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Thermosetting AESO-bacterial cellulose nanocomposite foams with tailored mechanical properties obtained by Pickering emulsion templating

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ABSTRACT

This study reports on the development of nanocomposite foams, prepared by Pickering emulsion templating, with promising tailored-properties, simply tunable by their composition. The selected multi-component monomer mixtures comprise acrylated epoxidized soybean oil (AESO), 1,6-hexanediol diacrylate (HDD) and divinylbenzene (DVB), chosen by their renewable-origin or resemblance to renewable ones, and above all due to their varying stiffness or crosslinking-ability. The Pickering water-in-oil emulsions, after their fast stabilization using cyclohexane and acetylated bacterial cellulose, were used as templates for the polymeric foams production. These original materials were thermally stable up to approximately 320 °C, and had a Young's modulus varying between 3.41 and 16.39 MPa, being the highest results prompted by the use of HDD or DVB.

1. Introduction

Nanocomposite polymer foams are a class of nanomaterials with growing interest in several areas, including catalysis, insulation and biomedical and pharmaceutical applications, due to their porous nanostructure, high surface area and diversity of polymeric structures [1,2]. These nanostructured materials can be obtained by means of different approaches, among which the most typically used involves polyurethane foaming [3—6], but emulsion templating has emerged as an effective way to prepare polymer based foams with precise morphologies [1]. For instance, Pickering emulsion templates that are uniquely stabilized by small particles are exceptionally stable owing to the permanent adsorption of the particles at the interface between the continuous and dispersed phases.

Medium or high internal phase (MIPE or HIPE) Pickering emulsion templates can be used to produce polymer based nanocomposite foams, if the components of the continuous phase are polymerizable [7]. Moreover, an appropriate selection of the stabilizing particles and of the continuous phase endows the design of environmentally-friendly bio-based foams seeking for alternatives to petroleum-based porous materials. For example, nano- and micro-sized particles of biological origin (e.g. particles derived from cellulose, lignin, starch and proteins) have been successfully used to prepare Pickering emulsions [8]. Bio-based particles present several advantages, when compared to the classically used synthetic inorganic particles, namely sustainable connotation, biodegradability and compatibility with several applications, including food and biomedical ones [8].

Cellulose nanofibrils (CNF) and nanocrystals (CNC) are of particular relevance because of their singular mechanical and surface properties, high availability and easiness to modify [9—11]. However, to the best of our knowledge, apart from several studies dealing with the stabilization of Pickering emulsions with nanocellulose fibrils or crystals, e.g. Refs. [12—14], only a couple of studies reported the production of sustainable cellulose nanocomposite polymers foams by Pickering emulsion polymerization. In a pioneering study, Blaker et al. described macroporous

thermosetting and UV-cured cellulose nanocomposites from MIPES and HIPES water-in-acrylated epoxidized soybean oil (AESO) emulsions stabilized by hydrophobized bacterial cellulose (BC) nanofibrils [15]. The hydrophobized cellulose samples were obtained via silylation or acetic acid modification of BC fibrils and the water-in-oil emulsions prepared through an organic phase exchange method or instead using AESO directly, followed by thermal or photopolymerization, respectively. Though, this work provided a comprehensive study about the preparation of the emulsion templates and corresponding foams, the composition of the foams was focused in a one-component AESO foam and moreover no detailed thermal or mechanical characterization was provided. In a different study, expandable polystyrene beads containing well-dispersed water microdroplets, as blowing agent, were produced through Pickering emulsion polymerization of styrene in w/o/w system using CNF [16]. Under appropriate conditions, these beads can be expanded to form low density nanocomposite foams. However, in this case the continuous phase, styrene, is not 100% bio-based. In another vein, porous materials from CNFs have been prepared using Pickering aqueous dispersions [17]. The use of chemically modified CNFs allowed preparing cross-linked foams with water durable and wet-resilient features.

These few studies clearly highlight the versatility and simplicity of this approach as an alternative to prepare innovative functional bio-based materials. Moreover, as this field is still poorly explored, it opens the possibility for the creation of panoply of new materials. For example, the use of multicomponent continuous phases has never been investigated as a way to tailor the properties of these foams.

In the present study, novel nanocomposite foams with tailored mechanical properties were obtained by Pickering emulsion polymerization of multicomponent continuous phases stabilized by acetylated bacterial cellulose. An appropriated selection of monomers, namely AESO, 1,6-hexanediol diacrylate, and divinylbenzene, was underwent taking in consideration their renewable-origin or similarity to renewable-based compounds, respectively. Likewise, this selection was also based on the monomers' varying stiffness or crosslinking-ability. The oil phase of the new emulsions was also composed of cyclohexane to enhance their stabilization time. The structural and morphological features, mechanical, thermal and also thermomechanical properties of the ensuing thermosetting foams were extensively studied.

2. Experimental

2.1. Chemicals and materials

Bacterial cellulose (BC) in the form of wet membranes (three-dimensional network of nano and microfibrils with 10–200 nm width) was produced using the *Gluconoacetobacter sacchari* bacterial strain and conventional culture medium conditions, as described elsewhere [18]. Acrylated epoxidized soybean oil (AESO), divinylbenzene (DVB, 80%), 1,6-hexanediol diacrylate (HDD, 80%), calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$, $\geq$99%) and acetic anhydride ($\geq$99%) were purchased from Sigma Aldrich-Chemicals Corp. Cumene hydroperoxide ($C_6H_5C(CH_3)_2OOH$, 80%) was supplied by Alfa Aeasar, cyclohexane (CH) was purchased from Panreac, and concentrated sulfuric acid (96%) from Acros Organic.

2.2. Bacterial cellulose acetylation

BC, previously disintegrated using a Ultra-Turrax equipment (11000 rpm, 1 h) and dispersed in acetone, was acetylated using a well-established protocol described elsewhere [19]. Briefly, the fibers (20 g) were mixed with acetic anhydride (300 ml) and sulfuric acid (1 ml), and heated at a temperature of 30 °C, for 4 h, under a nitrogen atmosphere. The ensuing acetylated BC fibers were isolated by filtration and thoroughly cleaned (washing the fibers with acetone, ethanol, water, and again ethanol). Then, these fibers were Soxhlet extracted with ethanol during 12 h to further remove any residual impurity. These acetylated BC fibers are referred hereafter as Ac−BC.

2.3. Emulsions preparation

Oil-in-water (o/w) emulsions were typically prepared by using, as the oil phase, $\approx$ 10 ml of AESO, or $\approx$ 10 ml of a mixture of AESO and CH, or instead using $\approx$ 10 ml of a mixture of AESO, CH and DVB and/or HDD in different relative proportions (Table 1). Typically, they were dispersed in 10 ml of water containing Ac−BC (0.5 wt% in respect to the water amount), $CaCl_2 \cdot 2H_2O$ (4 wt% in respect to the water amount) and $C_6H_5C(CH_3)_2OOH$ (3 wt% in respect to the AESO amount), and promptly homogenized by vigorous stirring using a vortex, during 1 min. The ensuing emulsions were allowed to rest at room-temperature and, at every 24 h, they were stirred and again allowed to rest until stable emulsions were reached. Table 1 summarizes the main emulsions compositions (E1-E7) prepared in this study.

2.4. Characterization of the emulsions

The stability of the w/o Pickering emulsions were assessed by following the movement of the emulsion boundary visually, at regular time intervals (every 24 h). The emulsion stability index (ESI) was calculated by taking the ratio between the volume of the emulsion at the time of assessment and the total volume of the mixture, and the internal phase volume ratio (Φ) was calculated from the ratio of water droplets phase volume and the emulsion volume. Optical microscopy images of the emulsion droplets were also captured with an IDS UI124DML numerical camera mounted on an Olympus Microscope BX51, with magnifications of ocular $\times$10 and objectives $\times$5 or $\times$10.

2.5. Pickering emulsions polymerization

Radical thermopolymerization reactions were carried out by heating the stable emulsions (E1-E4) at 80 °C, during 24 h, and using $C_6H_5C(CH_3)_2OOH$ as thermoinitiator (3 wt% relatively to the monomers amount). Radical photopolymerization was carried out by irradiating the stable emulsion (E0) with an UV light using a mercury lamp (with a wavelength >280 nm and power of 100 W), during 10 h.

The ensuing foam materials were cleaned with acetone and dried under vacuum, at 50 °C, during 24 h. Table 1 summarizes the correspondence between the emulsions (E0-E4) and the ensuing related foams (F0−F4).

Table 1
Experimental data for the emulsions preparation and related foams.

Emulsion	% H₂O	oil phase				Resulting Foam[a]
		%AESO	%CH	%DVB	%HDD	
E0	50	50	–	–	–	**F0**
E1	50	38	12	–	–	**F1**
E2	48	36	12	4	–	**F2**
E3	49	37	12	–	2	**F3**
E4	48	35	11	4	2	**F4**

[a] F0 was obtained by UV-photopolymerization reaction and F1−F4 were obtained by thermopolymerization reactions.