Journal of Colloid and Interface Science 333 (2009) 145–151

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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Synthesis of cationic polymer-grafted cellulose by aqueous ATRP

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ARTICLE INFO

Article history:
Received 23 September 2008
Accepted 25 January 2009
Available online 29 January 2009

Keywords:
Atom transfer radical polymerization (ATRP)
Cellulose fibers
Cationic polymer

ABSTRACT

We describe the synthesis of cellulose fibers densely grafted with the cationic polymer poly[2-(methacryloyloxy)ethyl]-trimethylammoniumchloride (PMeDMA) through aqueous ATRP. The hydroxyl groups present on the cellulose surface were exploited to initiate the ATRP polymerization of MeDMA. We first grafted a bromide initiator, known to be an efficient initiator for ATRP, on the cellulose surface from which the polymer was then directly grown. The resulting fibers/PMeDMA complex was analyzed with infra-red, XPS and SEM techniques and present clear evidences that the polymer is present on the cellulose surface. In order to better characterize the polymer, sacrificial initiators were also added in the mixture and subsequently recovered for analysis. Size exclusion chromatography shows that the polymerization in this heterogeneous medium was controlled. Finally, we show that the mechanical properties of test hand sheets made from modified pulp are markedly improved by the grafting of the cationic PMeDMA.

1. Introduction

An important challenge in pulp and cellulose chemistry is the modification of chemical and physical properties of natural cellulose fibers. The incorporation of polymer in cellulose materials provides a significant route to change and improve different properties such as flexibility, wetting properties, charge, as well as the strength of networks [1]. Grafting of polymer onto cellulose surface with vinyl monomers has been performed with different techniques, such as peroxidation or the use of xanthate, and different polymers such as styrene, methyl methacrylate and acrylamide [2,3].

These methods are however uncontrolled, it is impossible to predetermine the molecular weight of the polymer and the molecular weight distributions are very broad. For specific applications better-defined polymer is often required, which has led to the synthesis of well defined cellulose grafted (co)polymers. Synthesis of well-defined cellulose grafted polymers using a living controlled polymerisation on the surface of carboxymethyl and hydroxypropyl cellulose has been realized through the use of Barton ester intermediates and nitroxide mediation [4]. Recently, atom-transfer radical polymerization (ATRP) grafting of hydroxypropyl cellulose with PMMA and *tert*-butyl acrylate was also achieved [5], together with ATRP grafting of cellulose fibers (filter paper) with block copolymers PHEMA–PMA [6].

Cellulose/polymer composite can be obtained either by adsorption or by grafting of the polymer onto cellulose surface. However, a much stronger link between polymer and cellulose surface is obtained with the polymer grafted to the oxygen of the glucosidic unit of cellulose surface. There are two different ways of synthesizing cellulose graft polymer. The first, "graft to", uses a reaction of functional group of the pre-made polymer with an active site on the surface. The advantage of this grafting procedure is that the molecular weight and the molecular weight distribution of graft polymers are controlled. However, this technique is limited by a poor grafting density due to a lack of accessibility to the reactive surface groups caused by a steric hindrance. The second one is based on a "graft from" technique in which the polymer grows from the solid surface by initiators previously introduced onto the surfaces. This method ensures the synthesis of polymer chains covalently attached to the surface and can bring about a higher grafting polymer density. In addition, combined with controlled polymerization this approach leads to the formation of polymers with controlled molecular weight and narrow polydispersity.

Grafting of polymer and subsequent controlled polymerization on cellulose surface is usually performed on soluble cellulosic compound such as hydroxypropyl cellulose [5], or previously formed networks of fibers such as filter paper [6]. However, little attention has been paid to grafting of well-defined polymer directly on the surface of natural cellulose fibers. This situation is important to facilitate the potential papermaking applications of the fibers,

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doi:10.1016/j.jcis.2009.01.050

although problems with poor reproducibility of the synthesis and in production of non-homogeneous products [7] must be tackled.

The pulp and paper industry already extensively uses cationic polymers to increase the mechanical properties of cellulose fibers, in part due to the negative charge carried by fibers in aqueous media. Use of polymers such as cationic polyacrylamide or cationic starch which adsorb to the fibers surface is already well established and understood [1]. Nevertheless, several problems may arise from polymer desorption and reconfiguration [8]. Furthermore, the conventional method to prepare well-defined cationic polymers involves a synthesis with controlled polymerization followed by a post-quaternization step [9]. However, this last step is toxic or requires elevated temperature and long reaction times to achieve high degrees of quaternization [9,10].

Atom-transfer radical polymerisation (ATRP) [11,12] allows the synthesis of polymer with predefined molecular weight and narrow molecular weight distribution. It can also be used in protic media and for a wide variety of monomers. The first direct polymerization of a cationic quaternized monomer was performed via ATRP using MeDMA in protic media and ambient temperature [13] and PMeDMA with star-like structure, based on a cyclodextrin core and using a β-cyclodextrin, was also obtained by ATRP polymerization of MeDMA [14]. Both studies of ATRP of MeDMA were realized in homogeneous media. Direct polymerization of cationic monomers MeDMA via ATRP thus seems to be a promising route to obtain well-defined cationic polymers grafted onto fibers surface.

We report here the synthesis of cellulose–cationic polymer composite prepared by aqueous ATRP of cationic MeDMA on cellulose fibers. We first concentrate on the synthesis and characterization of the cellulose–cationic polymer composite. Test paper sheets containing various proportions of modified fibers were then prepared and their mechanical properties were studied in view of possible papermaking applications.

2. Materials and methods

2.1. Materials

Cellulose (Kraft pulp, 99% of cellulose), 2-bromo-2-methylpropionyl bromide (98%, Aldrich 25,227-1), 2,2′-bipyridyl (>98%, Fluka 14453), triethylamine (99.5%, Aldrich 47,128-3), *tert*-butylmethacrylate (tBuMA, 98%, Aldrich 46,335-3) was distilled under vacuum just before use, [2-(methacryloyloxy)ethyl]-trimethylammoniumchloride (MeDMA, 75 wt% solution in water, Aldrich 408107) was purified by extraction with diethyl ether. Tetrahydrofuran (THF, 99.5%, SDS 0700248) and toluene (>99.5%, Fluka 89861) were distilled and degassed by bubbling nitrogen for 30 min just before use. Copper(I) bromide (98%, Aldrich 21,286-5) was used as received. The water used in all experiments was de-ionized and distilled prior to use. Ion exchange resin (Aldrich 21,653-4), used for removal of ATRP copper catalyst.

2.2. Measurements

2.2.1. Size exclusion chromatography (SEC)

Size exclusion chromatography (SEC) was carried out using a Waters 2690 liquid chromatograph equipped with three columns, Waters Styragel 5 μm, 10^4 Å, 500 Å and 100 Å (columns, injection and refractometer temperature, 40 °C; injection volume, 100 μl; solvent, $NaNO_3$ (0.1 M), 1 ml/min). Size exclusion chromatography was calibrated with PEG standards.

2.2.2. Fourier transform infra-red (FTIR)

Fourier transform infra-red (FTIR) spectroscopy was used to investigate the nature of the chemical bonds for both modified and PMeDMA-grafted cellulose. Measurements were performed with a Perkin-Elmer System 2000.

2.2.3. X-ray photon spectroscopy (XPS)

X-ray photon spectroscopy (XPS) is a surface-sensitive technique that provides elemental composition information of a sample for depth of a few nanometers. A Kratos Axis Ultra spectrometer was used to evaluate the atomic concentrations present on the functionalized surface from the integral of elemental peaks intensities.

2.2.4. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was used to obtain the visual appearance of the test paper hand sheets at high resolution (micrometer scale). Measurements were taken with a Jeol JSM-5500 scanning electron microscope.

2.2.5. Zeta potential

Zeta potential measurements were performed to evaluate the effect of the cationic polymer modification on the anionic cellulose surface using a Zetasizer nano series from Malvern Instruments. The apparatus measures how fast a particle moves in a liquid when an electrical field is applied. The Zeta potential of original, non-modified cellulose is found to be −26.65 mV.

2.2.6. Hand sheet preparation and testing

Paper test sheets with basis weight of 60 g/m^2 were prepared using A.3 PAPTAC standard [15]. The hand sheets are first used for further by XPS and SEM techniques. Mechanical tests are also performed on hand sheets containing various proportions of modified and non-modified fibers (in mass proportion of 0%, 5%, 10%, 25%, 50%, 75% and 100% of modified fibers). Tensile and tear mechanical properties are examined on each set of hand sheets. Tensile properties are measured with an Instrom 4201 tensile tester according to PAPTAC D.6H standard [15]. The apparatus measures the tensile strength (the force needed to break the sample per unit width of the sample). The tensile index is then obtained by dividing the Tensile strength by the basis weight. Tear properties are measured with an Elmendorf ProTear Tearing tester of Thwing-Albert (PAPTAC standard D.9 [15]). The Tear index measures the average force needed for a previously formed crack to keep moving. In addition, the thickness of each hand sheet is measured (PAPTAC method D.4 [15]) and the density of the hand sheets is calculated from the basis weight.

2.3. Preparation of cellulose

The pulp was disintegrated in a British Disintegrator in deionized water at ambient temperature for 5 min. The pulp was then filtered; the consistency was determined and conserved. The general conditions of the experimental part for the synthesis of cellulose grafted bromide and the ATRP polymerization were as described before [16].

2.3.1. Product 1: Preparation of Br-grafted cellulose

The cellulose fibers were washed with acetone, methanol and water prior to use, ultrasonicated for 30 min, filtered and the consistency was determined. To a round bottom flask were added 8 g of fibers (3.84×10^{-2} mol, using cellulose as a basis unit), 10.80 ml of triethylamine (7.68×10^{-2} mol) and 400 ml of dry CH_2Cl_2. To the reaction mixture, stirred at room temperature under nitrogen, was added drop-wise 9.50 ml of 2-bromoisobutyryl bromide (7.68×10^{-2} mol) over a period of 15 min. The reaction mixture was stirred at room temperature for 24 h. The salt was removed by filtration. After washing with water the product was subjected to washing/filtration/ultrasonication/filtration with acetone and water in order to remove any non-grafted Br-initiator from the fibers [17].