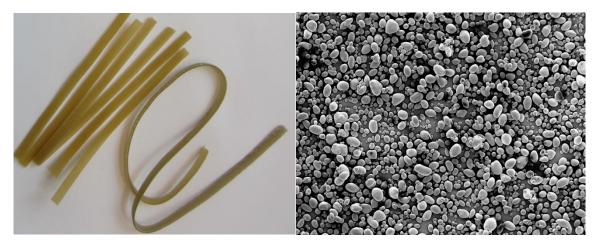
Bioplastics from natural polymers

Faraz Muneer

Introductory paper at the Faculty of Landscape Architecture, Horticulture and

Crop Production Sciences 2014:4

Swedish University of Agricultural Sciences



Alnarp, 2014

Photos: wheat gluten and potato starch based biocomposites (left) and starch granules (right)



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Summary

Petroleum based plastics are beneficial to the society; however, they are non-biodegradable and create numerous health and environmental problems. Therefore, it is important to find alternative resources for plastics production, which are more environmentally friendly and sustainable. Natural polymers from plants e.g. wheat gluten protein, potato starch, and polymers produced by bacteria are such resources. These polymers have been shown as being suitable for making environmentally friendly bioplastics due to their functional properties. Recent studies have reported the potential use of these natural polymers to produce plastics with promising mechanical and gas barrier properties. However, depending on the application the properties such as moisture susceptibility in the environment and strength of these polymers are not satisfactory and there is a need for improvement. One of the solutions is to combine the properties of two polymers in one composite material with unique characteristics. Wheat gluten an inexpensive byproduct of bioethanol industry with unique structural properties in combination with other natural polymers such potato starch and protein, as well as bacterial polymers, can be used for producing a wide range of bio-based materials and composites with interesting structural and functional properties.

Introduction

Synthetic to biopolymers

The petro-chemical based polymers are beneficial to the society for their use in different applications such as packaging, construction, automobiles, electronics and medical applications etc. However, use of synthetic plastics for short lived application is not sustainable due to an increased environmental concern of plastic waste. The plastics waste not only end-up in landfills but also in fresh water lakes, rivers and oceans creating numerous environmental and health problems for the whole ecosystem. Furthermore, proliferated increase in synthetic plastics production lead to higher energy consumption and greenhouse gas emissions together with release of hazardous chemicals (Thompson et al., 2009).

Therefore, replacement of synthetic polymers with plant based polymers such as wheat gluten and starch make the basis for a sustainable and eco-friendly plastic production (Mohanty et al., 2005). Biopolymers obtained from field grown crops such as wheat, corn, potato, soy, and starch, as well as microbial polymers such as poly-hydroxy butyrate (PHB), have been studied widely (Mohanty et al., 2002, Kolybaba et al., 2003). Biopolymers such as, wheat gluten and starch have shown interesting gas barrier and tensile properties suitable for the production of biobased plastics (Wretfors et al., 2009, Altskär et al., 2008, Thunwall et al., 2006). However, there is a concern that the biobased materials tend to lose their functional properties at high moisture contents, which may not be a problem under dry condition (Blomfeldt et al., 2010). Therefore, there is still a need to improve the performance of the biobased materials to be able make them suitable for industrial applications.

Wheat gluten

Wheat gluten is a byproduct from the bioethanol industry, relatively inexpensive, abundantly available and mostly used for animal feed and baking industry (Johansson et al., 2013). In addition, wheat gluten has shown interesting film formation, gas barrier, mechanical strength and biodegradability properties suitable for developing green plastics with unique properties (Olabarrieta et al., 2006). The wheat gluten proteins are divided into two groups depending on their solubility in aqueous ethanol solution and their molecular weight (Wieser, 2007). The non-soluble high molecular weight proteins are called glutenins, while lower molecular weight proteins are gliadins, soluble in ethanol solution (Wieser, 2007, Wrigley et al., 1988). The gliadins are responsible for intra-molecular and glutenins for inter-molecular disulphide linkages, and during heating, processing, gliadins also become a part of the polymeric network (Johansson et al., 2013).

Because of wheat gluten's thermoplastics nature, it has been used for making films (Ullsten et al., 2009, Ullsten et al., 2006), natural fiber based biocomposites (Muneer et al., 2014, Wretfors et al., 2009, Wretfors et al., 2010, Kunanopparat et al., 2008) and reinforced nano-composites (Kuktaite et al., 2014) with barrier and mechanical properties suitable for packaging applications. Hemp fiber reinforced wheat gluten composites have shown increased E-modulus and tensile stress values similar to their synthetic counterparts (Wretfors et al., 2009, Wretfors et al., 2010, Muneer et al., 2014). Similarly, wheat gluten reinforced-clay nano-composites have shown improved oxygen barrier properties being suitable for packaging (Kuktaite et al., 2014).

Wheat gluten structure

Wheat gluten polymer structural conformation is of immense importance during baking and plastic production (Johansson et al., 2013). However, during plant growth, the polymer structure in wheat gluten is affected by several factors, including genotype and growing environment during the grain production process (Johansson et al., 2013). During plastic production, the addition of chemical additives, plasticizers, and temperature play an important role in modification of the polymer structure (Gällstedt et al., 2004, Olabarrieta et al., 2006). At certain temperature and plasticizer content, the wheat gluten proteins tend to form highly complex polymerized networks stabilized by disulphide linkages (Gällstedt et al., 2004). Furthermore, the high polymerization behavior of wheat gluten at higher temperature has also shown positive effects in improving the mechanical properties of the materials (Olabarrieta et al., 2006).

The analysis of wheat gluten protein secondary structure suggests that a higher temperature contribute to a conversion of α -helices (unorganized structural form) to β -sheets (an organized structural form) improving the properties of the materials (Ullsten et al., 2009, Kuktaite et al., 2011). Morphology studies using small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) of wheat gluten protein based materials with or without additives have shown that molecular and atomic changes in protein take place during thermo-processing of the materials (Kuktaite et al., 2011, Kuktaite et al., 2012, Rasheed et al., 2014). It was observed that the formation of hierarchical hexagonal close packed structure in wheat gluten (Kuktaite et al., 2012) and gliadin based materials with and without additives were related to improved properties of the materials such as strength (WG) and extensibility (gliadin) (Rasheed et al., 2014). Furthermore, changes in the hierarchical additives added (e.g. NH₄OH and urea) (Kuktaite et al., 2012).

Potato starch

Starch is one of the potential biodegradable polymers which can replace synthetic polymers for limited time applications such as packaging and disposable cutlery. Starch is stored in plants in the form of semi-crystalline granules composed of two glucose polymers, amylose and amylopectin, having specific structures e.g. straight chains for amylose and highly branched chains for amylopectin (Flieger et al., 2003). Potato starch has shown suitable properties for film formation using extrusion and film blowing techniques, which have great potential for packaging applications (Altskär et al., 2008, Thunwall et al., 2006, Thunwall et al., 2008). When producing starch based materials, heating, mixing and shear stress contribute to the breakdown of the starch granules making it a thermoplastics material with interesting tensile properties (modulus and strength) and gas barrier properties (Altskär et al., 2008, Van Soest and Borger, 1997, Forssell et al., 2002, Thunwall et al., 2006).

In order to improve the tensile properties of the starch based materials, chemically modified hydroxy-propylated or oxidized potato starch as well as high amylose starch were developed by genetic engineering and have been used as raw material for plastics (Huang et al., 1999, Lourdin et al., 1995, Van Soest and Borger, 1997, Stagner et al., 2011, Thunwall et al., 2006). Tensile properties of the modified starches as compared to the native starch based materials were found to be better.

Different ratios of the main components of starch i.e. amylose and amylopectin tend to have profound effect on the physicochemical and functional properties of the materials (Van Hung et al., 2006). The starch with high amylose content or altered chain lengths in amylopectin fractions proved to have positive effects in improving the properties of the materials (Van Hung et al., 2006, Van Soest and Borger, 1997). Though, high amylose starches have high viscosity and high temperature during processing is needed for destruction of initial crystalline structure and to obtain higher performance of the material (Altskär et al., 2008).

Biocomposites

A composite is a combination of either two or more polymers, or a polymer reinforced with natural or synthetic fibers. The purpose of making composites is to utilize the properties of matrix and fibers in order to produce a material with higher strength. Recent studies have reported the use of wheat gluten and soy proteins which were reinforced with hemp, jute and bamboo fibers to make biocomposites with improved mechanical properties (Reddy and Yang, 2011, Huang and Netravali, 2009, Muneer et al., 2014). Few studies have reported the use of wheat gluten, rice proteins, egg albumin together with starch to obtain biocomposites with improved functional properties of the materials (Gonzalez-Gutierrez et al., 2010, Yang et al.,

2011). Egg albumin and corn/potato starch composites have shown suitable strength for packaging applications. Wheat gluten and nano-particles based composites have shown interesting structural and oxygen barrier properties (Kuktaite et al., 2014). Biocomposites solely based on biopolymers such as WG, potato starch, potato proteins, PHB and plant fibers in different combinations can be of interest for making a composite with unique functional properties.

Concluding Remarks

In conclusion biobased polymers are fascinating materials with unique properties which are suitable for biobased plastics production. However, in order to make them suitable for packaging applications their properties such as strength and susceptibility to harsh environmental conditions need to be improved. Combination of various sets of biocomposites can lead to improvement of the processing window for interesting products with improved structural and functional properties.

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