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Review

A review: Starch-based composite foams

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ABSTRACT

The large quantities of the petroleum-based foam materials used have raised concern due to their negative effects on the environment, predominantly single-use articles in packaging applications. Thus, considerable efforts have been put forth to develop environmentally friendly alternatives and, in particular, starch foams. Many techniques including extrusion, hot-mold baking/compression, microwave heating, freeze-drying/solvent exchange, and supercritical fluid extrusion can be used to produce starch foams with different cellular structures and properties. Starch by itself is, however, rather weak and water sensitive. To improve microstructure, mechanical and thermal properties, moldability, water resistance, lightness and other properties of starch-based foams, many approaches, e.g., chemical modification of starches, blending with various biodegradable polymers, incorporation of natural fibers, and addition of nanofillers, have been attempted and are intensively reviewed in this article.

Contents

1. Introduction

The synthetic polymers have replaced metals, glasses, ceramics and wood in many applications, chiefly in the area of packaging. The main commodity plastics, the so called “big five”, which are polyethylene (PE), poly(propylene) (PP), polystyrene (PS), poly(vinyl chloride) (PVC), and poly(ethylene terephthalate) (PET) have revolutionized the packaging industry in a variety of forms such as films, flexible bags, rigid containers and foams. Non-degradability of these petroleum-based packaging polymer products, however, has raised an environmental concern for suitable disposal [1]. Particularly, single-use packaging materials have been identified as the most suitable items to be replaced by biodegradable materials from renewable resources [2,3]. Due to the enormous amount of polystyrene used in foam packaging and food serving applications

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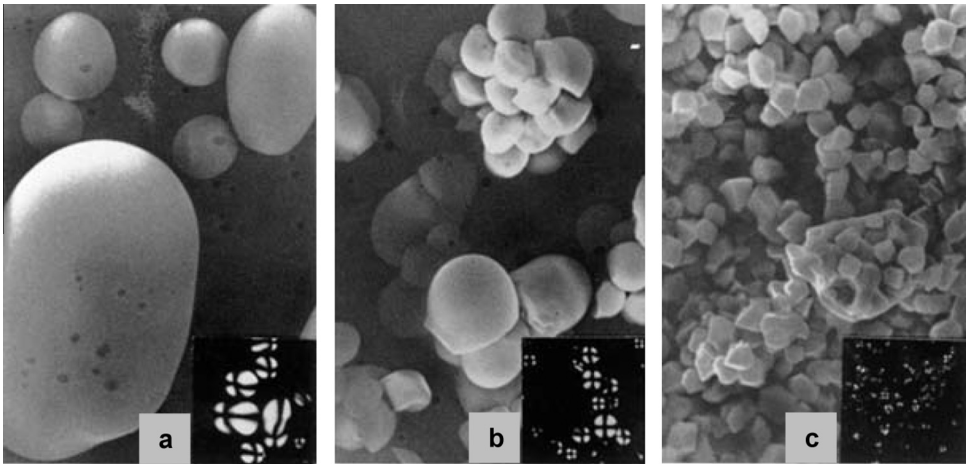

Fig. 1. Starch granules observed by scanning electron microscopy: (a) potato; (b) cassava; and (c) rice starches. The corresponding granules under polarized light are shown in insets [33].

as well as its difficulty to collect and to recycle, the development of various technologies for producing starch-based foams as polystyrene replacements has been initiated [4].

Starch by itself is, however, rather brittle and water sensitive. Various approaches have been investigated aiming to overcome these problems. Plasticizer (usually water and glycerol) is commonly added into starch to improve the foam product flexibility. Addition of plasticizer also enables melting of a plasticized starch below its decomposition temperature, leading to a significant improvement in starch processability as a thermoplastic [5,6]. Incorporation with some additives such as $CaCO_3$, talc, and salts (e.g. NaCl and $CaCl_2$) have also shown to reduce processing time, but raise aesthetic value of the starch-based foams and improve the foam cell structure then their mechanical strength [3,7–9]. Furthermore, in order to enhance water resistance and strength of the foams, chemically modified starches have been studied as well as various biodegradable polymers, for example, poly(lactic acid) (PLA), poly(ε-caprolactone) (PCL), poly(vinyl alcohol) (PVA), chitosan, poly(hydroxyester ether) (PHEE), poly(hydroxybutyrate-co-valerate) (PHBV), poly(butylenes-succinate) (PBSA), butane diol-terephthalate-adipate terpolymer (PBAT), cellulose acetate (CA), poly(ester amide) (PEA) have been blended with starches [7,8,10–17]. Another approach is to add reinforcing agents into a starch matrix which has been proved to be an effective method to obtain high-performance starch-based composite materials. A number of natural ligno-cellulosic fibers such as jute, flax, aspen, corn, soft wood, eucalypt cellulose, kraft pulp, sugarcane bagasse, cotton linter, hemp, α-cellulose, and wheat bran as well as some nanofillers such as clays and nanocelluloses have been used to reinforce starch foams [2,6,10,16–31]. Since both components are biodegradable, the composite as the integral part is also expected to be totally biodegradable. This material, therefore, can be referred as ‘a truly biocomposite or eco-friendly foam’.

The present review article deals with the research and development of starch-based foams in the past decade with a discussion on various processing techniques of the starch-based foams. The effects of various natural fibers, additives, other biopolymers, modified starches, and nanofillers on structure and properties of the resulting starch-based composite foams will be discussed.

2. Starch

Starch, present in most green plants, is produced from wide variety of sources, renewable, low cost, and inherently biodegradable or can be completely converted by microorganisms to carbon dioxide, water, mineral and biomass, with no negative environmental impact or ecotoxicity [5,32]. It is the major form in which carbohydrates are stored in a common constituent of higher plants. It exists in small, dense, discrete packages called granules that are insoluble in cold water [33]. Granules of starch accumulate at high concentrations in reproductive structures like cereal grains (e.g., wheat, rice, maize, barley, rye, oats, millet, sorghum) and in vegetative structures such as tubers (potatoes) and roots (cassava and taro). Starch granules occur in all shapes and sizes (spheres, ellipsoids, polygons, platelets, irregular tubules); their dimensions normally range from 2 μm to >100 μm, depending on the botanical source and type as shown in Fig. 1 [33,34].

Two major starch polymers are amylose and amylopectin. Amylose is an essential linear polymer with α-1–4 linked glucopyranosyl units. It is the smaller of the two polymers: molecular weight is around the order of 10^4 to 10^5 and a degree of polymerization (DP) of 250–1000 D-glucose units [33]. Amylopectin is a highly branched molecule with $(1 \rightarrow 4)$-linked α-D-glucopyranosyl units in chains joined by $(1 \rightarrow 6)$ linkages. Amylopectin is one of the largest molecules found in nature with molecular weight in the order of 10^6 to 10^8 corresponding to a DP of around 5000–50,000 D-glucose units. Normal starches, such as normal maize, rice, wheat and potato, contain 20–30% amylose and 70–80% amylopectin [34]. The orientation of amylose and amylopectin molecules inside a starch granule is very interesting and has been intensively investigated. It was reported that the starch granule has both amorphous and crystalline regions arranged in the grain in an onion like structure. Amylopectin chains are primarily responsible for the crystallinity of starch, forming a double helical crystalline structure. Amylose is present in the amorphous structure and part of the amylose is present as a helical complex with the lipids. It is located adjacent to or intertwined with amylopectin to maintain the integrity of the granule [33–35].

In food processing operations, understanding thermal behavior of starches is very important and, therefore, it has been extensively studied. As compared to conventional thermoplastics, thermal behavior of starches is much more complex because the various physicochemical changes could occur during heating starches, for instance, gelatinization, melting, glass transition, crystallization, change of crystal structure, volume expansion, molecular degradation, and motion of water. All these thermal behaviors depend upon the ratio of water to starch content [36–39]. At low water content, the glass transition is a key event determining the change in polymer mobility. Starches exist in a glassy state at sufficiently low temperatures where large-scale molecular motions stop. By