MULTIFUNCTIONAL LIGHTWEIGHT BIO-NANOCOMPOSITES STRUCTURES

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Abstract

Multifunctional lightweight bio-nanocomposite structures were prepared through a controlled nucleation and growth of gas bubbles in a thermoplastic matrix based on thermoplastic protein (zein) reinforced with nanoparticles, lignin and cellulose fibers. Cellular structures were successfully obtained by using a mixture of gases N_2/CO_2 (80/20) as blowing agent in systems containing low percentage of lignin and cellulose fibers. The possibility of tailoring the functional as well as the structural properties of biopolymers through the use of nanocomposites and natural fibers allowed for the development of novel bio-composites with improved specific mechanical properties as well as with higher thermal and acoustic insulation properties.

1 Introduction

When inspired by nature for the design of "efficient" materials we are extremely striken by the complexity of the hierarchical structures of natural foams. Vegetable and animal tissues are built by assembling, in a multiscale approach from nano to micro-scale, biomacromolecules such as polysaccharides and/or proteins, often with inorganic molecules. Fibrous and/or bulk materials are combined in full and empty spaces to generate highly anisotropic and lightweight structures.

We have developed a new generation of multifunctional bio-based composite structures where cellular structures are generated within a thermoplastic matrix of the corn protein zein reinforced with lignin and cellulose fibers. Zein is found in corn endosperm and has been the object of research as well as industrial interest (being commercially available since 1938) for its film-forming ability and its unique hydrophobicity, which is due to its high content of non-polar amino acids, [1]. It is industrially interesting due to the availability in large amounts as by-products of agricultural and biofuel processing activities (for example, ethanol production). Thermoplastic processing of zein is possible if a suitable plasticizer is used in combination with heat and shear. In this way, denaturation of the hierarchical structure of zein proteins and the development of molecular entanglements can be promoted, [2,3].

Lignin is an integral cell wall constituent, which provides plant strength and resistance to microbial degradation. It is an abundant and renewable biomaterial widespread in plants. Industrial lignin, which is a byproduct of the paper industry, exists in the black liquor of the pulping industry. Chemically, lignin is a high reactive macromolecule due to its functional groups such as phenolic, aromatic rings, methoxy and alcohol groups that are sites for

chemical modification and/or reaction. Addition of lignin in the application of polymer not only is an effective method in using renewable biomass energy, but also provides improvement of mechanical properties, heat and fire resistance [4-7]. However, the variation/improvement of characteristics could strongly dependent upon chemical functional groups of both lignin (alkaline lignin, sodium lignosulfonate) and natural polymers.
The formation of cellular structures in natural polymers has been mostly studied in the context of food engineering and in particular in the preparation of bread and cooked snacks [8-9]. The utilized technologies are different from the gas foaming technologies used for thermoplastic polymers. In fact bread and cooked snacks are produced via mixing (aeration) and fermentation with gas evolution processes. Recently, however, plastic processing technologies (stream-based extrusion) have been used to produce foams with different formulations including starch for different application such as packaging and insulation [10], while the gas foaming technologies to produces foams from thermoplasticized proteins has been reported by Salerno et al. [11]
Objective of this work was to study the processing and properties of bio-nanocomposites based on thermoplastic zein with the aim of developing fully bio-based lightweight composite materials. Lignin and cellulose fibers were employed to improve moisture resistance and mechanical properties as well as to control bubble nucleation during the formation, in situ, of the cellular structure.

2 Materials and testing methods

2.1 Thermoplastic zein (TPZ)

Maize zein protein was purchased in powder form by Sigma-Aldrich (Italy). Poly(ethylene glycol) 400 (PEG400) was used as plasticizer and was purchased from Fluka (Italy). Thermoplastic zein (TPZ) was processed by using an internal mixer using the following procedure. The zein powder, as received by the supplier (water content of 7%wt) was mixed with 25%wt PEG 400 in a beaker using a spatula to provide a crude blend. The blend was then subjected to shear stresses in a twin counter-rotating internal mixer (Rheomix 600 Haake, Germany) connected to a control unit (Rheocord 9000 Haake, Germany) to perform the thermoplasticization. Mixing temperature, speed of rotation and mixing time were 70°C, 50min^{-1} and 10min, respectively.

2.2 Bio-nanocomposite

In order to investigate the effect of lignin on hierarchical structure and on foamability of TPZ, two different ligninic systems were used, alkali lignin (average Mw=28000 ca., code 370959, Sigma Aldrich, Italy), hereafter denoted as AL and lignosulfonic acid-sodium salt (average Mw =52000 ca., code 471038, Sigma Aldrich, Italy), hereafter denoted as LSS, with two different functional groups (SH for AL and OH for LSS). TPZ/AL and TPZ/LSS were prepared by using a melt mixing method. AL and LSS were first added to PEG in amount such that the final concentrations of AL were 1 and 10 wt.% of zein+PEG system. The same thermoplasticization procedure described above for TPZ was employed.
Cellulose fibers used in absorbent products (fluff fibers) were employed as reinforcing fibers in foams.

2.3 Multifunctional foams

Foaming experiments were carried out by using a batch process on disc-shaped samples (10mm in diameter and 2 mm in thickness). The samples were placed into the pressure vessel and kept with 80-20vol% N_2-CO_2 blowing mixture for 3 hours at 70°C and at saturation pressure of 170 bar [12]. After gas solubilization, samples were cooled to the desired foaming temperature (T_f =50-60°C). The pressure was then quickly released to ambient to allow

foaming. To stabilize the cellular structure, foams were immediately removed from the vessel and allowed to cool at room conditions.

3 Results and discussion

SEM micrographs of foams obtained from TPZ, TPZ-1AL and TPZ-1LSS systems, with a foaming temperature of 55°C are shown in Figure 1. Microcellular structures were obtained both from neat TPZ and TPZ-BNCs at low lignin content (1%). Furthermore, we observed a higher number of cells only in the formulation containing small amount of AL with a slight reduction of foam density from 0.53 g/cm^3 to 0.45 g/cm^3. Foams prepared from TPZ-1LSS showed, instead, a lower cell number and higher foam density (0.75 g/cm^3) with respect to both TPZ and TPZ-1AL.

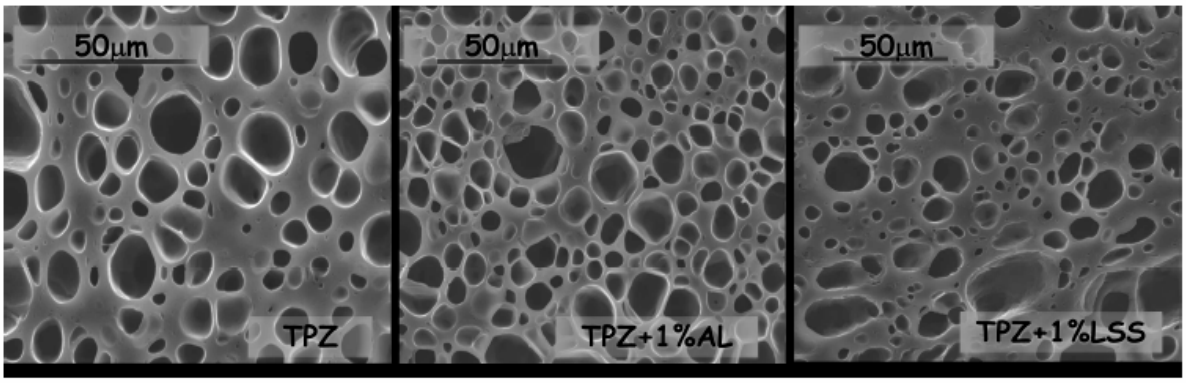

Figure 1. SEM micrographs of TPZ-BNCs foamed with N_2/CO_2 80/20vol% at P_{sat}=170bar and T_f=55°C.

At higher lignin content (10% of both AL and LSS) foaming did not occurred. These results can be correlated to an extensive modification of materials properties as function of lignin type and content, including secondary structure and thermo-mechanical properties of zein.
FTIR and XRD analysis have proved that the presence of lignin during the thermoplasticization process contributed to the modification of the protein secondary structure [13]. As a consequence, the viscoelastic properties of these systems as function of temperature were significantly modified and resulted in different nucleation and growing mechanisms of the gas bubbles during the foaming process. In particular, the addition of small amount of lignin (1% AL and LSS) in TPZ contributed to reduce the elastic modulus above the glass transition of almost one order of magnitude, from $4.0*10^6$ to $5.0*10^5$ in the case of 1% of AL, and from $4.0*10^6$ to $8.0*10^5$ in the case of 1% of LSS (Table 1). As observed by FTIR analysis reported by Oliviero et al. in [13], this effect could be associated to the increasing of "disordered" phase in zein secondary structure as a consequence of modification/disruption of the α-helix structure and the β-conformations induced by the presence of the lignin.

TPZ-BNC	AL (wt%)	LSS (wt%)	Foam density (g/cm^3)	E'(30°C)/E'(50°C)
TPZ	0	0	0.53	$4.0*10^8/4.0*10^6$
TPZ-1Al	1	-	0.45	$4.0*10^8/5.0*10^5$
TPZ-10AL	10	-	-	$1.0*10^9/5.0*10^7$
TPZ-1LSS	-	1	0.75	$4.0*10^8/8.0*10^5$
TPZ-10LSS	-	10	-	$1.0*10^9/1.0*10^8$

Table 1. Effect of lignin concentration on foam density and elastic modulus before (30°C) and after (50°C) the glass transition of the TPZ bio-nanocomposites

A different trend was observed at higher amount of lignin. In these cases, the materials showed higher elastic modulus both below and above the glass transition temperature. It is worth to observe that the reduction of elastic modulus around the glass transition was only 1 order of magnitude at 10% of LSS, suggesting the presence of strong crosslinking effects resulting from the interactions between the protein macromolecules and the modified lignin.

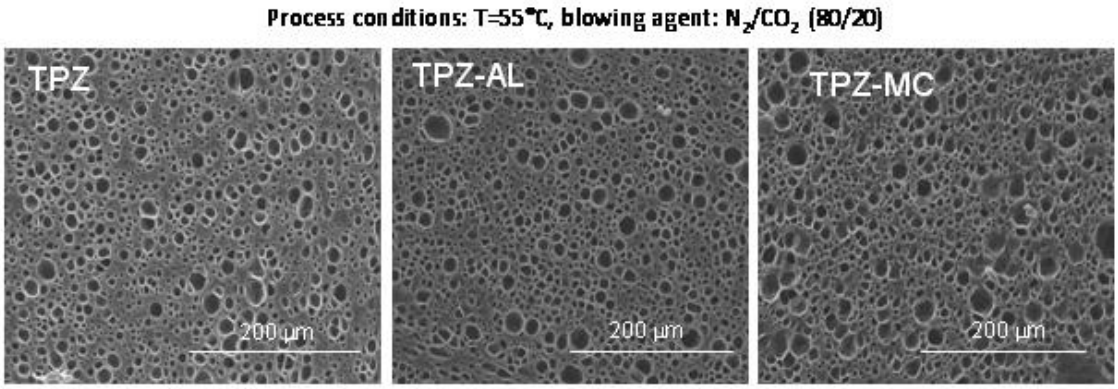

Figure 2. Cellular structures of TPZ foams: neat TPZ (left), TPZ-lignin (center), TPZ containing microcellulose fibers (right)

Cellular structures can be successfully generated from composites based on TPZ and fluff micro-cellulose fibers (MC). As shown in Figure 2, very similar cellular structures can be obtained when using small amount (1%) of AL or micro cellulose fibers (1%). All the systems reported in Figure 2 are characterized by a cellular morphology having bimodal cell size distribution. Cell size and cell density are not remarkably affected by the addition of lignin and of cellulose fibers

However, in the case of TPZ reinforced with cellulose fibers, we observed the formation of a certain numbers of larger pores around cellulose fibers (detail *b* in Figure 3). Poor adhesion between fibers and matrix is usually responsible for this behaviour. Smaller cells around fibers were instead observed in case of good adhesion (detail *a* in Figure 3)

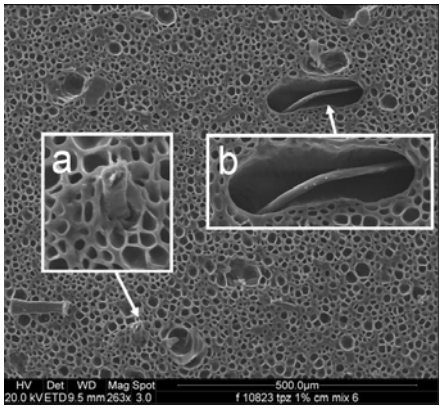

Figure 3. Cellular structures of TPZ foams reinforced with micro cellulose fibers.

4 Conclusions

Proteins, lignin and cellulose fibers represent three important bio-based polymers that can be successfully combined to prepare environmental friendly composite materials. Cellular structures can be obtained by using gas foaming techniques. In this way, lightweight bio-

based composites with improved specific mechanical properties as well as with higher thermal and acoustic insulation properties can be developed. i

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