

Modification of hydrophilic cellulose fibers by monolayer growth of polystyrene chains using ATRP

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Received: 4 January 2013 / Accepted: 19 February 2013 / Published online: 28 February 2013
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Abstract The chemical modification of biopolymer-based materials by grafting synthetic polymers has received considerable attention in recent years, inasmuch as there are wide varieties of monomers available. Nowadays, the most abundant biomacromolecule, cellulose, has attracted considerable attention due to its biodegradable, biocompatible, and renewable characteristics. In this study, the surface of hydrophilic cellulose microfibrils was successfully modified by polymerization of hydrophobic polystyrene using atom transfer radical polymerization (ATRP) technique in dispersion medium. In this medium, only the outer surface of the macroinitiator is available for the polymerization, so the grown polymer chains are formed as monolayer on the surface of the macroinitiator. This type of modification not only increases the mechanical properties of the cellulose backbone, but also turns the hydrophilic characteristics of cellulose into hydrophobic state. For this purpose, in the first part of this research, chloroacetylated cellulose was synthesized as macroinitiator. In the second part, the acyl content of the macroinitiator and the degree of substitution, which show the efficiency of the esterification reaction, have been determined by basic hydrolysis of the macroinitiator with KOH and back-titration of the excess alkali with HCl. Finally, the chloroacetylated cellulose was modified by graft copolymerization of styrene using ATRP method. The

polystyrene chain growth is confirmed by the atomic force microscopy images.

Keywords Cellulose microfibrils · Surface modification · ATRP · Monolayer

Introduction

The synthesis of cellulosic graft copolymers with tailored surface properties is of great interest due to their wide range of potential applications. For instance, graft copolymers can be used as antibacterial surfaces [1], thermoresponsive smart materials [2], membrane materials [3], controlled drug delivery vehicles [4], ion-exchange materials [5], sorption agents for the removal of heavy metals [6], and reinforcing agents in composite materials [7, 8].

The interest in using natural cellulose fibers in composite materials is constantly growing due to their availability as renewable natural resources, ease of fiber surface modification, low cost, good mechanical properties, low density compared with their inorganic counterparts, and recyclability [9]. However, the high moisture absorption of hydrophilic cellulose fibers can lead to composite failure due to the formation of weak interfacial interactions between the natural fibers and the polymer matrix. The most efficient way to reduce the hydrophilicity of cellulose fibers and to improve their compatibility and adhesion to other hydrophobic composite material components is to modify the cellulose surface by controlled grafting with hydrophobic monomers.

The grafting of hydrophobic monomers, such as methyl methacrylate, styrene, acrylonitrile, butadiene, and vinyl acetate onto cellulose substrates can enhance the adhesion of the grafted materials to hydrophobic fibers [10, 11].

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