HOMOGENEOUS GRAFTING COPOLYMERIZATION OF METHYLMETHACRYLATE ONTO CELLULOSE USING AMMONIUM PERSULFATE

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The homogeneous grafting of methylmethacrylate (MMA) onto cellulose was carried out by using ammonium persulfate as initiator. DMAc/LiCl was used as solvent for the dissolution of cellulose and medium for the homogeneous graft copolymerization. The efficient reaction conditions of the grafting reaction were confirmed by weighing methods. The results showed that the efficient reaction conditions were as follows: reaction time, 2 h, mass ratio of MMA/cellulose, 1/1 (g/g), mass ratio of initiator/cellulose, 6/50 (g/g), and reaction temperature, 80 °C. Under these conditions, the GP of cellulose under homogeneous conditions reached 76%, higher than that obtained under heterogeneous conditions. The grafted polymer was characterized by FTIR, SEM, TG-DTA and XRD. The results showed that the original crystalline structure was destroyed during the dissolution process of cellulose, which helped to improve the effectiveness of the grafting copolymerization reaction.

Keywords: homogeneous grafting, cellulose, methylmethacrylate, grafting percentage, N,N-dimethylacetamide/ lithium chloride

INTRODUCTION

Cellulose is a naturally occurring polysaccharide and the most abundant organic raw material. As the most affluent biopolymer resource in the world, cellulose has attracted much attention for preparing novel polymers and materials. [1-3]

To improve the properties of cellulose and enlarge its utilization range, modification methods of physical and chemical properties of cellulose have been continuously studied to investigate the required properties.[4-8] Grafting onto cellulose is possible by growing a polymer chain on the active sites of the cellulose backbone, where cellulose contains so many functional hydroxyl groups. Depending on the chemical structure of the monomer grafted onto cellulose, graft copolymers gain new properties, such as hydrophilic or hydrophobic character, improved elasticity, water absorption, ion-exchange capabilities, and heat resistance.[9-12]

Of the various methods capable of initiating graft copolymerization onto cellulose, persulfate initiation is very effective. When heated, persulfate ions in solution can decompose to produce sulfate ion-radicals and hydroxyl radicals:[13]

$$S_2O_8^{2-} \rightarrow 2SO_4^{-\bullet} \quad (1)$$

$$SO_4^{-\bullet} + H_2O \rightarrow HSO_4^- + HO^{\bullet} \quad (2)$$

In this case, the vinyl polymerization may be initiated by either the $SO_4^{-\bullet}$ radicals or the $HO^{\bullet}$ radicals. In the absence of reducing agents, however, the $SO_4^{-\bullet}$ radicals easily disappear, according to the following reaction:

$$2SO_4^{-\bullet} \rightarrow \text{Endproducts} \quad (3)$$

In our previous work, grafting of methylmethacrylate (MMA) onto undissolved cellulose by using ammonium persulfate as initiator was carried out in a heterogeneous system.[14] The grafting percentage (GP) was too low, 44% only. In this work, we attempted to improve the GP by homogeneous grafting copolymerization. To achieve homogeneous cellulose reactions, suitable

solvent systems that could both dissolve cellulose and provide a feasible reaction environment were prerequisites.

The discovery of new solvents for cellulose dissolution opened the possibility of performing derivatization and/or grafting reactions under homogeneous conditions, thus assuring important advantages, such as a better control of the degree of substitution,[11] a more uniform distribution of substituents along the polymer and a higher conversion yield.[15-17] N,N-dimethylacetamide/ lithium chloride (DMAc/LiCl) was one of the most efficient solvent systems for cellulose. Its dissolving capacity could reach 13 wt%.[18]

This paper mainly presents the results of studies on the homogeneous graft copolymerization of MMA onto cellulose by using ammonium persulfate as initiator and provides a comparison of the grafting copolymerization under homogeneous and heterogeneous conditions. The efficient conditions of the homogeneous grafting reaction were examined by weighing methods. The graft copolymers were characterized by the grafting parameters, FTIR spectroscopy, scanning electron microscopy (SEM), thermogravimetric analysis (TG-DTA) and X-ray diffraction (XRD). The grafting parameters, such as the grafting percentage (GP) and grafting efficiency (GE) were calculated by the following equations:

$$\mathrm{GP} = (W_2 - W_0)/W_0 \times 100 \quad (4)$$

$$\mathrm{GE} = (W_2 - W_0)/W_1 \times 100 \quad (5)$$

where W_0, W_1, and W_2 were the weights of native cellulose, monomer, and graft copolymer, respectively.

EXPERIMENTAL

Materials and equipment

Cotton linter (cellulose) was used as cellulose material. All the other reagents were of analytical grade and used as received. Infrared (IR) spectra were recorded using a TENSOR27 FTIR spectrometer in the range of 4500-400 cm^{-1}. SEM images were taken on a JSM-6700F scanning microscope. The sample was coated with a thin layer of gold in vacuum before examination. Thermogravimetric (TG) analysis and differential thermal analysis (DTA) of the samples were carried out on a Pyris Diamond TG-DTA analyzer (STA449C/3/F, Germany). The TG-DTA analyses were performed with a sample weight of 14.2 mg, a heating rate of 10 °C/min, and flowing nitrogen (20 mL/min). X-ray diffraction (XRD) analysis of the samples was carried out on an X-ray diffractometer (D/max-2500/PC, Rigaku Co. Ltd., Tokyo) by a reflection method using a Cu Kα target at 40 kV and 60 mA. The diffraction angle ranged from 5° to 60°.

Preswelling and dissolution of cellulose

Since grafting relied on diffusion of reagents to the backbone site, swelling was crucial. The following preswelling procedures of cellulose were carried out to increase the reactivity before the grafting. Cellulose was preswelled in DMAc at 160 °C for 0.5 h. Then the mixture was filtered to obtain the preswelled cellulose. The dissolution of cellulose was carried out according to the literature.[19] A stock solution of LiCl in DMAc (8%, w/w) was prepared by dissolving 7.4 g LiCl in 100 mL DMAc. The preswelled cellulose was added to DMAc/LiCl in a three-neck flask. The mixture was stirred at 100 °C for 2 h to guarantee the complete dissolution of the cellulose. The flask was continuously purged with gaseous N_2.

Grafting of cellulose with MMA under homogeneous conditions

Following the complete dissolution of the cellulose, the temperature was lowered to 70-90 °C, then a solution of ammonium persulfate (APS) in DMSO, the initiator, was added; after stirring for 15 min, a predetermined volume of MMA was added to the reaction. When the reaction was complete, the product was isolated by precipitation into excess deionized water, filtered, and washed several times. Finally, the grafted sample was extracted with acetone in a soxhlet apparatus for 48 h to dissolve all the homopolymer and dried to constant weight.

Preparation of membranes

The membranes of cellulose and grafted cellulose were prepared by the phase inversion technique.[20-22] Firstly, grafting reaction was carried out under the efficient reaction conditions. As the reaction was complete, the solution was placed under vacuum for 24 h at room temperature to obtain the solution of grafted cellulose. Secondly, the casting solution was cast on a glass plate using a doctor blade. The glass plate was quickly immersed in the gelation bath. The membrane sheets were subsequently stored in deionized water for 24 h to remove the residual DMAc/LiCl completely to obtain the membrane. These casting and gelation conditions were maintained constant throughout, because the thermodynamic conditions would largely affect the performance of the

resulting membranes.[23]

RESULTS AND DISCUSSION

Effect of reaction time on grafting

The effect of reaction time on grafting is presented in Figure 1. As shown in Figure 1, both GP and GE indicated a gradual increase with time during the time period of 1.5 to 2 h and leveled off 2 h later, reaching a saturated grafting value. The reduced amount of monomer and free radicals in the reaction system with an increase in reaction time led to the leveling off effect.[24] Therefore, the optimal reaction time was 2 h for the homogeneous grafting of MMA onto cellulose.

Effect of monomer amount on grafting

The GP was found to increase with an increase in the mass ratio of monomer to cellulose (Figure 2), which could be due to the greater availability of the monomer molecules in the proximity of the cellulose increasing the chance of the molecular collision and hence grafting. The continuous decrease of GE with an increase in monomer amount may be associated with the fact that increasing numbers of monomer molecules led to an increase of the likelihood of homopolymerization versus graft copolymerization.[25] When the mass ratio of MMA to cellulose was 1/1 (g/g), both GP and GE were relatively higher.

Effect of initiator dosage on grafting

Figure 3 shows the effect of the mass ratio of APS to cellulose on the graft copolymerization of MMA onto the cellulose backbone, as the other reaction variables were maintained constant. Both GP and GE exhibited an increase at first, followed by a decrease, with an increase in the initiator dosage. The increase of GP may be ascribed to the increase of macroradicals generated by increasing levels of APS (radical initiator) on the glucose unit of cellulose, and therefore, more available sites of cellulose to react with MMA. When the mass ratio of APS to cellulose was increased by more than 6/50 (g/g), the concentration of persulfate radicals increased and consequently initiated more of the homopolymerization of MMA, which resulted in a decrease in both GP and GE.[26]

Effect of reaction temperature on grafting

The effect of reaction temperature on grafting was investigated by changing the temperature from 70 °C to 90 °C, while keeping the other reaction variables constant. As may be noted from Figure 4, both GP and GE reached a maximum at 80 °C. A comparatively high temperature was helpful in increasing the bimolecular collisions for APS and cellulose, which led to the increase of cellulose macroradicals, and therefore enhanced the graft copolymerization of MMA onto cellulose. On the other hand, the GP and GE decreased with a further increase in temperature, probably due to the enhanced possibilities of termination and chain transfer at a relatively higher reaction temperature.[27] Therefore, the efficient reaction conditions were as follows: reaction time, 2 h, mass ratio of MMA/cellulose, 1/1 (g/g), mass ratio of initiator/cellulose, 6/50 (g/g), and reaction temperature, 80 °C. Under these conditions, the GP of cellulose reached 76%.

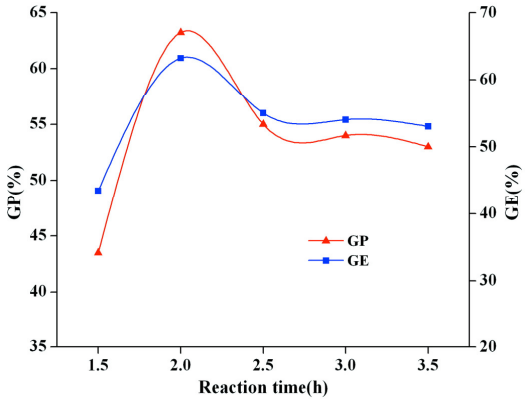

Figure 1: Effect of reaction time on grafting (conditions: mass ratio of MMA/cellulose, 1/1 (g/g), mass ratio of initiator/cellulose, 5/50 (g/g), and reaction temperature, 80 °C)

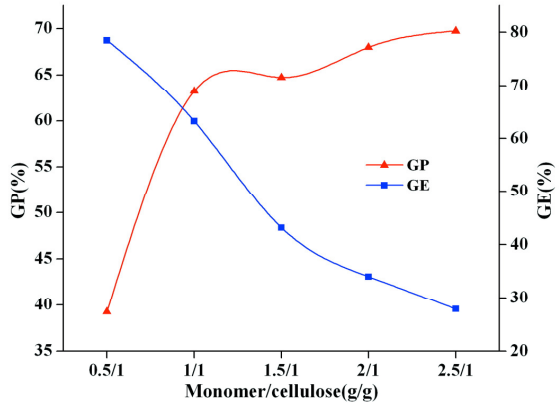

Figure 2: Effect of monomer amount on grafting (conditions: mass ratio of initiator/cellulose, 5/50 (g/g), reaction time, 2 h, and reaction temperature, 80 °C)

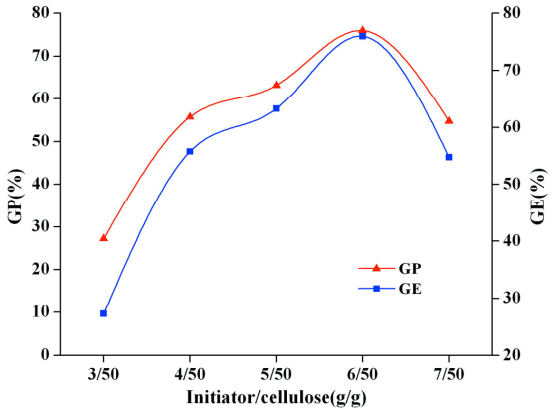

Figure 3: Effect of initiator dosage on grafting (conditions: mass ratio of MMA/cellulose, 1/1 (g/g), reaction time, 2 h, and reaction temperature, 80 °C)

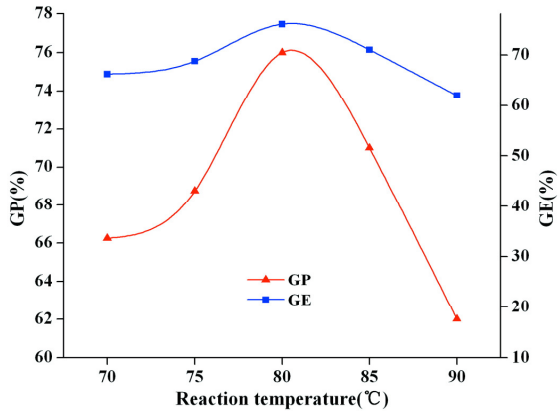

Figure 4: Effect of reaction temperature on grafting (conditions: mass ratio of MMA/cellulose, 1/1 (g/g), mass ratio of initiator/cellulose, 6/50 (g/g), and reaction time, 2 h)

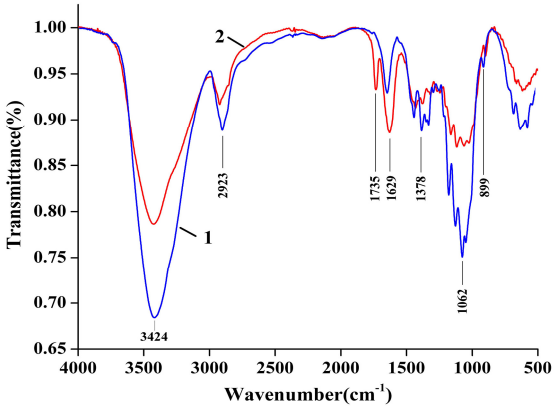

Figure 5: FTIR spectra of native cellulose (1) and its graft copolymer (2)

FTIR spectra analysis

Figure 5 presents the FTIR spectra of the native cellulose and its graft copolymer sample. As can be seen from the figure, the spectrum of the native cellulose exhibits the vibration of hydroxy group at 3424 cm^{-1} and the characteristic absorption peak of C–O at 1062 cm^{-1}. Moreover, the spectrum also reveals the β-glycosidic bond characteristic absorption peak at 899 cm^{-1} and cellulose characteristic peaks at 2923 cm^{-1}, 1629 cm^{-1} and 1378 cm^{-1}. A different infrared spectrum was observed for the grafted polymer (Figure 5). This indicated that the molecular structure of the native cellulose had changed. The new peak at 1735 cm^{-1} corresponded to the –C=O group of the MMA, which confirmed the introduction of the MMA side chain into the cellulose backbone by graft copolymerization.

Scanning electron microscope (SEM) observation

In this study, the native cellulose membrane and its graft copolymer membrane were prepared via the phase inversion method. SEM pictures of the cellulose membrane (Figure 6a) and the graft copolymer membrane (Figure 6b) also confirmed grafting, whereby a distinguished change was observed in the surface morphology after grafting. It could be seen that the smooth surface changed into a rough one with small clusters. This may be explained by the polarity difference between cellulose and MMA and the interruption of

intermolecular hydrogen bonds and crystalline regions in cellulose.

Thermostability of membranes

The TG and DTA curves of the membranes are shown in Figure 7. At a low temperature, 7.06 wt% weight loss for the cellulose membrane and 8.98 wt% weight loss for the grafted cellulose membrane were observed, owing to slight dehydration. On further heating, there was a sharp weight loss. The decomposition of the cellulose membrane occurred at 290 °C with about 66.81 wt% weight loss, and the decomposition of the grafted cellulose membrane occurred at 300 °C with about 71.63 wt% weight loss. The weight loss of the grafted cellulose membrane was higher than the weight loss of the cellulose membrane at both low and high temperatures. The thermopositive peaks of the cellulose membrane and grafted cellulose membrane occurred at 601.2 °C and 623 °C, respectively, and were caused by some reactions with cellulose.

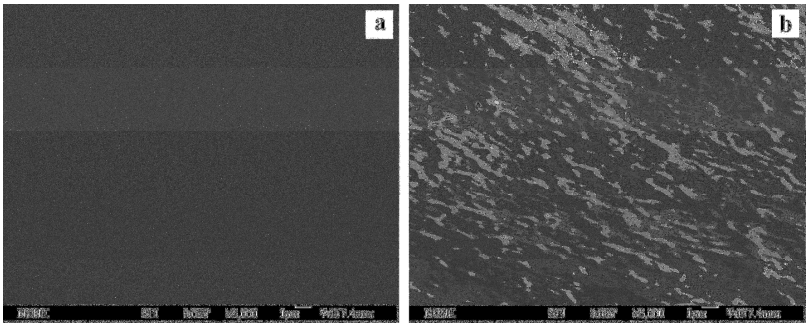

Figure 6: SEM of native cellulose membrane (a) and graft copolymer membrane (b)

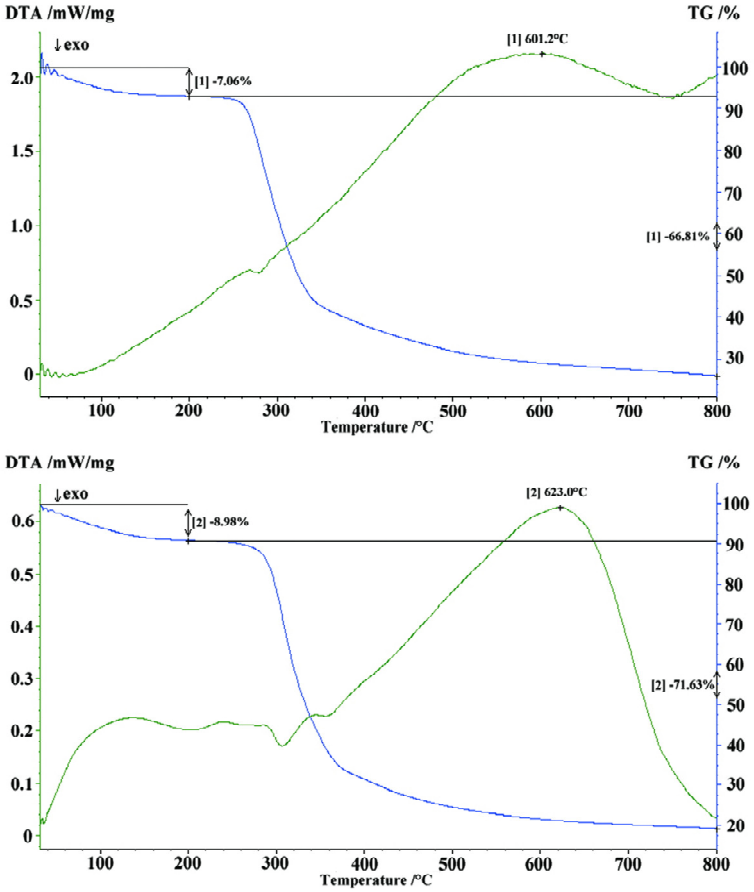

Figure 7: Thermograms of native cellulose membrane (1) and grafted cellulose membrane (2)

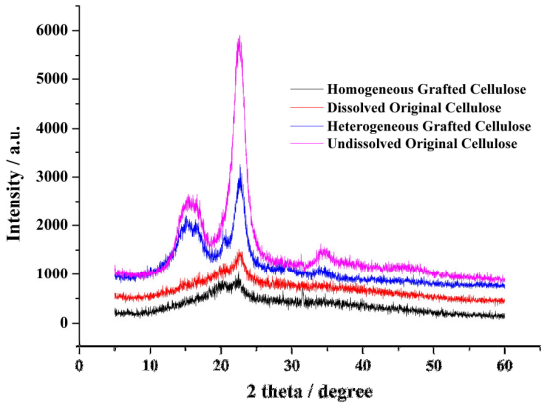

Figure 8: XRD patterns of original cellulose and its graft copolymers under homogeneous and heterogeneous conditions

X-ray diffraction (XRD) analysis

Figure 8 shows the XRD patterns of the original celluloses and its graft copolymers under homogeneous and heterogeneous conditions. As can be seen, the two curves of undissolved original cellulose and heterogeneous grafted cellulose both exhibited strong diffraction peaks at 2θ = 15.38° and 22.84°, which are characteristic diffraction peaks of cellulose I crystal.[28] Therefore, the crystalline structure of cellulose molecules was not destroyed after the grafting reaction under heterogeneous conditions, which indicated that the heterogeneous grafting copolymerization of cellulose mainly occurred in the amorphous region of the cellulose structure.

Moreover, the significant diffraction peaks at 15.38° disappeared in the two curves of the dissolved original cellulose and homogeneous grafted cellulose and the crystallinity of the two celluloses was obviously lower than that of the other two celluloses, suggesting that the original crystalline structure was destroyed during the dissolution process of cellulose. Those structural changes were vital for the effectiveness of grafting copolymerization processing and therefore the grafting reaction could occur in the crystalline region of the cellulose structure under homogeneous conditions, which was the reason why the GP of the homogeneous grafting reaction was higher than that of the heterogeneous grafting reaction.

CONCLUSION

Under the homogeneous conditions of the DMAc/LiCl system, MMA was grafted onto cellulose successfully. The efficient reaction conditions were as follows: reaction time, 2 h, mass ratio of MMA/cellulose, 1/1 (g/g), mass ratio of initiator/cellulose, 6/50 (g/g), and reaction temperature, 80 °C. Under these conditions, the GP of cellulose under homogeneous conditions reached 76%. The grafted polymer was characterized by FTIR, SEM, TG-DTA and XRD.

The results indicated that the original crystalline structure was destroyed during the dissolution process of cellulose, which helped to improve the effectiveness of the grafting copolymerization reaction. Therefore, the GP of the homogeneous grafting reaction was higher than that of the heterogeneous grafting reaction.

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