European Polymer Journal 79 (2016) 109–120

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Macromolecular Nanotechnology

Cellulose nano-biocomposites from high oleic sunflower oil-derived thermosets

Maryluz Moreno [a], Ilaria Armentano [b], Elena Fortunati [b], Samantha Mattioli [b], Luigi Torre [b], Gerard Lligadas [a], Joan C. Ronda [a,*], Marina Galià [a], Virginia Cádiz [a]

[a] Departament de Química Analítica i Química Orgànica, Universitat Rovira i Virgili, C/ Marcel.lí Domingo 1, 43007 Tarragona, Spain
[b] Materials Engineering Center, UdR INSTM, Strada di Pentima 4, 05100 Terni, Italy

ARTICLE INFO

Article history:
Received 8 February 2016
Received in revised form 19 April 2016
Accepted 19 April 2016
Available online 20 April 2016

Keywords:
Nano-biocomposites
Cellulose nanocrystals
Renewable resources
Thermosets
Thiol-Michael addition

ABSTRACT

Thiol-Michael addition of pentaerythritol tetrakis(3-mercaptopropionate) (PE3MP) to a high oleic sunflower oil derivative containing enone groups (ETG), has been used to prepare vegetable oil derived renewable thermosets in an efficient way and under mild conditions. The same formulation has been used to prepare nano-biocomposites by incorporating into the polymerization mixture, 1 wt%, 5 wt% and 10 wt% of cellulose nanocrystals (CNC) modified with Beycostat A B09® as surfactant. The chosen methodology allows a good dispersion of the nano filler in a low polarity reactive media which still is a challenging approach. The morphological, thermal and mechanical properties of the different nano-biocomposites were evaluated and compared with the pristine thermoset. Morphological analysis shows that good dispersion of the nanofillers is achieved in all formulations. Mechanical properties show an improvement of the Young Modulus for all nanofiller contents, showing a maximum at 5 wt% loading (32 and 78 MPa for the pristine and 5% CNC nano-composite respectively) that has been related with the reinforcement effect of the modified CNC. CNC dispersion also affects positively the surface properties, thus reducing drastically the contact angle values (78.0–16.0° for the pristine and 10% CNC nano-composite respectively). Finally, protein adsorption was measured in order to evaluate potential application of these materials as biosensors and cell growing supports.

1. Introduction

The last two decades have witnessed an exponential growth in the interest for using bio-based products, which has been driven by the need for replacing petroleum based materials, reducing the fuel consumption and for producing materials with lower environmental impact [1,2]. Natural vegetable oils are considered to be one of the most important classes of renewable resources because of the wide variety of possibilities for chemical transformations, universal availability, and low price and they are preferred by the chemical industry [3]. To date, a huge amount of thermoplastic and thermosetting oil-based biomaterials have been developed by using a variety of synthetic transformations [4–6] and they are also increasingly considered for the production of greener composites [7]. The wide range of possible combinations of vegetable oils, chemical modifications, polymerization routes and nature of fillers used as reinforcement phases allows tailoring composite properties to fit the requirements of structural or functional materials. Moreover, there is a clear trend to increase the percentage of

* Corresponding author.
E-mail address: juancarlos.ronda@urv.cat (J.C. Ronda).

http://dx.doi.org/10.1016/j.eurpolymj.2016.04.018
0014-3057/

"green"-based raw materials in the formulations of commodities as well as speciality polymers/composites for high added value applications [8,9]. Cellulose is the most abundant natural biopolymer and shares with vegetable oils its renewable, biodegradable and non-toxic character. Extracted from natural fibres, its hierarchical and multilevel organization allows different kinds of macro-, micro- and nano-scale fillers to be obtained [10]. Obtained by partial acid hydrolysis, cellulose nanocrystals (CNC) have been the focus of an exponentially increasing number of works exploring their use as nanofillers to improve mechanical and barrier properties of nano-biocomposites [11–14].

Plant oil-derived thermosetting materials have been widely obtained by polymerization or copolymerization with vinylic monomers using cationic or radical initiators [15]. Under these conditions, high temperatures and long curing cycles are usually needed due to the lack of reactivity of the internal double bonds in fatty acids. To overcome this drawback, chemical modification of vegetable oils to introduce more reactive groups (i.e. acrylate, maleate, epoxy) has been extensively used [16,17]. These reactive triglyceride derivatives can be crosslinked at lower temperatures and produce denser networks when combined with appropriate multifunctional reagents. Thiol-ene addition has recently resurged as an efficient tool to functionalize double and triple bonds under very mild conditions [18]. Thiol-ene addition to double bonds constitutes an example of "click chemistry" because the reactions are in general fast and efficient, high yielding, have clearly defined reaction pathways/products and presents tolerance to many different reaction conditions/solvents [19]. Thiol-ene based methodologies have recently attracted an extensive interest in the synthesis, post-modification or surface decoration of polymeric materials due to the high functional group tolerance and mild conditions usually required. The main drawback in both, academic and industrial applications, is the strong unpleasant smell of most thiol compounds. Thus, thiol-ene addition has been used to prepare elastomeric networks by reaction of vinyl ether, allyl ether, acrylate or maleate containing soybean oil [20,21] with the commercially available multifunctional thiols: trimethylolpropane tris(3-mercaptopropionate) and pentaerythritol tetrakis(3-mercaptopropionate) (PE3MP).

In a previous work we developed a new reactive enone containing triglyceride (ETG) [22] which has been effectively used to prepare thermosets and flame retardant thermosetting resins by aza- and phospha-Michael addition [23,24]. The addition of thiol groups to α,β-unsaturated carbonylic compounds constitutes a key reaction in biosynthesis as well as in the synthesis of biologically active compounds [25]. The reaction can be performed in solventless conditions and low temperatures through the activation of thiols with nucleophiles/bases [26] or the olefin acceptors with Lewis acids [27].

Recently, we studied the thiol-Michael addition of 1-octanethiol and 2-mercaptoethanol to a regioisomeric mixture of enone containing methyl oleate isomers. Under the studied conditions, thiol-Michael addition proceeds in a smooth way at moderate temperatures using 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) as the more effective catalyst [28].

Following these considerations, the thiol-Michael addition of PE3MP to the enone-containing triglyceride derived from high oleic sunflower oil, has been exploited in this work to produce elastomeric thermoset networks and cellulose nanocrystal (CNC) based nano-biocomposites under mild conditions. The effect of modified CNC on the morphological, mechanical, thermal and surface properties of the matrix was investigated. Moreover, their influence on the protein adsorption behavior was assessed. The utilization of renewable resources is in turn discussed as a novel and appropriate route to sustainable nano-biocomposites with modulated mechanical properties. It is expected that the use of vegetable oil-based resins as dispersing media for the CNC would enhance the biocompatibility of the resulting systems; moreover the nanocomposite formation from a reactive media under mild conditions would facilitate or simplify the preparation of film and coating of devices for these applications.

2. Experimental part

2.1. Materials

High oleic sunflower oil (minimum 80% oleic acid) was supplied by Coreysa, pentaerythritol tetrakis(3-mercaptopropionate) (PE3MP) (Aldrich), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) (Aldrich), meso-tetraphenylporphyrin (TPP) (Aldrich), triethylamine (Scharlau), acetic anhydride (Scharlau), microcrystalline cellulose powder (Aldrich), Beycostat A B09® (CECCA S.A.), Dowex Marathon MR-3 ion exchange resin (Aldrich) and bovine serum albumin culture medium (BSA, Aldrich) were used as received. Dichloromethane (DCM) was dried by refluxing over P_2O_5 and distilled immediately before use.

2.2. Synthesis of the α,β-unsaturated ketone derivative of high oleic sunflower oil (ETG)

Enone containing triglyceride was prepared starting from 70 g (79.1 mmol) of high oleic sunflower oil following a reported procedure [22] as a white cereous solid (mp. 22–26 °C) containing 2.3 α,β-unsaturated ketones per molecule (determined by ^{1}H NMR) with 76% yield.

2.3. Synthesis and modification of cellulose nanocrystals

Cellulose nanocrystals (CNC) were prepared from microcrystalline cellulose by sulfuric acid hydrolysis following the procedure used by Cranston and Gray [29]. Hydrolysis was carried out with 64 wt% sulfuric acid at 45 °C for 30 min with