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Surface-initiated atom transfer radical polymerization of butyl acrylate on cellulose microfibrils

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ABSTRACT

Surface-initiated atom transfer radical polymerization (SI-ATRP) of butyl acrylate (BA) on cellulose microfibrils (CMF) was conducted to create controllable hydrophobic chains on CMF. The macroinitiator, CMF-Br, was prepared by the esterification of hydroxyl groups on CMF with 2-bromoisobutyrylbromide (BIBB); followed by the ATRP of BA using two catalyst systems, $Cu^{I}Br$/2,2′-bipyridine (BPY) and $Cu^{I}Br$/pentamethyl-diethylenetriamine (PMDETA). The molecular weight (MW) and polydispersity of the grafted PBA cleaved from CMF via hydrolysis was determined using GPC. The results indicated that the PMDETA system exhibited relatively poor control over the ATRP; whereas the BPY system produced the PBA with tailored chain lengths and relatively narrow polydispersities but experienced a rather slow polymerization process. To optimize the polymerization with the CuBr/PMDETA system, several influencing factors were investigated, including the type of solvents, reaction temperature and the use of co-catalyst $Cu^{II}Br_2$. The hydrophobic-modified CMF is of great potential as reinforcements biocomposites.

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1. Introduction

Biocomposites or nanocomposites based on cellulose microfibrils (CMF) attract strong interest because of the combination of properties of the biomaterials (mechanical, biodegradable, inexpensive, and renewable) and the polymer (higher melt point, chemical resistance, low density and plasticity) (Amash & Zugenmaier, 1998; Dufresne, Cavaille, & Helbert, 1996; Mohamed, Mostafa, & Alain, 2005; Otto van den, Michael, Jeffrey, & Christoph, 2007; William et al., 2005). However, the exploitation of these properties requires the nano-particles well-dispersed in the polymer matrices. Unfortunately, CMF cannot develop its reinforcement capacity in polymer composites because of the poor adhesion to common non-polar matrices, such as polypropylene. This is mainly attributed to the high polarity and hydrophilicity of CMF. The poor compatibility causes agglomeration of CMF and weakens the interaction with polymer matrices, which induces a reduction of mechanical properties (Belgacem & Gandini, 2005). One of the approaches to enhance the interaction is to render the surface of CMF hydrophobic via grafting, thus improving various physical and chemical properties; including the heat resistance, elasticity, ion-exchange capabilities, resistance to abrasion and wear, oil and water repellency, and antibacterial activity (Gupta & Sahoo, 2001; Vigo, 1998). Of these modifications, the grafting of hydrophobic polymers, such as methyl methacrylate, styrene, acrylonitrile, and butyl acrylate, onto cellulose strengthens the CMF adhesion to hydrophobic polymers significantly (Zhang & Chen, 2002), which is crucial when cellulose fibers are used as reinforcements in composites (Carlmark & Malmstrom, 2003).

The surface of cellulose fibers have been modified by graft polymerizations via various methods in the past (Castellano, Gandini, Fabbri, & Belgacem, 2004; Favier, Chanzy, & Cavaille, 1995; Kalaprasad & Alain, 2003; Uchida & Ikada, 1997; Zadorecki & Ronnhult, 1986). Most of them are based on “grafting onto” and “grafting from” techniques. For the “grafting onto” method, strong hindrance between grafted polymer chains prevents attachment of further ones and then limits the graft density (Carlmark & Malmstrom, 2003). In “grafting from” method, chain scission can occur and does not necessarily render the cellulose backbone intact (Koening & Roberts, 1974). Also it is impossible for these methods to predetermine the length of each pendent chain or arm and the molecular weight distribution. The surface-initiated atom transfer radical polymerization (SI-ATRP) technique has attracted intensive interest for the surface grafting high-density polymer with the controllable molecular weight, molecular weight distribution, and well-defined structure (Liu & Guo, 2006; Pyun, Kowalewski, & Matyjaszewski, 2003). Furthermore, almost all the polymers formed were chemical-bonded onto the matrices and no non-grafted polymers were obtained in the SI-ATRP process. Up to now, the SI-ATRP technique has been successfully employed to graft

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polymers to various surfaces such as silicon (Matyjaszewski, Miller, Shukla, & Immarporn, 1999; Zhao & Brittain, 1999), silica (Shah et al., 2000), gold (Li, He, Cui, & Li, 2007), magnetite (Marutani et al., 2004) and porous substrates (Ejaz, Tsujii, & Fukuda, 2001). Furthermore, SI-ATRP has also been used to graft polymers onto cellulose fiber (David, Katja, Helge, & Søren, 2005; Glaied, Dubé, Chabot, & Daneault, 2009; Josefina et al., 2008; Valter, Marco, Simone, & Giulia, 2007; Zampano, Bertoldo, Bronco, & Simona, 2009), macroscopic cellulose fibers (Anna & Eva, 2003; Josefina & Eva, 2006; Plackett, Jankova, Egsgaard, & Hvilsted, 2005; Robert, Anna, Anders, Eva, & Isabel, 2007; Sang & Xiao, 2009), cellulose powder (Coskun & Temüz, 2005) and cellulose nanocrystals (Gaelle, Lindy, & Wim, 2009; Singh et al., 2008). For instance, the surface-initiated ATRP of acrylamide was conducted on silica at room temperature by using a catalyst system of $CuCl/CuCl_2$/tris(2-dimethyl-aminoethyl)-amine (Xiao & Wirth, 2002). It was found that the thickness of the polyacrylamide film is proportional to the monomer concentration but not to reaction time. Carrot, Diamanti, Manuszak, Charleux, & Vairon (2001) reported the silica enanocomposites with a hard core and a soft shell using SI-ATRP of butyl acrylate. Kong, Tadashi, Jiro, and Tomokazu (2001) successfully prepared homopolymer and block amphiphilic brush on silicon wafers by combining the self-assembled monolayer of initiator and ATRP. The amphiphilic block copolymer brushes consisting of PAAM and PMMA blocks were obtained by using the homopolymer bush as a macroinitiator for the follow-up ATRP polymerization of the second monomer. To our knowledge, few studies have been performed on the surface of cellulose fibers via SI-ATRP.

In this work, the SI-ATRP of butyl acrylate (BA) onto CMF was conducted in an attempt to render CMF hydrophobic. The resulting hydrophobic-modified CMF could be further used as reinforcement for polymer, polypropylene (PP) in particular, to generate biocomposites which are of interest for automobile application. Compared with cellulose fibers, CMF appears to be much smaller. The relatively large specific areas are expected to facilitate the graft polymerization for surface modification. In the current work, the selection of butyl acrylate for SI-ATRP is based on the fact that PBA on CMF surfaces would not only improve the compatibility between CMF with polymer matrix of PBA, but also act as elastomeric interfacial layer which is of great, potential in improving the impact strength of the resulting biocomposites. To maximize the performance of the PBA-modified CMF, various influencing factors, such as polymerization conditions, the choice of ligand and solvent, and the use of deactivator have been investigated in this work in an attempt to achieve the optimal control of SI-ATRP of BA on CMF.

2. Experimental

2.1. Materials

Cellulose microfiber (CMF; mean particle size 60 μm; bulk density 0.3 g/cm^3), derived from cotton linters (obtained by mechanical treatment), was obtained from Aldrich. The CMF powders were dried in a vacuum oven at 60 °C for 24 h prior to use. Butyl acrylate (BA), also from Aldrich, was first washed with dilute NaOH solution to extract the polymerization inhibitor, and then washed with distilled water, followed by drying and distillation under vacuum before use. Cu^IBr was purified by stirring it in acetic acid for 24 h, washing with methanol, and then drying. 1-methyl-2-pyrrolidinone (NMP) was purified by distillation over CaH_2. 2,2′-Bipyridine (BPY) from Aldrich was purified by recrystallization in cold hexane and dried in vacuum oven for 24 h. Triethylamine (TEA), 4-(dimethylamino) pyridine (DMAP), 2-bromoisobutyryl-bromide (BIBB), N,N,N′,N′,N″-pentamethyl-diethylenetriamine (PMDETA), $Cu^{II}Br_2$, toluene, 1-butanol and dimethylformamide (DMF), all from Aldrich, were used as received. Spectrum® Membranes with approximate molecular weight cut off (MWCO) at 1000 Da were used as dialysis tubes for the separation of undesired compounds or unreacted agents.

2.2. Synthesis of CMF-Br

To a three-necked round-bottom flask, 10 g of dried CMF particles, 250 ml of NMP solvent, 0.1 mol of TEA and 0.05 mol of DMAP were added. 50 ml of NMP solution containing 0.092 mol of BIBB was then added dropwise over 1.5 h at 0 °C after the system was degassed and backfilled with nitrogen for three cycles. The reaction proceeded under nitrogen at 0 °C for 24 h and continued at room temperature for 48 h. The resulting product, macroinitiator CMF-Br, was filtered and washed with ethanol to remove the impurities. The final product was dried at 60° in vacuum oven for 24 h.

2.3. General procedure for the SI-ATRP of BA

In a typical example, the polymerization of butyl acrylate was carried out under nitrogen, in a dried three-neck round-bottom flask (50 ml) equipped with a magnetic bar. CMF-Br (1 g, 0.8 mmol of Br), PMDETA (0.167 ml, 0.8mmol), Cu^IBr (0.115 g, 0.8 mmol) 20 ml of DMF were added into the flask, which was then sealed with a rubber septum and glass stoppers. The flask contents were then cycled between vacuum and nitrogen three times to remove oxygen. Degassed butyl acrylate (4.45 ml, 31 mmol) was added using a syringe. The flask was then immersed in an oil bath heated at 90 °C. The grafting yields at different time intervals were determined by thermogravimetrical analysis (TGA) measurement of aliquots collected from the reaction mixture and purified by filtration and washing with methanol. After the reaction was complete, the reaction mixture was cooled to room temperature and the final products were purified by filtration and washing with methanol for several times to remove Cu complexes.

Grafting yield (G_y), the weight percent of PBA grafted on CMF based on the initial weight of CMF, was calculated according to the following equation:

$$G_y = \frac{W_{\mathrm{PBA}}}{W_{\mathrm{CMF}}} \qquad (1)$$

where W_{PBA} and W_{CMF} are the weights of PBA grafted onto CMF and the total weight of grafted CMF, respectively; both were determined by TGA measurements.

2.4. Cleavage of PBA grafts from CMF-PBA surface

In order to investigate the molecular weight and polydispersity of PBA grafts on CMF surface, CMF-PBA samples were extracted overnight in methanolic HCl to cleave covalently bound PBA from the CMF-PBA. The fibers were then filtered off and rinsed with distilled water. The extracted solution containing the cleaved was analyzed using GPC. It is noteworthy that after hydrolyzed CMF-PBA, the linear polymer remained in the solution is poly(acrylic acid) (PAA) due to the removal of ester groups over the hydrolysis. Therefore, the molecular weight of the cleaved polymers obtained from GPC represents the MW of PAA, which is proportional to that of PBA chains.

2.5. Characterization

The infrared spectra of CMF-Br were recorded between 4000 and 400 cm^{-1} on a Perkin-Elmer Spectrum 100 FT-IR.

Using a SDT Q600 TA instrument, the decomposition measurements based on TGA were conducted at the temperatures ranging

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