STUDY ON GRAFTING COPOLYMERIZATION OF METHYL METHACRYLATE ONTO CELLULOSE UNDER HETEROGENEOUS CONDITIONS

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The grafting copolymerization of methyl methacrylate on cellulose was carried out under heterogeneous conditions using ammonium persulfate as redox initiator and water as dispersing system. The effects of reaction time, temperature, dosage of initiator and dosage of monomer on grafting yield (%G) and grafting efficiency (%GE) were investigated. Analysis of both reference and grafted cellulose samples was carried out by means of Fourier Transform Infrared Spectroscopy (FT-IR), scanning electron microscopy (SEM), thermogravimetry-differential thermal analysis (TG-DTA) and X-ray photoelectron spectroscopy (XRD). The results showed that methyl methacrylate had been grafted successfully on the amorphous area of the fiber.

Keywords: cellulose, methyl methacrylate, swelling, grafting copolymerization

INTRODUCTION

The depletion of fossil fuels and their rising costs are presently of major concern and are therefore driving an increasing interest towards the development of novel materials derived from renewable resources.[1] Cellulose is a renewable, biodegradable and abundant natural polymer resource, which is synthesized by photosynthesis.[2,3] Cellulose has received a great deal of attention due to its physical properties and chemical reactivity.[4] In recent years, environmental awareness has driven research into the modification of biofibres such as cellulose to increase their functionality and expand their applications. The grafting of synthetic polymers onto cellulose is an effective technique for modifying its properties.[5-8]

Grafting copolymerization of vinyl monomers onto cellulose has the advantage of allowing to obtain properties of both monomer and cellulose.[9,10] Understanding the structure of cellulose is a pre-requisite to controlling its modification.[11] Cellulose can be characterized as a high molecular weight homopolymer of β-1,4-linked anhydro-D-glucose units in which every unit is corkscrewed at 180° with respect to its neighbors. Approximately 36 individual cellulose molecules are brought together into larger units known as elementary fibrils, which pack into larger units called microfibrils, and these are in turn assembled into the familiar cellulose fibers.[12,13] The relative amounts of crystalline cellulose and amorphous cellulose have a considerable influence on the properties of the cellulose fibre. According to its molecular structure, cellulose is an active chemical due to the presence of the three hydroxyl groups in each glucose residue. In most instances, the hydroxyl groups in positions 2 and 3 behave as secondary alcohols, while the hydroxyl group in position 6 acts as a primary alcohol. These hydroxyl groups are mainly responsible for the reactions of cellulose.[14,15]

The reaction of cellulose should not simply be regarded as being that of a trihydric alcohol that is similar in its chemistry to sugars having three hydroxyl groups. The reactivity of these three hydroxyl groups under heterogeneous conditions can be affected by their inherent chemical reactivity. Accessibility treatments of cellulose can be performed in various ways, such as swelling, solvent exchange, inclusion degradation or mechanical grinding. Among these, swelling is the most frequently used activation method for cellulose modification. Cellulose undergoes swelling in solutions of acids, bases, and salts as well as in some organic solvents. Swelling agents generally penetrate the highly ordered regions, and split bonds between chains and fibrils of cellulose. Thus, cellulose can behave as an acid, as a base and as an amphoteric species, depending on the prevailing medium in which it is present. This logic helps in explaining the increased cellulose grafting efficiency that can occur under acidic conditions.[16,17]

Although the grafting of vinyl monomers onto cellulose has already been described under heterogeneous conditions, the grafting of methyl methacrylate in an aqueous medium has not been reported so far in the literature, to the best of the authors' knowledge. Therefore, we investigated the grafting of methyl methacrylate as co-monomer onto cellulose in an aqueous medium. In addition, we evaluated the effects of reaction time, temperature, initiator dosage and monomer dosage on grafting yield (%G) and grafting efficiency (%GE).

EXPERIMENTAL
Materials
The cellulose material (DP=1130) used in this study was a bleached hardwood chemical pulp kindly provided by a Qingdao paper mill. Methyl methacrylate (MMA) (Bodi Chemical Holding Co., LTD, Tianjin, China) was purified by extraction with an aqueous sodium chloride sodium hydroxide solution and dried over sodium sulfate. The ammonium persulfate (Bodi Chemical Holding Co., LTD, Tianjin, China) was of reagent grade and used without further purification.

Swelling
A sample of 5.0 g purified cellulose was crushed into flocculent fiber using a grinder. Then the fiber was added to a certain amount of N,N-dimethyl acetamide and pre-activated under 160 °C. Cellulose was swollen

for 30 minutes at this temperature. Then, the swollen cellulose was filtered using a filter flask.
Grafting copolymerization
The pre-activated cellulose sample was placed in a four-necked round-bottom flask equipped with a reflux condenser, a thermometer and an electrically operated stirrer. An amount of 95 g water was added into the flask to disperse the cellulose. When the temperature of the whole system reached 80 °C, the initiator (ammonium persulfate) and MMA were added to start the reaction. After the reaction, the grafted cellulose was washed with water and ethanol and dried to a constant weight at 60 °C. In order to remove the PMMA formed in the reaction, the product was mixed with acetone and agitated for 24 h to dissolve the homopolymer.

Characterization
Fourier transform infrared (FTIR) spectra were recorded using a TENSOR27 FTIR spectrometer in the range of 4000–500 cm^{-1}. The phase transformation analysis of the samples was conducted by wide-angle X-ray diffraction (WXRD) using an X-ray diffractometer (D/max-2500/PC, Rigaku Co. Ltd., Tokyo) with CuKaa radiation (40 kV, 60 mA) in the range $2\theta = 5°–60°$. SEM images were recorded on a JSM-6700F scanning microscope. The samples were coated with a thin layer of gold in a 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, German). The TG/DTA analyses were performed with a sample weight of 14.2 mg, a heating rate of 10 °C/min, and under flowing nitrogen (20 mL/min).

Characteristic grafting parameters
Grafting yield (%G) and grafting efficiency (%GE) were calculated as follows:[18-19]

$$G = \frac{M_1 - M_0}{M_0} \tag{1}$$

$$GE = \frac{M_1 - M_0}{M_2 - M_0} \tag{2}$$

where M_0 is the quantity of the cellulose, M_1 is the quantity of the pure grafted product, M_2 is the quantity of the crude grafted product.

RESULTS AND DISCUSSION
Effect of reaction time on grafting yield and grafting efficiency
The grafting yield and grafting efficiency of methyl methacrylate on cellulose was studied by varying the reaction time from 1 h to 3 h. As can be seen from Figure 1, the grafting yield and grafting efficiency showed an increasing trend up

to a reaction time of 2.5 h and then started to decrease. The initial increase in grafting was caused by the diffusion of monomer molecules to the growing chains and other active sites on the cellulose. The reduction in the extent of grafting at l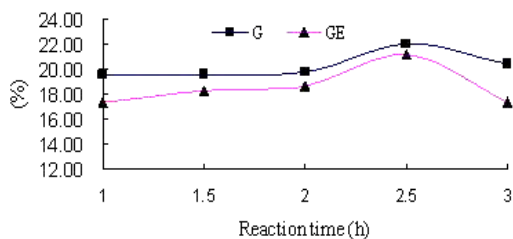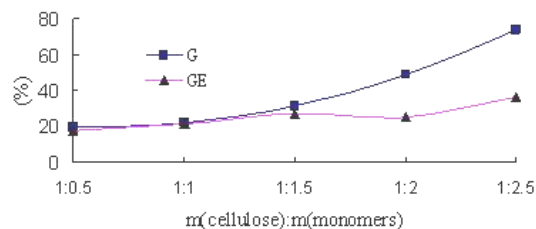onger reaction time (>3 h) was due to the decrease in the extent of swelling of the cellulosic chains and the concomitant steric hindrance exerted by the chains already grafted onto the cellulose.

Figure 1: Effect of reaction time on grafting

Figure 2: Effect of monomer amount on grafting
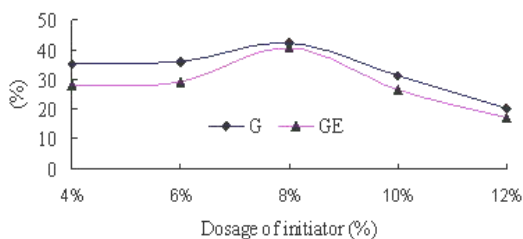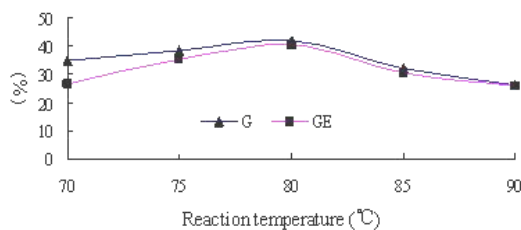

Figure 3: Effect of initiator dosage on grafting
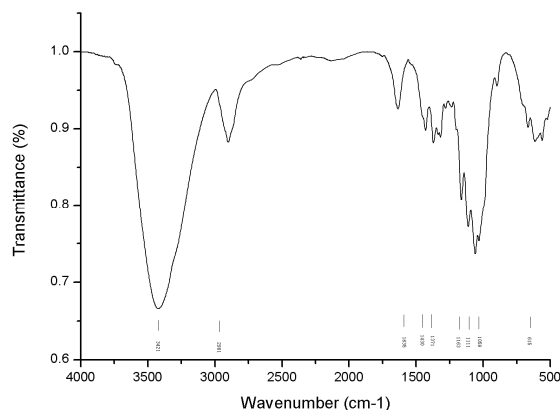

Figure 4: Effect of reaction temperature on grafting

Figure 5: FTIR spectra of native cellulose

Effect of monomer dosage on grafting yield and grafting efficiency

In order to investigate the effect of monomer dosage on the grafting parameters, the grafting copolymerization process was carried out at different dosages of monomer. Initially, the grafting yield and grafting efficiency showed a slow rise up to the cellulose to monomer mass ratio of 1:1.5, as can be observed from Fig. 2. However, after this, as the monomer dosage was further increased, the grafting yield grew remarkably due to the intensified formation of ungrafted homopolymers and copolymers.
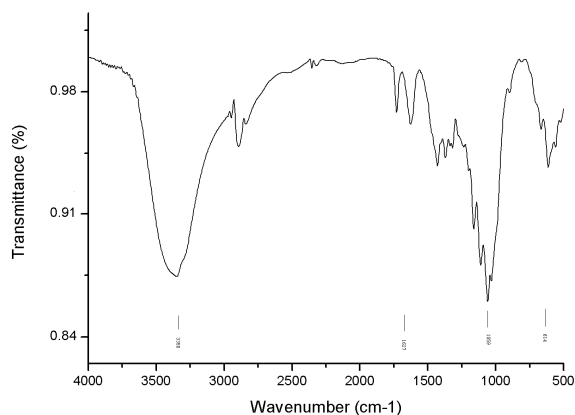
Figure 6: FTIR spectra of graft copolymer

Effect of initiator dosage on grafting yield and grafting efficiency

Initiation via the use of ammonium persulfate involves the generation of initiating species on the swollen cellulose substrate backbone. This is usually carried out by saturating the cellulose substrate with ammonium persulfate. The effect of initiator dosage on the (%G) and (%GE) onto cellulose was studied by varying the dosage of ammonium persulfate (compared to cellulose) from 4% to 12%. Initially, ammonium persulfate promoted the formation of more active sites on the cellulose backbone. The percent (%G) and (%GE) increased up to a concentration of 8% of ammonium persulfate, but showed a decreasing trend when the dosage of ammonium persulfate was further increased beyond 8%. The decreasing trend indicates that a higher concentration of ammonium persulfate is unable to form active sites on cellulose, but starts participating at the termination of the grafted growing chains on cellulose and of the homopolymer chains in solution.

Effect of reaction temperature on grafting yield and grafting efficiency

In order to study the effect of temperature, we studied the grafting of methyl methacrylate on cellulose at different temperatures, ranging from 70 to 90 °C; the results are presented in Figure 4. The grafting yield (%G) and grafting efficiency (%GE) increased with a rising temperature up to 80 °C. However, with a further rise in the temperature, (>80 °C), both grafting yield (%G)

and grafting efficiency (% GE) decreased. At a temperature <80 °C, the increase in the number of active sites on the cellulose backbone may have been caused by the high decomposition rate of the initiator and the formation of more sites on the cellulose. When the temperature was further increased beyond 80 °C, the (%G) and (%GE) and the molecular weights of the grafted chains and homopolymer chains showed a decreasing trend, which may have been caused by the high rate of termination of immature growing chains because of mutual combination or chain transfer to the solvent or monomer molecules.

FT-IR spectroscopy of ungrafted and grafted cellulose

Fig. 5 shows the FTIR spectra of pristine cellulose. As can be noted, the spectra indicate the presence of the characteristic bands of cellulose, such as the O–H stretching vibration of hydroxy at 3421 cm^{-1}, the characteristic absorption peak of C-O at 1059 cm^{-1} and the C–H bending vibration of CH-O at 1430 cm^{-1} etc.

Fig. 6 presents the FTIR spectra of grafted cellulose. The figure reveals two weak absorption peaks of methyl asymmetric stretching vibration at 2962 cm^{-1} and 2872 cm^{-1}. There is also a clear absorption peak corresponding to an ester group at 1750 cm^{-1}, which indicates that the methyl methacrylate was grafted onto the cellulose surface. Under heterogeneous conditions, the activity and accessibility of the hydroxyl groups are not high, but acrylic monomers can be grafted onto the cellulose backbone after activation.

SEM analysis of ungrafted and grafted cellulose

Fig. 7 (a) illustrates a SEM image of pulp fibre ground by the physical method. It may be remarked from the image that the cell wall of the fiber surface was destroyed because of physical grinding and the surface of the fiber is covered with a great number of fissures. Fig. 7 (b) and (c) show SEM images of the fiber that was grafted by methyl methacrylate. Although the product retains the original fibrous structure of the pulp, the surface of the fiber becomes noticeably rougher, and there are a lot of materials attached to it. The presence of methyl methacrylate on the fiber surface was confirmed by FTIR, which allows us to speculate that it is the methyl methacrylate side chains that grafted onto cellulose.

TG-DTA analysis of ungrafted and grafted cellulose

Fig. 8 presents the TG and DTA curves of grafted cellulose. As can be seen from the figure, the decomposition of cellulose occurred at about 150 °C, causing a weight loss of about 35.69 wt%. The thermopositive peak at about 236.8 °C was caused by some cracking reactions of cellulose. On further heating, there was a sharp weight loss, this decomposition stage occurred at 240 °C involving a weight loss of about 37.12 wt%. The endothermic peak at 443.6 °C was due to decomposition or cracking reactions. The thermopositive peak at about 605.4 °C was caused by intramolecular rearrangement.
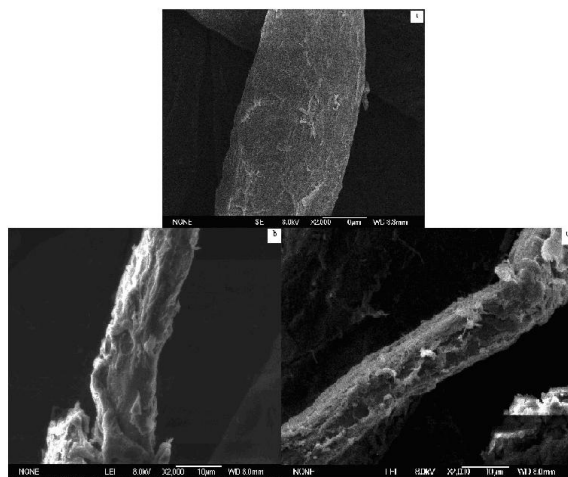

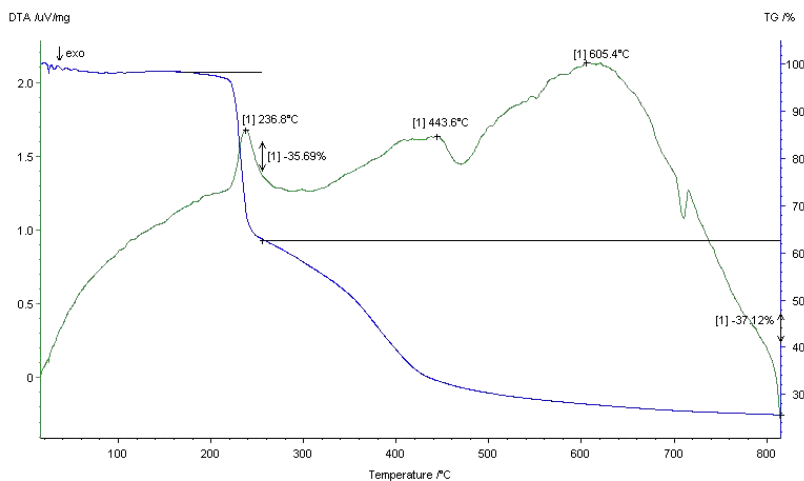Figure 7: SEM of native cellulose (a) and graft copolymer (b), (c)

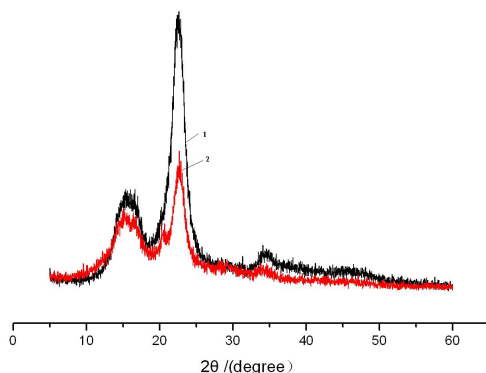

Figure 8: Thermograms of grafted cellulose

Figure 9: XRD patterns of original cellulose (1) and its graft copolymers (2)

XRD analysis of ungrafted and grafted cellulose

Fig. 9 shows the XRD spectra of pristine and grafted cellulose samples. Both curves present the characteristic crystalline peaks at $2\theta = 15.155°$ and $22.659°$, indicating the presence of cellulose I crystalline structure. The two curves are identical, which allows us to conclude that the crystalline structure of the cellulose molecules was not destroyed, i.e. the grafting polymerization occurred in the amorphous area of cellulose rather than in its crystalline area.

CONCLUSION

Methyl methacrylate was successfully grafted onto cellulose under heterogeneous conditions. The ideal reaction conditions were identified as follows: grafting temperature of 80 °C; grafting reaction time of 2.5 h; initiator dosage of 8% compared to cellulose; and m (cellulose): m (monomer) of 1:1.5. The characterization of the samples by FT-IR, SEM, TG-DTA and XRD analyses confirmed that methyl methacrylate had been grafted successfully on the amorphous region of the fiber.

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