Thermal investigation of 'molten starch'

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Abstract Detailed thermal analysis studies have shown that a 'molten starch' phase is obtained during controlled heating of starch. Before the 'molten' stage, depolymerisation of starch produces lower molecular weight compounds like dextrins, oligo, di- and monosaccharides, as well as other types of compounds. These compounds should have ideal properties for plasticizing starches because of the similarities of the molecules, helping lower phase changes in collaboration with molecular weight decrease. Interestingly, it was found previously that these materials only act as adhesives in a narrow temperature range around 523 K (250 °C) (Shuttleworth et al. J Mater Chem 19(45):8589–8593, 2009). Materials were investigated using thermal and mechanical analyses of single lap joints.

Keywords Starch · Adhesives · Modulated DSC · STA

Introduction

Starch is a carbohydrate material found abundantly in food plants. It is mainly composed of essentially linear amylose—molecular weight range 1×10^5–1×10^6 g mol^{-1} and the much larger, highly branched amylopectin—molecular weight range 1×10^7–1×10^{-9} g mol^{-1} [1, 2]. These polysaccharides make up starch in varying relative mass fractions, and can differ largely dependent upon the starch source. The resultant composition has a major impact on the starch's physical properties, such as the gel formation, viscosity, solubility and the strength of films that can be formed [3, 4].

Applications of starch-based products include being used as sizing agents and binders in the textile and paper industries [5]. They also continue to be heavily used in the adhesives industry, despite the introduction of synthetic alternatives [6].

Although starch adhesives are well established, modification is often required to overcome problems, such as poor water resistance and the occurrence of mould, which are inherent to starch [7]. This is reflected in the dramatic increase in their price compared to the native unmodified material. Additives are also typically used to improve the rheological stability and stickiness (tack) of the final starch adhesive, but the properties are still too poor for adhesion of starch-to-metal surfaces.

Extensive modification and degradation of starch's molecular structure occur when granules are heated. The extent to which these changes occur depends on the temperature and time involved, and, under extreme conditions, it results in complete loss of carbohydrate character [8]. Starch materials with good cohesive and stability properties may be obtained at high temperature due to de- and repolymerisation reactions. However, decomposition also occurs at high temperatures that can convert material into char that has poor mechanical characteristics. Degradation reactions of starch initially involve depolymerisation, hydrolysis, possibly oxidation, and dehydration.

Pyrolysis of starch has attracted attention since 1913, when Bautlin historically first reported on the product yields from the decomposition of rice starch that had been heated from 373 to 773 K over a period of 7 h [9]. The decomposition of starch within this range shows two maxima in the yield of gaseous products evolved. The first at around 523 K is due to carbon dioxide and carbon

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monoxide in the ratios 2:1, respectively, and the second at approximately 673 K is due to the formation of methane and unsaturated hydrocarbons.

It has been reported that there is a temperature interval, observed during high temperature heating, where starch exists as a soft material [10]. In this mobile phase, there may be a large range of material properties such as good binding strength, better wetting ability and an enhanced surface activity. By exploiting these properties, it is expected that a greater adhesion can be achieved, with potential chemical synergy between 'molten' starch and an aluminium surface contributing further.

This article focuses on understanding the thermal processes that occur between the onset of depolymerisation and decomposition to find the optimum temperature region for applying molten starch in metal adhesion.

Experimental

To a series of aluminium plates (50 ± 0.17 mm $\times$ 15 ± 0.05 mm $\times 0.6 \pm 0.02$ mm), ~ 3 g of 5% w/v gelatinised starch as prepared by Shuttleworth et al. [11] was used to coat a 20 mm length of one end of the aluminium plates. These were then dried at 323 K (50 °C) for 2 h to leave an evenly distributed starch layer (~ 0.16 g). Two coated ends were then stacked parallel on top of each other to form a single lap adhesive joint, a 500 g metal plate load was then applied to maintain pressure whist heating. Samples were then held at 513, 525 (252 °C) and 533 K for varying periods of time to assess the level of thermal conversion on adhesive strength.

The strength of the laminated single lap adhesive bond formed between the two aluminium films was measured using an Instron 3367 Dual Column System with a cross-head speed of 5 mm min^{-1}. The test was carried out in accordance with ASTM D-3165 guidelines [12].

TGA of the starch samples was carried out on a Stanton Redcroft 625 TG/DTA using approximately 10 mg sample accurately weighed into an aluminium sample pan. An empty aluminium pan was used as reference. The sample was then heated at different heating rates to different temperatures under a nitrogen flow (60 mL min^{-1}). Samples were analysed using the dedicated software for the Stanton Redcroft 625 TG/DTA.
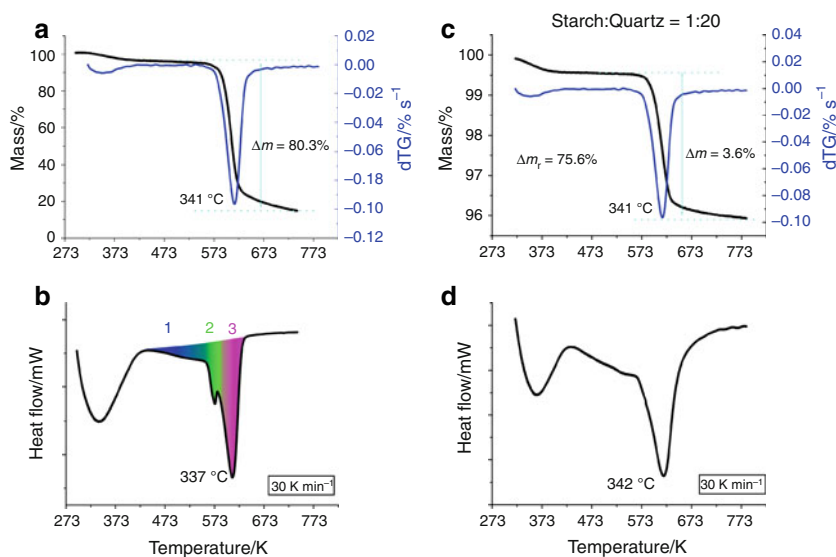
Starch samples were loaded in T zero aluminium DSC pans, sealed and analysed relative to an empty aluminium reference pan. The samples were all first equilibrated in the Modulated Differential scanning calorimeter (MDSC) cell at ambient for 10 min and then heated to 493, 503, 513, 523, and 533 K. The heating rates were 5 K min^{-1} to 453 K, 1 K min^{-1} to 473 K and 0.1 K min^{-1} in respect of upper temperature. All the samples were run with a 50 mL min^{-1} flow of nitrogen and were a sample size of approximately 3 mg. MDSC was performed using a TA Instruments model Q 2000 [13]. The calibration was carried out in the same manner as Picker and Hoag [14].

Results and discussion

Vacuum-dried starch was heated on a Stanton Redcroft STA 625 at a constant rate of 30 K min^{-1}. The results are reported in Fig. 1.

Figure 1a and b show two plots, one representing the change in mass, and the other the change in the heat flow of the material. The % mass change shows that the starch material is losing approximately 3–4% mass from the

Fig. 1 STA trace of starch heated at 30 K min^{-1}, **a** TG and dTG trace, **b** DSC trace whereas, **c** and **d** are the same but are heated in the presence of quartz in a ratio of 1:20

starting temperature to about 403 K which also corresponds to a large, broad endothermic transition in the DSC trace. This loss is probably due to residual moisture attached to the material coming off as the temperature of the environment is raised. The next event is an endothermic deviation in the heat flow base line, which is marked in Fig. 1b as region 1. This is followed by a change in mass starting around 523 K with the maximum mass change occurring at 614 K. This is where the main decomposition of the material occurs, representing approximately 80% mass loss. The DSC is interesting within this region, as there seems to be two endothermic transitions (Fig. 1b, region 2 and 3). The last occurs around 563–573 K and represents the onset of the main decomposition, and the peak of the second is found at 610 K, coinciding with the dTG peak.

Inspection of the sample after heating showed that the material had expanded in structure to produce a carbon-like foam. Foaming of the structure during heating would lead to an endothermic artefact in the energy signal that would hinder any further analysis and interpretation of the data. From previous study, it was found that region 2 was caused by the foaming of the material [10]. Region 3 correlated to the major mass loss and region 1—from the early study of Katz and others—is the start of the depolymerisation of the material [8].

Katz initially discovered this through X-ray diffraction experiments on starch pyrolysed at different stages [8]. At 453 K the diffraction patterns lost their sharpness, and also the starches became a lot more soluble in cold water, which is characteristic of the production of dextrins. The second difference Katz notice was that at 483–493 K an entirely amorphous pattern was produced, with the corresponding birefringence of the granules being destroyed. Although Katz's results concern starch samples kept at a given temperature and, which have not undergone a progressive heating (as in the previous study) [10], they nonetheless suggest that starch decomposition may be a complex process [15].

The starch samples show a colour evolution from the onset (region 1), ranging from ecru to light brown, brown, matt black, and a final black metallic hue. The samples also decrease in solubility to water as the initiation of foaming begins (region 2), indicating loss of OH groups and possible start of cross-linking. This is verified with reports suggesting that at around this temperature thermal condensation takes place between the hydroxyl groups of the starch chains to form ether segments and liberation of water molecules and other small molecular species [16]. Dehydration of neighbouring hydroxyl groups in the glucose ring has also been reported, resulting in the formation of C=C bonds or the actual breakdown of the glucose ring [17]. Aldehyde groups were formed probably at end groups

where the glucose ring opens. As to the mechanism of starch decomposition, it is probable that it proceeds via an ionic pathway through depolymerisation, and dehydration could be initiated by some sort of homolytic splitting of an hydroxyl group from the pyranose ring, which could subsequently react with an hydrogen from the surrounding area forming a water molecule [18]. A radical reaction has been ruled out, as it has been reported that only charred starch samples containing unpaired spins are observed by Electron Paramagnetic Resonance (EPR) Spectroscopy [19, 20].They postulated that this stability could be due to lipids complexed with the helical structures within the starch acting as radical scavengers. However, the high thermal stability of cassava and triticale starch suggested that the property of the starch matrix could also be involved as the stabilizing factor. This is important to ensure that thermal food production of starches is safe [19, 20].

To mitigate the effect of foaming, and prevent the occurrence of region 2 quartz was added in excess (1:20). It was postulated that this would aid the diffusion of any gas build up and analysis of the data. The results of this process can be seen in Fig. 1c and d. With the quartz mixed starch sample, there is no region 2, although the quartz has not altered the decomposition path as both the dTG and peaks in the heat flow occur at the same temperature in Fig. 1a and c and Fig. 1b and d.

Previous study has shown that as the heating rate is decreased, regions 1 and 3 shift to lower temperatures and tend to overlap each other, merging in a single signal with a maximum at 525 K for heating rates below 0.15 K min^{-1} [10]. This unique temperature, where the material resides in a molten state with an increased chemical activity and no charring opens up new possibilities for starch materials.

Using the following equation, the activation energy associated with the decomposition process (E_{act}), observed in region 3, can be calculated using the peak temperature in this region (T_{p3}) and the heating rate (β_H) applied:

$$\ln\left(\frac{RT_{p3}^2}{\beta_H}\right) = \frac{E_{act}}{R}\left(\frac{1}{T_{p3}^2}\right) + \ln\left(\frac{E_{act}}{k_0}\right)$$

where k_0 is the pre-exponential factor [21, 22] (Fig. 2).

As a good correlation is observed between the peak temperature and the heating rate, the decomposition of the molten starch is considered a simple process with high activation energy (147 kJ mol^{-1}). MDSC analysis was carried out on starch heated to 493, 503, 513, 523, and 533 K. respectively, with the trace for 523 K shown in Fig. 3.

The signal for heat flow follows the heat capacity signal until 348–373 K when it sharply increases when all further detail is lost. This increase is better evaluated using the non-reversing heat flow signal where the trace is similar
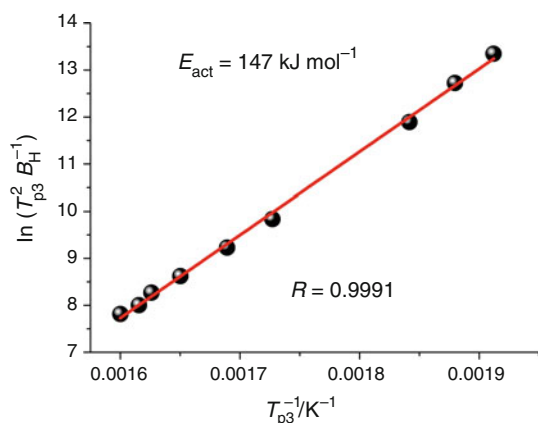
Fig. 2 Calculation of the activation energy associated with sample decomposition

Fig. 4 Reverse heat flow of starch heated to 493 K, which had previously been treated to increments between 493 and 533 K
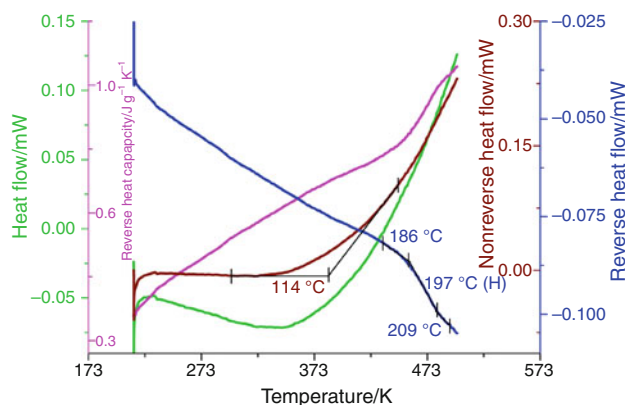

Fig. 3 MDSC trace of starch treated at 523 K, with heat flow, and both the non- and reversing heat flow and reversing heat capacity signals included

Fig. 5 Schematic of lap joint and pictures of the adhesive joint after failure

[23]. For all the samples tested, the extrapolated onset of the signal deviation occurs at a temperature of 387 ± 3 K. These data and those of Fig. 1a suggest that the cause is loss of any residual bound water. The benefits of MDSC as a technique is highlighted when evaluating the reversing heat flow signal where the sample that was pre-treated at 523 K reveals a glass transition staring at 459 K. This in the overall heat flow signal is over-shadowed with the loss of residual water masking the transition. The reversing heat flow can be seen for all the samples tested in Fig. 4.

The reverse heat flow signals for the samples pre-treated at 493 and 503 K follow heat capacity with the signal decreasing gradually with increasing temperature. However, the sample pre-treated at 513 K shows the start of an endothermic deviation in the baseline at 479 K, which decreases in temperature when heated at 523 K as discussed previously. This is indicative of a general decrease in molecular weight, possibly self-plasticisation and overall general softening of the polymer structure explaining the
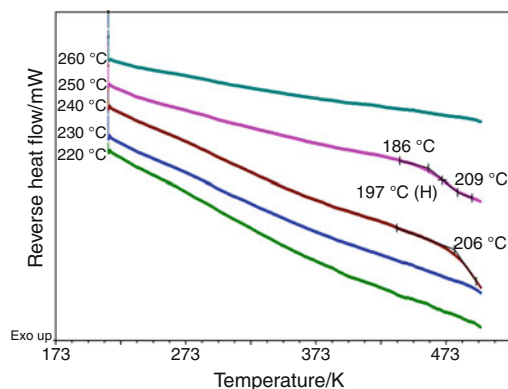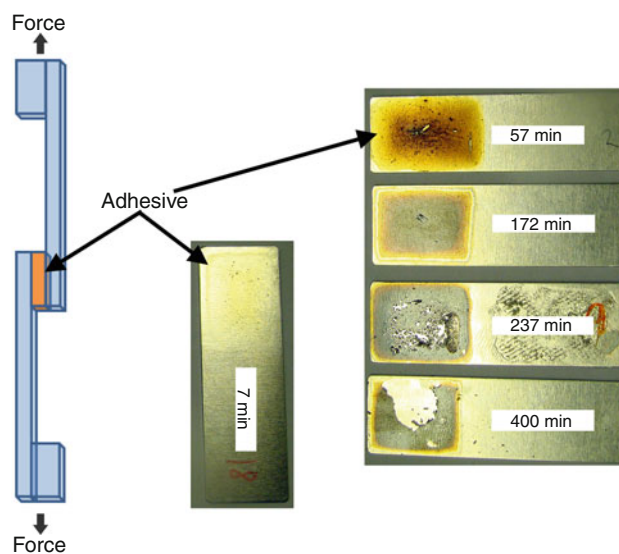
point of 525 K where the material can foam/shows molten character. Evaluation of the sample heated to 533 K shows no endothermic deviation in the sample baseline, probably due to its extensive curing and charring, and confirming the significance of the region around 523 K.

From these tests, 'molten' starch adhesives were tested for bonding aluminium as shown in Fig. 5 and within the "Experimental" section.

Bonding of the aluminium plates at 513 and 533 K showed no adhesive properties despite the cure time. However, all the samples prepared at 525 K bonded the aluminium plates, with the respective lap joints being loaded under tension and tested on a tensiometer, the results of which can be seen in Table 1 [12].

The results show that the best cure time at 525 K is at 172 min. It is expected that significant enhancement of bond strength would occur if the aluminium surface of the

Table 1 Effect of cure time 525 K (252 °C) on the average break load of the bonded single lap joint

Time at 525 K min^{-1}	Average adhesive strength/MPa
7	0
57	0.16 ± 0.02
172	0.58 ± 0.09
237	0.39 ± 0.06
400	0

plates had been pretreated to remove the oxide layer. The oxide that forms on aluminium hinders chemical bond formation to the adhesive, and possesses a weaker boundary layer in which to attain good interfacial contact between the surface and the adhesive.

Conclusions

It can be concluded that there is a narrow temperature range where 'molten starch' can be used to adhere aluminium.

At around 523 K, there is a special phase transition point at which starch decomposes without the production of carbon oxide. The polymer produced during this transition exhibits both good adhesion and cohesion properties. This material could eliminate the need for non-renewable adhesives in the adhesion of metals.

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