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Effects of crosslinking modes on the film forming properties of kelp mulching films

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ABSTRACT

To solve the serious environmental pollution caused by traditional plastic mulching film, a biodegradable kelp mulching film (KMF) with excellent film forming properties was fabricated using kelp as the raw material. In this paper, the effects of different crosslinking modes with Ca^{2+} and H^{+} on the film formation of KMF were investigated. Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) results indicated that the synergistic gelation of calcium alginate and alginic acid existed in Ca^{2+}-H^{+}-KMF, implying that the KMF simultaneously crosslinks with Ca^{2+} and H^{+}. And the Ca^{2+}-H^{+}-KMF exhibited the best physical and mechanical properties among the five differently crosslinked KMFs. Studied results suggested that KMF simultaneously crosslinked by 2% Ca^{2+} and 1% H^{+} for 15 min had the best overall performance. The maximum tensile strength (TS) and elongation at break (EB) were 66.72 MPa and 7.68%, at the same time, the water vapour permeation (WVP) and water solubility (WS) were 8.05×10^{-11} g/(m·s·Pa) and 7.75%. Using kelp in agricultural mulching films reflects the ecological concept of making full use of resources, thus the KMF can be regarded as a sustainable ecological alternative to traditional plastic mulching films in agriculture.

1. Introduction

Plastic mulching film is a modern agricultural implement that is being widely used to reduce moisture consumption, increase soil temperature, inhibit weed growth, protect crops from diseases, avoid the leaching of soil nutrients, and consequently improve crop yields [1,2]. In China, the consumption of plastic mulching films for agriculture is about 1,200,000 tons per year; the area covered by the plastic mulching films is around 20,000,000 hm^2, and it is projected to increase by 8–10% in the next ten years [3]. However, the use of such vast quantities of low-density polyethylene plastic mulching films results in large quantities of plastic detritus that is usually burnt in the fields, resulting in severe environmental pollution [4]. Moreover, plastic mulching films degrade over hundreds of years in the soil, and since erosion by wind and rain results in the breakdown of the film into pieces, its collection and disposal is extremely costly and time-consuming [5]. The accumulation of the plastic residue in the soil causes the soil to harden, followed by reducing soil permeability and fertility, resulting in a seriously decreased crop yield [6]. According to the reported statistics, when the amount of plastic residues in the soil reached 58.5 kg ha^{-1}, the yield of vegetables would decrease by 14.6–59.2%, wheat by 9–16%, and maize by 11–23% [7,8]. Thus, the long-term and over-use of plastic mulching films causes severe problems for environmental protection as well as agricultural production.

To solve the abovementioned problems, numerous literature on biodegradable mulching films have been reported in recent years [1,9–14]. These films include partially biodegradable films and fully biodegradable mulching films, but partially biodegradable films could not radically solve the pollution of plastic residues. So for, several types of natural polymers such as starch, cellulose, chitosan, alginates, proteins, or combinations thereof have been used to study fully biodegradable films [15–17]. Unfortunately, most of these films have either unsatisfactory mechanical properties or poor water barrier properties. Moreover, because the extraction of these natural polymers such as alginate extracted from brown algae is both expensive and energy-intensive [18,19], fully biodegradable film is a considerable cost for the farmers to be widely used in the fields. Thus these drawbacks are largely limits its practical application in agricultural production.

Kelp, which is the most common brown algae, is an industrially valuable and versatile commodity, producing foods, cosmetics and fertilizers from phycocolloids and alginates [20]. In recent years, kelp has emerged as a potential future source of feedstock for the production of chemicals and biofuels [21–23]. As reported by the 2013 Chinese Fishery Statistical Yearbook, the yield of kelp, which is the highest in

*Abbreviations:*KMF, kelp mulching film

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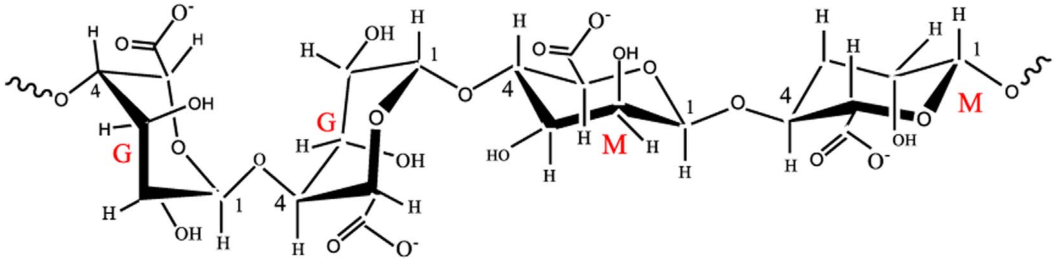

Fig. 1. The GG blocks (left), GM blocks (middle), and MM blocks (right) of alginates.

the world, has reached 979,000 tons per year. Kelp is rich in alginates as the polysaccharide in its matrix and cells. Alginate is a copolymer of 1–4 linked α-L-guluronate (G) and β-D-mannuronate (M) residues arranged alternately in GG or MM blocks together with GM blocks [24,25]. While the G-block residues give rise to fold and rigid structures, the M-block segments develop in linear and flexible structures in the molecular chains (Fig. 1) [26]. Alginate is one of the most studied materials for film applications due to its excellent film forming properties [25,27,28]. The idea of employing kelp in agriculture as biodegradable mulching film has come up due to various reasons – its good film forming properties due to the rich presence of alginates, it is renewable, abundant, and a biodegradable natural material. Furthermore, brown algae have been proven to be the most effective substrates to absorb the toxic heavy metals existing in the soil, thus significantly improving food safety [29,30]. In addition, the opaque KMF can prevent the passage of the photosynthetically active radiation (PAR) to inhibit weed growth [26]. At the end of their life, KMFs could be buried directly into the soil where bacterial flora transforms them into carbon dioxide or methane, biomass and water without generating waste that requires disposal. Using kelp in agricultural mulching films reflects the ecological concept of making full use of resources, thus the KMF could represent a sustainable ecological alternative to the traditional plastic mulching film.

Biodegradable films containing alginates are usually formed via crosslinking with polyvalent cations to improve their mechanical properties, water resistance, and rigidity [31]. Crosslinking methods of these films have been largely investigated in the case of Ca^{2+} [31–33]. A few previous studies involved H^+ in the crosslinking medium to optimize the physical and mechanical properties of the films containing alginates [27,34]. However, crosslinking modes with Ca^{2+} and H^+ as the crosslinking agents are rarely studied. As Ca^{2+} bind fundamentally to G residues, the crosslinking process involves preferentially G blocks of the alginates existing in kelp to form the calcium alginate gel according to "egg-box" model (Fig. 2) [26,35]. Since literature indicates that soluble alginate in the salt form can be converted into insoluble alginic acid in free acid form at acid pH [36], H^+ might involve both

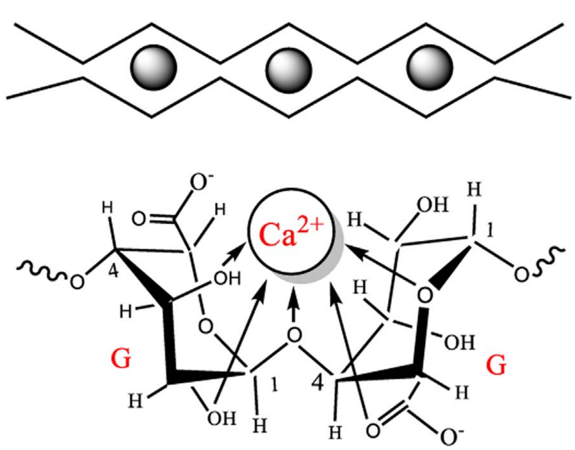

Fig. 2. GG blocks of alginates crosslinking with calcium ions.

the −COO groups of the G and M blocks of alginates (Fig. 1) to form the alginic acid gel to increase crosslinking density, and consequently improve the film forming properties of KMFs. Thus, the effects of different crosslinking modes with Ca^{2+} and H^+ on the film formation of KMF were investigated. In addition, previous studies mainly focused on the macro-properties and less on the micro-characteristics of biodegradable mulching films. The SEM and FTIR results are used to illuminate the micro-characteristics and to analyse the crosslinking mechanism of the KMFs in this work.

Therefore, the main objective of the current study was to fabricate a biodegradable KMF using kelp as the raw material, and to investigate the effects of different crosslinking modes with Ca^{2+} and H^+ on the film forming properties in terms of the microstructure, thickness, water solubility, mechanical and water vapour permeation properties. These studies are used as parameters for evaluating the applicability of KMFs as agricultural mulching films.

2. Materials and methods

2.1. Materials

Kelp was purchased from a local supplier (Qingdao, China) and was selected as the raw material with uniform quality to ensure that the data were comparable. Glycerol and hydrochloric acid were obtained from Bodi Chemical Co. (Tianjin, China), and calcium chloride and sodium carbonate were procured from Sinopharm Chemical Reagent Co. (Shanghai, China). Calcium chloride and hydrochloric acid were used as the crosslinking agents, while glycerol was used as the plasticizer.

2.2. Preparation of Na^+-KMF

The procedure for the preparation of Na^+-KMF is as follows: 10 g of dried kelp was cleaned and soaked in tap water (kelp/tap water = 1:40) for about 10 h and later mashed to a pulp. To this pulp, 1.6 g of Na_2CO_3 and 2.0 g of glycerol were added, and the entire mixture was maintained at 80 °C for 2.5 h with constant stirring to convert the insoluble alginate salts of kelp into soluble sodium alginate. The pulps were milled to less than 18 μm particle size using a colloid mill (JMS-50, China), and placed under vacuum about 1 h to remove any bubbles and form homogeneous solutions. The solutions were gently poured onto clean acrylic plates (70 g solution/plate) with 15 cm diameter and dried in an air oven at 60 °C for 5 h. The resulting Na^+-KMF with thicknesses of 0.040 ± 0.010 mm was then peeled off the plates and later crosslinked.

2.3. Crosslinking

To investigate the effects of different crosslinking modes with Ca^{2+} and H^+ as the crosslinking agents on the film forming properties of KMF, five differently crosslinked KMFs were prepared by immersing Na^+-KMF in different crosslinking solution for different time as shown in Table 1. Furthermore, to determine the combined effect of Ca^{2+} and H^+ on the film forming properties of KMF, the Na^+-KMF were