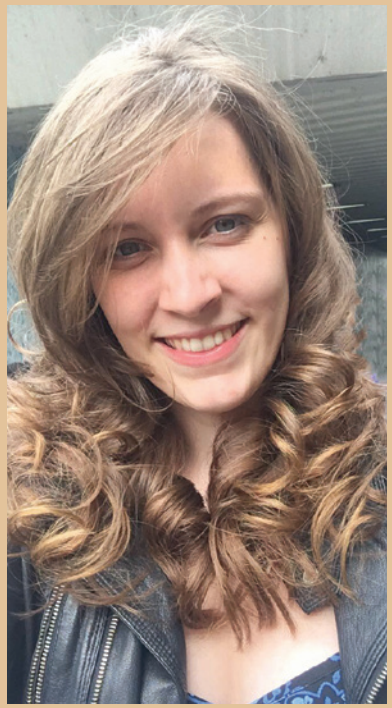
Rhiannon Heard



Rhiannon Heard obtained her Masters in Engineering at the University of Oxford in July 2017, where she was in receipt of two scholarships; The IMechE Land Rover Spen King Sustainability Award 2013 and The IET Diamond Jubilee Scholarship 2013. Rhiannon's Masters' thesis entailed research on micromechanics of pharmaceutics and she achieved first place in the Mechanical Engineering Category, The Ibex Industrial Brushes 4th year Project Mechanical Engineering Award 2017, in the annual poster competition at the University of Oxford. Upon completion of her degree Rhiannon presented her findings at the bi-annual Microscience Microscopy Congress 2017 in Manchester; for which she was in receipt of a travel bursary. This summer after receiving the Royal Microscopical Society Summer Studentship she undertook a project investigating quasi-static loading of polymers using in-situ microscopy techniques as detailed in this article. In October, Rhiannon will continue her research within microscopy when she commences her DPhil at the University of Oxford.

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