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Synthesis and characterization of hydroxypropyl methylcellulose and ethyl acrylate graft copolymers

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Abstract

The synthesis of hydroxypropyl methylcellulose-*g*-poly (ethyl acrylate) was carried out by potassium persulfate induced graft copolymerization in homogeneous aqueous medium. By varying the reaction conditions, graft copolymers with different percentage of grafting were prepared. These graft copolymers were characterized by fourier transform infrared spectra (FTIR), transmission electron microscopy (TEM), scanning electron microscopy (SEM), thermogravimetric analyses (TGA), X-ray diffraction analysis (XRD), and dynamic light scattering (DLS) methods. The molecular weight of grafted and ungrafted polymer chains determined by gel permeation chromatography (GPC) increased with increasing monomer and matrix concentration but decreased with increasing initiator concentration and reaction temperature. The mechanical properties of graft copolymers were measured as function of the percentage of grafting. In addition, the equilibrium humidity adsorption behavior and the disintegration time of the grafted copolymer films were also studied.

Keywords: Graft copolymer; Hydroxypropyl methylcellulose; Ethyl acrylate; Cellulose derivatives; Characterization; Property

1. Introduction

Graft copolymerization is a useful technique for modifying the properties of the most abundant natural cellulose and cellulosics polymers (Bianchi, Bonazza, Marsano, & Russo, 2000; Bikkullova, Druzhinina, & Abronin, 2005; Canche-Escamilla, Rodriguez-Trujillo, Herrera-Franco, Mendizabal, & Puig, 1997; Chauhan, Guleria, & Sharma, 2005b; Coskun & Temuz, 2005; Elisabetta et al., 2005; Estella, Enrico, Laura, & Saverio, 1998; Khan, 2005; Mishra & Bajpai, 2005; Okieimen, 1998; Okieimen, Sogbaike, & Ebhoaye, 2005; Pradeep, Saikia, & Dass, 2004; Roman-Aguirre, Marquez-Lucero, & Zaragoza-Contreras, 2004; Trivedi, Kalia, Patel, & Trivedi, 2005). It is important to mention that not only pure cellulose have been modified but also several cellulose derivatives, either in pure or raw form. In recent years, Chauhan et al. reported the graft copolymerization of certain vinyl monomers onto hydroxypropyl cellulose (HPC) in order to obtain new polymeric materials for environmental management and investigated the optimum grafting conditions as well as the utilization as the sorption agent of some metal ions (Chauhan, Guleria, & Mahajan, 2001; Chauhan & Mahajan, 2002a, 2002b; Chauhan, Mahajan, Sddiqui, & Gupta, 2004b, 2004a; Chauhan, Singh, Chauhan, Verma, & Mahajan, 2005a, 2005b). They used pine needles from the huge forest of the Western Himalayas as a source of cellulose. Cellulose was derivatized to HPC, the useful water-soluble cellulose ether, and then, HPC was graft-copolymerized with the vinyl monomers. In addition, some reports on cellulose derivatives focus on the graft copolymerization of vinyl monomers onto ethyl cellulose (EC) in homogeneous organic solvent medium (AbdelRazik, 1990, 1992, 1994, 1996a, 1996b, 1997a; AbdelRazik, 1997b; Aggour, 1999; Aggour & AbdelRazik, 1999; Shen, Yu, & Huang, 2005). In some studies (Biswal & Singh, 2004; Vasile, Bumbu,

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Dumitriu, & Staikos, 2004; EI-Hady & Ibrahim, 2004; Okieimen & Ogbeifun, 1996; Zhang, Tan, & Li, 2000), carboxymethyl cellulose (CMC) has also been grafted with vinyl monomers in a homogeneous solution system, and the grafted copolymer obtained has been used as membrane substrates (Ibrahim, Flefel, & EI-Zawawy, 2002).

Among the cellulose derivatives, hydroxypropyl methylcellulose (HPMC) is an important potential material with a wide range of applications in drugs, textiles, foods, and paper. HPMC is formed by its reaction with chloromethane and epoxy propane. The structure of HPMC is shown in Fig. 1. It has a number of hydroxypropyl groups, introduced into the cellulose molecule, which promote its water solubility. HPMC is also easily available and very cheap. However, there are few reports on the graft copolymerization of HPMC in homogeneous aqueous medium. In our previous paper (Wang & Xu, 2006), the graft copolymerization of ethyl acrylate (EA) onto HPMC initiated by potassium persulfate (KPS) was carried out in an aqueous homogeneous medium under various conditions to determine the optimum conditions for the graft copolymerization. In this paper, we focus on the characterization and the properties of the HPMC and EA graft copolymer, and the results obtained were also used to elucidate the relationship between the structure of the graft copolymer and the properties of it. Furthermore, the grafted chains on the HPMC backbone can hinder the penetration and the absorption of water molecules onto cellulose chains.The decreasing of absorbed water is an indicator of the protective effect given to HPMC by grafting copolymerization, and the graft copolymers obtained could have utility in applications of the tablet coating materials.

2. Experimental

2.1. Materials

Hydroxypropyl methylcellulose (Taian Ruitai Cellulose Co., Ltd, Shandong, China) was dried in a vacuum desiccator on calcium chloride. Ethyl acrylate (Tianjin Chemical Reagent Co., Inc., Tianjin, China) was washed with 5% sodium hydroxide and stored below 5 °C after vacuum distillation. The potassium persulfate was reagent grade chemicals and used after recrystallization. All other reagents were laboratory grade chemicals and were used as such.

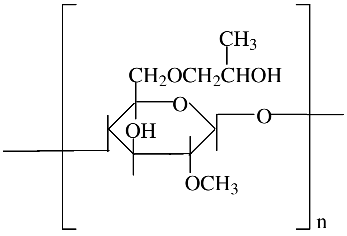

Fig. 1. Structure of hydroxypropyl methylcellulose.

2.2. Graft copolymerization

The graft copolymerization of EA onto HPMC was carried out by adding a calculated amount of HPMC (6 g) in a three-necked round-bottom flask containing a known amount of distilled water. The flask was fitted with an electrically operated stirrer and kept in a water bath maintained at 60 ± 1 °C. The solution was purged with nitrogen gas for about 30 min before adding KPS (0.15 g) into the flask. Then, EA (6 g) was charged into the flask to initiate the graft copolymerization after KPS interacting with HPMC for 5 min. The reaction mixture was stirred at a constant rate to avoid the adverse effect of stirring on graft copolymerization. The reactants were allowed to react about 4 h before the reaction was terminated.

2.3. Isolation of the grafted and ungrafted polymer chains

The rough product contained the HPMC graft copolymer and the PEA homopolymer was dried to a constant weight at 60 °C in a vacuum. The HPMC graft copolymer was separated from the PEA homopolymer by extraction (72 h) with acetone utilizing a Soxhlet apparatus. The PEA homopolymer (ungrafted PEA chains) was recovered from the acetone solution by reprecipitation into distilled water. Then, the two separated products were dried again under a vacuum. Finally, the purified copolymer HPMC-g-PEA obtained was hydrolyzed in 72% H_2SO_4 solution at 30 °C for 4 h to obtain the grafted PEA chains.

2.4. Definition of the grafting parameters

The monomer conversion was obtained gravimetrically. Percentage of grafting (G) and grafting efficiency (G_E) were calculated with the following equation after the HPMC-g-PEA, grafted PEA chains, and the HPMC were weighed

$$G(\%) = \frac{\text{Weight of PEA Grafted}}{\text{Weight of HPMC}} \times 100$$

$$G_E(\%) = \frac{\text{Weight of PEA Grafted}}{\text{Weight of EA Reacted}} \times 100$$

3. Characterization and properties testing

FTIR spectra analyses were used to identify the graft copolymerization. The FTIR spectra of HPMC, PEA, and the grafted HPMC after 72 h of acetone extraction samples were recorded on KBr pallets using Nicolet 5DX Fourier transform infrared spectrophotometer.

Water dispersion samples for transmission electron microscopy (TEM JEOL CX-100II) were prepared by diluting in distilled water, dispersing, and depositing on perforated carbon films supported on copper grids.

Scanning electron microscopy (SEM) was utilized to examine the surface morphology of the grafted HPMC film samples. For this, the film samples were coated with a thin