



Hydrophobic modification of wood via surface-initiated ARGET ATRP of MMA

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ABSTRACT

To convert the hydrophilic surface of wood into a hydrophobic surface, the present study investigated activators regenerated by electron transfer for atom transfer radical polymerization (ARGET ATRP) as a method of grafting methyl methacrylate (MMA) onto the wood surface. The wood treated with 2-bromoisobutyryl bromide and with the subsequently attached MMA via ARGET ATRP under different polymerization times (2 h, 4 h, 6 h, 8 h) were examined using scanning electron microscopy, Fourier transform infrared spectroscopy, and thermogravimetric analysis. All the analyses confirmed that PMMA had been grafted onto the wood surface. Water contact angle measurement proved that the covering layer of PMMA on wood made the surface hydrophobic. Polymerization time had a positive influence on the contact angle value and higher contact angle can be produced with the prolongation of the polymerization time. When the reaction time was extended to 8 h, the contact angle of treated wood surface reached 130° in the beginning, and remained at 116° after 60 s. The ARGET ATRP method may raise an alteration on the wood surface modification.

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1. Introduction

Wood is a natural polymer composite with chemical components consisting of abundant cellulose, hemicelluloses, lignin, slight amount of extractives, and inorganic substances. The greatest disadvantage of untreated wood is its hydrophilicity; moist wood is vulnerable to attack by fungi and termites, resulting in the loss of dimensional stability. The numerous hydroxyl groups result in the hydrophilicity of wood. Thus, by converting the hydrophilic hydroxyl groups into larger hydrophobic groups via chemical modification, the water absorption and dimensional stability of wood can be considerably altered. This will be beneficial to the applicability and service life of wood. Numerous approaches are available for the protection or modification of wood, such as acetylation and silylation [1], treatment with silicon compounds [2], coating by plasma polymerization [3,4], coating by sol–gel process [5,6], and nanocrystal coating by hydrothermal process [7,8], among others.

Atom transfer radical polymerization (ATRP) is a controlled radical polymerization technique that has been proven useful for

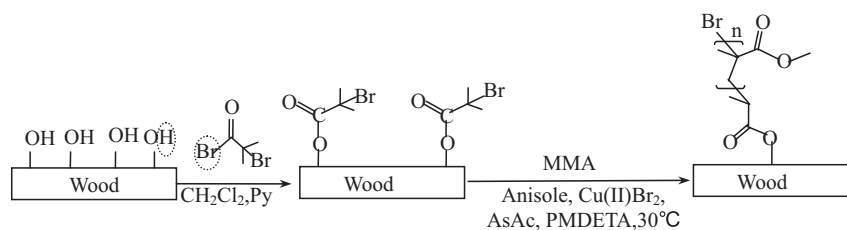
the synthesis of functional macromolecules with controlled and complex architectures [9]. Surface-initiated ATRP has also been proven to be a suitable technique for the natural fiber-grafting of cellulose because the available hydroxyl group on the surface can be easily converted to α -bromoesters, which are known to be excellent initiators for ATRP [10,11]. Numerous monomers have been grafted onto cellulose via ATRP, such as methyl methacrylate (MMA) [12,13], styrene (St) [14,15], methyl acrylate (MA) [16], 2-(dimethylamino)ethyl methacrylate (DMAEMA) [17], glycidyl methacrylate (GMA) [18], *N*-isopropylacrylamide (NIPAAm) [19], 4-vinylpyridine (4VP) [19], ethyl acrylate (EA) [20], etc.

In 2006, a new approach in conducting ATRP was developed by Matyjaszewski and co-workers [21] (Scheme 1). The relevance of this method lies in the significant reduction of the amount of copper, which can act as a catalyst in the ATRP system. Secondly, the conduct of the reaction can proceed even with limited amount of air [22] if large excesses of reducing agents (ascorbic acid, tin(II)2-ethylhexanoate, metallic copper) are added. Lastly, the procedure of deoxygenation can be omitted. This technique is called activators regenerated by electron transfer for atom transfer radical polymerization (ARGET ATRP). A number of researches on surface modification of materials have been conducted by this method [22–24].

The purpose of the present work is to improve wood properties by converting hydrophilic hydroxyl groups into larger hydrophobic groups by grafting polymers on the wood surface via ARGET ATRP. The present study can improve the surface water repellency and dimensional stability of wood by the synthesis of functional

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Scheme 1. ARGET ATRP of MMA from wood surface.

macromolecule coating with controlled and complex architectures, which will raise a potential method for wood surface modification.

2. Experimental

2.1. Materials

Poplar wood (*Populus tomentosa*) was cut into specimens of 5 mm (longitudinal) \times 10 mm (tangential) \times 10 mm (radial) in size and extracted using a benzene alcohol mixture [25]. Anisole, 2-bromoisobutyryl bromide (BIBB, 97%), copper(II) bromide (Cu(II)Br_2 , 99%), N,N,N',N'-pentamethyldiethylenetriamine (PMDETA, 99%), pyridine (99%), and ethyl 2-bromoisobutyrate (99%) from the Energy Chemical were used without further purification. Ascorbic acid (AsAc, 99%), dichloromethane (CH_2Cl_2), tetrahydrofuran (THF, 99.8%), and methanol (MeOH, 99.8%) from Tianjin Baishi Chemical Industry Co. Ltd. were also used without further purification. Methyl methacrylate (MMA, 99.5%) was acquired from Energy Chemical, but distilled under reduced pressure from calcium hydride (CaH_2).

2.2. Preparation of specimen

2.2.1. Immobilization of BIBB on wood surface

This method was adopted from Zampano [20]. Wood specimens were placed in a 150 mL round-bottomed flask equipped with a condenser tube and a magnetic stirring bar, then a mixture of BIBB (13.79 g), pyridine (4.75 g), and CH_2Cl_2 (60 mL) were added to the round-bottomed flask as the initiator and heated at reflux temperature (70°C) for 30 min. Subsequently, the wood specimens were removed from the flask and thoroughly washed with CH_2Cl_2 and THF (10 min for each solvent). Soxhlet extraction with ethanol for another 8 h followed to completely remove any unreacted and unbounded materials. The specimens were dried under vacuum of 0.07 MPa (C.A. 525 mmHg) at 50°C .

2.2.2. Grafting MMA from the initiator-functionalized wood surface

The wood specimens, which had been initiator-modified with BIBB, were immersed into a 100 mL round-bottomed flask containing a mixture of anisole (15 g), MMA (15 g, 0.15 mol), Cu(II)Br_2 (12.77 mg, 57.18 μmol), PMDETA (130 mg, 0.75 mmol), and a large excess of AsAc. The flask was degassed with nitrogen for 5 min and sealed with a rubber septum, before being placed in a thermostatic oil bath at 30°C . Four parallel experiments with polymerization times of 2 h, 4 h, 6 h, and 8 h were conducted, and the available products were labeled as Wood-MMA-*n*h, where *n* represents the reaction time (h). Reference materials consisted of untreated wood (wood) and the initiator-modified wood (wood-Br). The resulting products were subjected to thorough rinsing in THF, DCM, MeOH, and THF, and finally dried in a vacuum oven at 50°C . The process is outlined in Scheme 1. This process required no special instruments, and reaction was realized at low temperature and atmospheric pressure.

2.3. Characterization

The chemical composition of the wood surface was determined by Fourier transform infrared (FTIR) spectroscopy (Magna-IR 560, Nicolet). For the FTIR analysis, thin sample disks were prepared by grinding and pressing small amounts of the wood specimens with potassium bromide. The surface morphology was characterized using a FEI-SEM Quanta 200 microscope operating at 12.5 kV. The surface hydrophobic property was evaluated with a JC2000A contact angle analyzer produced by Powereach. The thermal gravimetric analysis of wood was recorded on a Perkin-Elmer TGA-7 thermogravimetric analyzer in the temperature range of 38 – 685°C at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. The X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer (D/max 2200, Rigaku, Japan) with Ni-filtered $\text{Cu-K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) at 40 kV and 30 mA. Scattered radiation was detected in the range of $2\theta = 5^\circ$ – 30° at a scan rate of $3^\circ/\text{min}$.

Table 1

The graft ratio of PMMA on wood surface at different conditions.

Monomer	DP_{target}	Reaction time/h	Graft ratio, %
MMA	100	8	5.68
MMA	200	8	6.85
MMA	400	8	6.99
MMA	400	2	2.36
MMA	400	4	3.42
MMA	400	6	3.52
MMA	–	2	3.93
MMA	–	4	6.44
MMA	–	6	9.47
MMA	–	8	12.84

DP_{target} = the molar ration of monomer to sacrificial initiator.

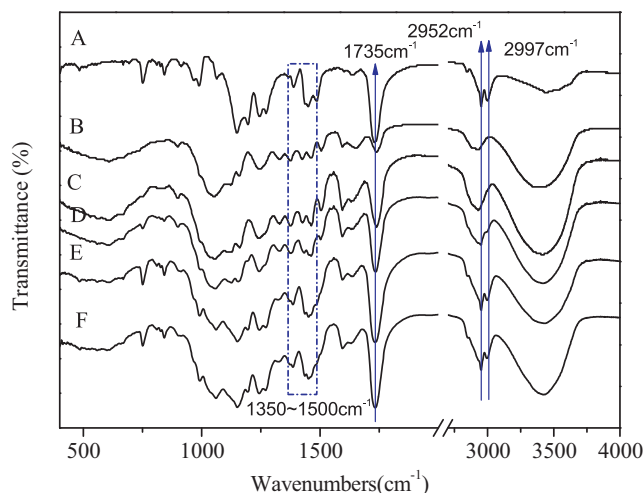


Fig. 1. FTIR spectra of (A) PMMA, (B) untreated wood, (C) wood-PMMA-2h, (D) wood-PMMA-4h, (E) wood-PMMA-6h and (F) wood-PMMA-8h.

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