Functionalising cellulose waste as a replacer for starch, as a functional food ingredient

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Introduction

Future projections predict a challenge to feed over 9 billion people by 2050. As a result, it is essential we begin to produce food more sustainably by reducing food waste and increase our recovery of novel ingredients from this waste. Cellulose is the most abundant polymer, naturally contained within the plant cell wall with hemicellulose, pectin and lignin. Modification of cellulose via ball milling and fibrillation from the native polymorph 1 to polymorph 2 in pea plant waste could potentially be optimised, as a functional food ingredient instead of starch.

Materials and methods

Pea plant biomass material
Pea pod, vine, stem and leaves (biomass) collected from a farm in East Yorkshire. Processing by juicing using an Anndy TD-1002 (Anndy producers, China).

Lyocell material
Commercially regenerated cellulose (Lenzing, Austria).

Ball mill processing
Pea plant was dried for 24 hours at 105°C. 0.5g of dried pea plant were ball milled using a planetary micro mill pulverisette 7 (Fritsch GmbH, Germany) at 600rpm with 10 minutes of milling then 10 minutes of pause for various milling times. Each Zirconium oxide pot contained 6 zirconium oxide balls with a diameters of 10mm.

Microscopy
An optical microscope (EVOS f1, AMG, Washington, USA) for light microscope images of the ball milled samples before rehydration. A polarized light Microscope (Olympus BX61, USA) was used for polarized light.

Rehydration of ball milled material
Rehydration of ball milled particles (1 g) were mixed with 14, 9 and 4mls of water respectively. Stir mixed for 4 hours using a magnetic flee on a magnetic stirrer (Fisher scientific, United kingdom). These were compared to the same weight of ball milled particles, but rehydrated in 99mls of water by hand mixing the sample, then using a Rotavapor 11 at -1°C on a rotating setting of 4 (Buchi Labortechnik AG, Switzerland) until the required evaporation of water had occurred, to equate to the same volume.

Colloid mill
Fryma MZ50 toothed colloid mill (Winkworth machinery ltd, UK) at a rate of 3350 rpm.

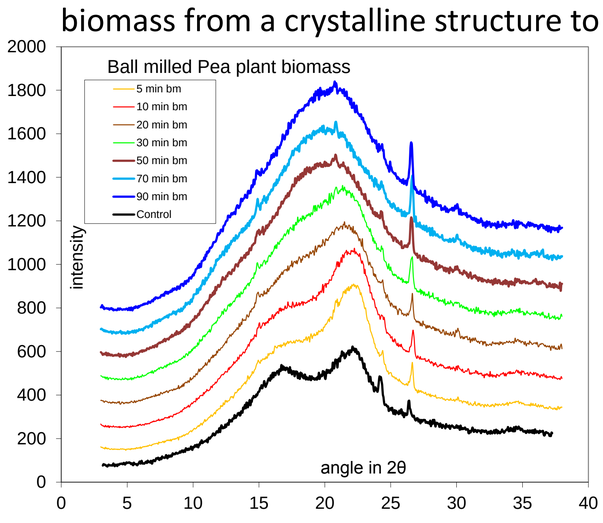
Wide angle X-ray diffraction
X-ray measurements for determining crystallinity were carried out using a Bruker D5005 (Bruker AXS, United Kingdom). Using a start angle of 2 $^{\theta}$, a finishing angle of 38$^{\theta}$ and a step angle of 0.05$^{\theta}$. With recording times every 2.5 seconds and a spin rotation of 60 rpm. Total acquisition time for each sample was 40 minutes.

Solid state cross polarization magic angle spinning Nuclear Magnetic Resonance
Solid state CP-MAS NMR were carried out on a Bruker (Karlsruhe, Germany) Avance 600 NMR spectrometer with narrow bore magnet and 4mm triple resonance probe. Samples measured between 5-7% moisture content operating at a decoupler power of 50 MHz with a contact time of 2 ms and a 2s recycled delay. Including, a 10s dwell time, a sweep width of 331ppm (parts per million). Finally, the number of scans recorded were 8192 and chemical shifts were referenced to ^{13}C.

Results and Discussion

Ball milled pea plant biomass

Figure 1 depicts the results from wide angle x-ray diffraction of ball milled pea plant material at varying milling times, which determine the amount of crystallinity within the sample. Ball milled pea plant biomass became amorphous within 50 minutes of ball milling according to x-ray diffraction. Therefore showing that ball milling is an effective method of changing the cellulose forms of pea plant biomass from a crystalline structure to an amorphous one.



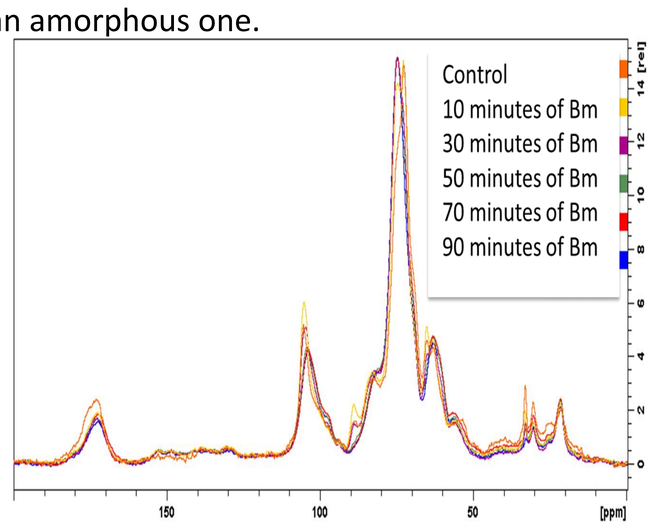


Figure 1: X-ray diffraction on varying ball milled times for pea plant biomass.

Figure 2: solid state CP-MAS NMR on varying ball milled times for pea plant biomass.

Figure 2 shows the results of solid state CP-MAS NMR on ball milled pea plant biomass at varying milling times, which also helps to quantify the amount of crystallinity within a sample but additionally aids to characterise chemical interactions ongoing within a sample. The analysis showed that ball milled pea plant biomass became amorphous within 50 minutes of ball milling. This supports results from the X-ray diffraction. However, the NMR did show complicated evaluation as there are contributions from hemicellulose, lignin and pectin. Further evaluation of the data will reveal the impact of ball milling on their functionalisation.

The figures 3a. and 3b. depict polarised light microscopy of rehydrated stir mix and rotary evaporated amorphous ball milled samples (10% moisture). These show that once the samples are rehydrated that some of the sample recrystalises, confirmed by x-ray diffraction.

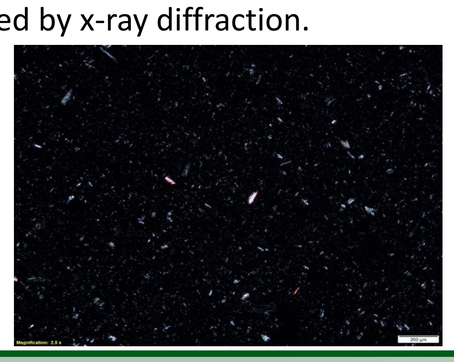
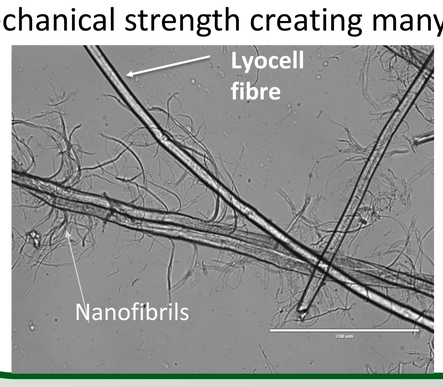


Figure 3a: Rehydrated to 10% stir mixed ball milled pea plant biomass.

Figure 3b: Rehydrated to 10% rotary evaporated ball milled pea plant biomass.

Fibrillation

Figures 4a. and b. show the effects of using a colloid mill on both Lyocell fibres and Pea plant biomass fibres. Such processing clearly fibrillates Lycocell fibres, whereas modified processing is required to fibrillate the more complex pea fibres. This means that they produce a high surface area, with low density and high mechanical strength creating many potential applications as binders, filaments and textural agents.



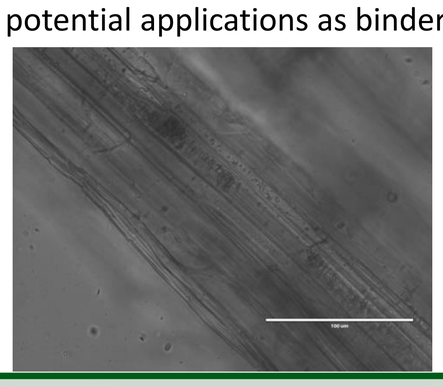


Fig 4a: Light microscopy of fibrillated Lyocell fibres, processed for 2 minutes.

Fig 4b: Pea plant fibres not fibrillated.

Conclusions and Outlook

- We have shown that pea biomass fibre material within 50 minutes of ball milling has become amorphous, this is supported by NMR. We have also shown that once the ball milled amorphous material is rehydrated it then recrystalises. The colloid mill is currently ineffective method in creating fibrillated pea plant fibres but was effective for Lyocell fibres.
- Our future work will involve further investigation into mechanical methods of fibrillating pea plant biomass fibres, comparing their rheological properties for application as a functional food ingredient.

References :
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