Thermoplastic Starch Reinforced With Cellulose

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Polymers derived from petrochemical sources are extremely widely used due to their excellent mechanical properties and ease of processing. There are however environmental concerns over their use including resource depletion, energy consumption in manufacture and end-of-life disposal.

In reaction to these concerns, biodegradable polymers and polymers from renewable sources are being sought. Starch can be processed into a plastic which fulfils both of these criteria and has properties similar to conventional plastics which allow it to be processed using existing equipment.

In its raw state, starch consists of carbohydrate polymers bound together in small crystallites[1]. The application of heat and/or shear in the presence of an appropriate plasticiser such as water, glycerol, ethylene glycol or glucose can cause the polymer chains to unravel and interpenetrate forming a viscous, amorphous mass. At high starch solids the result, generally known as thermoplastic starch (TPS), readily melts and flows allowing it to be extruded and moulded.

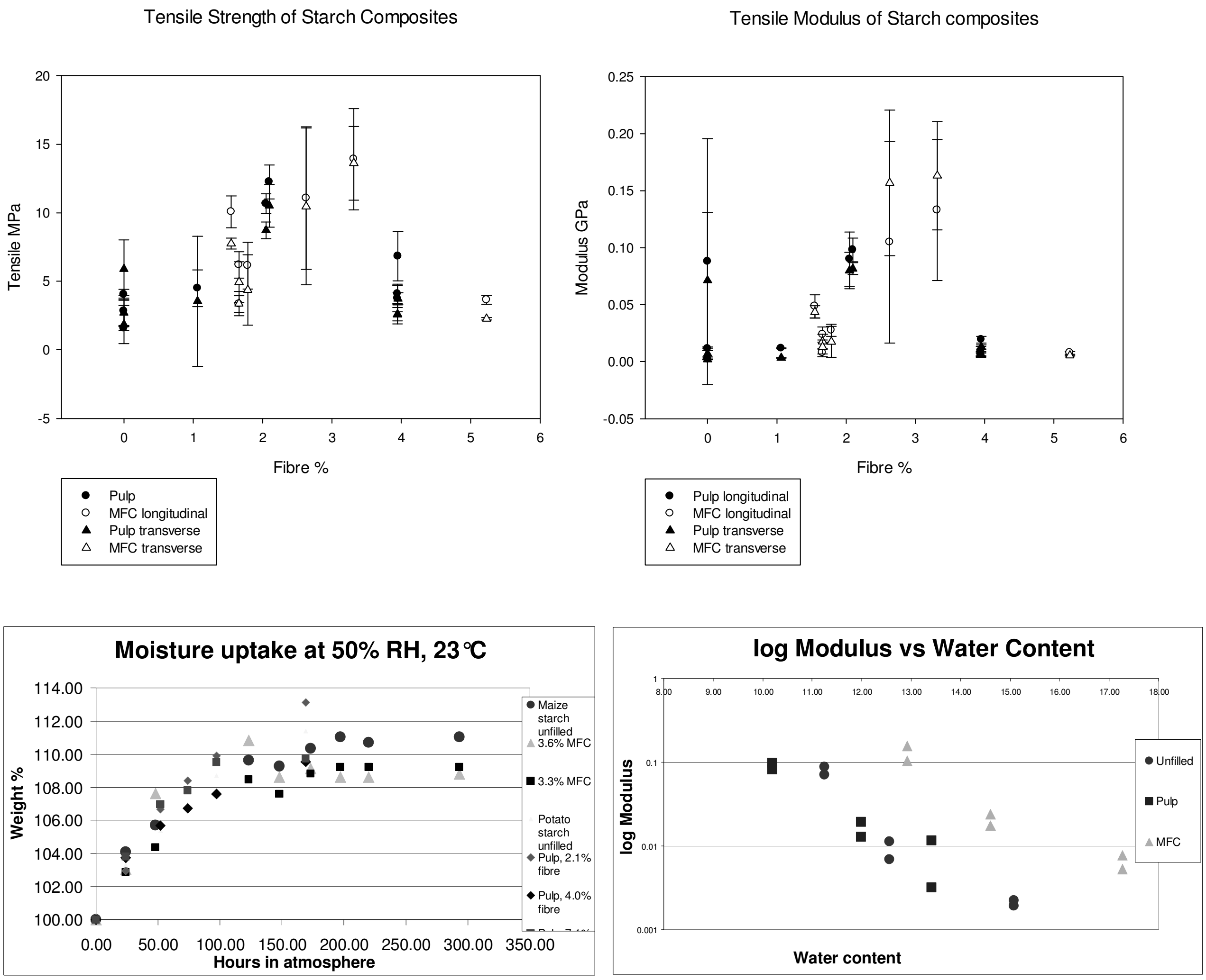
Compared to conventional polymers, TPS has poor mechanical properties. Its other disadvantage is that it is hygroscopic and its mechanical properties are sensitive to moisture. It was hypothesised that the inclusion of fibrous fillers would improve the strength of thermoplastic starch (TPS) and that hydrophilic fillers which are incompatible with conventional polymers could be used for this purpose.

Due to the hydrophilic character of both components, cellulose fibres may be expected to bind well with and reinforce a TPS matrix. Wood pulp, microcrystalline cellulose[2] and other cellulose fibres[3,4] have been found by other groups to have a significant reinforcing effect on TPS[5]. The aim of the current work is to compare the reinforcing effect of microfibrillated cellulose (MFC) with equivalent unprocessed wood pulp and with literature values. It was also hoped that since MFC absorbs water very slowly on its own, as a filler it might reduce the water sensitivity of TPS.

A formulation and process were developed involving the use of a two-roll mill and press to shear and heat the starch and form it into sheets. A transparent plastic was formed which was found to be hygroscopic, increasing in mass by 10% on conditioning at 50% relative humidity.

Composites were made using both unrefined pulp and microfibrillated cellulose (MFC). In all cases some reinforcing effect was found for the fillers, however there was not much difference between them . The samples were found to degrade over an extended conditioning period, which could be due to retrogradation - the rearrangement of molecules back into crystallites.

Water content of the samples after conditioning was measured by thermogravimetric analysis. There was a correlation between water released on heating with both tensile strength and modulus independent of fibre content, indicating that mechanical properties of TPS are very sensitive to the amount of water contained in them, that this property is challenging to control accurately even with careful conditioning and that MFC and pulp fillers make little difference to the water sensitivity.



Clockwise: Tensile Strength vs filler content, Young's modulus vs filler content, modulus vs mass released on heating to 170°C, mass increase on conditioning at 50% RH

References

(1) Parker, R.; Ring, S. G. *Journal of Cereal Science* **2001**, *34*, 1–17.

(2) Orts, W. J.; Shey, J.; Imam, S. H.; Glenn, G. M.; Guttman, M. E.; Revol, J.-F. *Journal of Polymers and the Environment* **2005**, *13*, 301–306.

(3) Kaushik, A.; Singh, M.; Verma, G. *Carbohydrate Polymers* **2010**, *82*, 337–345.

(4) Martins, I. M. G.; Magina, S. P.; Oliveira, L.; Freire, C. S. R.; Silvestre, A. J. D.; Neto, C. P.; Gandini, A. *Composites Science and Technology* **2009**, *69*, 2163–2168.

(5) Avérous, L.; Halley, P. J. *Biofuels, Bioproducts and Biorefining* **2009**, *3*, 329–343.

(6) Sandhu, K. S.; Singh, N. *Food Chemistry* **2007**, *101*, 1499–1507.

(7) Curvelo, A. A. .; de Carvalho, A. J. .; Agnelli, J. A. . *Carbohydrate Polymers* **2001**, *45*, 183–188.

(8) Ma, X.; Chang, P. R.; Yu, J. *Carbohydrate Polymers* **2008**, *72*, 369–375.