



## Preparation of Cellulose Graft Copolymer Based on Combination of Ionic Liquids and Microwave Heating†

DAN-HUI LIU<sup>1</sup>, WEI LUO<sup>1</sup>, YU-ZHEN WEI<sup>2</sup>, CHUN-XIANG LIN<sup>1,3,\*</sup>, CHAO-YANG DU<sup>4</sup> and MING-HUA LIU<sup>1,3</sup>

<sup>1</sup>College of Environment & Resources, Fuzhou University, Fuzhou 350002, P.R. China

<sup>2</sup>Fujian Gaoke Environmental Protection Research Institute Co. Ltd, Fuzhou 350002, P.R. China

<sup>3</sup>Fujian Provincial Technology Exploitation Base of Biomass Resources, Fuzhou 350002, P.R. China

<sup>4</sup>Fujian Southeast Century Environmental Protection Co. Ltd, Fuzhou 350002, P.R. China

\*Corresponding author: Fax: +86 591 22866087; Tel: +86 18250167816; E-mail: [linchunxiang2002@163.com](mailto:linchunxiang2002@163.com)

Received: 22 July 2014;

Accepted: 22 August 2014;

Published online: 1 September 2014;

AJC-15903

Cellulose is a promising raw materials available and can be modified through a variety of chemical modifications to obtain functional materials. Cellulose-g-acrylamide copolymer was prepared in a homogeneous medium by using N,N'-methylenebisacrylamide as crosslinker without any radical initiator under microwave radiation. 1-Butyl-3-methylimidazolium chloride an ([Bmim]Cl) ionic liquid is an environment friendly and effective reaction medium, was chosen to dissolve cellulose and the homogeneous graft polymerization of acrylamide onto cellulose. Due to the effect of microwave heating, the reaction time was significantly shorten: 1 min microwave heating was adequate, compared with 0.5-5.0 h, as conventional heating was used. The influences of monomer concentration, crosslinker dosage, microwave power and reaction time were investigated the obtained cellulose graft copolymer was characterized by IR spectrum, TGA and SEM. A feasible reaction mechanism of grafting based on microwave heating was put forward.

**Keywords:** Homogeneous, Ionic liquid, Graft polymerization, Cellulose, Microwave, Acrylamide.

### INTRODUCTION

Due to the increasing critic requirements of environmental protection and the gradual depletion of nonrenewable resources<sup>1</sup>, it is absolutely essential to obtain new products derived from renewable resources through green processed. In recent years, the development of bio-sourced materials have attracted great interest all over the world owing to their advantages in low cost, reproducibility, non-toxicity and biodegradation. Cellulose is regarded as one of the most abundant natural resources on earth, it is also a promising raw materials available for the preparation of various functional materials in terms of cost. Cellulose can be modified through a variety of chemical modifications to possess new abilities by introduction of new functional groups. Graft copolymerization is regarded as an effective technique to modified cellulose. Some research results on cellulose and vinyl monomers have been applied to adsorbing material, flocculating agent *etc.*<sup>2</sup>. Currently oxidation-reduction systems are used to grafting vinyl monomers onto cellulose<sup>3</sup>. Meanwhile homopolymer has suppressed grafting procedures and the quality of products. Microwave irradiation<sup>4</sup>

using the commercial household microwave oven as efficient thermal energy has got more and more attention owing to the significant promotion of reaction efficiency over conventional reaction<sup>5</sup>. Microwave heating can make reactants heated straightforward and well-proportioned throughout the reaction process. It can make the materials heat evenly and quickly. Grafting of butyl acrylate<sup>6</sup>, propenoic acid<sup>7</sup> and acrylic amide<sup>8,9</sup> onto the starch based on microwave irradiation has been researched recently employing redox initiators. Graft of vinyl functional monomers onto natural resources under microwave conditions in a short reaction time without any redox initiator/catalyst were reported in recent research.

Ionic liquids (IL) has been proven an excellent solvent<sup>10</sup> and reaction media<sup>11,12</sup> for the cellulose dissolution and modification. The interesting properties of ionic liquid including non-volatile, non-flammability, thermal and electrochemical stability as well as highly polar has drawn much attention around the world. Meanwhile, the use of ionic liquids as microwave-absorbing reagents may conduce to heat with high efficiency and reduce the reaction time greatly because of the good ionic conductivity and polarizability. In the present

†Presented at 2014 Global Conference on Polymer and Composite Materials (PCM2014) held on 27-29 May 2014, Ningbo, P.R. China

research, the grafted copolymerization of acrylamide with cellulose employing [BMIM]Cl as a reaction medium can obtain higher plurinativity in a small amount of time without any radical initiator/catalyst.

## EXPERIMENTAL

Cotton linter was used as received. The ionic liquids (IL) 1-N-butyl-3-methylimidazolium chloride ([Bmim]Cl), m.p. 73 °C, was purchased from Henan Lihua Pharmaceutical Co., Ltd.; All the other reagents were of analytical grade and used as received. A SANYO microwave oven (EM-300s), produced by Hefei SANYO Electric Appliances Factory, Ltd., China, was employed in these studies; FT-IR were obtained from a AVAT-AR 360 (USA Niclet Company). Thermal stability of samples was tested on a TGA 500 thermogravimetric analyzer (TA Instruments USA) in N<sub>2</sub> atmosphere.

**Microwave cellulose solubilization:** The cotton linter without any preprocessing as the cellulose raw material was dissolved in the molten ionic liquids ([Bmim]Cl) and heated in a domestic microwave oven for a little while. The flask was removed from the microwave oven between pulses, shaken or vortexed and replaced in the oven. This procedure was repeated until a clear, colorless, viscous solution was obtained. Ionic liquids are heated with exceptional efficiency by microwaves and care must be taken to avoid excess localized heating that can induce cellulose pyrolysis.

**Homogeneous graft of cellulose with acrylamide under microwave irradiation:** When the cellulose was completely dissolved, certain amount of acrylamide (AM) and N,N'-methylenebisacrylamide (N,N'-MBA) in DMSO were mixed into the cellulose/ionic liquids solution and then, the mixture was shaken manually and radiated under certain microwave power for required time. After that, the reaction vessel was taken out from the oven and made the formation cool naturally and then isolated into superfluous deionized water or isopropyl alcohol, filtered and washed adequately. At last, the grafted samples were purified employing acetone solution as medium in a Soxhlet extractor for 24 h to dissolve the product.

The following formulae were used for the calculation of grafting percentage (GP %) and grafting efficiency (GE %):

$$\text{Grafting percentage (GP \%)} = \frac{(W_2 - W_0)}{W_0} \times 100$$

$$\text{Grafting efficiency (GE \%)} = \frac{(W_2 - W_0)}{W_1} \times 100$$

where W<sub>0</sub>, W<sub>1</sub> and W<sub>2</sub> are the weights of the raw cellulose, the graft copolymer and the acrylamide, respectively.

## RESULTS AND DISCUSSION

**Optimization of the microwave irradiation and exposure time:** The best microwave power was chosen by employing a well-defined medium: 0.5 g of cellulose in 10 g [Bmim]Cl, 1.5 g acrylamide and 0.05 g crosslinker. The reactant were disposed with various reaction times (t) and power outputs (P) under microwave heating. In order to better control the reaction temperature system, the highest power chosen was 350 W. The grafting percentage (GP %) was determined for

each experiment (Table-1). A maximum was reached for an irradiation power of 120 W for 60 s. Increasing reaction time beyond 60 s resulted in temperature increase and cellulose pyrolysis as attested by a drop in grafting percentage (GP %) (Table-1) and brown colour. For these reasons, the optimum microwave was chosen at 120 W for 60 s in the following study.

TABLE-1  
GRAFTING PERCENTAGE (GP %) WITH DIFFERENT MW POWER AND IRRADIATE TIME AT FIXED CONCENTRATION OF CELLULOSE/BminCl (0.5 g/10 g), AM/CE (3 g/1 g)

No.	MW power (W)	GP % in different exposure time (s)				
		30	45	60	75	90
1	120	23.7	47.6	57.2	50.7	40.2
2	250	33.1	49.3	50.7	41.3	33.8
3	350	39.3	40.5	37.2	33.9	25.3

**Effect of monomer concentration:** GP % and GE % increase initially with monomer concentration but then decrease after 3 g/g cellulose (Fig. 1). At the first stage, the growth owes to the better utilization rate of the monomer molecules in the proximity of the cellulose (CE) raising the possibility of the molecular impact and thus grafting. Then when it is up to the highest point, the homopolymerization of acrylamide could cause the decrease.

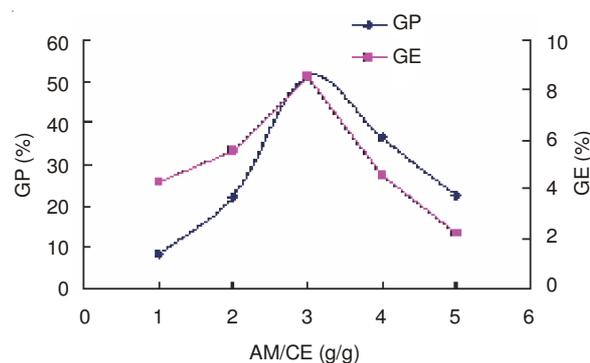


Fig. 1. Effect of monomer concentration

**Effect of crosslinker dosage on grafting reaction:** In the case of other conditions fixed, the effect of crosslinker dosage on grafting procedure was studied. The collection of grafting percentage and grafting efficiency and the dosage of crosslinker was showed in Fig. 2. The results turn out that with the increase of amount of crosslinker, grafting efficiency and grafting percentage increase initially and then the grafting degree drops when the dosage of crosslinker surpasses 0.1 g/g cellulose.

**FT-IR spectra:** Fig. 3 shows the FTIR spectra of the ionic liquid-reconstituted cellulose and the grafted copolymer. The characteristic peaks at 1634.59 and 1262.99 cm<sup>-1</sup> for the derivatives represent amide I (C=O stretching) and amide II (C-N stretching) bands, respectively. Moreover, a broad absorption band in 3500-3100 cm<sup>-1</sup> region for the derivatives are ascribable to the stretching frequency of the -OH and -NH<sub>2</sub> groups, which become stronger than that of the native cellulose. It turned out that intramolecular hydrogen bonds was taken shape in the product.

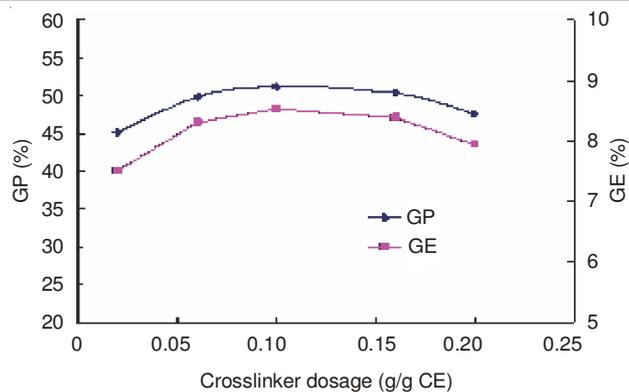


Fig. 2. Effect of crosslinker dosage

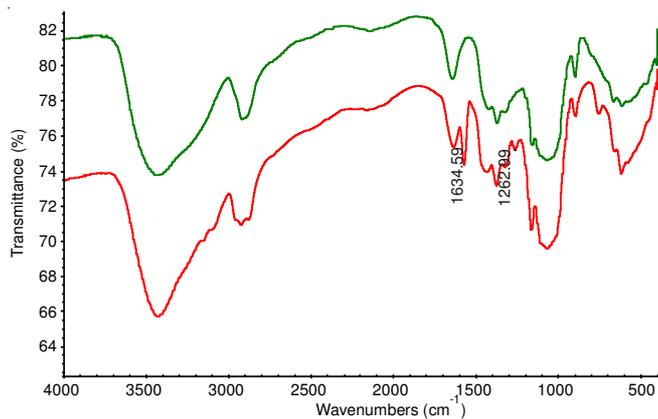


Fig. 3. FTIR spectra of the ionic liquid-reconstituted cellulose and the grafted copolymer

**Thermogravimetric analysis:** Thermogravimetric analysis of cellulose and graft copolymer were shown in Fig. 4. It showed that there was two stages occurred both in the thermal decomposition of cellulose and graft copolymer. The phase one weight of cellulose occurred at 270 °C and continued up to 390 °C with 28 wt % residues; the phase two started at 390 °C and last until 500 °C remaining 13 wt %. While the graft copolymer was decomposed mainly at 230 °C with 44 wt % residues and another process at 360 °C with 34 wt % residues

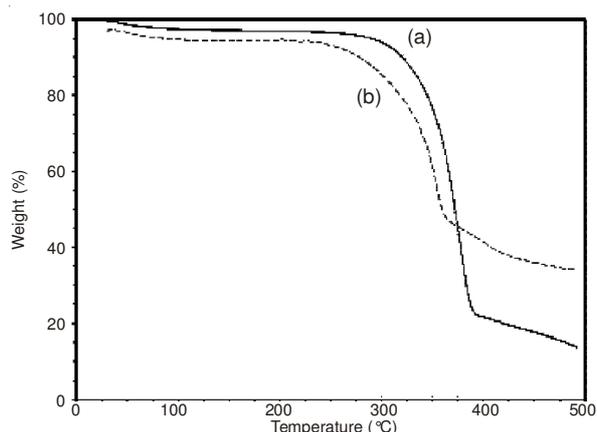


Fig. 4. TGA of cellulose (a) and grafted cellulose (b)

at 500 °C. The results implied that the cellulose graft copolymer showed a little decrease in thermal stability during 230-360 °C. However higher stability when temperature was high (above 375 °C).

**Scanning electron microscopy:** Fig. 5 showed the SEM images of cellulose and cellulose graft copolymer. It could be seen that after graft reaction, the smooth surface of the cellulose [Fig. 5(A)] was disappeared and the shaggy morphology is obviously presented [Fig. 5(B)]. The distinguished change in the surface of cellulose also confirmed that the grafting reaction took place.

**Mechanism:** Ionic liquids are good microwave-absorbing reagents, which could give rise to heat with high efficiency and a significantly shortened reaction time. Cellulose is a natural macromolecule compound with a lot of hydroxyl groups. The pressing energy is improbable to store in a specific form and it will flow from hydroxyl groups to neighboring molecules (acrylamide) under the action of the nonconductive heating. The nonconductive heating leads to bond rupturing producing radical sites at oxygen and nitrogen atoms. Researches have showed that microwaves impact on lowering of Gibbs energy of activation and then a suppositional free radical mechanism for the grafting under the microwave irradiation has been put

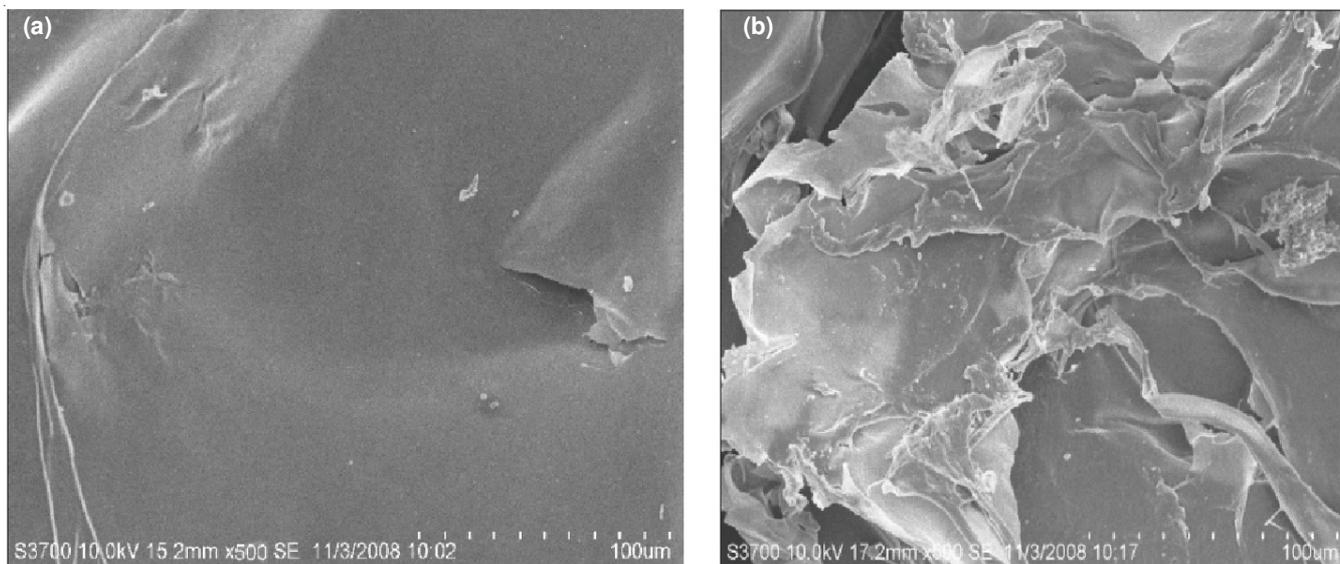
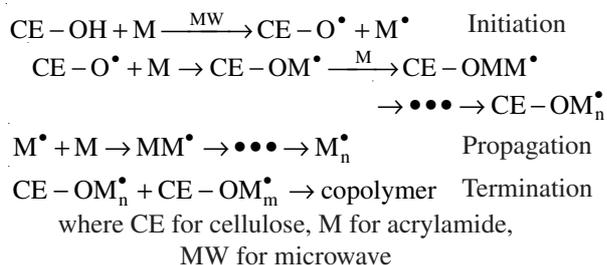


Fig. 5. SEM of cellulose (a) and grafted cellulose (b)

forward. O-H bonds at cellulose obtain microwave energy and will cleave generating monomer free radical and macro radical (**Scheme-I**).



**Scheme-I:** Mechanism under microwave irradiation

### Conclusion

The graftomer of cellulose and acrylamide was homogeneously synthesized at 120 W MW power in just 1 min under microwave without any initiator using an ionic liquid [Bmim]Cl. Further the grafting percentage of acrylamide on cellulose was 51.2 % under optimal conditions and the structure of cellulose graft copolymer was characterized by FT-IR, TGA and SEM.

### ACKNOWLEDGEMENTS

The research was financially supported by Science and Technology Project of Fujian Province Educational Department (JK2013004, JA12040), Science & Technology Development Fund of Fuzhou University (2012-XY-10, 2014-XQ-11).

### REFERENCES

1. A.K. Jain and A. Suhane, *Adv. Eng. Appl. Sci.*, **1**, 23 (2012).
2. K. Littunen, U. Hippi, L.S. Johansson, M. Österberg, T. Tammelin, J. Laine and J. Seppälä, *Carbohydr. Polym.*, **84**, 1039 (2011).
3. E. Lam, K.B. Male, J.H. Chong, A.C.W. Leung and J.H.T. Luong, *Trends Biotechnol.*, **30**, 283 (2012).
4. D. Marquardt, C. Vollmer, R. Thomann, P. Steurer, R. Mülhaupt, E. Redel and C. Janiak, *Carbon*, **49**, 1326 (2011).
5. Z. Cao, H. Ge and S. Lai, *Eur. Polym. J.*, **37**, 2141 (2001).
6. A. Santhana Krishna Kumar, C. Uday Kumar, V. Rajesh and N. Rajesh, *Int. J. Biol. Macromol.*, **66**, 135 (2014); .
7. J. Wu, G. Meng, Z. Liu et al., *Technol. Rev.*, **30**, 39 (2012).
8. J. Shu, X.J. Li and D.B. Zhao, *Adv. Mater. Res.*, **148-149**, 799 (2011).
9. K. Bhunia, S.S. Sablani, J. Tang and B. Rasco, *Comp. Rev. Food Sci. Food Safety*, **12**, 523 (2013).
10. C. Abrusci, J.L. Pablos, T. Corrales, J. López-Marín, I. Marín and F. Catalina, *Int. Biodeterior. Biodegrad.*, **65**, 451 (2011).
11. M. Petkovic, K.R. Seddon, L.P.N. Rebelo and C. Silva Pereira, *Chem. Soc. Rev.*, **40**, 1383 (2011).
12. S. Mallakpour and Z. Rafiee, *Prog. Polym. Sci.*, **36**, 1754 (2011).