International Journal of Biological Macromolecules 67 (2014) 91–98

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

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

# Effect of $Fe_3O_4$ on the sedimentation and structure–property relationship of starch under different pHs

S. Palanikumar, P. Siva, B. Meenarathi, L. Kannammal, R. Anbarasan *

*Department of Polymer Technology, Kamaraj College of Engineering and Technology, Virudhunagar 626 001, Tamilnadu, India*

ARTICLE INFO

*Article history:*
Received 24 August 2013
Received in revised form 5 February 2014
Accepted 4 March 2014
Available online 19 March 2014

*Keywords:*
Starch
Ferrite
VSM
Sedimentation velocity
Characterizations

ABSTRACT

The nanosized ferrite ($Fe_3O_4$) was synthesized and characterized by analytical techniques such as Fourier transform infrared (FTIR) spectroscopy, UV–visible spectroscopy, fluorescence spectroscopy and transmission electron microscopy (TEM). The structure–property relationship of starch was studied under three different pHs namely 3.8, 7.1 and 12.5. The starch treated under acidic condition was degraded. In a similar manner, the structure–property relationship of starch in the presence of ferrite nanoparticles at three different pHs, as mentioned above was studied. The starch/ferrite nanocomposite prepared under acidic condition showed a degraded structure. Further, the polymer/nanocomposite systems were characterized by analytical techniques such as FTIR, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), vibrating sample measurement (VSM), TEM and scanning electron microscopy (SEM). Finally, the settling velocity of starch under three different pHs both in the presence and absence of $Fe_3O_4$ was carried out to ensure the role of pH and effect of $Fe_3O_4$ on the settling velocity of starch.



## 1. Introduction

Starch is a renewable, very abundant polysaccharide, biocompatible, colorless, biodegradable and water insoluble amorphous fibrous substance and is characteristic of the source of the starch. Starch is ubiquitous, polysaccharide, naturally occurring cheapest food, biodegradable polymer worldwide and the extraction of which includes different processes such as washing, peeling, rasping, sieving, settling, pulverization and drying [1,2]. During the separation process, 5% of starch remains in the medium as slime. Quick isolation and separation of starch in the medium must be carried out otherwise degradation occurs due to the various fungal activities. The biodegradation of starch during the isolation process leads to the loss of economy as well. In order to isolate starch from aqueous medium quickly various techniques are adopted. Among which flocculation and pH adjustment are two important methodologies. The settling velocities of starch under different experimental conditions were done by Sajeev et al. [3]. In 2010, Yang and co-workers [4] reported about the neutral starch microspheres by using epichlorohydrin as a cross linker. Flocculating behavior of cationic starch derivatives was elaborately studied by Wei and research team [5]. Ultracentrifugation is also one of the methods used for the isolation of starch [6]. Starch was isolated from the source through phase separation method by using gallachtomannan [7]. Electro flocculation of cassava starch was studied by Sajeev et al. [8]. Rate of sedimentation of starch by using pectin was reported in the literature [9]. The other research team had also reported about the sedimentation of starch at different experimental conditions [10]. The above literature review indicates that starch can be settled with the aid of additives and contaminants and sometimes may be harmful to the human beings health. To avoid such an unwanted situation and at the same time to boost up the settling velocity of the starch without any harmful effect, the present investigation is made. Moreover, we know that iron is a bio-metal with high magnetic power under the influence of magnet which leads to the fast settling velocity of starch or any material which can be adhered on the surface of $Fe_3O_4$. Above all, we would like to introduce a new methodology for the fast settling of starch under different pHs without adding any additives and by saving time and money. By thorough literature survey we could not find any report based on the study of effect of pH on the structure–property relationship of starch. In the present investigation, for the first time, we studied the effect of pH and $Fe_3O_4$ on the structure–property relationship of starch particularly in the sedimentation velocity. The starch and its nanocomposites have applications in various fields. Starch is a bio-food material and it should be carefully utilized for our present and future generations. The present investigation signals an advent of a new era in the naturally occurring food

* Corresponding author. Tel.: +91 4549 278171.
*E-mail address:* anbu_may3@yahoo.co.in (R. Anbarasan).

http://dx.doi.org/10.1016/j.ijbiomac.2014.03.012
0141-8130/

material and its importance in human life, i.e. the complete isolation of starch without wastage during its extraction process from the source material.

## 2. Materials and methods

### 2.1. Materials

Starch, NaOH pellet, Ferric chloride ($FeCl_3$), Ferrous sulphate ($FeSO_4$) and hydrochloric acid (HCl) were purchased from Reachem, India and used without any further purification. Double distilled (DD) water was used for the experimental purpose. In the present investigation only one type of starch was used for experimentation. The potato starch was purchased from Reachem, India as a readymade sample.

### 2.2. Synthesis of ferrite nanoparticles

30 g ferric chloride and 15 g ferrous sulphate were mixed with 200 mL of DD water and stirred for about half an hour at 45 °C. The stirring was continued for another 2 h at room temperature for nucleation. Then 10 g NaOH in 20 mL of DD water was added to the mixture in drop wise manner. This resulted in the formation of a black colored precipitate and it was dried in the oven for about 6 h at 110 °C. The size of the thus obtained $Fe_3O_4$ nanoparticle was determined by using TEM technique as 10–25 nm. In the present investigation, the ferrite synthesis procedure was referred from the reported literature [11,12].

### 2.3. Reaction of starch at different pHs

2 g starch was mixed with 25 mL of water and stirred for about 6 h at 45 °C and then it was allowed to dry in the oven at 110 °C, ground to get fine powder. In a similar way 2 g starch was mixed with 25 mL of 1 M HCl and stirred for about 6 h at 45 °C, dried and the resulting sample was ground to fine powder. In the same way 2 g starch was mixed with 25 mL of 0.5 M NaOH and stirred for 6 h, dried in hot air oven at 110 °C and ground to get fine powder.

### 2.4. Reaction of starch/ferrite nanocomposite at different pHs

2 g starch and 0.50 g ferrite nanoparticle was mixed with 25 mL of DD water and stirred for about 2 h at room temperature and then it was allowed to dry in the oven at 110 °C and ground to get fine powder. In a similar way starch/ferrite nanocomposites were prepared as mentioned above at different pHs.

### 2.5. Determination of sedimentation velocity

The settling velocity of starch in the presence and absence of ferrite nanoparticle under three different pHs was determined by using the following formula [10].

$$v_0 = \frac{g d_s^2 (\rho_s - \rho_w)}{18 \mu_w} \quad (1)$$

where, $V_0$ – free falling velocity in $ms^{-1}$, $g$ – acceleration due to gravity in $ms^{-2}$, $d_s$ – diameter of average particle size of starch was determined from SEM images and also from the particle size analysis report, $\rho_s$ – density of starch particle in $kg\,m^{-3}$, $\rho_w$ – density of water in $kg\,m^{-3}$, $\mu_w$ – viscosity of water in $kg\,m^{-1}\,s^{-1}$. The key idea behind the present investigation is, under the influence of magnet the ferrite nanoparticles can move fast toward the force of attraction and also toward the gravitational force of attraction. During this travel process, the physisorbed polymer molecules also move toward the magnetic and gravitational forces through the secondary forces of attraction like hydrogen bonding, Vander walls forces etc. Starch exhibited a wide range of particle size while treated under acidic and alkaline pH in the absence of ferrite. In this case, the particle size analysis was carried out and their average particle size was determined by using arithmetic mean method. The other systems are not having that much wide range of particle size. According to this formula, the average particle size of starch was determined as 2642.8 nm and 2385.7 nm, respectively, for acidic and alkaline pH. The schematic diagram of sedimentation of starch under the influence of magnet is given in Fig. S1.

Supplementary Figure 1 related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ijbiomac.2014.03.012.

### 2.6. Characterization

Fourier transform infrared (FTIR) spectrum was taken by using Shimadzu 8400 S, Japan model instrument from 4000 to 400 $cm^{-1}$ by KBr pelletization method [13]. Jasco V-570 instrument was used for UV–visible spectrum measurements. 2 mg of sample was dissolved in 10 mL of water under ultrasonic irradiation for 10 min and subjected to UV–visible spectral measurements. Photoluminescence spectrum was measured with the help of PL, Jasco Model FP-6000, Japan, instrument from 300 to 700 nm. DSC and TGA were measured by using Universal V4.4A TA Instruments (simultaneous DSC and TGA analyzer) under nitrogen atmosphere at the heating rate of 10 K/min from room temperature to 373 K. X-ray diffraction (XRD, XS08, BRUKER, USA) was recorded with an advanced instrument and scanning from the $2\theta$ value of 2–60° at a scanning rate of 2°/min [14]. The surface morphology of the samples was scanned by scanning electron microscopy (SEM, JSM 6300, JEOL model) instrument [15]. The samples were lyophilized on glass slides and then coated with gold. The samples were observed under a SEM instrument. Transmission electron microscopy (TEM) was carried out by using a JEOL 2010 instrument and was operated at 200 kV. The samples were prepared after drying on carbon coated Cu grid and observed under a TEM instrument. Magnetic measurements were carried out with a superconducting quantum interference device magnetometer (Lakesore-7410-VSM, USA) with magnetic fields up to 7 T at 32 °C [16].

## 3. Results and discussion

For the sake of convenience, the present investigation is subdivided into two parts namely: (i) characterizations of nanosized $Fe_3O_4$ and (ii) characterizations of starch/$Fe_3O_4$ nanocomposites at different pHs.

### 3.1. Characterization of ferrite

The FTIR spectrum of ferrite synthesized in the present investigation is shown in Fig. 1a. The important peaks are characterized below: The spectrum showed one broad peak around 3363 $cm^{-1}$ due to the —OH stretching of intercalated water molecules. The —OH bending vibration appeared at 1574 $cm^{-1}$. The metal-oxide stretching can be seen at 566 $cm^{-1}$ with higher % transmittance and sharpness. This explains the crystalline nature of the ferrite nanoparticles [17]. The remaining peaks are associated with the carbonate stretching. Appearance of a sharp M—O stretching peak confirmed the structure of ferrite. The UV–visible spectrum of ferrite is represented in Fig. 1b. It showed one broad hump around 372.5 nm due to the scattering of light by nanoparticles. Appearance of this peak confirmed the structure of ferrite [17]. The photoluminescence spectrum of ferrite is shown in Fig. 1c. One peak appeared at 381.8 nm with less intensity [18]. This confirmed the biomedical applications of ferrite particularly in the bio-imaging field.