Chapter 12
Biodegradable Nanocomposite Foams: Processing, Structure, and Properties

Shasanka Sekhar Borkotoky, Tabli Ghosh and Vimal Katiyar

Abstract The biodegradable nanocomposite foams can be developed using different fabrication techniques where the use of various kinds of bio-based nanofillers helps in tailoring the foam properties. A brief discussion on different techniques of fabrication, their economic viability, and industrial feasibility in regards to the polymeric foams is made in this chapter. Moreover, the available different biodegradable polymeric foams and their processing in the recent past years is detailed. However, the chapter mainly focuses on the biodegradable poly (lactic acid) (PLA)-based nanocomposite foams and their recent developments and breakthroughs. The addition of nanofillers for fabricating the foam greatly affects various foam properties such as cell size, cell density, and porosity. Other important properties such as thermal properties, mechanical properties, and wettability are also affected by the nanofiller materials. The degradation of PLA-based nanocomposite foams is greatly influenced due to the addition of various bio-based nanofiller materials. In this regard, the tailor-made properties of various biodegradable foams make them promising candidate in different areas of research.

Keywords Poly (lactic acid) · Biodegradable · Foams · Fabrication · Characterization

1 Introduction

Foam is an entity consisting of gaseous voids (75–95%) in liquid or solids. Synthetic foams can be developed from various materials including glass, metals, ceramic, polymer, and rubber. Among various available foams, the polymeric foams have some unique properties and some added advantages such as low weight, low density, and less usage of materials compared to non-foam materials. Further, the cost of production can also be reduced by the specified factors. The elastomeric foams have been widely utilized in different fields of applications such as insulation materials,

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sound-absorbing materials, and cushioning. Thus, the polymeric foaming technology is growing day by day and has established as one of the major areas of research. Further, the development of porous material is gaining importance day by day with the discovery of new areas of applications [1].

The polymeric foam industry was initially developed during 1930s to 1950s, where polystyrene (PS) foam was firstly developed in 1931. The development and use of foam took an established shape in 1980s. The recent area of research is focused on improving the properties of the foam, which is the driving force for developing new foam-based materials. The polymeric foams are generally classified according to different parameters such as material use, structure, nature, mechanism, cell size, and others as shown in Fig. 1. However, the polymeric foams can also be broadly classified into two major parts: non-degradable foams and biodegradable foams [2]. Non-degradable polymeric foams mainly dominate the current market share of the total polymeric foams. However, a continuous effort has been made to replace the available non-degradable foams by biodegradable foams due to the increasing market share of polymer foams. The recent shares by volume in various applications of polymeric foams are shown in Fig. 2 (based on a market report of Smithers Rapra, 2015). According to this, the polymer foams have major application in construction materials and find applications in furniture, automobiles, packaging, refrigeration, and others. A recent market survey suggests that the use of high-performance polymeric foams will increase ~4.8% annually due to the growth in emerging technologies (based on the market survey of Smithers Rapra, 2018). However, the above foam market is mainly dominated by the non-degradable conventional foams.

Moreover, the demand for the biodegradable polymeric foams in different new areas is rapidly increasing day by day. Researchers are also trying to find new areas of replacement to the conventional non-foamed polymers by developing composites, blends of biodegradable foams. As the ultimate disposal of non-degradable

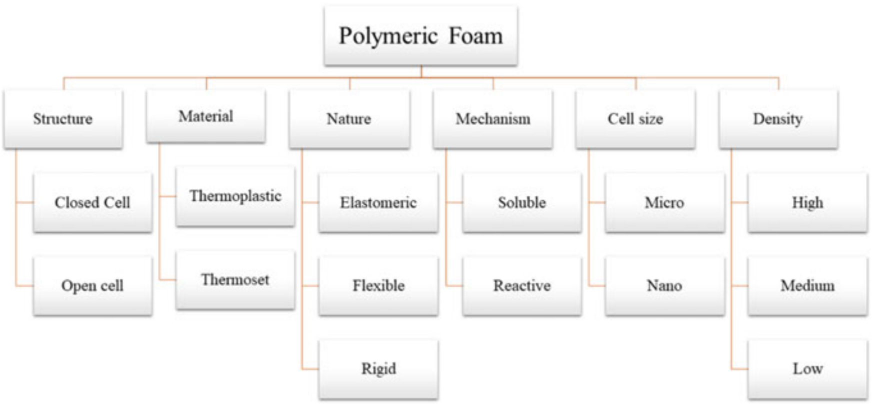

Fig. 1 Classifications of polymeric foams based on different parameters

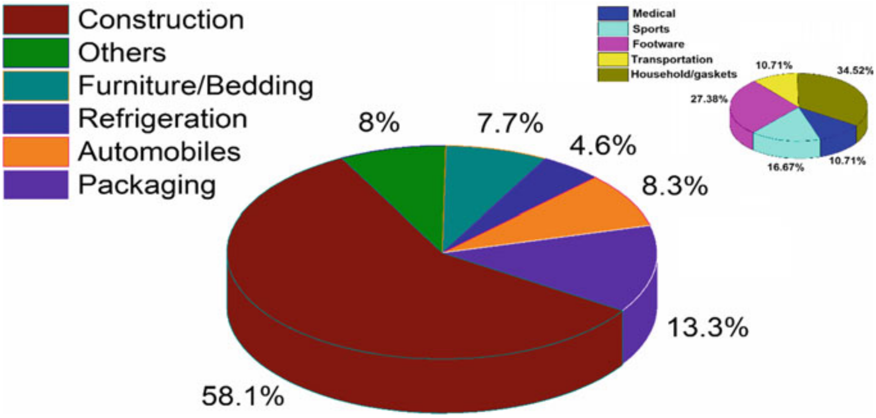

Fig. 2 Global market shares of polymeric foams in different segments

polymer foams is a major concern in the environmental point of view, the environmentally friendly technologies are now a primary requisite in this regard followed by the international agreements like the Kyoto protocol, Montreal protocol, and so on. Hence, the need for bio-based and biodegradable foams is gaining attention in recent years. Bio-based and biodegradable foams show a tremendous and promising impact in different fields like biomedical, food packaging, industrial, engineering, and advance applications. Some of the recently used biodegradable polymeric foams include starch, poly(hydroxyalkanoates) (PHAs), poly(3-hydroxybutyrate) (PHB), poly (lactic acid) (PLA), poly(ε-caprolactone) (PCL), and poly(3-hydroxybutyrate-co-hydroxyvalerate) (PHBV). The first developed biodegradable polymeric foam is starch, which is further improved for various properties. Biodegradable polymer foams have some inferior properties, which need to be modified to compete with the non-degradable polymeric foam materials for targeted applications. In this regard, the major differences between the biodegradable and non-degradable foams are illustrated in Fig. 3, where biodegradable foam-based materials provide non-toxicity, biocompatibility, and eco-friendly nature causing no harmful effect to the environment.

In recent years, a variety of biodegradable polymer materials are gaining importance for the fabrication of tailor-made foam materials for multifaceted advanced applications. However, one of the promising biodegradable polymers, which are gaining attention among the scientific community for the replacement of conventional polymeric foam, is PLA. Recent researches on bio-based foams are mainly focused on the development of PLA-based foams. Besides, PLA, the other biodegradable polymeric foams include PCL, polybutylene succinate (PBS), PHBV, cellulose, their blends, composites, etc., which are being used for wide application.

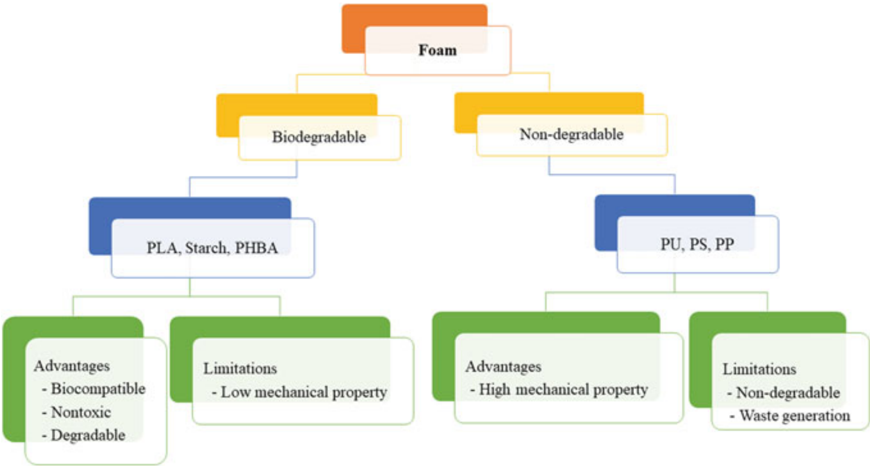

Fig. 3 Degradable and non-degradable foams

1.1 Poly (Lactic Acid) (PLA)

PLA is a bio-based and biodegradable polymer synthesized from natural resources including corn and carbohydrate-based feedstock. PLA has the properties comparable to some non-degradable petroleum-based polymers. The schematic illustration of the life cycle of biodegradable PLA can be observed in Fig. 4, where the composting and

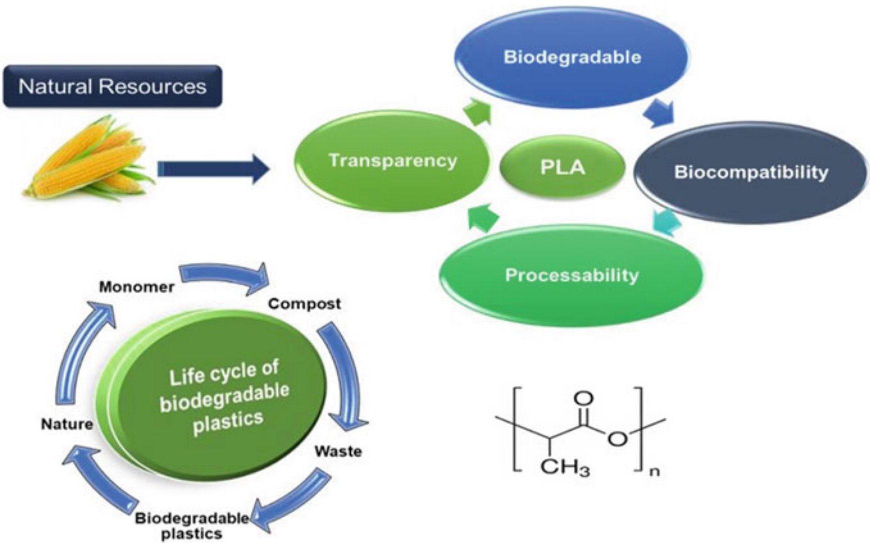

Fig. 4 Life cycle of poly (lactic acid)

biodegradation processes reduce environmental waste. Additionally, PLA has good processability which increases the market value of PLA-based foam materials. PLA is mainly synthesized by ring opening polymerization (ROP) of lactide monomer [3]. PLA is a thermoplastic which is glossy, transparent, and semi-crystalline in nature. The production of PLA requires less energy (up to 25–55%) compared to the energy consumed in the production of petroleum-based non-degradable foams. The content of D-isomer present in PLA influences its ultimate properties. The thermal degradation of PLA leads to the release of non-toxic materials such as CO_2, H_2O, and lactic acid due to hydrolysis of ester linkages. The mechanical and other properties of PLA are comparable with most of the petroleum-based conventional polymers. The properties of PLA can be improved by tuning it with the addition of different nanofillers, plasticizers, chain extenders, etc. [4].

However, one of the limitations of PLA is its low melt strength. The short degradation time of PLA makes it unsuitable for engineering applications. Another limitation of PLA is low thermal properties. The current researches on PLA are mainly focused in the directions to tune these limitations. PLA-based foams are mainly utilized in sophisticated bio-based medical applications like cell culture, tissue engineering, and so on due to its biodegradability. Simultaneously, it can be useful in other advanced applications by tailoring its properties for specific applications. The other applications include packaging, housewares, automobile parts, cushioning applications, insulation, furniture, high-grade decorative items, and electrical appliances. A focused study has to be performed to make it suitable for different applications [5].

2 Fabrication of Polymeric Foams

Polymer foaming can broadly be carried out in different established processes classified as batch foaming process and continuous foaming process. The batch process is mainly limited to the research in development fields to investigate the newly developed materials and their foaming behavior. On the other hand, the continuous process is an economically and industrially viable scale-up process in larger magnitude. A continuous process is achieved by an extrusion technique, consisting of steps like mixing with additives and pressurization of inert gases [6].

2.1 Batch Foaming Process

Fabrication of polymeric foams can be performed by using batch process. In this process of fabrication, foamed samples are prepared batch-wise. It is a discontinuous foaming process, and the reproducibility of this process is very good by maintaining exact process parameters. This process is mainly utilized to investigate the initial foaming behavior of polymers and composite systems. The process is also industrially viable with some limitations. In this process, carbon dioxide or nitrogen is mainly

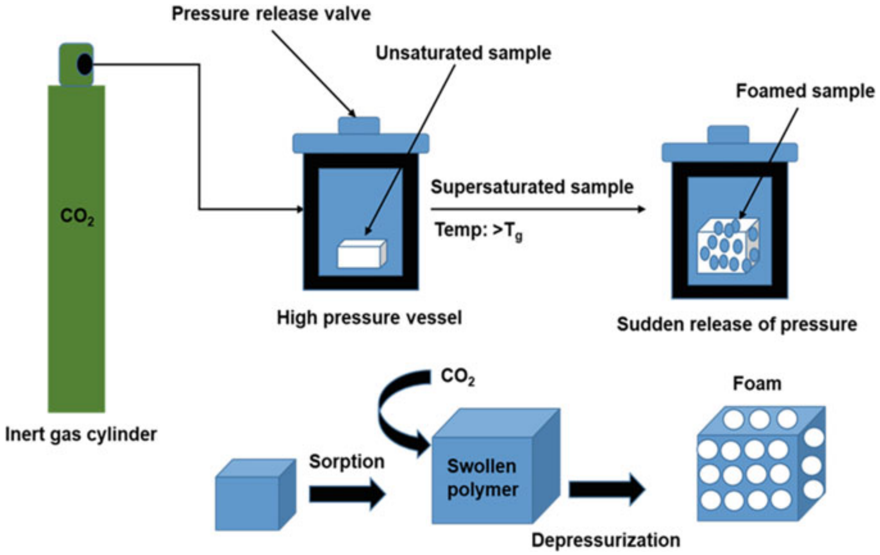

Fig. 5 A schematic representation of batch foaming process

used as physical blowing agent (PhyBA). A schematic diagram of the process is represented in Fig. 5. Since earlier days, two different methods have been generally utilized in the batch foaming process. In the first process, the pressure drop initiates the foaming in the polymer sample resulting in thermodynamic disequilibrium. The method is very useful to understand the different foaming parameters as well as the influence of additives or blending on cell nucleation. In the second technique, the thermodynamic disequilibrium is reached due to the increasing temperature. From this method, the foaming temperature and processing window of the foam can be evaluated for foam extrusion process.

2.2 *Continuous Foaming Process*

This process of fabrication of polymeric foam generally consists of extrusion (Fig. 6) and injection techniques. Different zones of the extruder can be operated at different temperatures, which make it possible to use temperature sensitive additives along with the polymer. This is one of the most beneficial CO_2-based foaming process techniques for the addition of different additives to the bio-based polymeric foams. In the die section of the extruder, the pressure is released and ultimately the polymer foam is generated. In this continuous process, the process parameters such as screw speed, saturation pressure, type and amount of additives (clay, plasticizer etc.), etc., can be optimized for obtaining tuned foam properties. The influence of the die geometry and temperature on the nucleation rate or the expansion ratio of the fabricated

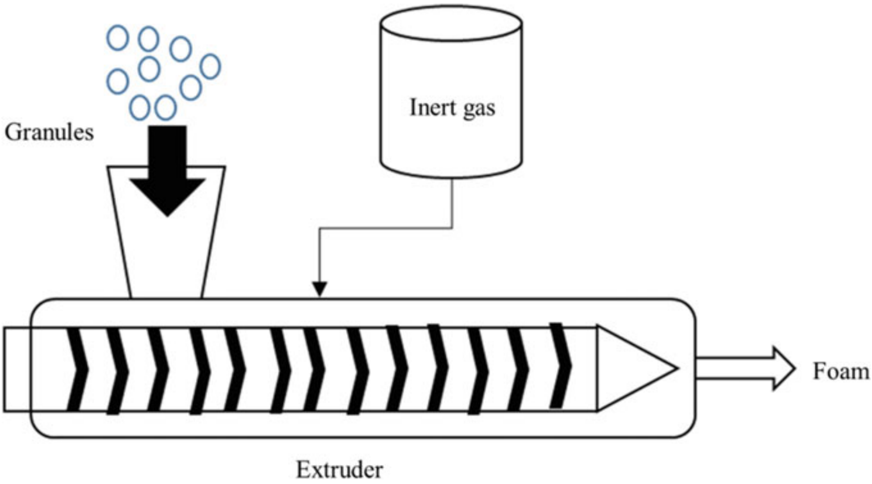

Fig. 6 A schematic representation of continuous foaming process

foams can be investigated by this process. In this process, the main advantage is the continuous high-speed production and scale-up of the technology. Different parameters like melt strength, viscosity, solubility, end groups, glass transition temperature, etc., affect the properties of the polymeric foams.

3 Polymer Foaming Technology

Polymer foaming is mainly achieved by two different techniques: physical foaming and reactive foaming.

3.1 Physical Foaming

In physical foaming, PBAs are used in the polymer melt. It also permits high-speed continuous foaming of the polymer by using extrusion and injection molding.

Physical foaming can be performed by using the following methods:

(a) Casting and leaching (C/L)
(b) Gas foaming
(c) Thermally induced phase separation (TIPS).

C/L Methods In C/L technique, the polymer is dissolved in a highly volatile solvent and cast in a bed of porogen. After evaporation of the solvent, the sample is placed in water for leaching out the porogens followed by drying. The leaching of porogens

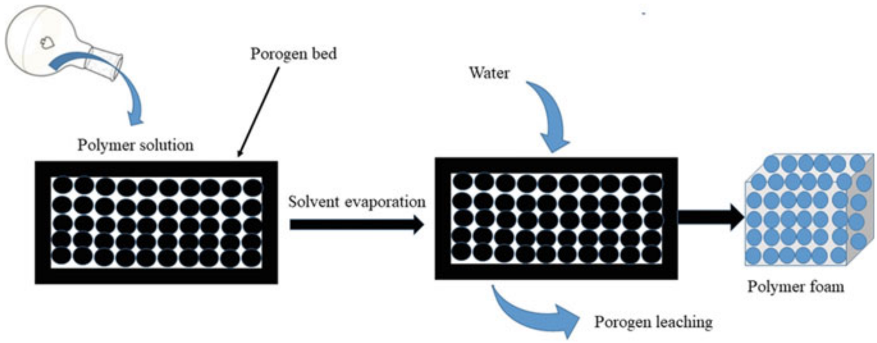

Fig. 7 Casting and leaching (C/L) technique of foam fabrication

ultimately leaves a porous structure. The selection of porogen is very important as it must be easily available and non-toxic in nature. Additionally, the porogen must be easily leached out after the solvent is evaporated. Mostly used porogens include salts like NaCl, KCl, etc. The size and amount of the porogen have the ultimate effect in cell size and cell density of the foams [7]. This technique is one of the cost-effective and easy methods to fabricate foams. The C/L method is represented in Fig. 7.

Gas Foaming Method In the gas foaming technique, different gases like nitrogen, carbon dioxide, etc., are used as PBA in the polymer melt. One of the greener approaches for gas foaming is using it in a supercritical state. Many investigations on polymer foam fabrication are reported using this technique. There are some criteria regarding the selection of PBA which includes safety, non-toxicity, transportation, reactivity, volatility, and economic viability.

TIPS Method Generally, two steps are followed for TIPS method of fabrication of foams. In the TIPS process of fabrication of foams, polymer pellets are partially foamed in the first step using PBA. These partially foamed pellets are transferred to a mold and again foaming has been performed using steam and low boiling liquid for extra foaming in the second step. Finally, a foamed structure is obtained taking the shape of the mold, and foamed beads are sticked to one another [8].

3.2 Reactive Foaming

In the reactive foaming technique, chemical reactions are carried out for the foaming of polymers. The production of gases in the chemical reactions fabricates the foamed structure. In this method of fabrication, the chemical blowing agents (CBA) are utilized for foaming of polymers. The selection of CBA has some minimum criteria including by-products, nucleating effects, processability with the base polymer, and color left-over in the polymer matrix.

4 Recent Advances in Biodegradable PLA-Based Foams

Generally, biodegradable polymeric foams like starch, PHBV, etc., are mainly used in food packaging applications. However, biodegradable PLA-based foams have the potential to replace the major market players (polypropylene, PS, etc.) in different commodity applications due to its unique properties. Recently, researchers are focusing toward the development of PLA-based sustainable foams due to its greener routes and comparable properties with some non-degradable foams. However, some improvements in the properties of PLA-based foams are still lacking compared to non-degradable foams. The improvement in the properties of PLA-based foams can be achieved by the incorporation of additives, flame retardants, plasticizers, and so on according to the ultimate application. Some investigations on PLA-based foams are found to be path-breaking towards the development of greener environment. Mainly, it is observed that PLA-based foams are developed using continuous extrusion foaming technique in the scale-up process. However, the investigations are also carried out in batch foaming to understand the parameters for improvements. PLA-based foams are used in various fields of biomedical applications including tissue engineering and cell culture. It is observed in the literature that most of the PLA-based foams used in bio-based sophisticated applications are fabricated by C/L technique due to its cost-effectiveness and less usage of machinery. Some of the recent developments observed in PLA-based foams are discussed in this section. The improvement in the thermal stability and crystallinity in PLA-based foams can be achieved by using additives like nanofillers, nanoclays, etc. The mechanical properties of PLA-based foams are very much dependent on the amount of closed and open cells present in the PLA foam matrix. Therefore, the increase in the closed cell percentage can easily achieve mechanical strength. The plasticizers in PLA-based foams improve the flexibility, which is a requirement in some sophisticated bio-based applications [9]. Recent studies reveal that for some applications related to cell proliferation, the large surface area is favorable along with wettability requirements, and PLA-based foams can be tuned to the desired properties by utilizing nanobiofillers [10].

A representative field emission scanning electron microscopy (FESEM) image of PLA-based foam is shown in Fig. 8, where the interconnected pores with cell walls are clearly visible in the micrograph. Generally, for the improvement in mechanical properties, foams are fabricated using extrusion or injection molding process using supercritical carbon dioxide as PBA. Some investigations on the improvements in mechanical properties of PLA-based foams suggest that using nanoclay (montmorillonite (MMT)) at lower concentrations in the PLA matrix improves the tensile strength of PLA foam. The nanoclay also helps in the generation of more nucleating cites which are also responsible for smaller pores in the matrix [11]. Similarly, an increase of specific tensile strength of PLA-based foams is also observed under foaming with compressed CO_2. The elongation at break increases up to ~15 times on foaming compared to unfoamed counterpart [12]. The reduction in cell size and increase in the cell density can also be achieved in PLA-based foams using a mixture of compressed CO_2 and N_2 (20:80 ratio) as PBA. Sequential addition of chain

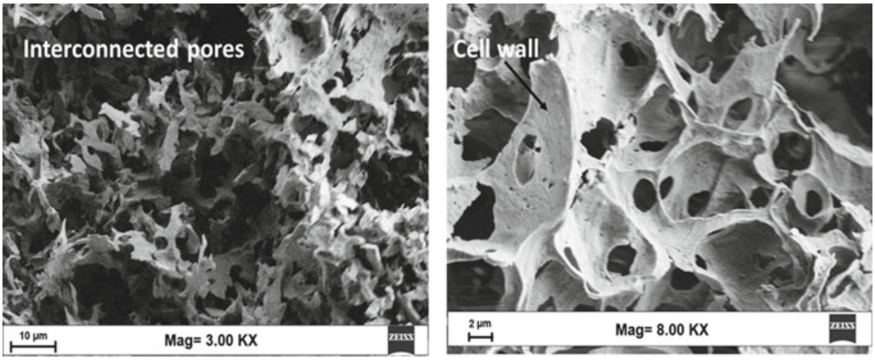

Fig. 8 FESEM micrographs of PLA-based foams fabricated at the Centre of Excellence for Sustainable Polymers (CoE-SusPol), IIT Guwahati

extenders such as 1, 4-butanediol and 1,4-butane di isocyanate in PLA gives high melt viscosity and elasticity to the PLA foam. Addition of crosslinkers in the PLA matrix improves the glass transition temperature (T_g) and thus affects the thermal properties [13]. Foaming of PLA in the presence of chain extender such as Joncryl 4368, which influences the polymer viscosity and crystallinity. Chain extender helps in the generation of smaller pores and improvement in cold crystallization temperature [14]. PS/poly(glycidyl methacrylate) random copolymer has also been used as chain extender in PLA matrix, which improves the viscous and elastic properties along with smaller cell generation in PLA foam using supercritical CO_2 as PBA [15].

Investigations are also observed for the fabrication of PLA-based foams for tissue engineering applications with very high interconnectivity of the pores. This is achieved by using foaming of PLA/PS blend and then extracting the PS phase, which leads to a highly interconnected porous PLA-foamed structure. The high interconnectivity of pores is suitable for the growing of human cells in the PLA foam matrix [16]. Similar types of PLA-based tissue engineering scaffolds can also be fabricated by using a solvent-free method. PLA and sucrose immiscible blends are first obtained from the extruder followed by solid-state foaming. The leaching of sucrose particles ultimately leaves a foamed PLA structure. A highly porous (porosity: 90%) structure with pore size ranging from 25 to 200 μm can be achieved by this process [17]. Some researchers utilize injection molding technique for the fabrication of high void fraction polylactide foams. Incorporation of talc in the PLA foaming process is under N_2 as PBA. They observed that talc/clay provides a more uniform cell structure with cell size <50 μm. The crystallization kinetics of PLA is also affected by different parameters like the pressure of the gas, the presence of nanoclay/talc, mold opening, and so on [18]. The continuous process of fabrication of low-density, microcellular PLA foams with crystallinity and well-controlled cell morphology has demonstrated by Wang et al. [19]. They have developed a tandem system utilizing CO_2 as PBA. They systematically investigated the extrusion foaming behaviors of linear and branched PLAs. They have concluded that molecular branching in PLA is responsible for melt strength and elasticity. The integrity of the cells and cell density increases with branching. The extrusion foaming of PLA with endothermic chemical foaming agent (CFA) has demonstrated by Matuana et al. [20]. They observed that void fraction is closely related to the melt flow index of PLA. Various other parameters like processing speed, CFA concentration, and melt flow index affected the cellular morphology of PLA foam. Hence, by maintaining these parameters we can tune the PLA-based foam morphology according to the desired applications. Improvements in cell density, reduction in cell size and increase in bulk compressibility of PLA-based foams can also be achieved by using tapioca starch and cloisite Na^+ in the PLA matrix by melt intercalation techniques. The PLA-based nanocomposite foams have superior and excellent properties compared to neat PLA foam due to the possible intercalation of nanoclays in the PLA matrix [21]. The average pore size of PLA-based foams can be achieved up to ~5 μm utilizing PLA/starch composite foaming by supercritical CO_2 in batch foaming process. The increase in crystallinity is observed in PLA/starch foams compared to neat PLA foam, which influences the mechanical properties along with the expansion ratio [22]. Similar kind of improvements in flexural and tensile strength in PLA/starch foams are noticed with the addition of plasticizers like glycerol, urea, and so on [23]. The maximum expansion ratio of ~50 for PLA-based foam can be achieved by using extrusion foaming of semi-crystalline PLA and thermoplastic starch blends. This system gives the minimum average pore size as ~25 μm [24].

Some improvements in PLA-based foams can also be accomplished by blending it with different other materials and subsequent foaming of the system. Blending of PLA with polymers like poly(butylene adipate-co-butylene terephthalate), poly(butylene adipate-co-terephthalate), PHBV, and so on has been demonstrated in recent past [25–27]. Extrusion foaming of the above PLA-based polymeric blends improves the mechanical and other properties of PLA foam. The decrease in the cell size (up to ~10 μm) and increase in the cell density is observed. The degree of crystallinity in PLA-based foams can also be improved by using flex-fiber composites and coupling agent [28]. Introduction of stereocomplex crystallites in the PLA matrix helps to improve the heat resistance property of microcellular PLA-based foam. A significant increase in cell density and decrement in cell size is also reported on the incorporation of stereocomplex crystallites [29]. Flame retardant property of PLA-based foams can be improved by using starch as a natural charring agent [30].

Introduction of hyperbranched polyester (HBP)/nanoclay in the PLA matrix by an injection molding process using N_2 as PBA has been reported by Pilla et al. [31]. They have achieved a maximum expansion ratio as 1.2 and minimum average cell size as ~10 μm. The addition of HBPs and nanoclay decreased the average cell size and increased the cell density of PLA-based foam. The development of first nanocellular PLA-based foams has been demonstrated by Fujimoto et al. [32]. They have fabricated PLA/layered silicate nanocomposite foam utilizing supercritical CO_2 as PBA in batch foaming technology. The expansion ratio of ~2.7 and average cell size of 360 nm can be achieved by this technique. The fabricated foam mainly consists of a closed cellular structure which enhances the mechanical properties of PLA-based foams.

Some improvements in the nanocellular PLA-based foam technology has been carried out by Ema et al. [33], where foam processing and cellular structure of polylactide-based nanocomposites has been studied. They used an autoclave for foaming and utilized the batch foaming technique using supercritical carbon dioxide (CO_2) as a foaming agent. They investigated the foam processing of neat polylactide (PLA) and two different types of PLA-based nanocomposites (PLACNs). The maximum expansion ratio of ~5 and minimum average cell size as ~200 nm is achieved by this technique. The dispersed nanoclay particles acted as nucleating sites for cell formation and the cell growth occurs on the surfaces of the clays. The PLACNs provided excellent nanocomposite foams having high cell density.

The degradation of PLA-based foams is a very important phenomenon. Some investigations on the degradation behavior of PLA-based foams can be observed in the literature. The enzymatic degradation of PLA-based foams can be enhanced by changing the pore size. It is observed that the degradation rate of nanocellular PLA-based foam is ~2 times higher than the microcellular foam with the same crystallinity. This phenomenon is due to the large surface area of the nanocellular foam which can accommodate a large amount of water facilitating the enzymatic degradation faster than microcellular foam [34].

5 Nanostructured Materials in PLA-Based Foams

The addition of nanobiofillers in the polymer matrix for tuning of various properties is also a growing field of PLA-based foams. Some investigations have been reported in literature about the usage of nanobiofillers like silk, cellulose, chitosan, gum Arabic (GA), nanoclay, etc., in the PLA-based foams. These nanofillers are derived from bio-sources and are abundantly available in nature. Therefore, the utilization of these fillers in the PLA foam matrix has economic and environmental aspects.

5.1 PLA- and Silk Fibroin-Based Nanocomposite Foams

Silk is a widely used material for improving the properties of PLA-based foam materials. The fabrication of microcellular biodegradable PLA/silk composite foams using supercritical CO_2 has been reported by Kang et al. The reduction in cell size and increase in cell density is observed with the increase in silk fibroins in the PLA matrix. By utilizing this technique, average cell size up to ~15 μm can be achieved [35].

5.2 PLA and Nanocellulose-Based Nanocomposite Foams

Cyclic tensile properties of PLA-based foams can be tuned by using cellulose nanocrystals (CNC) as demonstrated by Qiu et al. [36] using high-pressure batch foaming process. Improvement in the cell density and decrement in wall thickness is observed for PLA/CNC-based foams. Incorporation of cellulose nanofibers (CNF) in the PLA foam matrix has been reported in some of the investigations. Improvements in strain at break and high tensile toughness in PLA/CNF-based microcellular foams have been demonstrated in past years [37]. Viscosity of the fabricated PLA/CNF-based foams is also influenced by CNF content as reported by Youn Cho et al. [38]. They used supercritical carbon dioxide as a PBA. They also found that compared to neat PLA foam, the PLA/CNF nanocomposite foams exhibited decreased cell size as well as increased cell density and foam density due to the improved viscous properties. CNF mainly acts as a nucleating agent in the PLA matrix at low concentrations; however, at higher concentration, it hinders the chain movement of PLA. The introduction of CNFs significantly improves the morphology of PLA foams. Both the amount of CNFs and surface acetylation contribute to the reduction in cell size and an increase in cell density of PLA-based foam [39]. Improvements in mechanical, thermal, and wettability properties of PLA/CNC-based microcellular foams fabricated by C/L technique utilizing sucrose as porogen medium has been reported. The bionanofiller mainly acts as a nucleating agent in the PLA matrix in lower loadings and acts as a physical barrier for chain folding in higher loading. CNC nanobiofillers also help in crystallization of PLA-based foams. CNC also influences the thermal stability of the fabricated PLA-based foams. The cell density increases, and cell size decreases with increasing CNC content. The hydrophobicity of PLA-based foams improves with increase in CNC due to the change in morphology and the effect of nanofiller. CNC also helps in increasing the surface area of PLA-based foams. The energy of crystallization also increases with CNC loading. The thermal degradation investigation of PLA/CNC-based foams reveals the increase in activation energy with CNC at lower loadings indicating an increase in thermostability by uniform dispersion of CNC nanobiofillers in PLA foam matrix. A change of ~40–50 kJ/mol in activation energy has been reported for PLA/CNC foam system compared to PLA/CNC film system due to the generation of more surface area and more cites of degradation in PLA/CNC-based foams. However, CNC has no significant effect on the mechanism of degradation of PLA-based foams [40, 41].

5.3 PLA- and Nanochitosan-Based Nanocomposite Foams

Nanobiofillers like chitosan and GA act as plasticizing agents in the PLA matrix. Chitosan is abundantly available in nature. It comes from natural resources. Chitosan is a very useful bionanofiller. It has the approval of the Food and Drug Administration (FDA) as a non-toxic material and can be utilized in foods and other biomedical applications. However, due to its hydrophilic nature, some modifications in the surface have to be conducted to make it compatible with hydrophobic biopolymers. Chitosan microspheres have been utilized in PLA foam matrix for application of peptide carrier in biomedical fields [42]. Some investigations demonstrated the fabrication of PLA-based foams with chitosan for breast cancer cells [43]. Chitosan nanofiller has been widely utilized in poly (L-lactic acid) foam matrix for cell proliferation investigations [44]. On the other hand, poly (chitosan-grafted-lactic acid) scaffolds have been utilized for biocompatibility investigations [45]. PLA/modified chitosan (MC)-based microcellular foams have been fabricated by C/L technique. The ~2.3-fold increase in cell density and ~1.3-fold decrease in cell size have been demonstrated compared to neat PLA foams. The MC (oligomer-grafted-chitosan) improves the hydrophobicity of the fabricated PLA-based foams. The increase in the surface area has been reported with an increase in MC concentration due to the generation of smaller pores. MC acts as a nucleating agent in the PLA matrix. However, due to the presence of low-molecular-weight oligomers in MC, the thermal properties slightly decrease. The activation energy decreases with an increase in MC loading due to its plasticizing effect in PLA foam matrix [46].

5.4 PLA- and Nanogum-Based Nanocomposite Foams

GA is a polysaccharide obtained from trees like *Acacia senegal* and *Acacia seyal*. It has some added advantages like non-toxicity, biodegradability, and easy availability as it comes from natural resources. GA has Generally Recognized as Safe (GRAS) certification by United States Food and Drug Administration (USFDA). A recent investigation on PLA/modified GA (MG)-based microcellular foam demonstrated that MG acts as a plasticizer in the PLA foam matrix due to the presence of oligomer. MG helps in the generation of smaller pores in the matrix. From the porosimetric investigation, an increase in cell density and a decrease in cell size in PLA foam have been reported. The hydrophobicity of PLA-based foam increases with the increase in MG due to the change in surface morphology of PLA foam. However, a decrease in thermostability and thermo-mechanical properties has been reported [47].

From the above discussion, it can be concluded that the bio-based nanofillers can be effectively used in the PLA foam matrix to improve various properties. The use of bionanofillers in PLA foam matrix leads to the opening of a wider window of applications in the field of tissue engineering and cell proliferation for PLA-based foam.

6 Other Bio-based Sustainable Foams

Apart from PLA-based foams, some important and useful bio-based sustainable foam includes starch foam, cellulose foam, polyvinyl alcohol (PVOH), PCL, and ethylene vinyl alcohol (EVOH). Starch is the first developed biodegradable foam in the history of biopolymer foams. The starch foam was first developed in 1964 (US patent 3137592) and further modified as a hydrophobic porous starch foam in 1975 (US patent 3891624). Water-soluble PVOH foams were developed in 1992 (US Patent 5089535). The applications of these biodegradable sustainable foams are limited. The starch foam is mainly utilized in the food packaging industry. PVOH and EVOH are the two water-soluble foams mainly utilized in packaging, oxygen barrier, and multilayer packaging applications. The water solubility of these two foams makes it environmentally friendly in nature, and disposal after end life is very easy. PCL is also used in packaging applications, tissue engineering, high engineering advance application with the aid of various bio-based materials such as chitosan, cellulose, and others. The bio-based sustainable foams have some limitations in properties like low mechanical and thermal properties [48].

The improvement in the properties of these biopolymers is the current need. A wide range of applications needs to be investigated for these biopolymers. Among these biopolymer foams, starch attracts the scientific community due to its agricultural routes. As discussed in the earlier section, improvements in PLA-based foams can be carried out using starch as an additive. Starch foam has the capability to compete with PS foam in the loose-fill market. Biodegradable Green Cell® foam (GCF) can be fabricated from the proprietary corn–starch blend [49]. It is mainly targeted for protective packaging applications. Starch foam is already an established player in the loose-fill global market. Starch-based packaging peanuts are made from crop-based sources and are non-toxic in nature. The biodegradable peanut for packaging brand, Biofoam, can be fabricated from grain sorghum. Starch-based loose-fill biodegradable peanuts are soluble in water, whereas PS-based loose-fill packaging is not soluble in water. Therefore, a significant research is required to improve the starch-based foam to make it comparable with PS-based foams. The improvements in the technology are required to overcome the drawbacks like higher weight, dust creation, high cost, and lower resilience of starch-based foams for different packaging applications. On the other hand, some important factors like life cycle analysis, testing, new processing technique, and proper disposal methodology need to be properly addressed for these bio-based polymer foams to make it more applicable and cost-effective in the near future.

References

1. Klempner D, Sendijarevic V, Aseeva RM (eds) (2004) Handbook of polymeric foams and foam technology. Hanser Verlag
2. Lee ST (2004) Introduction: polymeric foams, mechanisms, and materials. In: Polymeric foams. CRC Press, pp 15–29
3. Auras RA, Lim LT, Selke SE, Tsuji H (eds) (2011) Poly (lactic acid): synthesis, structures, properties, processing, and applications, vol 10. Wiley
4. Nofar M, Park CB (2014) Poly (lactic acid) foaming. Prog Polym Sci 39:1721–1741. https://doi.org/10.1016/j.progpolymsci.2014.04.001
5. Auras R, Harte B, Selke S (2004) An overview of polylactides as packaging materials. Macromol Biosci 4:835–864. https://doi.org/10.1002/mabi.200400043
6. Sauceau M, Fages J, Common A, Nikitine C, Rodier E (2011) New challenges in polymer foaming: a review of extrusion processes assisted by supercritical carbon dioxide. Prog Polym Sci 36:749–766. https://doi.org/10.1016/j.progpolymsci.2010.12.004
7. Mane S (2016) Effect of porogens (type and amount) on polymer porosity: a review. Can Chem Trans 4:210–225
8. Li S, Chen X, Li M (2010) Effect of some factors on fabrication of poly (L-lactic acid) microporous foams by thermally induced phase separation using N, N-dimethylacetamide as solvent. Prep Biochem Biotechnol 41:53–72. https://doi.org/10.1080/10826068.2010.534222
9. Tripathi N, Katiyar V (2016) PLA/functionalized-gum arabic based bionanocomposite films for high gas barrier applications. J Appl Polym Sci 133. https://doi.org/10.1002/app.43458
10. Dhar P, Tarafder D, Kumar A, Katiyar V (2015) Effect of cellulose nanocrystal polymorphs on mechanical, barrier and thermal properties of poly (lactic acid) based bionanocomposites. RSC Adv 5:60426–60440. https://doi.org/10.1039/C5RA06840A
11. Hwang SS, Hsu PP, Yeh JM, Chang KC, Lai YZ (2009) The mechanical/thermal properties of microcellular injection-molded poly-lactic-acid nanocomposites. Polym Compos 30:1625–1630. https://doi.org/10.1002/pc.20736
12. Ji G, Wang J, Zhai W, Lin D, Zheng W (2013) Tensile properties of microcellular poly (lactic acid) foams blown by compressed CO_2. J Cell Plast 49:101–117. https://doi.org/10.1177/0021955X13477437
13. Di Y, Iannace S, Di Maio E, Nicolais L (2005) Reactively modified poly (lactic acid): properties and foam processing. Macromol Mater Eng 290:1083–1090. https://doi.org/10.1002/mame.200500115
14. Ludwiczak J, Kozlowski M (2015) Foaming of polylactide in the presence of chain extender. J Polym Environ 23:137–142. https://doi.org/10.1007/s10924-014-0658-7
15. Zhou M, Zhou P, Xiong P, Qian X, Zheng H (2015) Crystallization, rheology and foam morphology of branched PLA prepared by novel type of chain extender. Macromol Res 23:231–236. https://doi.org/10.1007/s13233-015-3018-0
16. Zhou C, Ma L, Li W, Yao D (2011) Fabrication of tissue engineering scaffolds through solid-state foaming of immiscible polymer blends. Biofabrication 3:045003
17. Ma L, Jiang W, Li W (2014) Solvent-free fabrication of tissue engineering scaffolds with immiscible polymer blends. Int J Polym Mater Polym Biomater 63:510–517. https://doi.org/10.1080/00914037.2013.854222
18. Ameli A, Nofar M, Jahani D, Rizvi G, Park CB (2015) Development of high void fraction polylactide composite foams using injection molding: crystallization and foaming behaviors. Chem Eng J 262:78–87. https://doi.org/10.1016/j.cej.2014.09.087
19. Wang J, Zhu W, Zhang H, Park CB (2012) Continuous processing of low-density, microcellular poly (lactic acid) foams with controlled cell morphology and crystallinity. Chem Eng Sci 75:390–399. https://doi.org/10.1016/j.ces.2012.02.051
20. Matuana LM, Faruk O, Diaz CA (2009) Cell morphology of extrusion foamed poly (lactic acid) using endothermic chemical foaming agent. Bioresour Technol 100:5947–5954. https://doi.org/10.1016/j.biortech.2009.06.063

21. Lee SY, Hanna MA (2008) Preparation and characterization of tapioca starch-poly (lactic acid)-Cloisite NA^+ nanocomposite foams. J Appl Polym Sci 110(4):2337–2344. https://doi.org/10.1002/app.27730
22. Hao A, Geng Y, Xu Q, Lu Z, Yu L (2008) Study of different effects on foaming process of biodegradable PLA/starch composites in supercritical/compressed carbon dioxide. J Appl Polym Sci 109:2679–2686. https://doi.org/10.1002/app.27861
23. Preechawong D, Peesan M, Supaphol P, Rujiravanit R (2005) Preparation and characterization of starch/poly (L-lactic acid) hybrid foams. Carbohydr Polym 59:329–337. https://doi.org/10.1016/j.carbpol.2004.10.003
24. Mihai M, Huneault MA, Favis BD, Li H (2007) Extrusion foaming of semi-crystalline PLA and PLA/thermoplastic starch blends. Macromol Biosci 7:907–920. https://doi.org/10.1002/mabi.200700080
25. Yuan H, Liu Z, Ren J (2009) Preparation, characterization, and foaming behavior of poly (lactic acid)/poly (butylene adipate-co-butylene terephthalate) blend. Polym Eng Sci 49:1004–1012. https://doi.org/10.1002/pen.21287
26. Pilla S, Kim SG, Auer GK, Gong S, Park CB (2010) Microcellular extrusion foaming of poly (lactide)/poly (butylene adipate-co-terephthalate) blends. Mater Sci Eng C 30:255–262. https://doi.org/10.1016/j.msec.2009.10.010
27. Zhao H, Cui Z, Sun X, Turng LS, Peng X (2013) Morphology and properties of injection molded solid and microcellular polylactic acid/polyhydroxybutyrate-valerate (PLA/PHBV) blends. Ind Eng Chem Res 52:2569–2581. https://doi.org/10.1021/ie301573y
28. Pilla S, Kramschuster A, Lee J, Auer GK, Gong S, Turng LS (2009) Microcellular and solid polylactide–flax fiber composites. Compos Interfaces 16:869–890. https://doi.org/10.1163/092764409X12477467990283
29. Jia P, Hu J, Zhai W, Duan Y, Zhang J, Han C (2015) Cell morphology and improved heat resistance of microcellular poly (L-lactide) foam via introducing stereocomplex crystallites of PLA. Ind Eng Chem Res 54:2476–2488. https://doi.org/10.1021/ie504345y
30. Wang J, Ren Q, Zheng W, Zhai W (2014) Improved flame-retardant properties of poly (lactic acid) foams using starch as a natural charring agent. Ind Eng Chem Res 53:1422–1430. https://doi.org/10.1021/ie403041h
31. Pilla S, Kramschuster A, Lee J, Clemons C, Gong S, Turng LS (2010) Microcellular processing of polylactide–hyperbranched polyester–nanoclay composites. J Mater Sci 45:2732–2746. https://doi.org/10.1007/s10853-010-4261-6
32. Fujimoto Y, Ray SS, Okamoto M, Ogami A, Yamada K, Ueda K (2003) Well-controlled biodegradable nanocomposite foams: from microcellular to nanocellular. Macromol Rapid Commun 24:457–461. https://doi.org/10.1002/marc.200390068
33. Ema Y, Ikeya M, Okamoto M (2006) Foam processing and cellular structure of polylactide-based nanocomposites. Polymer 47:5350–5359. https://doi.org/10.1016/j.polymer.2006.05.050
34. Bitou M, Okamoto M (2008) Fabrication of porous 3-D structure from poly (L-lactide)-based nano-composite foams. Effect of foam structure on enzymatic degradation. Polym Degrad Stab 93:1081–1087. https://doi.org/10.1016/j.polymdegradstab.2008.03.014
35. Kang DJ, Xu D, Zhang ZX, Pal K, Bang DS, Kim JK (2009) Well-controlled microcellular biodegradable PLA/silk composite foams using supercritical CO_2. Macromol Mater Eng 294:620–624. https://doi.org/10.1002/mame.200900103
36. Qiu Y, Lv Q, Wu D, Xie W, Peng S, Lan R, Xie H (2018) Cyclic tensile properties of the polylactide nanocomposite foams containing cellulose nanocrystals. Cellulose 25:1795–1807. https://doi.org/10.1007/s10570-018-1703-9
37. Dlouhá J, Suryanegara L, Yano H (2014) Cellulose nanofibre–poly (lactic acid) microcellular foams exhibiting high tensile toughness. React Funct Polym 85:201–207. https://doi.org/10.1016/j.reactfunctpolym.2014.07.016
38. Cho SY, Park HH, Yun YS, Jin HJ (2013) Influence of cellulose nanofibers on the morphology and physical properties of poly (lactic acid) foaming by supercritical carbon dioxide. Macromol Res 21:529–533. https://doi.org/10.1007/s13233-013-1057-y

39. Dlouhá J, Suryanegara L, Yano H (2012) The role of cellulose nanofibres in supercritical foaming of polylactic acid and their effect on the foam morphology. Soft Matter 8:8704–8713. https://doi.org/10.1039/C2SM25909E
40. Borkotoky SS, Dhar P, Katiyar V (2018) Biodegradable poly (lactic acid)/cellulose nanocrystals (CNCs) composite microcellular foam: effect of nanofillers on foam cellular morphology, thermal and wettability behavior. Int J Biol Macromol 106:433–446. https://doi.org/10.1016/j.ijbiomac.2017.08.036
41. Borkotoky SS, Chakraborty G, Katiyar V (2018) Thermal degradation behaviour and crystallization kinetics of poly (lactic acid) and cellulose nanocrystals (CNC) based microcellular composite foams. Int J Biol Macromol 118:1518–1531. https://doi.org/10.1016/j.ijbiomac.2018.06.202
42. Niu X, Feng Q, Wang M, Guo X, Zheng Q (2009) In vitro degradation and release behavior of porous poly (lactic acid) scaffolds containing chitosan microspheres as a carrier for BMP-2-derived synthetic peptide. Polym Degrad Stab 94:176–182. https://doi.org/10.1016/j.polymdegradstab.2008.11.008
43. Sahoo SK, Panda AK, Labhasetwar V (2005) Characterization of porous PLGA/PLA microparticles as a scaffold for three dimensional growth of breast cancer cells. Biomacromolecules 6:1132–1139. https://doi.org/10.1021/bm0492632
44. Jiao Y, Liu Z, Zhou C (2007) Fabrication and characterization of PLLA–chitosan hybrid scaffolds with improved cell compatibility. J Biomed Mater Res A 80:820–825. https://doi.org/10.1002/jbm.a.31061
45. Zhang Z, Cui H (2012) Biodegradability and biocompatibility study of poly (chitosan-g-lactic acid) scaffolds. Molecules 17:3243–3258. https://doi.org/10.3390/molecules17033243
46. Borkotoky SS, Pal AK, Katiyar V (2019) Poly (lactic acid)/modified chitosan-based microcellular foams: thermal and crystallization behavior with wettability and porosimetric investigations. J Appl Polym Sci 136:47236. https://doi.org/10.1002/app.47236
47. Borkotoky SS, Ghosh T, Bhagabati P, Katiyar V (2019) Poly (lactic acid)/modified gum arabic (MG) based microcellular composite foam: effect of MG on foam properties, thermal and crystallization behavior. Int J Biol Macromol 125:159–170. https://doi.org/10.1016/j.ijbiomac.2018.11.257
48. Ramesh NS, Lee S, Park CB (2007) Polymeric foams: science and technology
49. Arif S, Burgess G, Narayan R, Harte B (2007) Evaluation of a biodegradable foam for protective packaging applications. Packag Technol Sci 20:413–419. https://doi.org/10.1002/pts.770