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Functional biohybrid materials synthesized via surface-initiated MADIX/RAFT polymerization from renewable natural wood fiber: Grafting of polymer as non leaching preservative

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Crude wood fibers represent a wide class of renewable resources. The surface modification of such materials via covalent grafting of polymer offers new surface properties with non-leaching coating. The grafting of the polymer chains was achieved by surface-initiated controlled radical polymerization through a grafted xanthate chain transfer agent. Macromolecular design via interchange of xanthate (MADIX) technique was chosen to graft poly(vinyl acetate), polystyrene, poly(*n*-butyl acrylate) and poly(4-vinylbenzyl chloride)-polystyrene amphiphilic cationic copolymers. Water contact angle measurements highlighted the hydrophobization of the wood fiber surface with a nanoscaled polymer monolayer indicating the appropriate coverage of the fiber. X-ray photoelectron spectroscopy showed the successful grafting of the polymer after drastic washing procedure. The quaternization of the grafted polystyrene-*co*-poly(4-vinyl benzyl chloride) copolymers with tertiary amine allows the introduction of biocide quaternary ammonium functions while preserving the hydrophobic character of the modified wood fiber when introducing a long alkyl chain in the statistical copolymer. Finally, the cationic copolymer was subjected to *Coniophora Puteana* to evaluate its propensity to limit the fungi expansion.

1. Introduction

Surface treatment of renewable resources is known to improve the characteristic values of biocomposites by introducing new surface properties [1,2] or by favoring dispersion in a polymeric matrix [3]. In the context of wood development, we are concerned with tuning the surface properties of natural wood fibers by grafting polymer chains from the fiber surface. We aim to covalently attach the polymer in order to prevent any leaching of the coating, an important issue for environmental concerns. The grafting of hydrophobic polymer chains will contribute to the preservation of the wood fibers against external stress (humidity, fungi…) and the introduction of additional biocidal functions inside the polymer chains should bring benefit to the coating.

Surface-initiated controlled radical polymerization (SI-CRP) has proved to be a powerful method to graft polymer chains from a wide variety of surfaces (for example, silica nanoparticles [4], silicon wafer [5], ordered mesoporous silica [6,7], metallic surface [8], magnetic nanoparticles [9], carbon nanotubes [10,11], and polymer films [12,13]). The combination of "grafting from" and controlled radical polymerization techniques produces grafted polymer chains with controlled length exhibiting a high grafting density thanks to the simultaneous growth of polymer chains from the surface [14,15]. Since the first SI-CRP performed from a polysaccharide [16], many studies were devoted to SI-CRP of various polymers from pure cellulose fibers or Whatman filter paper as substrates, either by atom transfer radical polymerization (ATRP) [1,2,17–23] or by reversible addition fragmentation transfer (RAFT) [24–29] process through dithiobenzoate-based chain transfer agents. Recent reviews devoted to the modification of polysaccharide through controlled radical polymerization grafting highlights the interest of such strategy to generate high performance biohybrid materials [30,31].

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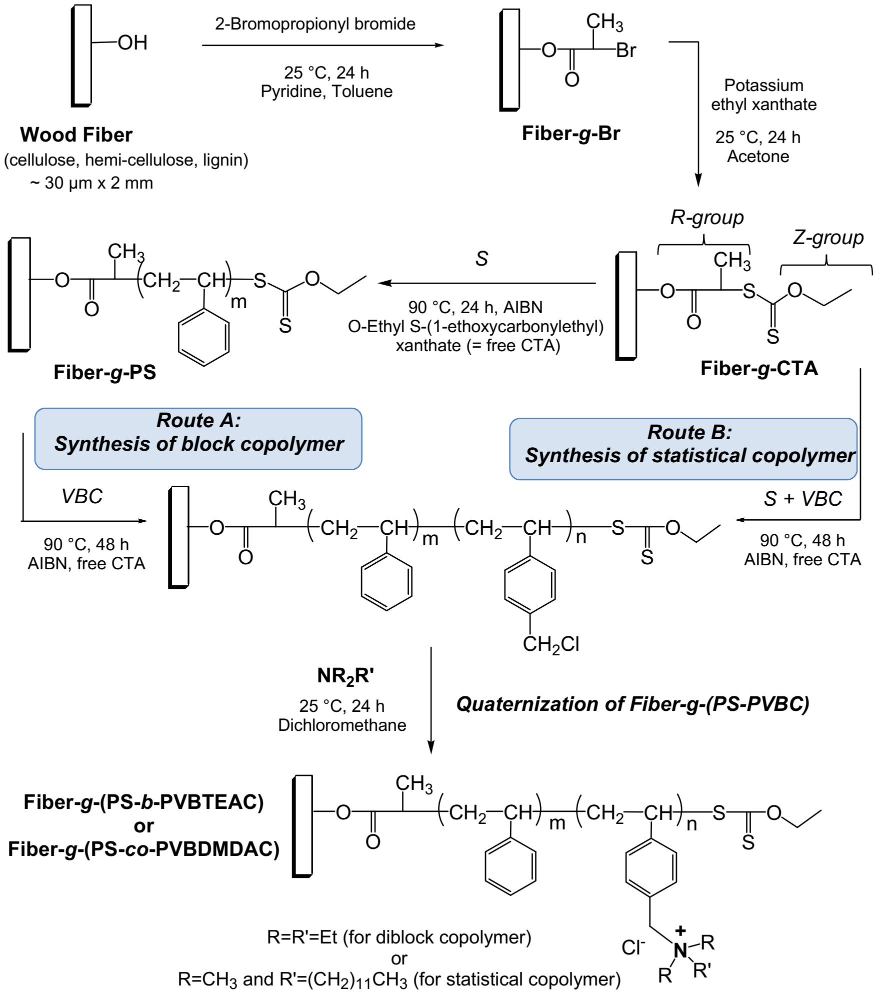
Herein, we present the surface modification of renewable raw wood fibers still containing cellulose and lignin derivatives. The polymer grafting is performed by SI-CRP through macromolecular design via interchange of xanthate (MADIX) process [32,33]. MADIX process is based on a reversible addition fragmentation transfer equilibrium involving xanthate agents, less colored species that dithiobenzoate-based chain transfer agents. Xanthates proved to be efficient chain transfer agents (CTA) to control the polymerization of a wide class of vinylic monomers such as styrenic [34,35], alkyl acrylates [36] and especially vinyl esters [37–42]. Indeed, xanthates are the only appropriate CTA to control the RAFT polymerization of vinyl acetate [37–42]. For the purpose of this work, the wood fibers are derivatized to introduce the chain transfer agent via the R-group [43] (see Scheme 1). The radicals are then created on the surface of the wood fibers by transfer reactions [44], which allows the growing of the polymer chains from the fiber surface. The straightforward attachment of the xanthate agent was performed in two simple steps using low cost commercially available reagents. The intermediate alkyl bromide was not used for ATRP polymerization to avoid both the use of amine-based ligands and the additional purification step for copper catalyst removal. For all the above mentioned reasons, MADIX polymerization was chosen for the present study for the surface-initiated polymerization of the selected styrenic, acrylic and vinyl ester monomers. Only one study previously reported the MADIX polymerization of VAc initiated from a soluble polysaccharide backbone (hydroxypropyl cellulose) using a xanthate agent grafted via the Z group [42].

The present work is devoted to the grafting of poly(vinyl acetate) (PVAc), poly(butyl acrylate) (P*n*BA), polystyrene (PS) and cationic amphiphilic PS-based copolymers from the raw wood fibers. P*n*BA and PVAc rise interest for their adhesive properties [45,46] whereas PS and cationic amphiphilic copolymers are known respectively for their hydrophobic character and biocide activity. The macromolecular features of the free chains are explored to assess the level of polymerization control. The fiber surface is analyzed by X-ray photoelectron spectroscopy to prove the success of the chemical surface modification. Finally, the properties of the polymer-grafted wood fibers are investigated in terms of wettability and the effect of the synthesized cationic polymer onto a fungi growing is studied. To the best of our knowledge, this is the first report of grafting polymer chains by controlled radical polymerization initiated from natural wood fibers which were not submitted to the delignification process.

2. Experimental section

2.1. Materials

Vinyl acetate (VAc, Sigma Aldrich, 99%), styrene (St, Sigma Aldrich, 99%) and 4-vinylbenzyl chloride (VBC, Sigma Aldrich, 90%) were purified through an inhibitor removal column (Sigma Aldrich). Pyridine (ABCR, 99%), acetone (Xilab, reagent grade) and toluene (Sigma Aldrich, 99.7%) were dried with molecular sieves (Aldrich, 4 Å pore diameter). 2,2′-azobis(isobutyronitrile) (AIBN, Acros, 99%), ethyl-2-bromopropionate (EBP, Fluka, 98%), 2-bromo-propionyl



Scheme 1. General scheme for the synthesis of polymer grafted wood fibers by surface-initiated MADIX/RAFT polymerization.