Carbohydrate Polymers 170 (2017) 89–98

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Guar gum benzoate nanoparticle reinforced gelatin films for enhanced thermal insulation, mechanical and antimicrobial properties

Sonia Kundu, Aatrayee Das, Aalok Basu, Md. Farooque Abdullah, Arup Mukherjee*

Division of Pharmaceutical and Fine Chemical Technology, Department of Chemical Technology, University of Calcutta, 92, A.P.C. Road, Kolkata 700009, West Bengal, India

ARTICLE INFO

Article history:
Received 21 February 2017
Received in revised form 17 April 2017
Accepted 20 April 2017
Available online 23 April 2017

Chemical compounds studied in this article:
Guar gum (PubChem CID: 44134661)
Citric acid monohydrate (PubChem CID: 22230)
Dimethyl sulphoxide (PubChem CID: 679)
Dimethyl amino pyridine (PubChem CID: 14284)
Benzoyl chloride (PubChem CID: 7412)
Lithium chloride (PubChem CID: 433294)
Glutaraldehyde (PubChem CID: 3485)
Glycerol (PubChem CID: 753)
Sodium hydroxide (PubChem CID: 14798)
Sodium chloride (PubChem CID: 5234)

Keywords:
Guar gum benzoate gelatin nanocomposite films
thermal insulation
antimicrobial properties
Hofmeister cation guided reaction

ABSTRACT

This work relates to guar gum benzoate self assembly nanoparticles synthesis and nano composite films development with gelatin. Guar gum benzoate was synthesized in a Hofmeister cation guided homogeneous phase reaction. Self assembly polysaccharide nanoparticles were prepared in solvent displacement technique. Electron microscopy and DLS study confirmed uniform quasi spherical nanoparticles with ζ-potential – 28.7 mV. Nanocomposite films were further developed in gelatin matrix. The film capacity augmenting due to nanoparticles incorporation was noteworthy. Superior barrier properties, reinforcing and thermal insulation effects were observed in films dispersed with 20% w/w nanoparticles. Detailed FTIR studies and thermal analysis confirmed nanoparticles interactions in the film matrix. The nanocomposite film water vapour permeability was at 0.75 g mm^{-1} kPa^{-1} h^{-1}, thermal conductivity 0.39 W m^{-1} K^{-1} and the tensile strength were recorded at 3.87 MPa. The final film expressed excellent antimicrobial properties against water born gram negative and gram positive bacteria.

1. Introduction

Associative interactions of polysaccharide and proteins are intriguing. Similar interactions are very useful for functionally superior and bio-safe materials design. Precise control over molecular association due to size, shape, conformations, van der Walls forces, ionic exchange or hydrophobic stacking interactions were experimented earlier for applications in pharmaceuticals, food packaging, environmental and biomedical areas (Dickinson, 2008; Ettelaie & Akinshina, 2014). There is a growing interest in recent years for complete understanding of similar macromolecular interaction (Semenova, 2016). Soft matter microstructures non-covalent interactions are pronounced in polymer blends (Sarika, Pavithran, & James, 2015). Apparently dissimilar forces were conjoined intelligently for bio-based materials functional enhancements. Best effects can be achieved when at least one or both macromolecules are incorporated in large surface colloid phases.

Guar gum (GG) is a galactomannan obtained directly from *Cyamopsis tetragonoloba* seed pericarp. GG blends well in protein helices and is frequently used in ice creams. Native GG exists in a three chain associative coil formation which hydrates hugely in water (Mukherjee & Basu, 2007). GG surface hydroxyl groups are however polar and facile hydrogen substitution products are known (Sharma, Kumar, & Soni, 2004). Different other GG derivatives are also known to take up un-restrictive formations in biopolymer blend environment (Bosio, Lopez, Mukherjee, Mechetti, & Castro, 2014). Some selective ones have found successful applications already in the commercial space. A cationic

* Corresponding author.
E-mail addresses: arupm1234@gmail.com, hdct1@yahoo.co.in (A. Mukherjee).

http://dx.doi.org/10.1016/j.carbpol.2017.04.056
0144-8617/

derivative guar hydroxypropyltrimonium chloride, 'Jaguar' for example interacts favorably with hair keratin and is used widely in conditioning shampoos. Jaguar deposits on the hair are efficient on small doses and strengthen hair over time. GG hydrophobic derivatives can undergo interesting self assembly formations while polar substituted biopolymers are useful in hydrogel network formations.

Gelatin is a food gelling protein obtained from partial hydrolysis of cattle bones. Gelatin dissolves in water and undergoes conformational transition when heated above 35 °C. Collagen type coil helix structures of gelatin at 35 °C provide enough cross-linking capacity and diffusion space in nanoscale. The protein is biocompatible, non-immunogenic, biodegradable film forming material. Gelatin was therefore investigated extensively in drug delivery, tissue engineering and food packaging areas (Badhe et al., 2017). Unfortunately, gelatin films express poor vapour barrier properties, high hydrophilicity and low mechanical properties. Attempts were made earlier for gelatin film property enhancement following polymer blending, oil emulsion incorporation, biocomposite design, chemical cross-linking (Mohajer, Rezaei, & Hosseini, 2017). Compatible nanomaterials induce specific advantages in biopolymer interfaces. Metal and metal-oxide nanoparticles were used earlier for functional and mechanical property enhancement of gelatin films. Films embedded with single wall carbon nanotubes were used for membrane separation and performance enhancements. Likewise, cerium oxide nanoparticles were incorporated in antioxidant type active gelatin films intended for cell growth and regenerative medicine applications (Shi et al., 2013; Marino et al., 2017).

Water retardant galactomannan nanoparticles incorporation in gelatin film was considered as one attractive exploration for film property augmenting. This work intends to develop polysaccharide derived nanoparticles and gelatin protein interact bio-safe films for packaging materials applications. To our knowledge this is a first ever study on fully bio-based protein-polysaccharide nanocomposite films design for functional property enhancements. Furthermore, high DS hydrophobic GGB nanoparticles were developed in Hofmeister ion guided homogeneous phase reactions and facile ouzo solvent diffusion techniques. Nanocomposite films were developed and property evaluated for intended applications.

2. Materials and methods

2.1. Materials

Reagent grade gelatin, citric acid (CA, $C_6H_8O_7{\cdot}H_2O$), dimethyl sulphoxide (DMSO, 99.9%), glycerol (98%), sodium hydroxide (NaOH), sodium chloride (NaCl), potassium bromide (KBr, IR grade), fused calcium chloride ($CaCl_2$), glutaraldehyde (25%) and uranyl acetate were from Merck (Mumbai, India). Dimethyl amino pyridine (DMAP), lithium chloride (LiCl) and benzoyl chloride (C_6H_5COCl) for synthesis were from Spectrochem (Mumbai, India). Guar gum (GG, CAS No. 9000-30-0) was received as gift from Nuevo Polymers (Gurgaon, India). Microbial growth media constituents beef extract, peptone and agar were from Himedia (Mumbai, India). Analytical grade methanol and ethanol used were from Merck.

2.2. Homogeneous phase synthesis for guar gum benzoate (GGB)

Native GG was washed free of debris and oligomers before starting any reaction (McCleary & Nurthen, 1983). Typically, 5.0 g of pre-washed GG was taken in 100 mL of 50% (v/v) aqueous isopropanol and soaked for 24 h. The solvent was decanted off and the GG remnant added into 80 mL of DMSO under magnetic stirring. LiCl (2 g) dissolved previously in 20 mL of DMSO was added into it, stirred and a homogeneous solution was obtained. The solution was transferred to a 250 mL three necked round bottomed flask placed over an electrical heating mantle. The flask was equipped with a reflux condenser, a nitrogen purging unit and a mechanical stirrer. The reaction temperature was maintained at 30 ± 2 °C throughout. DMAP (11.29 g) dissolved in 5 mL of DMSO was added and the reaction mixture was stirred at 80 rpm to equilibrate. Benzoyl chloride (12 mL) was then added dropwise under nitrogen purging (5 mL min^{-1}). The reaction mixture was stirred for additional 3 h for reaction completion and the content poured into ice cold aqueous ethanol (50% w/v, 200 mL). White precipitate GGB was collected after filtration and the product washed with distilled water. GGB was further soxlated against methanol and the leachants checked free from aromatics in UV spectrophotometer (EVO300 PC, Thermo Fisher, U.S.A). The GGB product (4.75 g) was preserved in screw cap bottles and kept in vaccum dessicator until application. Different polymer to the acid halide ratio was used to obtain biopolymer derivatives with different degree of substitution.

2.3. Guar gum benzoate nanoparticles (GGBnp)

Typically, 10 mL of GGB dissolved in DMSO (3 mg mL^{-1}) was taken in a dialysis bag (MWCO 12400, Sigma, U.S.A.) and placed against running water at room temperature for solvent diffusion. After 72 h the dialysis bag content was transferred in a flask and lyophilized (Eyela FDU 1200, Japan) at −52.3 °C and 19 Pa to powders for analysis. Alternatively, the bag content was transferred to screw cap bottles and preserved in refrigerators.

2.4. Nanocomposite films

Nanocomposite films were cast from gelatin solutions dispersed proportionately with GGBnp. Typically, 200 mg of GGBnp was added in 20 mL of distilled water containing 1 g of gelatin and 200 mg CA. The mixture was heated to 80 ± 2 °C under magnetic stirring at 200 rpm and a clear homogeneous solution was obtained. To this solution, 0.2 mL of glycerol (20% v/v) was added as plasticizer and the pH adjusted to 10 using drops of 1N NaOH. The mixture was heated for 10 min more and the solution poured onto polypropylene petridishes to cool for 24 h in an incubator maintained at 35 ± 2 °C. The films formed were then peeled off and kept in dessicators before analysis. Films without GGBnp were prepared similarly.

2.5. Characterization of guar gum benzoate and nanoparticles

C,H,N combustion analysis for GG and GGB was carried out in an analyzer (CHNS-932, Leco Corp., U.S.A). The results were compared against acetophenone standard samples. FT-IR studies for GG and GGB were carried out in a FTIR spectrometer (Jasco 6300, Japan). Samples were ground-mixed with KBr, pressed into pellets and scanned in wavelength range of 400–4000 cm^{-1} with background corrections. The X-ray diffraction studies for GG, GGB and GGBnp were carried out in a X'Pert Pro X-Ray diffractrometer (PW 3050/60, Philips, India) with Cu anode having Kα radiation (λ = 1.54060Å) at 40 kV voltage and 30 mA current. The sample diffractions were recorded in 10°–80° (2θ) range, step size 0.03°. The thermal analysis was carried out in Pyris Diamond TG/DTA (Perkin Elmer, Singapore). Samples were placed in platinum crucibles and heated incrementally (10 °C min^{-1}) up to 450 °C under N_2 purging.

The particle size, polydispersity index (PDI) and zeta-potential (ζ) of nanoparticles were recorded in DLS (Zetasizer® Nano ZS, Malvern Instrument Ltd., U.K). GGBnp in water were exposed to a 4 mW helium–neon laser beam, 633 nm, and the back scattering angle was at 173°. Analyses were carried out in triplicate and an