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Biodegradability and property characterizations of Methyl Cellulose: Effect of nanocompositing and chemical crosslinking

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Abstract

Broader range of biodegradability and other essential properties of Methyl Cellulose (MC) were achieved through nanocomposite formation and chemical crosslinking. Methyl Cellulose/Montmorillonite (MC/MMT) nanocomposites as well as MC-glutaraldehyde crosslinked films were characterized for thermal properties, tensile properties, moisture absorption, and biodegradability. MC/MMT nanocomposite films prepared by MMT suspension exhibited exfoliation which was confirmed by XRD and TEM results. In the chemical crosslinked system, the FTIR spectra revealed the crosslinkage between MC and GA. The tensile properties of the crosslinked films indicated that optimum GA content was 4.5 wt%. In addition, MC prepared from each method was capable of enhancing different properties. The MC/MMT nanocomposites could significantly improve tensile modulus (nanocompositing: 65%; crosslinking: 45%), while MC crosslinked film could outstandingly increase glass transition temperature (nanocompositing: 4 °C; crosslinking: 17 °C) and decrease moisture absorption properties (nanocompositing: 19%; crosslinking: 26%). The crosslinkage technique had more potential to hinder the biodegradation process. In 6 weeks, the CO_2 emission of crosslinked films was reduced around 80% in comparison with that of pure MC.

Keywords: Montmorillonite; Methyl Cellulose; Nanocomposite; Exfoliation; Biodegradability

1. Introduction

In the past 20 years, the production and the use of plastics in the world have been enormously increased, worsening the problems of the waste disposal. The growing interest in environmental impact of discarded plastics has been focused on the development of plastics, which are degraded more rapidly in the environment, leading to a complete bioassimilation of the plastics (Aminabhavi, Balundgi, & Cassidy, 1990; Crosby, 1981; Doi, 1990). Biopolymers can be used in those applications where biodegradability and/or the derivation of natural resources gives added value, particularly, where valuable petroleum-based plastics are used for applications with a short life time (Avella et al., 2005). For these reasons, throughout the world today, the development of biodegradable materials with controlled properties has been a subject of great research challenge to the community of material scientists and engineers (Gupta & Revagade, 2007; Mangiacapra, Gorrasi, Sorrentino, & Vittoria, 2005; Marras, Zuburtikudis, & Panayiotou, 2007; Yang, Yu, Feng, & Ma, 2006).

Methyl Cellulose (MC), a biodegradable polymer, is a modified type of cellulose being the most abundant biopolymer in nature. It is well known and of interest to be used as environmental friendly products, especially as coating or mulching film, because of its large availability, low cost, and easy processability. However, due to a biodegradable behavior of MC, it can be used only in limited applications.

There are two methods that can be used to potentially improve the biodegradability of MC. The first method is

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nanoreinforcement of pristine polymers to increase the lengths of the tortuous paths in nanocomposites in the presence of high clay content. When these lengths increase, the clay with high aspect ratio obstructs the diffusion of microorganism in the bulk of the film. That forces the decrease of biodegradability rate (Lee et al., 2002). The second one is to promote covalent linkages between polymer chains by crosslinking agent such as glutaraldehyde (GA). When crosslinkages occur, the gaps between polymer chains reduce. The water molecules, which are the media of microorganism, cannot penetrate through the crosslinked polymers. Both methods should modulate the biodegradability of polymers.

Polymer/clay nanocomposites have been the focus of academic and industrial attention in recent years because the final composites often exhibit a desired enhancement of physical and/or chemical properties relative to the pure polymer matrix e.g. increase of strength (Kampeerapappun, Aht-Ong, Pentrakoon, & Srikulkit, 2007), enhancement of thermal stability, and especially decrease of biodegradability rate even at very low clay contents (Lee et al., 2002; Li, Chen, & Xie, 2004; Wang et al., 2005). Montmorillonite (MMT) is one of the most important natural clays. The filler originally inherits a stacked structure of parallel silicate layers (Sinha & Okamoto, 2003). Depending on the extent of compatibility between the clay and the matrix, a microphase-separated conventional composite, intercalated, or exfoliated morphology can be obtained when directly mixed with polymer matrix (Krikorian & Pochan, 2003).

Crosslinking is one of the most popular methods used to modify water-soluble polymer in order to achieve desired properties. Some polymer characteristics could be altered by crosslinking such as swelling, permeability (Coma, Sebti, Pardon, Pichavant, & Deschamps, 2003; Park & Ruckenstein, 2001), drug releasing, transport properties, water uptake, mechanical properties, chemical stability, sponge structure as well as biodegradation rate (Wach, Mitomo, Nagasawa, & Yoshii, 2003). Several crosslinking agents for MC have been employed including dialdehyde. However, one of the most popular crosslinkers is glutaraldehyde (GA), a small molecule dialdehyde (Park & Ruckenstein, 2001).

In this work, MC/MMT nanocomposite films were prepared by solution intercalation using a homogenizer at the MC gelatinized temperature of 50–55 °C, to achieve intercalation of the stacked layers of MMT. The filler was suspended in water and dispersed under ultra high shear rate to form MMT gel suspension. This preparation method was applied in order to delaminate the layered silicate of MMT and to homogenously disperse the nanoparticles in MC matrix. Crosslinked MC was prepared by using GA as a chemical crosslinking reagent and hydrochloric acid as a catalyst in an aqueous solution. The effects of MMT and GA contents used on the biodegradability, physical properties, thermal properties and mechanical properties of MC nanocomposites, and crosslinked films were investigated, respectively.

2. Experimental

2.1. Materials

Methyl Cellulose (MC), Tylose H 6000 YP2, was purchased from SE Tylose GmbH & Co., KG, Germany whereas Polargel HV powder, trade name of Montmorillonite (MMT), was supplied by VOLCLAY International Co., Ltd. Glutaraldehyde (GA) solution (25 wt%, molecular weight = 100.11, Bp = 106 °C) under trade name of UNILAB was obtained from Ajex Finechem, New Zealand.

2.2. Preparation of nanocomposite films

2.2.1. Preparation of Montmorillonite suspension

The condition for preparation of MMT suspension by using a homogenizer (IKA T25 basic) was preliminarily investigated. The suitable preparation condition to ensure a completely exfoliated suspension was applied for the preparation of MMT suspension. The performed condition was Polargel HV suspension at 5 wt% and pre-swelling times of 8 days using a homogenizer at a constant mixing speed of 13,500 rpm for 5 min at ambient temperature.

2.2.2. Preparation of Methyl Cellulose nanocomposite films

MC/MMT nanocomposite films were prepared by mixing appropriate MMT suspensions obtained from Section 2.2.1 with aqueous MC solutions (2 wt%) by solution intercalation technique over the gelation temperature of MC (50–55 °C). In this study, mixing temperature was about 80 °C. A homogenizer was used for high shear mixing at 13,500 rpm for 5 min. The weight ratio of MC/MMT was varied as 100:0, 100:1, 100:2, 100:3, 100:5, and 100:10. About 30 ml of the obtained MC/MMT solution was poured onto a polystyrene mold. Dried films were obtained after the solvent was evaporated in an air-circulated chamber at ambient temperature. The thickness of the yielded nanocomposite films was in the range of 70–80 μm.

2.3. Preparation of crosslinked Methyl Cellulose films

Aqueous MC solutions (2 wt%) were prepared by dissolving MC powders in water and mixed for 1 min at 80 °C using a homogenizer with a speed of 13,500 rpm. GA and hydrochloric acid were added after the MC solution was cooled to room temperature. The investigated GA contents were varied at 0.5, 1.5, 3.0, 4.5, 6.0, and 12.0 wt%. In each solution, 2 drops of hydrochloric acid were added to yield a solution of pH 3. After stirring using a magnetic stirrer at 700 rpm for 1 h, the homogeneous mixture of MC and GA was obtained. Finally, the resulting dried films were washed by distilled water for 3 h to neutralize the films. The thickness of crosslinked films was approximately the same as that of the nanocomposite films.