Carbohydrate Polymers 151 (2016) 245–250

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Transparent sunlight conversion film based on carboxymethyl cellulose and carbon dots

Yaqin You, Haoran Zhang, Yingliang Liu*, Bingfu Lei*

Guangdong Provincial Engineering Technology Research Center for Optical Agriculture, College of Materials and Energy, South China Agricultural University, Guangzhou 510642, China

ARTICLE INFO

Article history:
Received 4 February 2016
Received in revised form 16 May 2016
Accepted 18 May 2016
Available online 20 May 2016

Keywords:
Carboxymethyl cellulose
Carbon dots
Composite
Sunlight conversion
Film

ABSTRACT

Transparent sunlight conversion film based on carboxymethyl cellulose (CMC) and carbon dots (CDs) has been developed for the first time through dispersion of CDs in CMC aqueous solution. Due to the hydrogen bonds interaction, CMC can effectively absorb the CDs, whose surfaces are functionalized by lots of polar groups. The results from atomic force microscopy (AFM), scanning electron microscopy (SEM) confirm that the composite film possesses a homogeneous and compact structure. Besides, the CMC matrix neither competes for absorbing excitation light nor absorbs the emissions of CDs, which reserves the inherent optical properties of the individual CDs. The composite films can efficiently convert ultraviolet light to blue light. What's more, the film is transparent and possesses excellent mechanical properties, expected to apply in the field of agricultural planting for sunlight conversion.

1. Introduction

Sunlight conversion film is a kind of functional film to change the wavelength of light, which shows great potential application in the field of agriculture. Based on plant physiology, the strongest absorption bands for the absorption of plant is located in blue light (400–500 nm) and red light (600–680 nm), motivating the synthesis of chlorophyll; while ultraviolet light (below 400 nm) goes against, affecting the normal growth of plants and inducing disease from insect pests (Poudel, Kataoka & Mochioka, 2008; Kadur et al., 2007). Especially, like tomato (Xu et al., 2012) and cabbage (Kim et al., 2015), they show strong demand for blue light. Therefore, it is significant that sunlight conversion film is improved to convert the ultraviolet light into blue light (400–500 nm). As we all know, sunlight conversion film is made up of two parts, including matrix and sunlight conversion agent, in which the latter plays a critical role in the performance of sunlight conversion properties. For sunlight conversion agent, many kinds of phosphors have been reported such as $CaS:Cu^{+}$ (Zhang, Li, Chen, Xiao, & Sun 2004), $CaAl_2O_4:Eu^{2+}$ (Li & Hintzen, 2006) and $Ba_3MgSi_2O_8:Eu^{2+}$ (He et al., 2009). Compared with these doped phosphor, carbon dots (CDs), which consists a fascinating class of fluorescence-based nanoparticles, have emerged as important fluorescence materials because of their excellent photostability, chemical stability, high biocompatibility, and cost-effective preparation (Qu, Wang, Lu, Liu, & Wang, 2012). Until now, CDs have gained increasing researchers' attention and a great number of CDs are available for their promising candidates in sensing (Qu, Chen, Zheng, Cao, & Liu, 2013), bioimaging (Bhunia, Saha, Maity, Ray, & Jana, 2013), catalysis (Zhang, Yuan, Liang, &Yu, 2015), and energy conversion/storage devices (Li et al., 2011). Except for the properties above, as for fluorescence material, CDs can effectively absorb certain characteristic wavelength, and the electronic transitions from the ground state to the excited state. On other hand, a part of energy is released in the form of a photon when transition from the lowest excited state to the ground state. Thus, the whole process of sunlight conversion is completed. However, there is no report on the sunlight conversion properties of the carbon dots.

As we all know, environmental concern is always a focus of the world, especially towards the unreasonable utilization of fossil fuels (Bilgen, Kaygusuz & Sari, 2004). Therefore, more and more attention is paid to search for alternatives to replace the non-renewable sources (Khan, Huq, Khan, Riedl, & Lacroix, 2014). And biodegradable natural polymer including cellulose (Dar, Garai, Das, & Ghosh, 2010; Burman, Ghosh, &Das, 2014; Ghosh & Moulik, 1998; Nag, Sadhukhan & Chattoraj 1988; Qi, Chang, & Zhang, 2009), starch (Dintcheva, La Mantia, & Arrigo, 2014), and chitin (Srinivasa & Tharanathan, 2007) is provided a broader development space. Carboxymethyl cellulose (CMC), the most widely used cellulose derivative, composed of β-D-glucose and β-D-glucopyranosyl-2-*O*-(carboxymethyl)-monosodium salt connected via β-(1,4-glycosidic) bonds (Fig. 1), which is prepared through the reaction between a cellulose alkali with sodium monochloroacetate (Paunonen, 2013). Due to its non-toxicity, bio-

* Corresponding author.
E-mail addresses: tliuyl@163.com (Y. Liu), tleibf@scau.edu.cn (B. Lei).

http://dx.doi.org/10.1016/j.carbpol.2016.05.063
0144-8617/

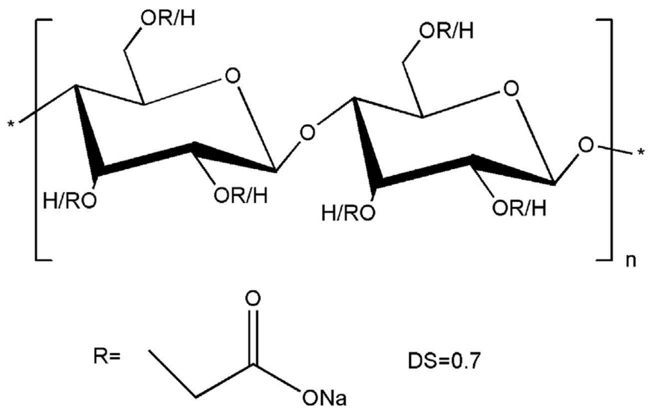

Fig. 1. Schematic structure of carboxymethyl cellulose.

compatibility, biodegradability, and hydrophilicity, CMC has been gained considerably public interest (Das, Mondal, & Ghosh, 2016; Chakraborty, Chakraborty & Ghosh, 2006; Wang & Su, 2014). Especially, the CMC film possesses high transparency in the spectral region and excellent film forming ability (Luna Martínez et al., 2011). Recently, a lot of interest has been paid in the synthesis of hybrid nanocomposites based on CMC with potential application. On one hand, the mechanical strength properties of film are improved effectively with the addition of graphene oxide in sodium carboxymethyl cellulose as high performance film (Yadav, Rhee, Jung, & Park, 2013). On the other hand, optical properties have been discussed in the luminescent films through situ precipitation of ZnS in sodium carboxymethyl cellulose aqueous solution (Luna Martínez et al., 2011). But the sunlight conversion properties of the composite film have scarcely been discussed.

It is known that CMC is a kind of hydrophilicity polymer, containing large number of hydroxyl groups. Besides, the CDs are biocompatible, whose surfaces are functionalized by lots of polar groups such as hydroxyl, carboxyl and amide groups. So it is promising to integrate CDs with CMC through simple hybrid process. In this work, we convey an effective route to prepare sunlight conversion film through combining the CDs with the CMC matrix. The preparation process can be divided into two parts, including synthesize of CDs and fabrication of film. Composite film was obtained by casting after the CDs dispersed in CMC aqueous solution. This process is demonstrated to be a “green” system to produce sunlight conversion films, without toxic vapor and fluid produced. In addition, from the perspectives of economic, compared to rare earth irons doped phosphors for sunlight conversion, the entail original materials is rather cost-effective involving in the synthesis of CDs, which can be produced in a large scale. Following, the obtained film was characterized by atomic force microscopy (AFM), scanning electron microscopy (SEM) to evaluate its structure. Besides, optical properties were analyzed by using UV–vis spectroscopy and fluorescence spectroscopy. The composite film presents optical transmission about 90% at 800 nm influenced by the amount of CDs in the composite films. Furthermore, the sunlight conversion effect of the composite film is analyzed through fluorescence spectrometer connecting an extra Xe lamp. In addition, the mechanical properties of the film are discussed.

2. Experimental

2.1. Materials

Carboxymethyl cellulose (viscosity: 800–1200 mPa s; DS = 0.7) and citric acid was acquired from Aldrich (Shanghai, China). Besides, the weight-average molecular weight (Mw) of CMC was determined in an aqueous solution by laser light scattering to be 12.0×10^4. Ethylenediamine was supplied by commercial sources in China, and was of analytical grade. All reagents were used as received without additional purification.

2.2. Synthesis of carbon dots

Carbon dots were prepared according to the literature (Zhu et al., 2013): firstly, citric acid (1.26 g) and ethylenediamine (1.61 ml) was dissolved in deionized water (30 ml). And then the solution was transferred to a poly (tetrafluoroethylene) (Teflon)-lined autoclave (50 ml) and heated at 200 °C for 5 h. After the reaction, the reactors were cooled to room temperature naturally. The product, which was yellow-brown and transparent, was separated by centrifugation and purified by dialysis. Finally, through vacuum distillation and desiccation, the brownish black solid was obtained. In order to weigh accurately, 10 mg of CDs was dispersed in 10 ml of deionized water for further steps.

2.3. Preparation of CMC/CDs film

In a typical process, 0.8 g of CMC was dissolved in 50 ml of deionized water at 60 °C until a transparent solution was formed. After added 200 μl of CDs solution (0.2 mg of CDs), the mixture solution was constantly stirred for 1 h at 60 °C. And then the resultant solution was subjected to centrifugation at 166.66 Hz (10000 rpm) for 10 min under ambient conditions for degasification. Finally, the composite solution was rapidly casted into a culture dish with side-to-side vibrations to make the solution well-distributed, and dried at 40 °C under vacuum for 24 h.

2.4. Characterizations

Transmission electron microscopy (TEM) images were recorded on a FEI-Tecnai-12 transmission electron microscope. The sample was diluted with ethanol, and then dropped to the copper grid for observation. The surface morphology of the films was analyzed by an atomic force microscope (AFM) (Dimension Edge, America). Scanning electron microscopy (SEM) observation was carried out with a MERLIN −Compact-FSEM microscope (Germany). For charactering the internal fine structure of the film, the cross section was prepared as follows. Firstly, the film was cut into rectangular strips in size of 0.5 × 2 cm. And then the cross section was obtained after the rectangular strips immersed in a container full with liquid nitrogen. Secondly, for available to test, both sides of the film are pasted on the glass strip through the conductive adhesive. Following, with the help of conductive liquid, the cross section of the film was vertically fixed on the copper table. At last, the cross section of the dried films were sputtered with gold and characterized with 3 kV accelerating voltage.

Thickness of the film was measured by a thickness gauge, and each value was expressed as an average of five measurements. The thickness of the film has been controlled to be about 40 μm. Relative errors in thickness of each film were within ±2 μm. Tensile tests were performed on a universal tensile tester (UTM 4204, Shenzhen SANS test machine, China) according to GB/T 1040.3-2006, equipped with a 200 N load cell. Rectangular strips 1.2 × 15 cm in size were cut from the films and tested with a span length of 10 cm at a rate of 5.0 mm min^{-1}.

Fourier transformed infrared spectroscopy (FT-IR) of the CDs in KBr discs were recorded with the region of 4000–400 cm^{-1} on a FT-IR spectrometer (Vertex 70, Germany). Absorption spectra were measured with a UV–vis spectrometer (Shimadzu UV 2550A, Japan) at a wavelength from 200 nm to 600 nm. The excitation spectra and emission spectra of the films were operated on a fluorescence spectrophotometer (F-7000, Hitachi, Japan). The sunlight conver-