

Chapter 13

Composite Foams Made from Biodegradable Polymers for Food Packaging Applications



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Abstract Polymeric foams are cell structures (porous microstructures) that have been frequently made from synthetic polymers for use in the development of food packaging. Due to the problems concerning the environmental impact caused by polymers from the petrochemical industry, the foams have been more recently studied from biodegradable polymers. However, the polymer materials obtained are usually susceptible to moisture, thus conditioning the collapse of the porous structure of the material. As an alternative, the composite foams have been investigated from nano-fillers such as clays, cellulose, nanoparticles, among others. This chapter aims to analyze the recent advances in the studies of composite foams.

Keywords Biopolymers · Composite materials · Polymer composites

13.1 Introduction

Foams produced from petroleum-based conventional polymers, such as polystyrene (PS) and polyurethane (PU), are widely used in the food packaging industry, because of their excellent properties and low production costs. However, these polymers do not undergo biodegradation and its recycling is unprofitable (Li et al. 2017). Hence, the increased customer awareness about the environment and the creation of government laws on environmental protection and waste disposal has encouraged scientists to develop new eco-friendly materials. Biodegradable polymers are an alternative to conventional ones, especially those produced from renewable

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resources since they can be mineralized by microorganism without negative environmental impact (Suárez and Gutiérrez 2017). Nevertheless, biodegradable polymer produce foams with poorer morphology, water and moisture resistance, and mechanical, thermal and barrier properties as compared to conventional polymer foams (Luzi et al. 2016; Mitrus et al. 2016).

13.2 Composite Foams

It has been reported that the formation of composite foams offers a solution to improve the properties of biodegradable polymers, especially when the filler has a dimension on the range of nanometers. The addition of a low nanofiller content as a reinforcement can provide a significant improvement of several properties, i.e. dimensional, mechanical and thermal stability. In addition, nanofiller may serve as nucleation agent for bubble generation and as a stabilizer of the nucleating bubbles by decreasing the cell coalescence with an increase of melt strength (Soykeabkaew et al. 2015; Zhao et al. 2015). In order to not alter the biodegradability and biocompatibility of biodegradable composite foams are added natural reinforcements, i.e. cellulose and clays. Cellulose nanocrystals (CNC) is a highly-crystalline and rod-like nanoparticle extracted from cellulose, which possesses several advantages such as sustainability, recyclability, non-toxicity, high surface area, low density, etc. When it is used as a filler of composite foams, CNC improves the thermal and mechanical properties and affect the polymer nucleating process (Srithep et al. 2012; Liu et al. 2014; Mi et al. 2014). On the other hand, nanoclays are layered silicate minerals, such as montmorillonite has high availability, versatility, low cost, and minimal adverse effects on the environment and human health. The individual clay particle presents a platelet structure, with a thickness of approximately 1 nm and lateral dimensions up to 1 μm . In nanocomposites, the nanoclays reinforcing efficiency, good barrier properties, and improved dimensional and thermal stability are strongly related to their aspect ratio and large surface area (Keshtkar et al. 2014; Kumar and Maiti 2015; Li et al. 2015). The most investigated biodegradable polymers for the developed of biodegradable composite foams are polybutylene succinate (PBS), polycaprolactone (PCL), polylactic acid (PLA), polyvinyl alcohol (PVA), and starch. In Table 13.1 are listed several works about edible nanocomposite foams based on the most used biodegradable polymers and CNC or nanoclays as the filler.

PBS is a biodegradable aliphatic polyester, which is obtained by polycondensation reaction of 1,4-butanediol and succinic acid, or by fermentation of agricultural crops containing cellulose, glucose, and lactose. For its reasonable production cost, outstanding biodegradability, melt processability, and chemical and thermal resistance PBS is a promising material. However, PBS presents some insufficient properties such as its linear molecular structure, low melt viscosity and strength, and its barrier properties (Chen et al. 2015; Hu et al. 2015; Luzi et al. 2016). Lin et al. (2015) developed biodegradable microcellular foams based on PBS and CNC by

Table 13.1 Edible nanocomposite foams with different biodegradable polymers as matrix and cellulose nanocrystals or nanoclays as filler

Polymer	Reinforcement	Foam processing	Reference
PBS	Cellulose nanocrystals (CNC)	Compressing method	Lin et al. (2015)
	Surface acetylated cellulose nanocrystals (ACNA)	Compressing method	Hu et al. (2015)
	Organically modified Cloisite®15A, Cloisite®20A, and Cloisite®30A	Baking method	Lim et al. (2011)
PCL	Cellulose nanocrystals	Supercritical CO ₂ injection	Mi et al. (2014)
	Organically modified Cloisite®30B	Pressure vessel	Di et al. (2003)
	Organically modified Cloisite®25A	Supercritical CO ₂ and ethanol atmosphere pressure quench	Tsimpliaraki et al. (2013)
PVA	Microfibrillated cellulose (MFC)	Supercritical CO ₂ extrusion	Zhao et al. (2014)
	Cellulose nanofibrils (CNF)	Freeze-drying method	Liu et al. (2014)
	Cellulose nanocrystals (CNC)	Baking process	Song et al. (2016)
	Pristine Na ⁺ montmorillonite	Extrusion	Li et al. (2015)
PLA	Cellulose nanocrystals (CNC)	Casting and leaching method	Borkotoky et al. (2017)
	Organically modified I.34TCN nanoclay	Supercritical CO ₂ extrusion	Liu et al. (2013)
	Organically modified Cloisite®30B	Supercritical CO ₂ extrusion	Keshtkar et al. (2014)
Starch	Cellulose nanofibrils (CNF)	Freeze-drying method	Svagan et al. (2008)
	Cellulose nanofibrils (CNF)	Freeze-drying method	Yildirim et al. (2014)
	Organically modified Cloisite®30B and Cloisite10A	Baking method	Matsuda et al. (2013)
	Wizkay TU-90 kaolin	Compressing method	Kaewtatip et al. (2013)

compressing method. Azodicarbonamide (AC) was the blowing agent and zinc oxide (ZnO) the blowing promoter. The flexural strength and modulus of the nanocomposite foam with 5 wt% of CNC was increased by 50% and 62.9%, respectively, as compared with the neat PBS foam. Behavior attributed to the stress transfer between the matrix and nanofiller. The cells morphology, structure and stability were also modified by the filler due to the nucleation effect of CNC.

Hu et al. (2015) studied the effect of the chemical acetylation modification of CNC on the properties of PBS biodegradable foams. The foaming process was made by compressing method, and AC and ZnO were the blowing agent and the blowing promoter. The chemical treatment to obtain acetylated cellulose nanocrystals (ACNC) promoted the compatibility with the matrix. Nanocomposite foams with 5 wt% of ACNC showed flexural strength and modulus improved by 50% and 31.4%, respectively, as compared to that the neat PBS foam. The good dispersion of

ACNC along the PBS matrix, and to the compatibility between nanocomposite foam components improved those properties. Additionally, it was observed that the microstructure was affected by the filler, increasing the density and average cell size. Clays are other nanofiller used as the reinforcement of nanocomposite foams. Lim et al. (2011) prepared PBS and organoclay nanocomposite foams by the baking method, employing AC, *N, N'*-dinitroso pentatetramine, and urea activator as the blowing agent. The nanocomposite with 2 wt% of clay displayed the better mechanical and thermal properties. The thermal degradation temperature, tensile strength, and elongation at break of composites with 2 wt% of the filler increased by 5, 64 and 470%, respectively, as compared to the neat PSB foam. The improved on the mechanical properties was due to the strong interaction between the PBS matrix and the nanoclay, which resulted in the transfer of stress to the nanofiller. Furthermore, it was observed that the blowing ratio depended upon the blowing temperature and time, and that nanocomposite foams had closed cells, which were oval-shaped.

Another biodegradable promising polymer is the PCL that is a hydrophobic and semicrystalline polymer, which presents low melting temperature at approximately 60 °C and exceptional blend-compatibility. PCL is synthesized by ring opening polymerization of ϵ -caprolactone using a variety of catalyst, and by ring opening polymerization of 2-methylene-1-3-dioxepane. PCL properties can be modified by adding functional groups. However, PCL has high degraded times and poor mechanical performance (Di et al. 2003; Mi et al. 2014). Mi et al. (2014) prepared CNC and PCL composites by injection molding with supercritical CO₂ as the blowing agent CNC acted as a nucleating agent and had a strong interface with the PCL matrix improving the tensile modulus, complex viscosity, and storage modulus. It was also found that nanocomposite foams presented fine cell structure.

Studying the effect of organically modified clay upon the crystallization and foaming process of PCL. Di et al. (2003) found that the crystallization kinetics increase by 81% with the addition of 5 wt% of the filler, because of the nucleating effect of the silicate layers, as compared to the neat PCL foam. Furthermore, the complex viscosity and density of the nanocomposite foams were higher than that of neat PCL foam. Likewise, Tsimliaraki et al. (2013) prepared PCL and organically modified clay nanocomposite foams by one-step or two-step press quench method, with supercritical CO₂ or CO₂-ethanol atmosphere as a blowing agent. The dispersion of the filler and the cell density and structure were better when the blowing agent was the mixture CO₂-ethanol. Besides, it was not found a significant difference between nanocomposite foams structure when the processing method was either one-step or two-step.

PVA is another biodegradable polymer widely studied as a matrix of edible nanocomposite foams, as a matter of fact, PVA foams has been extensively applied in the biomedical and pharmaceutical fields. PVA is a semicrystalline and water-soluble polymer with several advantages, for instance, its compatibility with organic and inorganic materials, good ion exchange, physical adsorption, chelation, polarity, biocompatibility, and versatility. However, PVA has narrow process window, which makes its melting temperature very close to its decomposition temperature (Mali et al. 2010; Debiagi et al. 2014; Li et al. 2015). Liu et al. (2014) developed

PVA and cellulose nanofibrils nanocomposite foams by the freeze-drying method. The addition of 30 wt% of CNF increased the Young's modulus, compressive stress and energy absorption by 75, 60.58 and 14.36%, respectively, as compared with the neat PVA foam. Those results were attributed to the effect of CNF on the foam morphology since composite foams with 30 wt% or lower CNF content presented smaller pore sizes with the larger surface area, which could support stronger compression forces. Those pores were composed of fibrils with amorphous PVA playing the role of cross-linker or glue. Comparatively, Zhao et al. (2014) prepared PVA and microfibrillated cellulose (MFC) by extrusion with water and CO₂ as the co-blowing agents and studied the effect of water, CO₂ and MFC content on the properties of the composite foam. It was observed that the addition of 0.5 wt% of MFC increased the crystallinity by 37.48% as compared to the neat PVA foam. This behavior was due to nucleation effect of the filler that contributed to cell nucleation and prevented large crystal formation. Moreover, it was perceived that the composite with 0.05 wt% of MFC prepared using 12.5 wt% of water and 9 wt% of CO₂ displayed the best properties. The cell density was increased by almost an order of magnitude and the cell size was decreased by 6.66%.

Likewise, the morphology, density, water uptake and mechanical properties of PVA and CNC nanocomposite foams, developed by Song et al. (2016) through the baking process, were modified with the addition of the filler. The foaming process was carried out with initial reaction times of 10 and 120 s, and calcium carbonate and formaldehyde were employed as the blowing and cross-linking agent, respectively. It was observed that the nanocomposite foam with 1.5 wt% of CNC and the initial time of 120 s displayed tensile strength and compressive modulus increased by 737.31 and 8.75%, respectively, as compared to the neat PVA foam and nanocomposite foams with 10 s initial reaction time. Those results were attributed to longer initial reaction time, allowing the formation of high density with small pore size foams, and to the strong interaction between the low CNC content that presented uniformly dispersion and the matrix. On the other hand, there have been also developed PVA nanocomposite foams with nanolayered silicates as the filler. Li et al. (2015) studied the effect of pristine montmorillonite on the properties of PVA nanocomposites foams prepared by extrusion and using AC as the blowing agent. The clay was intercalated during the extrusion forming the exfoliated and intercalated structures. Due to the strong interaction between the nanocomposite components, the melt elasticity and strength were improved. As a consequence of the increased melt strength and reduced crystallization time, the density of nanocomposite foam decreased.

Edible nanocomposite foams have also been prepared using PLA as a matrix. PLA is polyester synthesized by ring opening of lactide or L- and D-lactide acid, which can be produced from renewable agricultural materials. PLA is a biocompatible polymer that has low toxicity and produces foams with high surface area, high toughness and low thermal conductivity (Lee et al. 2008; Ding et al. 2016). However, due to its low crystallinity, low melt strength, low deflection temperature, and slow crystallization, PLA presents limited applicability in different manufacturing processes (Bocz et al. 2016). Borkotoky et al. (2017) developed PLA and CNC

nanocomposite foams by a novel and economic casting and leaching method and studied the filler effect on the morphology and thermal properties of the foams. It was observed that the addition of 3 wt% of CNC increased the foam density by 38.09% and decreased the pore size by 47.14%, as compared with the neat PLA foam, as a consequence of the nucleating effect of the nanoparticles, which formed a greater number of smaller size cells. The crystallinity of the nanocomposite with 3 wt% of CNC increased by 12.9%, reaffirming the nucleating effect of the filler.

Additionally, clays are also used as a filler of PLA nanocomposite foams. Liu et al. (2013) found that organically modified I.34TCN clay and the chain-extender BL 10069 N affected the properties of PLA foams prepared by the supercritical CO₂ extrusion method. The nanocomposite with 3 wt% of the clay presented the exfoliated and intercalated structures. It was also perceived that the addition of 3 wt% of the clay increased the complex viscosity, storage modulus, melt strength and cell density, besides it decreased the loss factor and pore size of the nanocomposite foam. The behavior of the complex viscosity was attributed to the intercalation and exfoliation of the nanoclay that impede polymer chains to move and the increased of the melt strength was related to the increase of the storage modulus, which was ascribed to the intercalation of polymer chains into the clay layers. Similarly, Keshtkar et al. (2014) studied the effect of organically modified clay and CO₂ content on the morphology, crystallization and rheological properties of nanocomposite foams prepared by extrusion with supercritical CO₂ as the blowing agent. The nanocomposite foam with 5 wt% of the filler, 9 wt% of CO₂ and prepared with die temperature at 115 °C displayed the best crystallization, cell density, expansion rate and complex viscosity. Those results were attributed to the crystallization and nucleation effects of the filler that were pronounced by the presence of plasticizing CO₂. Besides, the filler increases the melt strength, and thereby the foaming behavior.

Finally, the most used biodegradable polymer to prepared composite foams is the starch, which is a renewable and low-cost polymer produced by a vast variety of sources. Starch is the main form in which carbohydrates are stored in plants, cereal grains, tubers, and roots. The major starch polymer components are amylose and amylopectin (Soykeabkaew et al. 2015). Since it is a renewable resource, abundant, inexpensive and non-toxic, starch is considered the most used polysaccharide for foam packaging applications (Palma-Rodríguez et al. 2016). However, starch-based foams have poor water resistance and mechanical properties (Kaisangsri et al. 2014; Pornsuksomboon et al. 2016). Aiming to study the mechanical performance of nanofibrillated cellulose (NFC) and amylopectin potato starch nanocomposite foams, prepared by the freeze-drying method, Svagan et al. (2008) found that the best mechanical properties were for obtained adding 40 wt% of the filler. The Young's and yield strength of the nanocomposite foam with 40 wt% of CNF increased by 42.85 and 200%, respectively, as compared to that the neat starch foam. Furthermore, the density and the water content decreased by 7.69 and 23.63%, respectively. Besides the reinforcement effect of the nanofiller, the cell structure of the nanocomposite foams was a formed by a mixture of closed and open cells, which influence the mechanical behavior in the linear-elastic and cell collapse regions. The decreased in water content was due to the hydrophobic nature of the

nanofiller. Likewise, Yildirim et al. (2014) developed corn starch and CNF nanocomposite foams by the freeze-drying method, with different starch and CNF contents, and studied the mechanical flexural and compressive behavior of nanocomposite foams. The best mechanical performance was displayed by the nanocomposite foam with 6 wt% of corn starch and 1.5 wt% of NFC. The elastic modulus, modulus of rupture, compression modulus and compressive resistance of nanocomposites with 6 wt% of starch and 1.5 wt% of CNF increased by 109,869; 16,375; 5946 and 2212% as compared to the nanocomposite foam with 0.5 wt% of starch and 0.5 wt% of CNF.

Furthermore, starch-based nanocomposite foams with nanoclays as filler have been prepared. Matsuda et al. (2013) developed cassava starch and two organically modified clay (Closite[®]30B and Closite[®]10A) nanocomposite foams by the baking method and evaluated the influence of the content and the kind of filler upon the microstructural and mechanical properties. After 30 min of immersion, all nanocomposite foams had lower capacities of water absorption than the neat starch foam, due to the clays hydrophobicity, which is higher to Closite[®]10A. Both organoclays presented good dispersion along the matrix and formed the exfoliated structure. Also, both clays improved the stress at break, due to the strong interaction between the nanoclays and the matrix, which enhanced the mechanical reinforcement. Correspondingly, evaluating the effect of kaolin upon the morphology, water absorption and mechanical properties of starch foams that were prepared by compressing method. Kaewtatip et al. (2013) found that the addition of 15% of kaolin increased the Izod impact strength by 368%, as compared to the neat starch foam. Result attributed to the good dispersion and distribution of kaolin along the starch matrix, and to the kaolin efficiency absorbing and diluting impact energy. Additionally, the addition of kaolin the water absorption decreased by 6 and 8% after the nanocomposite foams were exposed at 55% of relative humidity for 7 and 45 days, respectively.

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