Carbohydrate Polymers 139 (2016) 90–98

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Nano $CaCO_3$ imprinted starch hybrid polyethylhexylacrylate\polyvinylalcohol nanocomposite thin films

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ARTICLE INFO

Article history:
Received 16 September 2015
Received in revised form
13 November 2015
Accepted 4 December 2015
Available online 12 December 2015

Keywords:
Nano composite film
Topology
Thermal conductivity
Antimicrobial properties
Tensile strength

ABSTRACT

Starch hybrid polyethylhexylacrylate (PEHA)/polyvinylalcohol (PVA) nanocomposite thin films are prepared by different composition of nano $CaCO_3$ in aqueous medium. The chemical interaction of nano $CaCO_3$ with PEHA in presence of starch and PVA is investigated by Fourier transforms infrared spectroscopy (FTIR). X-ray diffraction (XRD) is used in order to study the change in crystallite size and *d*-spacing during the formation of nanocomposite thin film. The surface morphology of nanofilms is studied by scanning electron microscope (SEM). The topology and surface roughness of the films is noticed by atomic force microscope (AFM). The tensile strength, thermal stability and thermal conductivity of films are increased with increase in concentrations of $CaCO_3$ nanopowder. The chemical resistance and biodegradable properties of the nanocomposite thin films are also investigated. The growth of bacteria and fungi in starch hybrid PEHA film is reduced substantially with imprint of nano $CaCO_3$.

1. Introduction

Polymer nanocomposites are involved in a great attention during last two decades for their academic importance and industrial applications. Nanocomposite thin films (NCTF) consist of an ultrathin barrier layer of a polymer chain with reinforcement of nanoparticles. The incorporation of nanostructured material would be eventually affects the physicochemical properties of NCTF. NCTF with nanofillers have attracted wide scientific and industry report due to the superior properties contributed by the nanofillers.

In present study, starch is used as a binder and an active agent for making the material biodegradable in nature. Starch is consists of two anhydroglucoses, amylose and amylopectin where, anhydroglucose polymers are arranged into a semi crystalline granular structure (Warren, Royall, Gaisford, Butterworth, & Ellis, 2011). The presence of pores in the granule surface and its interaction with amylase is a factor affecting the binding nature of starch. The binding property of starch with substrate is due to the loss of crystalline structure inside the starch granules. Hence binding of starch with substrate increases the biodegradability of the material, when it is hydrolyzed due to carboxymethylation mechanism. However, the limitation of using starch alone is due to its slow compatibility with hydrophobic polymers and having flammability properties. PVA is chosen as one of the component in present study due to its excellent film forming properties along with emulsifying surfactant and adhesive behaviors. PVA has the properties of non-toxic, odorless having high flexibility and tensile strength (Gokmen et al., 2015). Therefore, PVA is used as an additive in present investigation in order to improve the compatibility of PEHA matrix. In literature PVA has been used as an additive in order to study heat sealing property of the materials (Su et al., 2010).

Out of different acrylic polymers, polyethylhexylacrylate (PEHA) is important which is used in differential industrial applications. But its application becomes limited because of its non-biodegradable nature. Polysaccharide polymers like starch, chitosan and alginate are commonly used as host matrices (Brayner, Vaulay, Fievet, & Coradin, 2007; Djokovic et al., 2009; Vigneshwaran, Nachane, Balasubramanya, & Varadarajan, 2006; Vimala et al., 2010; Wei, Sun, Qian, Ye, & Ma, 2009) for degradation of polymers. Starch is one of the promising and popular biodegradable polymers obtained as granule sheet plant. However, there are several strong limitations to develop a starch-based film as it has poor tensile properties due to their hydrophilic nature and sensitivity to moisture content. One of the methods to overcome this limitation is to improve the strength of starch matrixes with organic or mineral fillers (Cyras, Manfredi, Ton-That, & Vazquez, 2008).

Nanoparticles are novel type of filler materials that displays a higher level of efficiency and improved the physicochemical, mechanical properties of starch-based films. $CaCO_3$ is one of the important nanoparticles which show unique properties like thermal conductivity, high melting decomposition temperature, high thermal stability, and oxidation resistance and in lubricating

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http://dx.doi.org/10.1016/j.carbpol.2015.12.009
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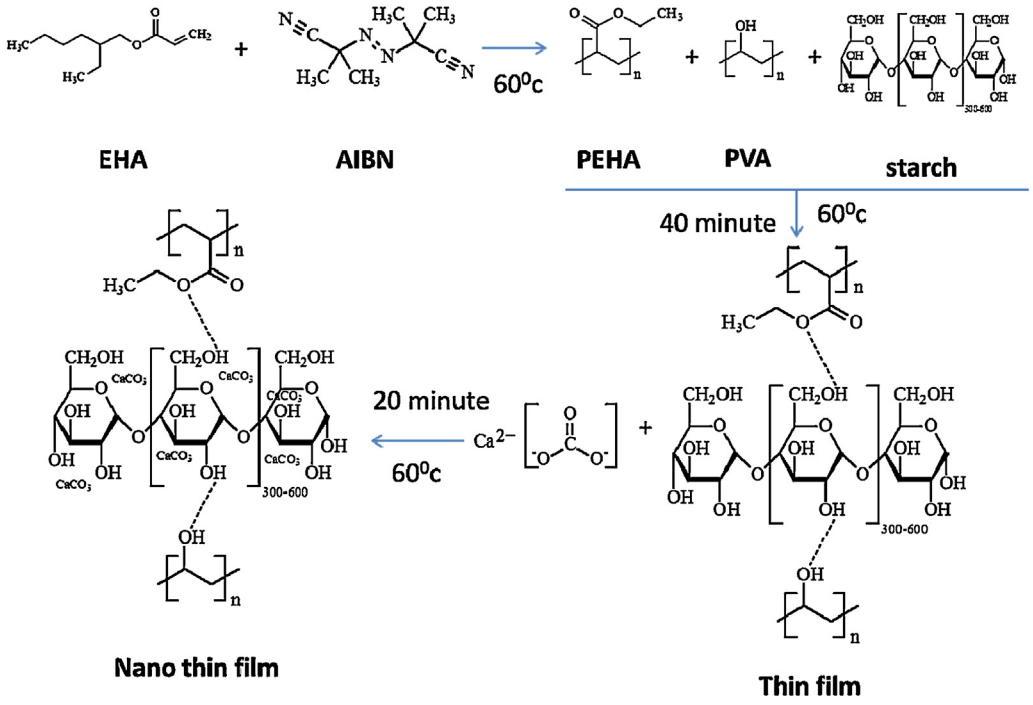

Scheme 1. Scheme for the synthesis of starch hybrid PEHA/PVA–$CaCO_3$ nanocomposite thin films.

materials as compared to other nano particles (Hosoda & Kato, 2001). Further, $CaCO_3$ nanoparticles are used as fillers in making of composite materials like plastics and paper industry (Kim, Douglas, & Gower, 2007). In present study, $CaCO_3$ is used as reinforcing agent in order to improve the properties of starch hybrid PEHA/PVA composite thin films. Now a day composite based on polymers and inorganic nanoparticles have focused a lot of attention and interest because of their academic and industrial applications. Nanocomposites synthesized from polymers, biopolymers and copolymers with reinforcement of inorganic nanoparticles are of great interest for packaging material with enhanced physical, thermal (Swain, Dash, & Pradhan, 2014a), mechanical (Kisku, Das, & Swain, 2014), gas barrier properties (Pradhan, Behera, & Swain, 2014), chemical resistance, fire retardant (Swain et al., 2014a; Swain, Patra, & Kisku 2014b) and processing characteristics (Li, Chen, Li, & Sun, 2011b).

Although preparation, characterization and study of different properties of inorganic nanopowder incorporated polymer and copolymer thin films are not rare, however the preparation of $CaCO_3$ dispersed starch hybrid PEHA/PVA composite thin films are new in the literature. In present study, we have synthesized starch hybrid PEHA/PVA–$CaCO_3$ thin film is a low cost *in situ* green polymerization technique. The chemical interaction, morphology, topology and surface roughness of synthesized nanocomposite films are studied. The influence of $CaCO_3$ nanopowder on the chemical–physical properties of the polymeric matrix is studied for structural, thermal conducting and tensile properties. In present investigation, the study of antibacterial properties in combination with chemical resistance, biodegradability, tensile strength, thermal conductivity and thermal stability shows the possibility for packaging applications.

2. Experimental

2.1. Materials

The monomer, 2-ethyl hexyl acrylate (EHA) is purchased from Sisco Research Laboratory (SRL) Mumbai; India. It is washed with 3% *ortho* phosphoric acid and with 5% sodium hydroxide to remove inhibitor followed by washing with distilled water. The washed monomer EHA is dried over calcium chloride and stored in refrigerator before use. The polyvinyl alcohol (PVA) is purchased from Loba Chemi (India). The surface active radical initiator α,α′-Azoisobutylronitrile (AIBN) (Spectrochem, 99.9%) is used as received. Potato starch is purchased from Fischer Scientific Pvt. Ltd, Mumbai, India. Calcium carbonate ($CaCO_3$) nano powder is obtained from Sisco Research laboratories Pvt. Ltd, India with average diameter of 50 nm. The water used for the experiment is distilled two times over alkaline permanganate solution.

2.2. Methods

2.2.1. Preparation of thin film

The starch hybrid PEHA/PVA composite thin film with reinforcement of $CaCO_3$ can be prepared by *in situ* polymerization method using aqueous solution. EHA (4.2×10^{-3}), AIBN (4×10^{-3}), PVA and starch in the ratio of 20:80, 40:60, 60:40, 50:50 and 80:20 are prepared in a conical flask under 60 °C temperatures and stirred for 40 minute. Then calculated amount of $CaCO_3$ (1 wt%, 3 wt%, 5 wt% and 8 wt%) is added to starch hybrid PEHA/PVA solution under same temperatures and stirred for 20 min. Then the $CaCo_3$ reinforced starch hybrid PEHA/PVA nanocomposites gel is poured in to a petridishes to make the films. A round, transparent, thin and flexible nanocomposites film is obtained after drying in a hot air oven at 70 °C. The structural representation of synthesis process is represented as Scheme 1.

2.3. Characterization techniques

FTIR spectra of nanofilms (in the form of KBr pellets) are recorded by using a shimadzu IR affinity-I Fourier transform infrared spectrophotometer in the range of 4000 cm^{-1} to 400 cm^{-1}. X-ray diffraction patterns are obtained using a Rigaku X-ray machine operating of 40 kV and 15 MA. The morphology and dispersion of nano $CaCO_3$ in starch hybrid PEHA/PVA thin films are