Renewable Thermoplastics – Starch Fatty Acid Esters as Alternatives to Synthetics

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Thermoplastics are an important class of polymers that find widespread use in a broad variety of applications. Because of environmental concerns regarding the lack of biodegradability of synthetic thermoplastics, green alternatives are increasingly studied that should be both based on renewable resources and biodegradable. In this regard, polysaccharide esters of naturally occurring fatty acids are in the center of interest.

Keywords: Thermoplastics; Polymers; Starch; Long-chain fatty acids; Starch esters

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Thermoplastics

Thermoplastics are a class of polymers that can be softened and melted by the application of heat. They can be processed either in the heat-softened state or in the liquid state, *e.g.*, by extrusion and injection molding. The thermoplastics represent roughly three quarters of the overall global consumption of plastics. Typical examples of thermoplastics are polyethylene, polypropylene, polyvinyl chloride, polyesters, and styrenics. All of these have a problematic property in common – they cannot be degraded by natural processes and hence contribute greatly to environmental problems. Therefore, a lot of research is being dedicated toward exploring green alternative materials and the best new ways to process biodegradable polymers based on renewable resources.

Bioplastics

It must be noted that bio-based polymers, *e.g.*, polyethylene from bio-based ethene obtained *via* the path from sugar – to ethanol – and finally ethylene, are usually not biodegradable. This editorial is intended to cover solely bio-based and biodegradable materials. Bioplastics are a class of polymers that are made fully or in part from renewable resources such as sugarcane and corn, or from polysaccharides including cellulose, starch, and others. Moreover, bacteria may produce polymers when a carbon source is in excess and at least one other nutrient essential for growth has been depleted. Bioplastics can be naturally "recycled" by biological degradation processes. Thus, bioplastics are sustainable alternatives to conventional petrochemical-based plastics. Their production has the potential to reduce the consumption of petroleum by about 20%. Today it is a necessity in many industrial applications such as food packaging, agriculture, horticulture, composting bags, hygiene, *etc.* to replace the synthetic polymers.

Thermoplastics Obtained from Natural Feedstock

As very recently nicely discussed (Ehman and Area 2021), polysaccharides provided by nature are alternatives of the utmost importance to petroleum-based polymers and comparable synthetic polymers made based on low molecular bio-based starting compounds such as polyethylene (*via* the path sugar–ethanol–ethylene and then polymerization).

Further examples are polylactic acids (PLAs). The unique macromolecule starch is degraded to sugars that are used as C-source in the fermentation process, applying *Lactobacilli* to obtain lactic acid for polymerization to the polyester.

Finally, bacteria-based thermoplastics are made from sugar of plant feed stocks to fuel this cellular process. The growth of the polymers within the bacteria occurs in a fermentation process. The polymer into the microorganism can be extracted easily. The most widely studied bacteria-based bioplastics produced are polyhydroxylalkanoates (PHAs) such as poly(hydroxybutyrate), which is synthesized by *Chlorella pyrenoidosa* after 14 days of cultivation. The most common polyesters of this type are poly(hydroxybutyrate) (PHB) and poly(hydroxyvalerate) (PHV). Although PHAs have the potential to be a competitive bioplastics, their commercial production has remained static.

Fully Bio-based Thermoplastics based on Starch

Thermoplastic starch may be obtained by adding plasticizers in a rather high percentage that are capable of hydrogen bonding with the starch hydroxyl groups, such as water, glycerol, and sorbitol. However, the properties tend to be disappointing. Moreover, the plasticizers may leave the material, yielding a loss of thermoplasticity.

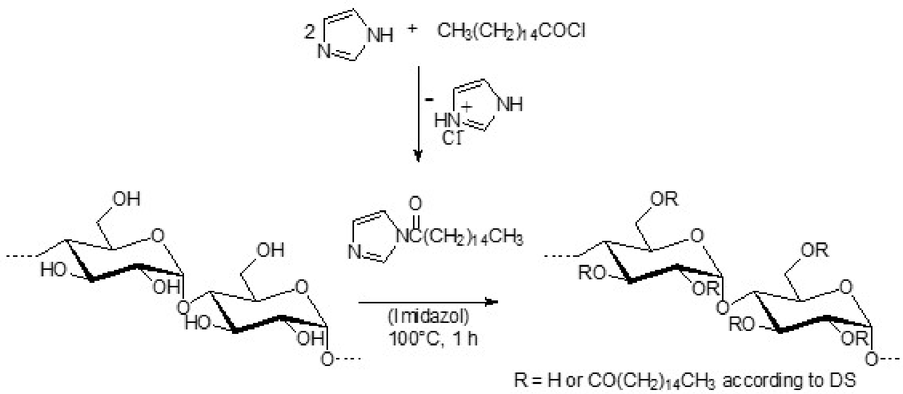

Fig. 1. Reaction scheme of esterification of starch applying imidazole as solvent, activator, and base

A different approach is the esterification of starch with long-chain substituents to obtain bio-based and thermoplastic materials (Grünler *et al.* 2009). The chemistry to make the starch esters is simple and efficient. A powerful, stable, and non-derivatizing solvent for starch, namely molten imidazole, has proved to act not only as solvent but also as activator and base (Jordan *et al.* 2014). The solvent fulfills the requirements for a state of the art solvent for the polysaccharide with respect to its non-toxicity, recyclability, non-flammability, stability, as well as its low price commercial availability. It is a suitable solvent for the shaping of starch and more importantly for homogeneous starch chemistry to prepare advanced starch derivatives with superior properties (Fig. 1).

Long-chain starch esters could be prepared using molten imidazole as solvent for the biopolymer. The advantage is the simplicity of the reaction mixture. The reaction proceeds via the imidazolide, which is formed *in situ* with an acid chloride applied as esterification agent. The starch esters obtained are highly pure; there is no hint of any impurities. The high quality of the products prepared is responsible for the occurrence of colorless melts. Although DSC measurements show a variety of thermal transitions, the formation of melts in the range of 40 to 255 °C could be observed with a hot stage microscope. The type and the amount of ester moieties can be varied to adjust the melting behavior. For instance, starch palmitates melt completely transparent within two distinct regions of the degree of substitution (DS) around 1.5 as well as between 2.2 and 3.0. Upon cooling, the melts form homogeneous films on different supports, including glass. They show good adhesion and should therefore be a suitable basic material for the preparation of composites, such as laminated glass. Recycling of imidazole is essential to make the process suitable for large-scale production, which could be realized by conversion of the imidazole into imidazole hydrochloride and isolation of this salt.

The starch esters can be processed by usual methods such as extrusion and melt blowing. It is important to note that no plasticizers are needed in the processes of thermal shaping (Fig. 2). The starch ester may be used for gluing paper, stone, wood, wood chips, and even glass. The thermoplastics starch ester applied between the two glass panes shown in Fig. 3 contains a UV-switchable dye (photochromic properties), which is useful to control the lighting conditions in rooms. It is also simple to prepare completely bio-based wood board with 5% starch stearate, as schematically presented in Fig. 4.

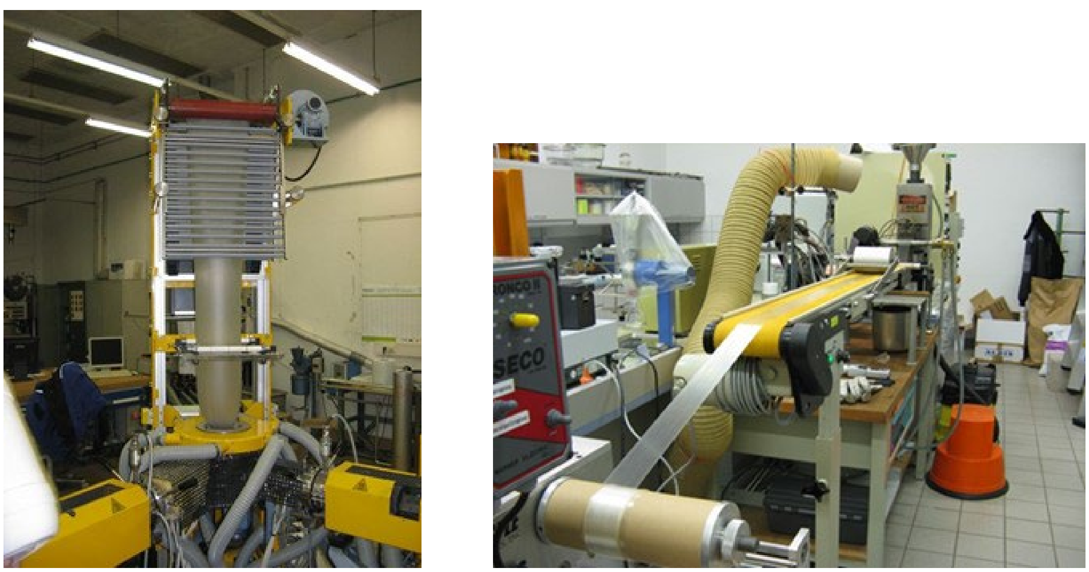

Fig. 2. Film production of starch palmitate by melt blown technique and extrusion of starch palmitate, which is possible without any additive (plasticizer)

Fig. 3. Starch palmitate (DS 1.5) containing photoactive dye laminated glass possessing photochromic properties (blue - under irritation with UV light)

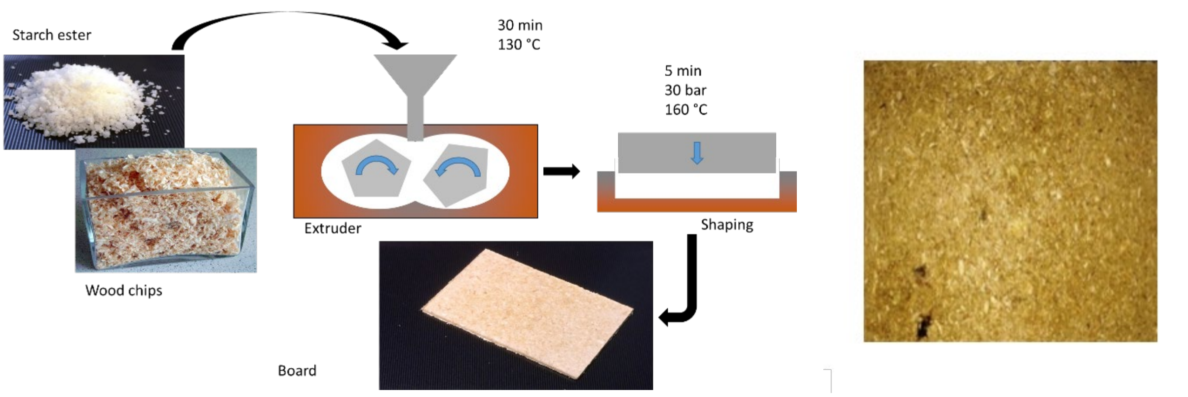

Fig. 4. Scheme of the preparation of completely bio-based wood board produced with 5% starch stearate

Conclusions

Esters of starch and other polysaccharides with long-chain fatty acids are promising novel thermoplastics. The thermal properties can be controlled by the fatty acid, by the degree of substitution, and by the molar mass of the biopolymer. They possess great potential to be used in usual thermoplastics applications, provided that the preparation can be carried out efficiently.

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