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Preparation and characterization of pre-silane modified ethyl cellulose-based microcapsules containing linseed oil

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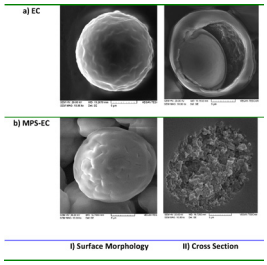
HIGHLIGHTS

- Ethyl cellulose was treated with three different trimethoxysilane coupling agents.
- Various techniques and methods confirmed silane grafting of ethyl cellulose.
- A solvent evaporation method was described for microcapsules preparation.
- Microcapsules were prepared with a regular spherical shape in the size of 5–35 μm.
- These microcapsules have a smart prospect in self-healing coatings applications.

GRAPHICAL ABSTRACT

Scanning electron micrographs of microcapsules. (a) EC, and (b) MPS-EC, (I) surface morphology and (II) cross section.



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ABSTRACT

In this study, ethyl cellulose (EC) was treated with three different trimethoxysilane coupling agents. Various characterization techniques were employed to evaluate silane modification of EC compound. Microencapsulated phase change materials based on linseed oil (LO) core and un-treated and silane-treated EC shell materials with ratio of LO to EC (70:30) were prepared by solvent evaporation method. Morphology and shape of microcapsules were studied using optical microscopy and scanning electron microscopy (SEM) equipped with energy dispersive X-ray analyzer (EDAX). The size distribution of microcapsules was evaluated using a particle size analyzer.

Fourier transform infrared spectra (FTIR) and nuclear magnetic resonance (NMR) analyses revealed chemical interactions between EC and three different types of trimethoxysilane. Chemical bond (Si—O—C) was formed by the reaction between Si—OH and the hydroxyl group of EC. The thermo-gravimetric analysis (TGA) showed 6–12 wt% silane grafting on the EC compound. Microcapsules with a uniform spherical shape 5–35 μm in diameter and 0.5–2.0 μm in shell thickness were successfully prepared using either un-treated or silane-treated EC. SEM micrographs of the fractured surface of acrylic coating containing LO filled EC-microcapsules showed matrix structure for microcapsules, as results of silane treatment of EC shell material.

The pre-silanized EC-microcapsules can improve mechanical properties of water-based self-healing coatings, due to better compatibility of microcapsules with polymeric matrix and possible chemical interactions between silane groups attached on EC-microcapsules and functional group of polymeric matrix.

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1. Introduction

Micro-encapsulation technology can be used in various fields of application including paper industries [1], food stuffs [2], pharmaceuticals [3], cosmetics [4], adhesive materials [5] and coating industries [6] to protect substrates from their surrounding environments. Among different categories of micro-encapsulations' applications, much attention has been paid to self-healing polymeric coatings [7,8]. Self-healing materials can be used for preventing crack propagation, increasing the coating's lifetime and reducing the cost of maintenance and repairing of the defected coatings [9]. In 2001, White et al. [10] proposed a novel approach to restore the mechanical properties of an epoxy-based coating in which urea-formaldehyde microcapsules containing dicyclopentadiene (DCPD) healing agent were used. Restoring has been obtained through the ring opening polymerization of DCPD in the presence of Grubbs' catalyst [11]. In this application, microcapsules containing healing agent break with external stimulus and the healing materials release within the crack lines, and come into the contact with the active agents therefore polymerization starts and the damage is restored [12].

In the recent years, many articles have been published about the self-healing properties of the coatings and composites [8–15]. Most of these researches focused on development of new encapsulation methods, their efficiency and optimizing the properties of solvent-based coatings, e.g., poly(urea-formaldehyde) (PUF) [9–14]. However, there are rare reports on water-based self-healing coatings [15–17]. Kumar et al. [15] fabricated microcapsules composed of vegetable oil as the core materials, surrounded by urea-formaldehyde shell polymer, applicable in water-based self-healing coatings. Mirabedini et al. [18] showed that the local release of encapsulated vegetable oil by ethyl cellulose, EC, upon external mechanical stress could plasticize the matrix and partly restore tensile properties. However, due to possible weakness of microcapsules/polymer matrix interface, fluctuation in the mechanical properties at microcapsules loading higher than 2 wt% was observed. Weak interactions at the matrix–microcapsule interface can diminish stress transfer to the capsules and retard the release of the healing agent used [19,20]. Therefore, enhancing the chemical or/and physical interactions between microcapsules and the host polymer matrix could significantly improve the self-healing characteristics in this system.

Mechanical properties of the coating materials can be improved by increasing physical entanglement between non-continuous phase (i.e., microcapsules) and continuous polymeric part, or/and enhancing chemical or physical interactions between the fillers and polymeric matrix [21–24]. Coupling agents and in particular, silane coupling agents (SCA) have gained much attention because of their particular structures that could simultaneously bind to the matrix and the microcapsules via chemical or physical interactions and improving the adhesion between microcapsule and polymer [23,24]. Nowadays, a few reports have been released regarding to SCA treatment of PUF microcapsule's shells to improve the interfacial interactions between the PUF microcapsule shells and surrounding epoxy matrix [19,20,25,26]. However, to the best of our knowledge there has been no published report on chemical modification of EC-microcapsules using SCA materials for self-healing coating applications.

In this study, in order to improve possible interactions between EC-microcapsules and polymeric matrix, EC was chemically modified using three different types of trimethoxysilane coupling agents. Various techniques were used to characterize silane-treated EC. Microcapsules with a 30:70 ratio of silane-treated EC as the shell-forming polymer and linseed oil, LO, as the core materials were prepared via a modified solvent evaporation method. Characteristics of microcapsules prepared using silane-treated EC are presented and discussed in here.

2. Experimental

2.1. Materials

EC powder (viscosity 10 cP, measured as a 5% (v/v) solution in toluene/ethanol 80:20, 48% ethoxyl content), LO, chloroform, sodium dodecyl sulfate (SDS) and Triton X-100 were obtained from Sigma–Aldrich (Oakville, Ontario, Canada). SCA consisting of (3-aminopropyl)-trimethoxysilane (APS), [3-(methacryloyloxy)-propyl]-trimethoxysilane, MPS, and [3-(2,3-epoxypropoxy)-propyl]-trimethoxysilane, EPS, were purchased from Merck Chemicals Co. (Darmstadt, Germany). All chemicals were analytical reagent grade and used as received without any further purification.

2.2. Silane modification of ethyl cellulose

EC was chemically modified by three different trimethoxysilane derivatives in order to improve possible interfacial interactions between the microcapsules and polymeric matrix. Briefly, 2 g EC powder was dissolved in 60 mL acetone by gentle magnetic stirring at ambient temperature for 1 h. In parallel, 1 g of the respective trimethoxysilane derivative was dissolved in 30 mL acetone under same conditions for 1 h. The ratio of the three different SCA to EC was considered as 1:2 (wt:wt). Then, EC solution was added dropwise to silane solution and kept under stirring and refluxed for further 7 h. Solvent content was removed by distillation and the residue silane-treated EC was rinsed with deionized water for several times, filtered and dried in a low pressure oven for 24 h at 25 °C [21].

2.3. Characterization of silane-treated ethyl cellulose

Fourier-transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy were used for characterizing of EC samples before and after silanization. FTIR spectroscopy was carried out in KBr pellet on a Bruker EQUINOX 55 FTIR spectrophotometer (Ettlingen, Germany), collecting 18 scans in the 400–4000 cm^{-1} range with 4 cm^{-1} resolution. CNMR spectra were recorded on a Bruker Avance 300 NMR MHz (Germany) equipment, from 0 to 200 ppm using tetramethylsilane as internal standard. Samples were dissolved in deuterated chloroform at ambient temperature. The thermal behavior of the un-treated and silane-treated EC (after drying in a low temperature oven at 80 °C for 3 h) was evaluated with TGA (PL-1500, Polymer Laboratories, UK), under N_2 atmosphere from room temperature up to 600 °C with a heating rate of 10 °C min^{-1}.

2.4. Preparation of microcapsules

LO-loaded microcapsules were prepared via a modified solvent evaporation method [17]. In a typical batch, 0.9 g silane-treated EC and 2.1 g of LO were separately dissolved in chloroform (18 mL) under magnetic stirring for 1 h. Then, LO solution was added to the EC solution and agitated for 30 min. The above-mentioned solution was added dropwise to an aqueous solution of SDS (1 wt%) and Triton X-100 (0.02 wt%) saturated with chloroform in a 150 mL beaker, under mechanical stirring at a constant speed of 1000 rpm with an axial three-bladed impeller stirrer (Heidolph RZR 2102, Germany) for about 10 min. During this process the temperature was gradually increased from 25 ± 2 °C to 40 ± 2 °C using a temperature-controlled water bath. To remove the solvent, the temperature was subsequently increased to about