

SYNTHESIS AND PROPERTIES OF GLYCIDYL-METHACRYLATE-GRAFTED
EUCALYPTUS FIBERS

G. YANG and H. M. ZHAI

*Jiangsu Provincial Key Laboratory of Pulp and Paper Science and Technology,
Nanjing Forestry University, Nanjing 210037, China*

Received November 21, 2011

To promote the value-added utilization of natural, renewable and sustainable eucalyptus fibers, a glycidyl-methacrylate-grafted fiber (GMAGF) was synthesized by grafting glycidyl methacrylate (GMA) onto bleached eucalyptus fiber induced by a Fe^{2+} - H_2O_2 -thiourea dioxide (TD) redox system, *via* cross-linking reaction of diallyl phthalate (DAP), followed by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and scanning electron microscopy (SEM) characterization. The effects of the dosage and concentration of DAP, H_2O_2 and TD and of the temperature of the reaction system on the grafting percentage (G%) and oil absorptivity (OAP) of GMAGF were studied. The main results obtained are as follows: (1) G% increased as the monomer dosage increased to a given content; (2) GMAGF crystallinity considerably decreased, compared to that of the original fiber; (3) GMAGF, carrying glycidyl groups and improving its non-polarity, is able to adsorb hydrophobic substance molecules like diesel; OAP rose with the increase of grafting percentage; a maximum OAP (17.6 g/g) improvement, by 320%, compared to the original fiber, was obtained when G% ranged from 85 to 90%, at a DAP dosage of 5.0%; (4) OAP was closely related to both G% and the cross-linked network formed between copolymers.

Keywords: glycidyl methacrylate, oil absorptivity, contact angle, grafted eucalyptus fiber

INTRODUCTION

Spilled and discharged oily wastes significantly impact our living environment.¹⁻² To minimize the impact of oil accidents upon the environment, much attention has been paid to finding efficient oil-absorbing materials. Cellulose, one of the most abundant natural materials in the world and an environmentally friendly and renewable biomaterial, has been used in many fields,³ which explains the growing interest manifested for its chemical modification, to improve its functions and to extend its applications.⁴ Grafting copolymerization applied for modifying natural cellulose has been widely reported worldwide. Since the hydrophilic hydroxyl groups from the cellulose surface sharply decrease its oil absorptivity (OAP), an improvement of the cellulose OAP can be achieved by introducing hydrophobic functional groups onto it.⁵⁻⁷ It has been reported that fiber assemblies made up of single natural and synthetic fibers, as well as blends of natural and synthetic fibers, showed a higher oil sorption

capacity of the high-density oil, compared to diesel oil.⁸ Abdullah *et al.*,⁹ who studied the physico-chemical and sorption characteristics of Malaysian Kapok with diesel and engine oil, showed that Kapok exhibited high hydrophobic-oleophilic characteristics, attributed to the hollow lumen and to its waxy surfaces. GMA is an attractive monomer with a reactive double bond and an epoxy group in the molecule.¹⁰ GMA-grafted cellulose (GMAGC) is an important intermediate, because the epoxy group in its molecule structure can form new functional groups by further chemical reaction. On the other hand, the ester structure of GMAGC can improve its polarity, which is advantageous for its OAP, as well.

Nowadays, the fast-growing eucalyptus with a height around 35 meters, only seven years old, can be harvested for pulping. The productivity of eucalyptus is twice that of softwood, as well as that of most of the other hardwoods. The production of eucalyptus pulp has become

significant since the 1970s. Thus, an important direction of investigation refers to the value-added utilization of renewable and sustainable bleached eucalyptus fibers (mainly composed of cellulose) as specific functional fibers. However, only few studies have been devoted to the synthesis of GMAGF from eucalyptus fiber and its OAP, and relatively little is known of their properties.

Therefore, in the present investigation, GMAGF was synthesized by grafting copolymerization of GMA onto bleached eucalyptus fibers (pulp) by a Fe^{2+} - H_2O_2 -thiourea dioxide (TD) redox system, *via* cross-linking of diallyl phthalate (DAP), and characterized by related methods. The effects of different grafting conditions on OAP were evaluated. The relationships among grafting percentage, contact angle and OAP were also analyzed.

EXPERIMENTAL

Materials

Bleached eucalyptus pulp (Votorantim Celulose e Papel), 0# diesel, ferrous ammonium sulphate, H_2O_2 (Shanghai Chemical Reagent Co., Ltd), TD (Shandong Qingzhou Friendship Chem. Co. Ltd) and DAP (Shanghai Yilin Materials Co., Ltd.) were of industrial grade and used as received. GMA (Kangyida Coating and Chemicals Co., Ltd., China) was distilled before use, to remove the stabilizers.

Synthesis

Synthesis was conducted according to literature data,¹¹⁻¹² with some modifications. The eucalyptus pulp was first impregnated in a freshly prepared aqueous $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (0.025%) for 20 min at 25 °C, at a pulp-to-liquor ratio of 1:50, then squeezed, washed thoroughly with distilled water and dried. A 2.5 g ferrous-containing sample, 200 mL water, GMA, hydrogen peroxide, TD and DAP were placed in a 250 mL four-necked flask. The grafting reaction was performed at the given temperature for 20 min, under nitrogen atmosphere. The graft copolymers and the homopolymer were separated through Soxhlet extraction with acetone for 24 h, and oven-dried at 60 °C under vacuum until constant weight. Percent grafting (%G) was calculated according to Kojima *et al.*,¹³ as follows:

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

where W_1 and W_0 denote the weight of the grafted eucalyptus fiber weight and of the original eucalyptus fiber, respectively. Grafting efficiency was not used to evaluate the synthesis characteristics, because our previous study indicated that grafting efficiency of this synthesis was always very high (over 92%).

Analysis methods

Epoxy group content

The epoxy group content was determined by HCl-dioxane titration.¹⁴

Contact angle

A predetermined weight sample was flattened and a drop of deionized water was applied to the surface to measure the contact angle. The camera of contact angle tester (JC-2000D) snaps automatically the image of the liquor drop (20 frames/s).

Oil absorptivity

5.0 g of GMAGF were immersed into 0# diesel for 5 min, after which the suspension was poured into a 30-mesh polyester bag. An oscillating bed was used to remove the redundant oil by shaking for 10 min. The rotating speed was of 220 rpm/min and the amplitude was of 30 mm. After shaking, the total weight of GMAGF with absorbed oil was obtained. OAP was calculated by dividing the total weight after shaking by the original weight of GMAGF.

FT-IR spectral analysis

The solid phase FT-IR spectra of the powdered sample with infrared grade KBr were obtained with a Thermo Nicolet Avatar FT-IR spectrometer.

X-ray diffraction analysis

The ungrafted and grafted eucalyptus fibers were analyzed by a Rigaku D/Max-RBX X-ray diffractometer with $\text{Cu K}\alpha$ radiation, at 40 kV and 50 mA. The diffraction angle ranged from 65° to 5°. The crystallinity of the sample (X_c , %) was calculated according to the following formula:

$$X_c (\%) = (F_c / (F_c + F_a)) \times 100$$

where F_c and F_a are the areas of crystalline and non-crystalline regions, respectively.

Scanning electron microscopy

Surface morphology of ungrafted and grafted eucalyptus fibers was analyzed with a NTC JSM-6390/LV scanning electron microscope (SEM).

RESULTS AND DISCUSSION

GMAGF synthesis

FT-IR spectroscopy

As shown in Figure 1, several additional peaks were found for GMAGF, compared to the eucalyptus cellulose without any treatment. The peak at 1733 cm^{-1} should be assigned to the $>\text{C}=\text{O}$ stretching vibration, indicating the presence of an ester group of GMAGF. The characteristic adsorption peaks at 906 cm^{-1} (asymmetrical stretching vibration of the epoxy group) and 850 cm^{-1} ($\text{C}-\text{O}-\text{C}$ stretching typical for the epoxide ring)¹⁵ evidence that grafting of

GMA onto fibers had occurred. The intensity of these characteristic peaks, corresponding to GMA functional groups, increased with the increase of grafting percentage. Peak intensity at about 3000 cm^{-1} , corresponding to the C–H stretching vibration of the epoxy group, increased obviously when G% increased from 86.1 to 217.1%. These results indicate that the eucalyptus fiber was successfully grafted with GMA.

XRD analysis

Figure 2 shows the XRD (X-ray diffraction) patterns of eucalyptus fibers and grafted fibers. As shown in Figure 2, a wider peak with low intensity was observed at around $2\theta = 22.48^\circ$. The crystallinity of eucalyptus fiber and the GMAGF value ($G\% = 217.1\%$) was of 69.8 and 26.2%, respectively. The decrease in crystallinity after grafting should be attributed to the randomness of the amorphous phase in the graft copolymers enhanced by grafting with GMA, which caused perturbation of the long-ranged spacing between chains.¹⁶

SEM analysis

Morphological investigation of the eucalyptus and GMA-grafted eucalyptus fibers was

conducted with a scanning electron microscope (SEM), the recorded images being shown in Figure 3. The smoothness and evenness of the fiber surface were observed on the original fiber. The changes in surface morphology after grafting with GMA clearly revealed that grafting affected the eucalyptus fiber surface. Surface unevenness resulted from polymer deposition during graft copolymerization. In addition, the grafted eucalyptus fiber was plumper than the original one, which might be caused by excessive grafting, affecting the fiber inner lumen wall.

Effects of synthesis conditions on OAP of GMAGF

The 0# diesel was used for OAP determination. The OAP of the original fiber was of 4.2 g/g.

Effect of temperature

The effects of temperature on OAP and G% of GMAGF are shown in Figure 4 (a). As temperature increased from 35 to 75 °C, OAP and G% of the grafted fiber first increased, after which OAP decreased, while G% remained constant. At a temperature of 55 °C, G% was of 86.1%, and the maximum OAP value was of 17.6 g/g, meaning an increase of almost 320%, compared to the original fiber.

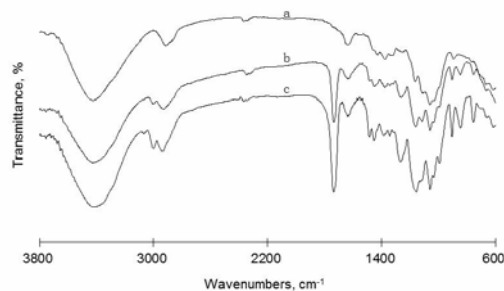


Figure 1: FT-IR spectra of original and grafted fibers at different grafting percentages: a, the original; b, G% = 86.1%; c, G% = 217.1%

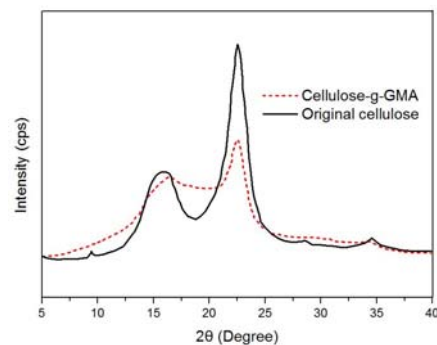


Figure 2: XRD patterns of original fiber and GMAGF

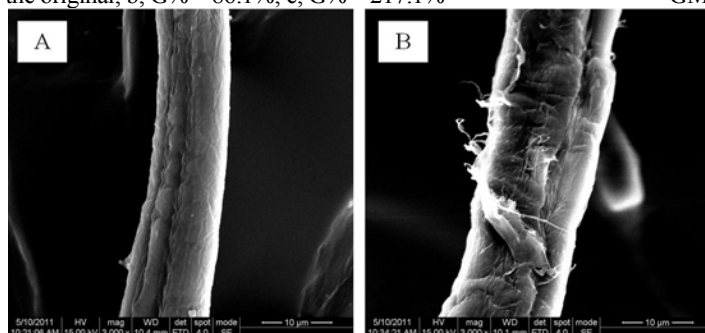


Figure 3: SEM images of (A) eucalyptus fiber and (B) GMAGF (%G = 217.1%)

At a temperature below 55 °C, the fiber macromolecule cannot be well grafted with the monomer. When temperature exceeded 55 °C, G% did not decrease sharply, and OAP decreased. The quick polymerization and decomposition of the cross-linking agent may make difficulty of cross-linked networks in the grafted cellulose.

Effect of monomer concentration

The effect of monomer concentration on OAP and G% of GMAGF is shown in Figure 4 (b). Graft copolymerization was carried out at various GMA concentrations, ranging from 0.035 mol/L to 0.420 mol/L. As GMA concentration increased, OAP first increased, after which it decreased. The maximum value was obtained at a GMA concentration of 0.14 mol/L, while G% kept increasing, which may be explained by the fact that GMA, containing an ester bond, is a hydrophobic monomer. From the beginning, due to the increase of GMA grafted into the fiber surface, surface polarity came down. More integrated holes appeared among the grafted fiber to capture the oily substance. However, too much grafted GMA would destroy the fiber crystalline area during grafting, exposing more hydroxyl groups. Meanwhile, the volume of holes may diminish. Since the oily substance has its own surface tension, it is difficult for the oil substance to get into the inner space of the holes, so that it remains on the surface.

Effect of H₂O₂ dosage

Figure 4 (c) indicates the effects of H₂O₂ dosage on OAP and grafting percentage. Graft copolymerization was carried out at various H₂O₂ dosages, ranging from 0.05 to 2.00 g/L. OAP first increased, then decreased to 12.0 g/g. The maximum value was achieved at 0.20 g/L of H₂O₂. The G% value had a similar trend. The cross-linked network could be influenced by H₂O₂ dosage. When the H₂O₂ dosage is low, the active sites appearing on the fiber are not sufficient for grafting, and the cross-linked networks are not well built to preserve the oily substance. When the H₂O₂ dosage exceeded 0.20 g/L, the decrease of G% may be caused by the termination of the growing grafted chains or by the initiation of homopolymerization, due to excess radicals.¹⁷ The lower relative molecular weight between the junction points of the grafted products form smaller volumes of the cross-linked network.

Effect of TD dosage

The effects of TD dosage on OAP and G% for GMAGF are shown in Figure 4 (d). Graft copolymerization was carried out at various TD dosages, ranging from 0.5 g/L to 8.0 g/L. With the increase of the TD dosage, OAP and G% first increased, then decreased. This may be explained by the function of TD in the Fe²⁺-H₂O₂ redox system. TD addition to the reaction system increased the grafting percentage, which improved oil adsorption. However, too much TD in the system could restrain the grafting reaction, which decreases the amount of monomer grafted onto the fiber, thus causing OAP decrease.

Effect of DAP dosage

The effect of DAP dosage on the OAP and G% of GMAGF is shown in Figure 4 (e). Graft copolymerization was carried out at various DAP dosages, ranging from 0 to 9.0% (based on bleached eucalyptus pulp). Figure 4 (e) shows that DAP addition did not affect the grafting process, the G% remaining almost the same. With the increase of the DAP dosage, OAP first increased, then dropped. The maximum value was obtained at a DAP usage of 5.0%. The first increase of oil adsorption was attributed to the cross-linked network, gradually built up *via* the effect of DAP, when more integrated holes appeared. However, too much DAP would produce more junction points, thus reducing the volume of holes in the network structure. Therefore, DAP may possibly change the cross-linked network among the grafted fibers.

Effect of liquor ratio

The effects of liquor ratio on OAP and G% of GMAGF are illustrated in Figure 4 (f). Graft copolymerization was carried out at various liquor ratios (g water per g bleached eucalyptus pulp), ranging from 30 to 60. The liquor ratio affects not only the concentration of cellulose, monomer and initiator dosage, etc., but also the dispersion of the reaction ingredients in the system. With the increase of the liquor ratio, oil adsorption and G% first increased, then decreased. The maximum value was reached at a liquor-to-solid ratio of 50. In addition, the grafted epoxy group could be hydrolyzed at this ratio.

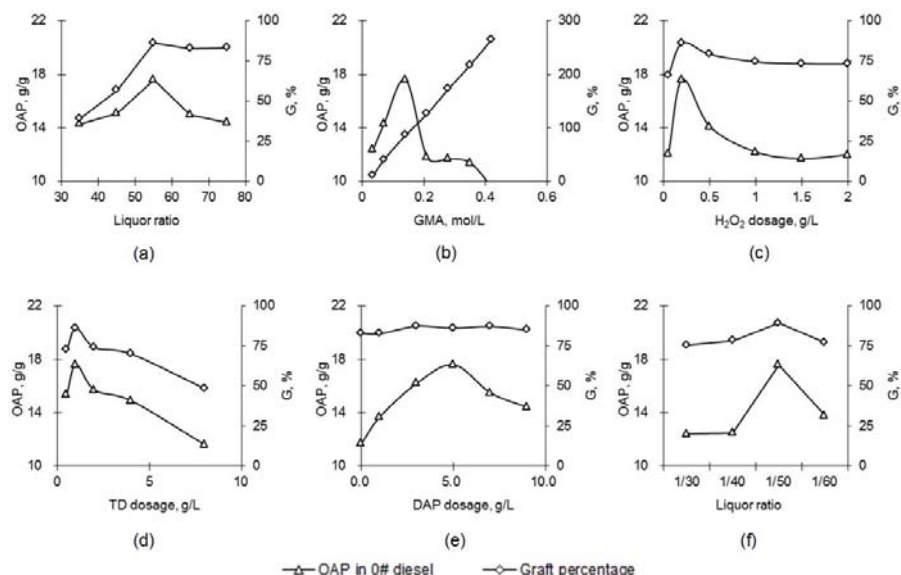


Figure 4: Effects of synthesis conditions on OAP and G% of GMAGF:

(a) temperature; (b) GMA concentration; (c) H₂O₂ dosage; (d) TD dosage; (e) DAP dosage; (f) liquor:solid ratio

Contact angle, epoxy content and G% of GMAGF

Contact angle is also known as the wetting angle formed when the liquor stands on the solid surface at thermodynamic equilibrium.¹⁸ In this study, the contact angle demonstrates hydrophobicity of the grafted fiber. As demonstrated in Figure 5, the variation trend of the contact angle was linear along with the increase of G%, when G% was below 90%. When

G% was between 90 and 170%, the variation trend gradually increased while, when it exceeded 170%, the contact angle remained unchanged. Meanwhile, with the increase of the grafting percentage, the epoxy content rose from 0.56 to 4.53 mmol/g. At first, grafting occurred onto the fiber surface, mostly in the amorphous region. With increasing of the GMA monomer, it was grafted onto the fiber backbone and G% increased.

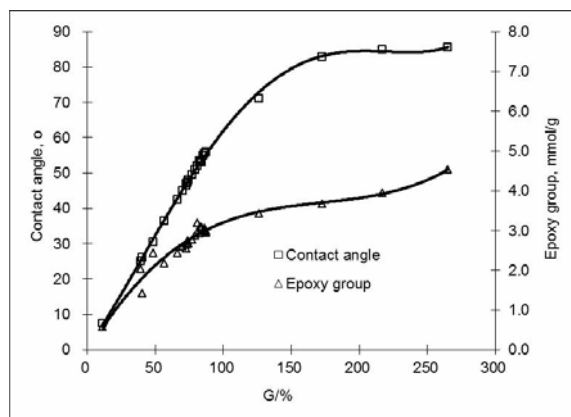


Figure 5: Relationships among grafting percentage, contact angle and epoxy group of FGGMA

The polar hydroxyl groups were replaced by the non-polar ester (also epoxy group) bond on the surface, which resulted in the increase of the contact angle and oil adsorption. However, a too

much grafted GMA did not bring the value of the contact angle to a higher level, causing the destruction of the crystalline region instead (according to the results of XRD analysis), which

was not beneficial to the surface non-polarity and construction of the cross-linked network. Over-grafted fiber would expose the inner hydroxyl, thus restraining the increase of contact angle. Fiber degradation would destroy the cross-linked network and reduce the size of holes inside the structure. The above analysis of the testing parameters shows that, under certain conditions, the increase of the contact angle could enhance the OAP of the grafted fiber.

CONCLUSIONS

Graft copolymerization of GMA onto bleached eucalyptus fiber was successfully conducted in a Fe^{2+} - H_2O_2 -TD redox system. A proper control of the dosage and concentration of DAP monomer, H_2O_2 and TD, as well as the temperature of the reaction system are important for the grafting percentage. G% increased linearly as the monomer dosage increased. The crystallinity of the graft copolymers greatly decreased, compared to that of the eucalyptus fiber.

The glycidyl-methacrylate-grafted fiber, carrying glycidyl groups and increasing non-polarity, is able to adsorb hydrophobic molecules like diesel. The OAP rose up with the increment in graft percentage. A maximum OAP (17.6 g/g), improved by 320%, compared to the bleached eucalyptus pulp, was obtained at a G% ranging from 85 to 90% and a DAP dosage of 5.0%. OAP may depend on both grafting percentage and the cross-linked network formed between copolymers. A detailed study on the latter is under way.

ACKNOWLEDGEMENTS: The financial support of the National Science Foundation of China (Grant No. 31070524), Major State Basic

Research Development Program of China, (Grant No. 2010CB732205) and Jiangsu Technology Innovation Special Funds Projects (Grant No. BZ2010069) is gratefully acknowledged.

REFERENCES

- ¹ Y. Liu, M. Xu and J. Liu, *Chem. Adhes.*, **32**, 46 (2010).
- ² W. Y. Chiau, *Mar. Pollut. Bull.*, **51**, 1041 (2005).
- ³ D. W. O'Connell, C. Birkinshaw and T. F. O'Dwyer, *Bioresource Technol.*, **99**, 6709 (2008).
- ⁴ H. Dong, Q. Xu and Y. Li, *Colloid. Surf., B*, **66**, 26 (2008).
- ⁵ E. Princi, S. Vicini and E. Pedemonte, *Eur. Polym. J.*, **42**, 51 (2006).
- ⁶ S. Hassanpour, *Radiat. Phys. Chem.*, **55**, 41 (1999).
- ⁷ S. Liu and G. Sun, *Carbohydr. Polym.*, **71**, 614 (2008).
- ⁸ R. S. Rengasamy, D. Dipayan and K. C. Praba, *J. Hazard. Mater.*, 186, 526 (2011).
- ⁹ M. A. Abdullah, A. Rahmah and U. Z. Man, *J. Hazard. Mater.*, 177, 683 (2010).
- ¹⁰ E. Vismaraa, L. Melonea and G. Gastaldi, *J. Hazard. Mater.*, **170**, 798 (2009).
- ¹¹ D. W. O'Connell, C. Birkinshaw and T. F. O'Dwyer, *J. Appl. Polym. Sci.*, **99**, 2888 (2006).
- ¹² R. N. Ronald, T. Kenji and S. Katsuhiko, *Water Res.*, **35**, 2724 (2001).
- ¹³ V. Singh, A. Tiwari, D. N. Tripathi and R. Sanghi, *Carbohydr. Polym.*, **58**, 1 (2004).
- ¹⁴ J. A. Kling and H. J. Polehn, *J. Polym. Sci., A: Polym. Chem.*, **33**, 1107 (1995).
- ¹⁵ S. R. Shukla and A. R. Athalye, *J. Appl. Polym. Sci.*, **54**, 279 (1994).
- ¹⁶ X. L. Wang, Y. Huang and J. Zhu, *Carbohydr. Res.*, **344**, 801 (2009).
- ¹⁷ V. D. Athawale and V. Lele, *Carbohydr. Polym.*, **35**, 21 (1998).
- ¹⁸ B. Vadgama and D. K. Harris, *Exp. Therm. Fluid. Sci.*, **31**, 979 (2007).