Salt modified starch: Sustainable, recyclable plastics

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Salt modified starch: sustainable, recyclable plastics

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The ubiquitous nature of starch makes it a tantalising basis of sustainable plastic manufacture. Extensive hydrogen bonding between chains, however, makes the plasticisation of starch difficult but this work shows that the incorporation of a simple quaternary ammonium salt can lead to a flexible plastic with mechanical properties similar to oil derived plastics. Compression-moulding produces a transparent material with mechanical strength which is similar to some polyolefin plastics. It is shown that the material can be extruded and/or compression-moulded and these processes improve further the mechanical strength of the samples. Most importantly, it is shown that these plastics are recyclable and ultimately compostable.

Introduction

Oil derived polymers have dominated material science for the past 50 years, but clearly the dwindling raw material makes the sustainability of polyolefins in their current form a significant issue. The search for biodegradable polymers from a sustainable source has largely centred on the use of polylactic acid, PLA, which is produced from starch and has found use in biomedical applications, packaging and disposable items such as cutlery and cups *etc.* However, the cost of PLA is still high when compared to petroleum based plastics due to the numerous processing steps required for its production from starch.[1]

A more sustainable and ultimately bio-inspired alternative is the use of thermoplastic starch (TPS) which is formed by the incorporation of small polar organic compounds such as water,[2] glycerol,[3] urea,[4] ethanolamine[5] and formamide[6] into a starch matrix. These compounds help to plasticise the starch by breaking the internal hydrogen bonding between the glucose rings in the starch, decreasing its crystallinity and making the structure more amorphous.[7] In nature, water fulfils this role, however, the ingress or egress of water is very dependent upon the temperature and humidity. For synthetic TPS the modifier is usually incorporated into the structure by using extrusion,[1] compression-moulding,[8] casting[9] or melt processing.[10]

The physical and mechanical properties of TPS vary significantly with amylose–amylopectin content, molecular weight, modifiers, water content and processing technique. Here we report the use of choline chloride (ChCl) as a plasticising agent with urea. The salt helps to break up the intramolecular hydrogen bonding in starch and acts as a bridge between the urea and sugar moieties. In addition, when ChCl and urea are mixed together, a significant depression in melting point can be seen.[11] The melting point of urea is 132–135 °C and ChCl decomposes

at 302–305 °C.[12] Both of these are close to or greater than the gelation temperature for starch which is typically between 80 and 160 °C. This creates significant difficulties in relation to efficient mixing of the modifier into the starch and limits the methods that can be employed for its plasticisation. It has, however, been shown that a 2 : 1 molar ratio of urea to ChCl produces a liquid with a freezing point of 12 °C so the mixture can be blended below the gelation temperature and processed after this with much greater ease.[12] In addition, for high melting solids such as urea, a volatile liquid such as water is often added to dissolve the modifier, and subsequently evaporated off through casting to form a film causing a more protracted, less energy efficient process.[7] Ionic liquids have been used previously as solvents for the modification of carbohydrates although the salt has usually been removed at the end of the process.[11,13] Biswas *et al.* acylated starch using DESs and showed that starch is soluble but could form a gel at high enough concentration.[14] Zdanowicz and Spychaj have recently used DESs as gelling agents for starch.[15] Ramesh *et al*.[16] added starch and lithium bis(trifluoromethanesulfonyl)imide to DESs to produce a polymer electrolyte. In the current study it is shown that amorphous transparent plastics can be produced using salts as modifying agents and the novelty of this approach is that starch is the major component and the benign salt is a minor component and is used as a plasticiser rather than a solvent. The effect of different processing techniques is also shown to significantly affect the properties.

Methods

Corn starch (Sigma Aldrich) was dried in an oven for 24 h at 70 °C before use. Urea and choline chloride (both Sigma Aldrich >99%) were used as received. The starch, urea and choline chloride were mixed in the appropriate amounts using pestle and mortar. The mixture was then placed in oven at 70 °C for one hour. Subsequently, it was then placed between two

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copper plates lined with a silicone sheet and with a 2 mm copper separator with a 10 cm square aperture. The sandwich was then placed in a hydraulic press and a force of 100 kN was applied to the sample for 10 min at 140 °C. The sample was then cooled back to room temperature in 5 min in the press with the force still applied. Differential scanning calorimetry was carried out using a Mettler Toledo DSC1 STARe system. Extrusion was carried out using a Prism TSE-24-TC co-rotating twin screw (20 L/D) extruder with a Prism volumetric feeder and an air swept face-cut pelletising system. The extruder has 5 temperature controlled zones; the first was held at 80 °C and the other 4 were maintained at 120 °C. The feed zone was maintained at 15 °C with a water cooler. The screw speed was set to approximately 120 rpm, at which the die pressure was ≈20 bar. The air swept face-cut pelletising system's blades were set at 95 rpm with only one blade set-up to cut.

Quartz crystal microbalance experiments were performed on AT-cut 10 MHz quartz resonators with unpolished Au electrodes (0.23 cm^{-2}). All experiments were carried out at a frequency range close to the resonance frequency of the quartz crystal using a Hewlett-Packard HP8751A network analyser operating in reflectance mode utilising a HP87512A transmission/reflectance test unit. Surface analysis was carried out using scanning electron microscopy (Philips XL30 ESEM). The tensile testing of the dog-bone shaped samples was carried out using an Instron 3343 tensile apparatus (Instron Ltd, Assembled, USA) with a load cell of 500 N. The material strain and stress were controlled by Instron Bluehill 2 software. Average values were taken from 6 samples.

Results

Starch samples were mixed with urea and choline chloride in a 2.16 : 1 : 1.16 weight ratio. On mixing, the slurry was placed in a brass former with a stainless steel plug at both ends and placed in an oven at 150 °C for 30 min. On cooling, the result was a soft, flexible, opaque, cheese-like substance. The same was repeated for a starch and urea mixture in a 1 : 1 weight ratio. Fig. 1 shows a photograph of the salt modified starch sample together with a series of SEM images which show the contrast between the granular structure of the dried corn starch (b) and the corresponding gelled samples using just urea (c) and urea and choline chloride (d). The starch can be clearly seen as granules of approximate size 9.8 μm in Fig. 1(b). However, on gelation the granular structure is partially absent from the urea

modified material (c) but totally absent from the salt modified starch (d). This shows that the salt, as predicted acts as an improved plasticiser for starch.

The process of this gelation has been investigated in two differing ways; differential scanning calorimetry (DSC) and the quartz crystal microbalance (QCM). DSC is a useful technique for studying the gelation temperature (T_g) of starch as the programmed temperature ramp employed in DSC enables the identification of the temperature at which a phase transition occurs. Fig. 2(a) and (b) show the differential scanning thermograms for the sample shown in Fig. 1 produced from a starch, urea and choline chloride mixture in a 2.16 : 1 : 1.16 weight ratio mixture. The DSC trace when the ungelled sample is heated from 0 to 145 °C shows a transition at 97 °C which corresponds to the gelation of the starch by the ChCl–urea mixture.

The shape of the calorimetry thermogram shown in Fig. 2(a) is different compared to examples of starch gelation from the literature which commonly show an endotherm—thought to be due to the melting of the crystalline regions within the starch.[17,18] The trace in Fig. 2(a) resembles much more closely that of a glass transition with the exception that this is an irreversible process indicating that a gelation of the starch has occurred. Once the sample has been gelled a thermoplastic material is formed. The DSC trace Fig. 2(b) shows the scan from −100 to 145 °C of the sample resulting from the gelation in Fig. 2(a) showing a glass transition with a midpoint at −16 °C. This value is rather low when compared to literature values for the glass transition of various TPS systems.[3–6] However, this is likely due to the high modifier concentration in this case (50 wt%). A subsequent sample containing 70% wt corn starch and 30% wt of the 2 : 1 molar ChCl : urea mixture the gelation point was slightly lower at 91 °C but the glass transition temperature was significantly higher at 24 °C. This is a value which is comparable to those found for more conventional starch : glycerol 70 : 30% wt mixtures.[19] However, direct comparisons with other literature values are difficult as different starch sources are generally used. Materials can be processed *via* a number of different ways to form its respective TPS and moisture content can vary significantly from anything between 0 and 20%.[1]

Quartz crystal microbalance (QCM) techniques and acoustic impedance spectroscopy have been used extensively to probe the viscoelastic effects in thin-film polymers.[20] Here we have used acoustic impedance QCM methods to investigate the physical transformations and consequential mechanical viscoelastic losses associated with the gelation–plasticisation of the starch. The
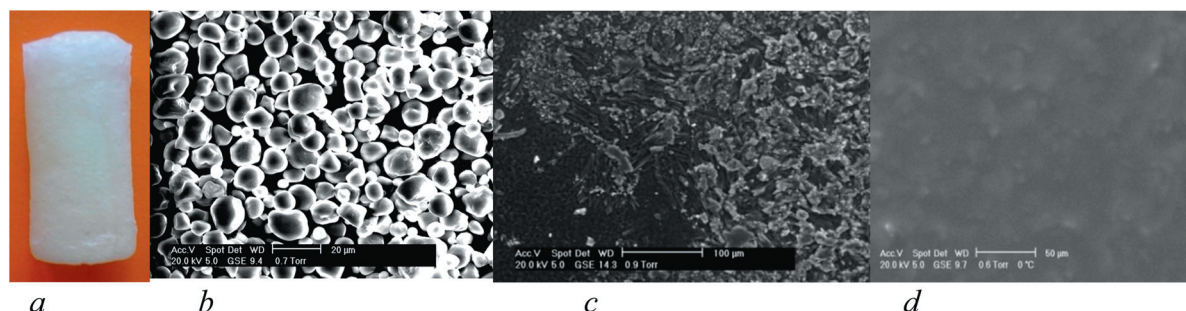

a   *b*   *c*   *d*

Fig. 1 Photograph of salt modified starch sample (a) SEM images of dry corn starch (b), corn starch plasticised with just urea (c) and corn starch plasticised with ChCl and urea (d).
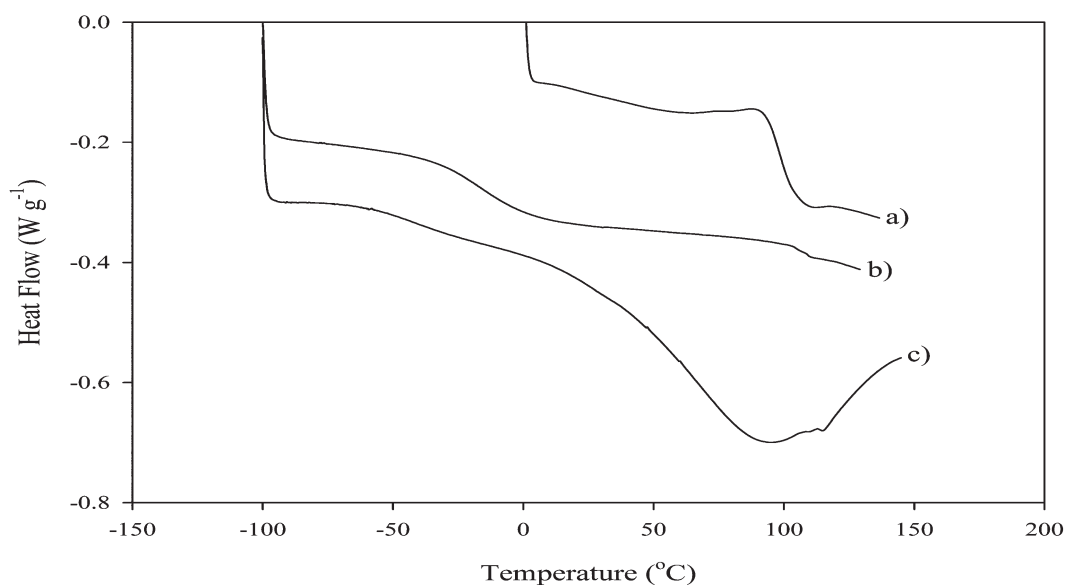
Fig. 2 Differential scanning thermogram of a corn starch, urea and ChCl mixture scanned from 0 to 145 °C at 10 °C min^{-1} (a) with the resultant sample then cooled to −100 °C then heated to 145 °C at 10 °C min^{-1} (b) and finally with extruded starch, urea and ChCl sample cooled to −100 °C then heated to 145 °C at 10 °C min^{-1} (c).

acoustic impedance spectrum of the resonant crystal is defined by the representation of electrical admittance, U/mS, as a function of frequency, f/MHz, where $U = 1/Z$ and Z is the a.c. electrical impedance of the resonant circuit containing the crystal. Changes in the position (peak frequency, f_o) and shape of the resonance resulting from contact are correlated with changes in coupled mass and viscoelastic mechanical losses associated with dissipation of mechanical energy from the shear mode resonance of the crystal into the viscoelastic material adjacent to it. To our knowledge this is the first time acoustic impedance QCM methods have been applied to gelation studies of starch based polymers. In a representative experiment approximately 0.5 cm^3 of slurry comprising the mixture of corn starch, urea and choline chloride, was added to a cell containing the resonant quartz crystal held at 140 °C such that the surface of the crystal was completely covered. The acoustic impedance spectrum, $U(f)$, was then continually recorded (*ca.* one spectrum every 4–5 s) over a frequency band width encompassing the crystal resonance for a total period of *ca.* 1300 s during which the slurry had solidified. A sample of the full data set is presented as a function of time in Fig. 3(a).

At the start of the experiment, shortly after the sample was placed on the crystal, the resonance line shape was very sharp and well defined having a centre frequency, f_o = 9.975 MHz. However, the line shape rapidly becomes very much broader and shifts to lower frequencies. This rapid broadening is consistent with additional mechanical loading of the crystal by a thick viscoelastic layer as the slurry is transformed. The centre frequencies, f_o, for all spectra were acquired *via* data fitting routines (described in detail elsewhere)[21,22] and are presented separately as a function of time in Fig. 3(b). Here it can be seen that initially the value of f_o rises immediately after addition of the slurry to the crystal to a maximum of f_o = 9.978 MHz at t = 50 s. This can be easily explained because the slurry is necessarily added to the heated cell at a lower temperature (typically r.t.)

hence initial heating of the slurry on contact with the cell reduces the local viscosity resulting in an increase in resonant frequency. Once thermal equilibrium is reached, the value of f_o becomes progressively smaller, reaching a minimum of 9.967 MHz at an elapsed time of *ca.* t = 130s. This downward trend in f_o can be accounted for in the following way; as the sample gelation progresses, $50 < t < 130$ s, the material becomes more rigid resulting in an increase of coupled mass to the crystal. The subsequent upward trend in f_o during the time period, $130 < t < 230$ s, probably arises because of heat dissipation as a result of continued sample gelation since this process is exothermic, Fig. 2. As gelation progresses and thermal equilibrium is approached, the material becomes progressively stiffer and the subsequent trend in f_o is continually downward.

Trends in f_o during the gelation process are also mirrored by trends in the peak intensity, U_o, data, Fig. 3(b). Here the maximum intensity, U_o, corresponds to the maximum in frequency, f_o as might be expected at the point of minimum viscosity and mechanical loss. However, the following minimum and subsequent maximum seen in the $f_o(t)$ data around $130 < t < 230$ s are much less pronounced in the $U_o(t)$ trace. This can be explained in terms of a travelling reaction front in the gelation process moving away from the surface of the crystal with time. In this case the composition of the gelling material is relatively constant behind (crystal side) the travelling front, resulting in a value of U_o that does not change much with time, but as the front travels away from the crystal, the gelled layer becomes thicker and the coupled mass is increased, resulting in a correlated frequency response. Also the peak resonance shape can be quantified in terms of the Q-factor, where $Q = (f_o/w)$ and w/Hz, is the half-height full-width of the resonant line. The Q-factor data, $Q(t)$, for the fitted acoustic impedance spectra are presented in Fig. 3(c) with the $U_o(t)$ data, Fig. 3(b), overlaid for clarity. This demonstrates that the initial sharpening of the resonance line is accompanied by a narrowing of the line (increase in Q)
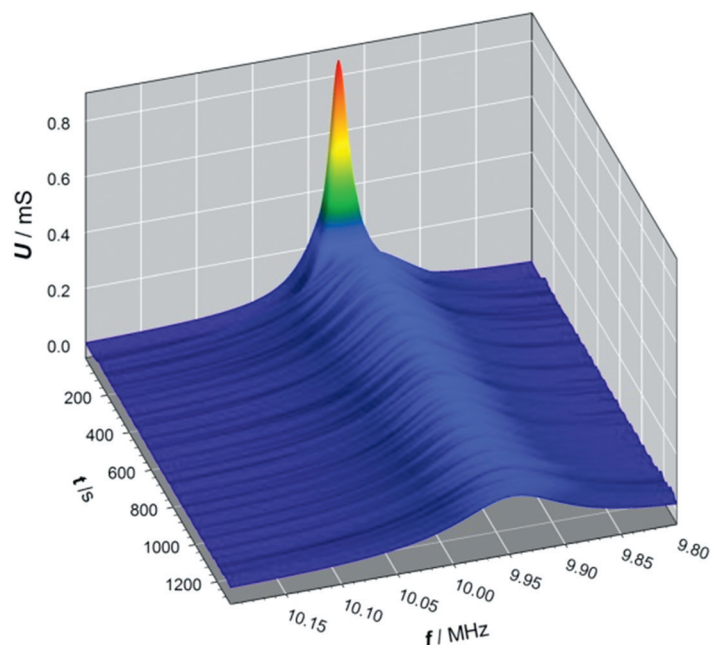
(a)
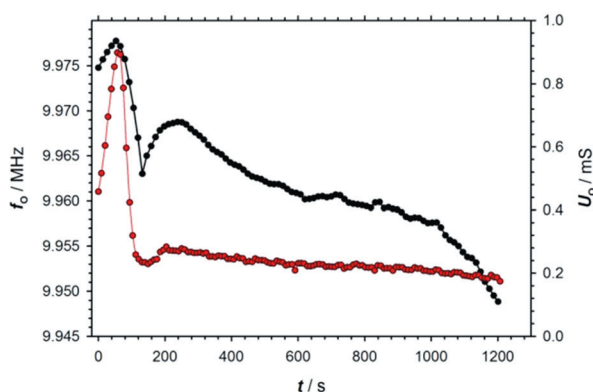
(b)
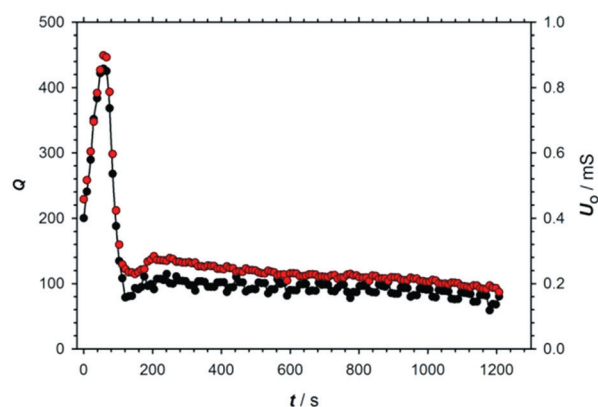
(c)

Fig. 3 Acoustic impedance data from QCM experiment for a starch, urea and choline chloride mixture in a 2.16 : 1 : 1.16 weight ratio held at 140 °C; (a) admittance spectra $U(f)$ presented as a function of time (101 spectra), (b) peak resonant frequency values, f_o, (black) and peak intensity values, U_o (red), derived from fitting of the spectra in Fig. 3(a), (c) Q-factor data (black) overlaid with U_o (red) data (Fig. 3(b)).

and subsequent attenuation is synchronised with concomitant line-broadening.

The viscosity of the fluid adjacent to a QCM crystal can be estimated from the Kanazawa equation (eqn (1)) where Δf is the difference in frequency between the resonance of the crystal in air and immersed in the viscous medium, f_0 is the fundamental frequency of the crystal resonance, in air, ρ_q and ρ_L are the respective densities of quartz and the liquid phase and μ_q is the shear modulus of quartz.[23] This can be easily rearranged to give the viscosity of the liquid phase, η_L, eqn (2).

$$\Delta f = -f_0^{3/2}\sqrt{\left(\frac{\rho_L\eta_L}{\pi\rho_q\mu_q}\right)} \qquad (1)$$

$$\eta_L = \left(\frac{\Delta f^2}{f_0^\varepsilon \rho_L}\right)\pi\rho_q\eta_q \qquad (2)$$

Using this method, the viscosity of the initial slurry ($t = 0$ s) was determined as 105 cP, this falling to a value of 80 cP at $t = 50$ s, corresponding to the peak in f_o. The viscosity subsequently increased to a value of 236 cP at $t = 130$ s during initial gelation and at the end of the experiment had reached a value of 464 cP. This final value is somewhat smaller than might be expected for a viscoelastic material, however, the shear mode acoustic wave penetrates only a layer of material adjacent to the crystal surface of the order of 10–20 µm thick. Consequently, the physical properties of this near-surface layer may be somewhat different to those of the bulk, particularly as the material continues to gel

and harden. For example, trapped liquid close to the surface as well as variations in composition could lead to a decrease in coupled mass or mechanical losses resulting in a calculated viscosity that is numerically lower than that expected for the bulk.

Interestingly, due to the inclusion of the choline chloride salt in the plasticising mixture, these samples are conducting. The conductivity was measured from the impedance spectrum across a thin film of the sample (approx 1.5 mm) sandwiched between two 20×40 mm nickel plates. The conductivity was found to be 2.18×10^{-7} S cm^{-1}. The use of starch for the generation of conducting polymer electrolytes is not new, there have been examples where a salt is extruded directly with the native starch[24] as well as examples where a salt has been added to other plasticisers (such as LiClO$_4$ in glycerol for example),[25] however, there have been very few examples where the salt has been integrated into the plasticizing mixture, such as the case here.[26]

The sample in Fig. 1a is opaque and it is our postulation that this occurs due to crystalline regions still being present within the sample. The observation that these samples are conducting shows that at least some of the ions included in the plasticiser mixture are free moving within the sample, thus suggesting that not all of the plasticiser has been used to plasticize the starch.

In addition to carrying out the starch gelation under ambient pressure, compression-moulding has also been employed. It was found experimentally that less plasticiser was required so starch, urea and choline chloride mixture in a 5.05 : 1 : 1.16 weight ratio mixture was used.

The samples produced from the compression-moulding were considerably different from those that were produced under ambient pressure. They were transparent, as shown in Fig. 4, which is likely due to the increased pressure causing a greater penetration of the plasticisers into the starch structure. The salt modified starch was totally transparent whereas that with just urea was still largely opaque showing again that the salt is better at plasticising the starch. In addition, these samples were found to be non-conducting showing the reduced mobility of the ions within the sample, again indicating better inclusion of the plasticisers into the starch granules.

After ageing the sample for 16 h at approximately 20 °C, the mechanical properties of the pressed samples were investigated with the results shown in Table 1. Due to the non-linear shape of

the strain–strain plot the modulus reported here is the chordal modulus between 1 and 1.5 N. This calculation determines the slope of the stress–strain curve between two specified points on the curve and constructs a straight line between specified lower and upper bounds and was chosen in preference to Young's modulus which relies on measuring the initial linear portion of a stress–strain curve. This is a standard method for polymer analysis. The modulus of the compression-moulded sample is significantly higher than that obtained from the QCM experiment shown above in Fig. 3. This shows that the compression process helps to modify the structure of the material. The non-compressed sample is opaque showing that it contains a significant amount of crystalline regions. The compressed sample is transparent showing that it consists of largely amorphous polymer.

As a control sample, an analogous material was made through compression-moulding incorporating urea into the material as opposed to the choline chloride–urea mixture that was used previously. This was also found to plasticise the starch very effectively producing a transparent sample that looked very similar to that in Fig. 4(a). However, on formation, the material readily changed from partially transparent to opaque as shown in Fig. 4 (b). SEM analysis showed the presence of crystalline regions which was attributed to the recrystallization of urea. This decorative effect also manifests itself in the mechanical properties: whereas the fresh material has similar properties to that of the urea and ChCl sample the sample quickly becomes very brittle

Table 1 Modulus, tensile strength and elongation at break of sample of 5.05 : 1 : 1.16 starch : urea : choline chloride compression-moulded at 100 kN and 150 °C for 10 min prior to cooling for 10 min under 100 kN. Starch : urea 7 : 3 by weight under same forming conditions

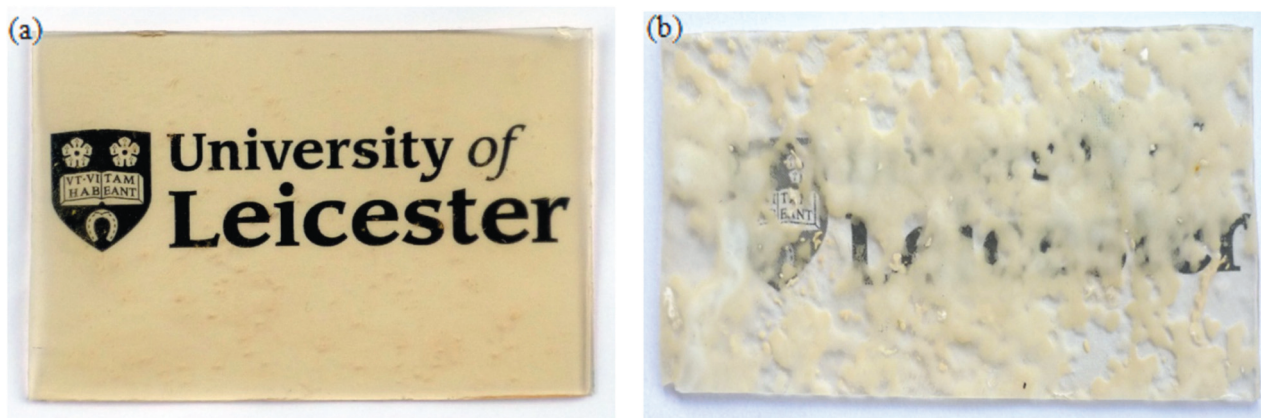| Composition/wt ratio	Modulus/ MPa	Tensile strength/ MPa	Elongation at break/%
Starch : urea 7 : 3	2.49 (±1.01)	1.19 (±0.22)	104.9 (±12.7)
Starch : urea : ChCl 5.05 : 1 : 1.16	238.6 (±5.2)	5.46 (±0.93)	19.3 (±1.55)
Starch : urea : ChCl 5.05 : 1 : 1.16 (extruded)	550.6 (±18.6)	12.00 (±1.10)	41.3 (±4.16)
Low density polyethylene	200–400	8–12	600

Fig. 4 Transparent sample prepared from compression-moulding of a 5.05 : 1 : 1.16 mixture of starch, urea and ChCl (a) and the sample prepared with corn starch : urea 7 : 3 ratio by weight (b).
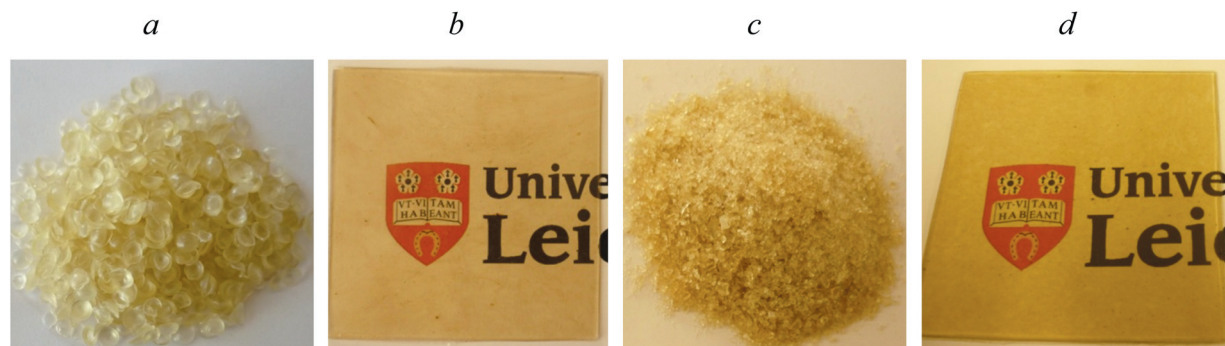
Fig. 5 Starch extruded with ChCl and urea as a modifier (a) compression-moulded (b) reground (c) then remoulded (d).

showing very little strength after a period of one week. The choline chloride–urea samples have remained amorphous for >6 months.

Table 1 shows that improved homogenisation of the starch–modifier mixture leads to significantly improved ultimate tensile strength for the salt modified starch. The extruded material is similar in strength and modulus to typical values for high density polyethylene. It should however be noted that it is significantly less ductile than HDPE. Fig. 5 shows some pellets of salt modified starch formed after extrusion together with a sheet formed by compression-moulding the pellets. Fig. 5c shows the sheet in Fig. 5b ground into a powder and Fig. 5d shows a sheet formed from that powder. This demonstrates that the salt modified starch is remouldable, recyclable and loses very little of its original transparency. Since all the components are compostable, it can be seen that these materials also pose very low chronic eco-toxicity threat unlike current plastics.

One of the key limitations of thermoplastic starch is its susceptibility to moisture absorbance. While it may be envisaged that the incorporation of a salt may make the material more hygroscopic in practice this was not found to be the case. A series of samples were made and left in 50% humidity and 20 °C for up to 6 days. Comparable samples were coated with polylactic acid to prevent moisture absorbance. The uncoated samples retained approximately the same weight over a 7 day period (±0.5 wt %) and the samples also retained a similar ultimate tensile strength (±12%) over the same period as the fresh sample (2.71 MPa). This was the same for the PLA coated samples and these did not vary by more than experimental error (0.2 MPa) over the period of the experiment.

Conclusions

This work has shown that the incorporation of a quaternary ammonium halide with urea into starch leads to a stronger, more flexible thermoplastic than samples containing only urea. The initial gelation process is found to be relatively rapid using quartz crystal microbalance. Simple heating of the ingredients led to a white opaque sample but compression-moulding produced a transparent sheet with markedly different properties. The compression-moulded samples have been shown to be recyclable, losing little of their original properties. Extrusion of the ingredients further improved the samples and it was shown that the materials were less susceptible to the absorption of water from the atmosphere than materials that just use urea as a modifier.

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