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Research paper

Crosslinked swellable clay/egg white bionanocomposites

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ABSTRACT

A series of non-soluble crosslinked bionanocomposites on the basis of natural egg white containing 5, 10, 15 and 20 wt.% of Na-montmorillonite clay were prepared via a facile mixing-drying method. The prepared bionanocomposites were characterized by X-ray diffractometry, transmission electron microscopy, Fourier transform infrared spectroscopy and scanning electron microscopy. The network, thermal, swelling and dehydration properties of bionanocomposites were investigated. The results revealed the creation of a partially delaminated morphology for the prepared bionanocomposites with a uniform dispersion of clay layers inside the egg white matrix. The role of clay as a crosslinker in the creation of a crosslinked egg white network was confirmed. The denaturation behavior of proteins of egg white was affected by incorporated clay to the bionanocomposites. In spite of the pure egg white, the prepared bionanocomposites could absorb water and swell in aqueous solutions. The swelling and dehydration rates of bionanocomposites exhibited an inverse dependency on the incorporated clay loading level and a direct dependency on the swelling temperature. The mechanism governing the mass transfer during the swelling and dehydration of bionanocomposites is Fickian and non-Fickian, respectively.

1. Introduction

For the design of biomedical devices, either natural or synthetic, it is necessary to use materials characterized by non-immunogenicity, biocompatibility and controllable biodegradability (Kundu et al., 2014; Sun and Tan, 2013). However, despite the remarkable potential and diversity of man-made synthetic biomaterials, their applications have been limited in some cases by challenges including biocompatibility and biodegradability. Due to the excellent biocompatibility as an intrinsic advantage, natural biomaterials have *re*-emerged as viable alternatives for synthetic biomaterials in biomedical engineering and attracted substantial attention of the scientific community (Kundu et al., 2014). A high degree of biocompatibility is achieved when a biomaterial interacts with the body without inducing any unacceptable toxic, immunogenic, thrombogenic, and carcinogenic responses, which with no doubt, could be achieved by natural biomaterials (Naahidi et al., 2013).

Nanocomposites are a novel class of composite materials consisting of at least a matrix phase (polymer, metal or ceramic) and a reinforcing phase, where the reinforcing agent, such as nanoparticles, has at least one dimension in the nanoscale range (1 to 100 nm) (Paszkiewicz et al., 2015). Compared with the conventional composites, nanocomposites demonstrate improved mechanical properties, electrical conductivity, thermal stability, gas barrier properties, fire retardancy and so on (Chen et al., 2012; Mauroy et al., 2015). Different kinds of small-scale inorganic nanoparticles such as gold, silver, copper oxide, carbon nanotubes, and various types of clay minerals, e.g., montmorillonite, laponite and kaolinite have been widely used in the production of polymer-based nanocomposites (Zhang et al., 2009, 2014). Among these inorganic materials, special attention has been drawn to clay minerals in order to prepare polymer–clay nanocomposites, because of their nanometric dimensions and intercalated properties. Furthermore, they are natural, abundant, and inexpensive minerals that have high mechanical strengths as well as high chemical resistances (Ray and Okamoto, 2003). Raw clays also have a considerable degree of biocompatibility, which makes them suitable in biomedical applications (Gormley and Addison, 1983).

Similar to the conventional materials used in biomedical engineering the application of most nanocomposites, which are mainly prepared by synthetic materials, is restricted due to the challenges of non-biocompatibility. Therefore, in recent years, special attention has been paid to the production of nanocomposites on the basis of natural biocompatible materials, so called bionanocomposites, for biomedical applications. Beside the biomedical applications, in line with recent environmental policies, increased attention has been paid to the development of bionanocomposites for several industrial applications, such as automotive, construction and packaging (Tingaut et al., 2010). In general, the term bionanocomposite refers to a nanocomposite where its constituents or at least the materials of the dominant matrix phase are biocompatible (Fernandes et al., 2013). The matrix phase in bionanocomposites is mainly a biocompatible and biodegradable polymer ideally derived from natural resources (e.g. chitosan). In terms of reinforcements, they might include plant fibers and by-products from lignocellulosic renewable resources or synthetic inorganic materials, as well as raw clays (Fernandes et al., 2013).

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Egg white (EW) as a natural and inexpensive source of high quality proteins such as ovalbumin, conalbumin, lysozyme, ovomucoid and ovomucin is of great interest for many industrial applications especially food and pharmaceutical industries (Braun and Gingras, 2012; Mann and Mann, 2011). Excellent biocompatibility and biodegradability of EW makes it a unique biomaterial for production of biomedical devices. However, due to the high solubility of EW either in the fresh or dried forms in water and aqueous solutions, it is not possible to prepare the solid medical devices using it. The main goal of the current study was to prepare the crosslinked EW bionanocomposites that in the future may be used as shapeable devices, e.g. drug delivery carriers, scaffolds and wound dressings, in regenerative medicine and tissue engineering.

In recent years, among the protein-based nanocomposites, special attention has been drawn to the production of albumin-based nanocomposites. Misak et al. (2014) prepared non-crosslinked albumin/drug-based nanocomposite microspheres and characterized them for advanced targeting of drug molecules. A more biocompatible drug delivery system could be obtained with a higher albumin concentration. The prepared albumin-based microspheres were suggested to treat inflamed tissues such as cancer tumors. Huang et al. (2010) synthesized albumin-conjugated copper sulfide nanocomposites. The prepared nanocomposites were approximate spheres with size distributions on a nanometric scale. The synthesized nanocomposites had a great potential application in biomedical engineering and microelectronics. In other research, carbon nanotubes (Gerasimenko et al., 2013; Bobrinetskiy et al., 2014) and Ag nanoparticles (Vimala et al., 2014) have been utilized in the production of albumin-based nanocomposites. Recently, Dianez et al. (2016) prepared bioplastic nanocomposites on the basis of spray-dried EW albumen using unmodified (Cloisite® Na^+) and organically modified clay (Cloisite® 30B) as reinforcements via a thermoplastic processing using glycerol and water as plasticizers followed by a compression moulding at high temperature and pressure (120 °C and 100 bar). They studied some morphological and thermomechanical properties of the resultant bioplastics. The organically modified clay had a hydrophobic character, leading to a poor compatibility with the albumen matrix that created large clay aggregates and consequently resulted in poor mechanical properties of the bioplastic nanocomposites. On the contrary, unmodified clay introduced into the matrix, led to improved thermomechanical properties even at a low clay loading level. Since the bioplastic nanocomposites did not have a three-dimensional crosslinked network, they demonstrated poor water uptake ability and the addition of clay to the albumen matrix did not significantly alter its water absorption.

In this work, non-soluble, crosslinked and swellable bionanocomposites on the basis of natural EW as matrix phase and Na-montmorillonite (Mt) as reinforcing and crosslinking agent were prepared via a facile mixing-drying method. Some structural, physical, thermal, swelling and dehydration properties of the prepared Mt–EW bionanocomposites were experimentally investigated to evaluate their potential for the possible production of biomedical devices.

2. Experimental

2.1. Materials

Mt having the exchangeable sodium ions with the cation exchange capacity (CEC) of 92.6 meq/100 g, molecular weight of 540.46 g/gmol, and density of 2.86 g/cm^3 was purchased from Southern Clay Products Inc., USA. Chicken eggs were purchased from retail stores in the Urmia area. The eggs were cracked and the white separated from the yolk and used in production of bionanocomposites without further treatments. The humidity and pH of EW were measured, on average, as 86.4 wt.% and 4.7, respectively. Double distilled water (DDW) was used in preparation of all dispersions, solutions and samples.

2.2. Preparation of bionanocomposites

The Mt-EW bionanocomposites were prepared using a simple mixing-drying method. For preparation of each bionanocomposite, first a Mt dispersion was prepared by well mixing of a predetermined amount of Mt in DDW at a mixing rate of ca. 500 rpm for 10 h. After preparation of the Mt dispersion, known amount of EW was added to the dispersion and completely mixed at 25 °C for 2 h with a mixing rate of ca. 50 rpm. The achieved uniform solution was casted as a film on a glass plate and then dried under vacuum at 25 °C. The abbreviation Ex is used here for prepared bionanocomposites for which x shows the weight percentage of Mt in completely dried sample. The designations and detailed compositions of the prepared Mt-EW bionanocomposites are summarized in Table 1. The processing procedure of bionanocomposites and the appearances of a typical bionanocomposite (E10) at dried and swelled states are illustrated in Fig. 1.

2.3. X-ray diffractometry (XRD)

The XRD was carried out on three typical bionanocomposites (samples E5, E15 and E20) and also on the pristine Mt powder and pure dried EW (sample E0), as references. Prior the test, all samples were completely dried in a vacuum oven. The XRD experiments were conducted with a diffractometer (Siemens D5000, Germany) equipped with monochromatic CuKα radiation ($\lambda = 0.154$ nm, 40 kV and 30 mA) at room temperature. Parallel beam optics was used with 1 mm entrance slit and 0.6 mm exit slit. Data were collected over the 2θ range of 3–50° at a scanning speed of 2°/min and a step scan size of 0.02° and a counting time of 0.3 s.

2.4. Transmission electron microscopy (TEM)

The morphology of typical bionanocomposites, i.e. E5 and E10, were observed by TEM. Prior to TEM observation, each sample was completely dried under vacuum and then embedded in an epoxy matrix. Then the samples were frozen in liquid nitrogen and cut to 70–100 nm thickness sections, perpendicular to the films, by means of a diamond knife. Subsequently, samples were placed onto 400 mesh copper grids. The observation was performed using a Philips (EM 208 S, Netherlands) microscope with an acceleration voltage of 100 kV.

2.5. Fourier transform infrared spectroscopy (FTIR)

The characteristic functional groups of the Mt, pure EW (E0) and Mt–EW bionanocomposite loaded with 5 wt.% of Mt (E5) were analyzed by FTIR. Each sample was completely dried under vacuum and then grounded with dried potassium bromide (KBr) powder and compressed into a disc, where the sample to KBr ratio was 1:100. The characterizations were performed using a Thermo Nicolet (FTIR NEXUS-670, USA) spectroscope. Spectra were collected in the range 400–4000 cm^{-1} with 2 cm^{-1} spectral resolution and 20 scans were performed for each sample.

Table 1
Designations and chemical compositions of the prepared bionanocomposites.

Sample designation	EW (wt.%)	Mt (wt.%)	DDW (wt.%)	Mt (wt.%) in dried bionanocomposite
E0	100	0	0	0
E5	84.5	0.6	14.9	5
E10	72.1	1.0	26.9	10
E15	62.0	1.4	36.6	15
E20	53.5	1.8	44.7	20