

## SYNTHESIS AND CHARACTERISTICS OF GRAFT COPOLYMERS OF POLY(BUTYL ACRYLATE) AND CELLULOSE FIBER WITH ULTRASONIC PROCESSING AS A MATERIAL FOR OIL ABSORPTION

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A series of materials used for oil absorption based on cellulose fiber grafted with butyl acrylate (BuAc) have been prepared by radical polymerization under ultrasonic waves processing. Effects of ultrasonic dose for the maximum graft yield were considered. The dependency of optimum conditions for oil absorption rate on parameters such as ultrasonic processing time and ultrasonic power were also determined. Fourier infrared (FT-IR) analysis was used to confirm the chemical reaction taking place between cellulose and butyl acrylate. The thermogravimetric behavior of the graft copolymer was characterized by thermogravimetric analysis (TGA). Scanning electron microscope (SEM) analysis was used to determine the surface structure of the grafted material. With the increase of the ultrasonic treatment dose, the surface of the ultrasonic processed material became more regular, and the material was transformed into a homogeneous network polymer having a good structure and good adsorbing ability.

*Keywords:* Cellulose; Ultrasonic wave; Oil absorption; Graft copolymerization

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### INTRODUCTION

In the course of a recent large oil spill (around five thousand barrels a day) in the Gulf of Mexico after an April 2010 offshore drilling rig explosion, efforts to manage the spill included controlled burning, dispersal, and plugging of the well bore. These efforts were only partly successful. There is now a growing concern worldwide about the urgent need to control accidental and deliberate oil releases during its extraction, transportation, and storage (Reynolds et al. 2001; National Research Council 2003). Another important threat to the environment is polycyclic aromatic hydrocarbons, which can be potent cell mutagens and carcinogens, and they affect a variety of biological processes (Pelkonen et al. 1982). Absorbent materials are popular due to their capability to collect and remove the oil from the oil spill site completely. Oil removal by removing the absorbent structure then becomes much easier (Adebajo et al. 2003; Valderrama et al. 2007). A wide range of materials for oil absorption have been employed, such as biomass (Tolba et al. 2011), polymeric materials (Ceylan et al. 2009), and macroporous inorganic material.

Compared with some traditional materials, some nanomaterials such as carbon nanotube sponges (Gui et al. 2010), nano fiber/inorganic composites (Flávia et al. 2009), and aerogels (Reynolds et al. 2001; Rao et al. 2007; Korhonen et al. 2011) have been studied. The unique properties such as large surface area, extremely high porosity, and very low density lead to characteristics such as hydrophobicity and oleophilicity, high uptake capacity, and high rate of uptake, which make those nanomaterials good absorbents.

Cellulose is one of the most available natural materials. It is a natural polysaccharide that is composed of poly-(1,4)-D-glucose residues, and it can be obtained from plants such as fruit, straw, woody vegetation, and so on (Zuluaga et al. 2009; Chauhan et al. 2005). Significant hot issues include the development of cellulose fibrils (Beck-Candanedo et al. 2005; Qu et al. 2010a), cellulose composites (Li et al. 2011; Qu et al. 2010b), and cellulose graft copolymers (Chauhan et al. 2004). In recent years, several papers on cellulose grafting material, by atom transfer radical polymerization (ATRP) (Vlcek et al. 2006), free radical graft copolymerization (Littunen et al. 2011), and simultaneous gamma radiation initiation method (Chauhan et al. 2005) have been published.

Since the mid 1990s, living radical polymerizations (LRP) such as atom transfer radical polymerization (ATRP) have been used extensively as a tool for the development of novel macromolecular structures (Wang et al. 1995). ATRP's positive attributes include simplicity, "livingness," cost, and robustness. The use of inexpensive copper catalysts and readily available initiators also makes it an interesting option for surface modification (Zoppe et al. 2010). Surface modifications of nanocellulose via ATRP have been reported; Xu et al. (2008) synthesized a novel amphotropic polymer through azo polymers grafting from cellulose nanocrystals via ATRP. Morandi et al. (2009) synthesized cellulose nanocrystals grafted by polystyrene chains via surface-initiated ATRP.

In 1962 Iwasaki et al. studied the effect of ultrasound on single fiber of wood pulp and found some interesting phenomena that affect the fiber (cellulose) cell wall. The middle layer S2 of secondary wall was dislocated, together with the removal of the outer S1 layer and swelling of the S2 layer. These variations resulted in fine fibrosis of the S2 layer. Thus, for a single fiber of cellulose, ultrasound plays a role of mechanical pulping (Iwasaki et al. 1962). Recently, ultrasonic radiation (high frequency sounds) has been widely used as a new technology for polymer synthesis (Widnersson et al. 2011; Natori and Natori 2011). The effects of ultrasound on a chemical process are both mechanical and chemical. Under ultrasonic waves, a microbubble will form and then collapse, with temperature in the bubble reaching thousands of degrees centigrade. Water molecules under this temperature will break and form radicals. Such radicals then initiate polymerisation in the same way as a conventional chemical initiator (Bradley et al. 2005; Teo et al. 2008).

In this study, we present a method for the production of cellulose grafted with butyl acrylate (BuAc). The materials are prepared via radical polymerization under ultrasonic waves processing. An obtained cellulose grafted butyl acrylate copolymer was characterized by scanning electron microscopy (SEM), Fourier transform infra-red spectrometry (FT-IR), and thermogravimetric analysis (TGA). The absorption behavior of the acetylated straw was tested using benzene and edible oil.

## EXPERIMENTAL

### Materials

Bleached wood pulpboard (sulfate cooking) made from eucalyptus wood was purchased from Shandong Huatai Paper Mill (Shandong Province, China). Butyl acrylate (BuAc) was purchased from Tianjin Fuchen Chemical Plant (Tianjin, China). This was treated with 2 M NaOH and dried overnight over anhydrous sodium sulfate. N,N-methylene-bis-acrylamide (DMAM) was purchased from Tianjin Jinke Chemical Plant.  $K_2S_2O_8$  and benzene were purchased from Shantou Xilong Chemical Plant. All chemicals used are of analytical grade.

### Preparation of the Materials

#### *Preparation of cellulose fiber*

First, the cellulose pulpboard (100 g) was dispersed in water to form a suspension and stored over night. Then, the suspension was disintegrated in a card breaker (ZBJ-1, Changchun, China) for 10000 revolutions. The suspension was then filtered with a vacuum filter.

Water retention value was calculated from the obtained cellulose fiber (lignocellulosic fibers). First, some samples were taken from the obtained cellulose fiber and weighed [ $M_1$  (g)]. They were then dried in an air oven at 105 °C to constant weight [ $M_2$  (g)]. The water retention value [WRT (%)] was calculated according to Eq. 1

$$WRT = (M_1 - M_2) / M_2 \cdot 100\% \quad (1)$$

In order to get 2.0 g of cellulose fiber, which was used in the next step, the weight of needed damp fiber [ $M_c$  (g)] was then calculated according to Eq. 2

$$M_c = 2.0 / (1 - WRT) \quad (2)$$

#### *Graft copolymerization of butyl acrylate*

Cellulose fiber (2.0 g) and butyl acrylate monomer (3 mL) were taken in 50.0 mL of distilled water in a three-neck flask under nitrogen flow and agitated for 10 min. The cross-linking agent N,N-methylene-bis-acrylamide (0.01 g) and the initiator  $K_2S_2O_8$  (0.05 g) were then added to the flask and ultrasonically processed for various time periods at 70 °C in an ultrasonic bath (Kun Shan, China, 40 KHz) provided by Kun Shan Ultrasonic Instruments Co., Ltd., China. After that, samples were extracted with ethyl alcohol by stirring for 12.0 h to ensure complete removal of the homopolymer, and dried at 50 °C in an air oven.

### Performance and Characterization of the Materials

#### *Adsorption of oils*

The samples were weighted [ $M_3$  (g)] and then placed in benzene or edible oil (sunflower seed oil) for 6 h. They were then packed out and drained for 2 min. After that, they were reweighed [ $M_4$  (g)]. The percentage absorptivity (g/g) was calculated according to Eq. 3.

$$\text{Absorptivity} = (M_4 - M_3) / M_3 \quad (3)$$

### Scanning electron microscope (SEM)

The fracture surfaces of cellulose fiber and cellulose grafted with butyl acrylate (BuAc-cellulose graft copolymer) were studied with a JSM5900 scanning electron microscope (SEM) under an accelerating voltage of 5 kV. Prior to the SEM examination all the surfaces were sputtered with gold.

### FT-IR characterization

FT-IR spectra of the native cellulose fiber and BuAc-cellulose graft copolymer were obtained using dried powdered samples on a Tensor 27 (Bruker, Germany) device in the range of 4,000 to 600  $\text{cm}^{-1}$ . Pellets were prepared from the mixtures of the samples and KBr (1:100 in weight). 32 scans were accumulated at a resolution of 2  $\text{cm}^{-1}$ .

### Thermal analysis

The thermal properties of cellulose fiber and BuAc-cellulose graft copolymer samples weighing between 5 to 10 mg were examined with a TGA (DTG-60, Shimadzu, Japan) device in a temperature range between room temperature (25  $^{\circ}\text{C}$ ) and 600  $^{\circ}\text{C}$  at a rate of 20  $^{\circ}\text{C}/\text{min}$  under nitrogen flow.

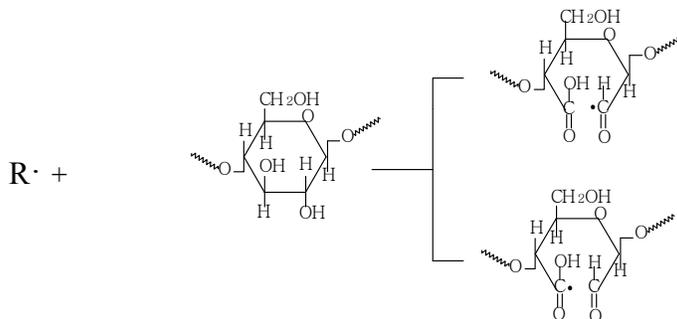
## RESULTS AND DISCUSSION

### Reaction Mechanism

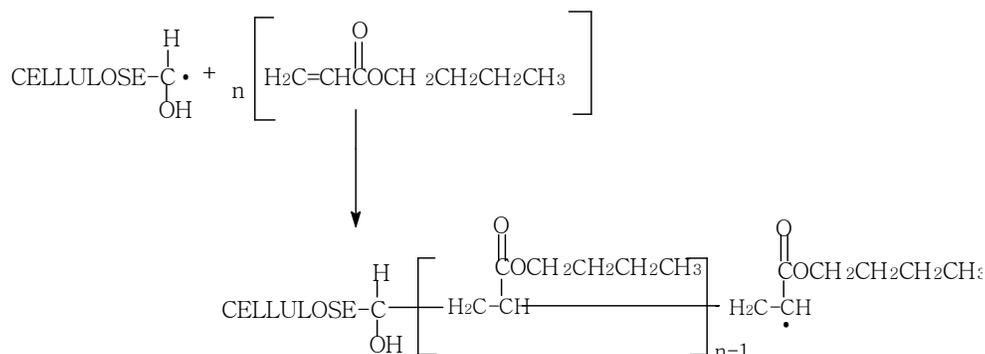
The first step in the mechanism is the generation of radicals by the decomposition of  $\text{K}_2\text{S}_2\text{O}_8$  and the broken of water molecules under ultrasonic waves.



In the active centre formation, the radical ( $\text{R}^{\cdot}$ ) may attack the cellulosic hydroxyl to produce macroradicals:



Once the cellulosic radicals are produced, they react with the monomers to generate the graft copolymer.



### Effects of the Ultrasonic on the Graft Copolymerization

On increasing the duration of ultrasonic treatment from 0 min to 20 min in the 5 h reaction time, the experimental data obtained showed significant differences in the rates of polymerization. The weight of the copolymer increased from 3.65 g. to 4.30 g., which can be attributed to formation with a higher dose of chemical initiator. With a further increase in the total dose of ultrasonic processing time from 20 min to 30 min, the weight of the copolymer increased slowly. The reason may be the limited amount of butyl acrylate monomer, so the chemical initiator obtained from broken water molecules disappeared without initiation reaction. From these results we can conclude that the overall polymerization and the grafting processes with this monomer require a very low dose of ultrasonic processing.

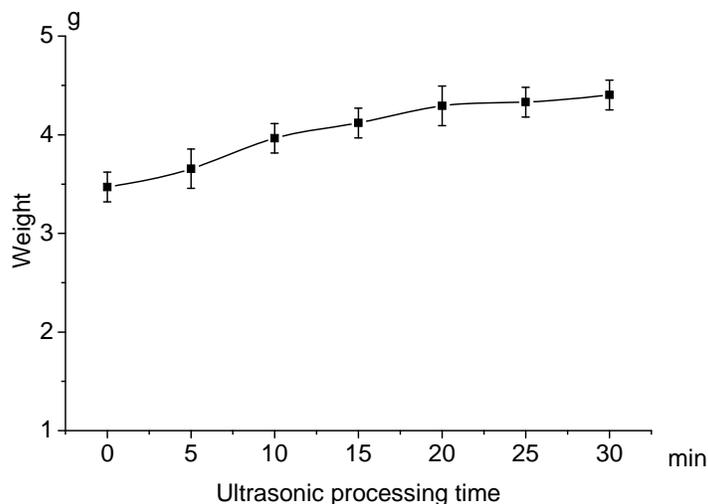
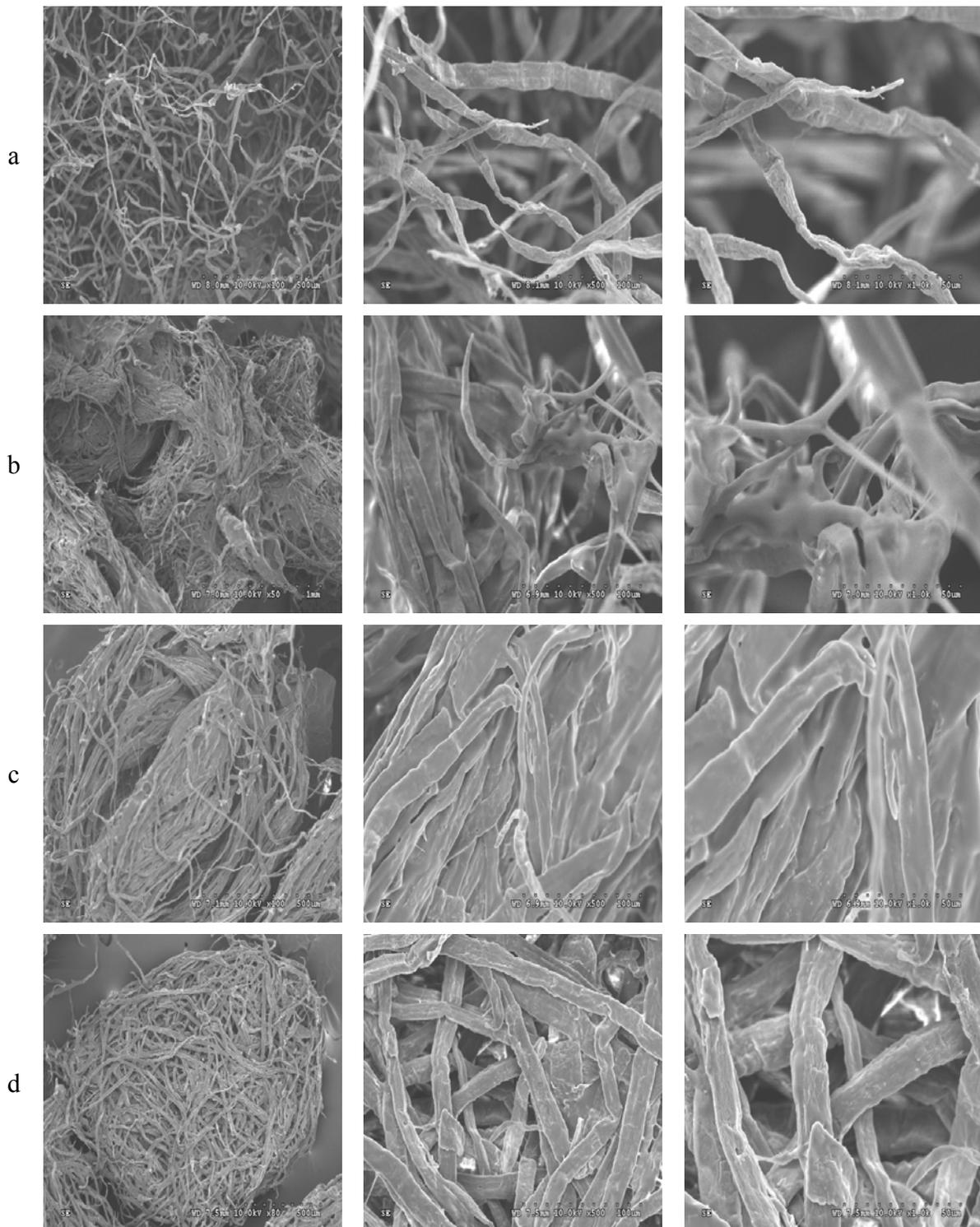


Fig. 1. Effect of ultrasonic dose on product yields

### Structure of Cellulose and the Grafting Copolymerization

The surface structure of the cellulose and the BuAc-cellulose graft copolymer obtained was analyzed using SEM. The results showed that the appearance was affected by ultrasonic treatment time.

The surface morphology of the pure cellulose is shown in Fig. 2a, and the result of BuAc-cellulose graft copolymerization obtained without ultrasonic processing is shown in Fig. 2b. Comparing Fig. 2a and Fig. 2b, one can see a significant difference in

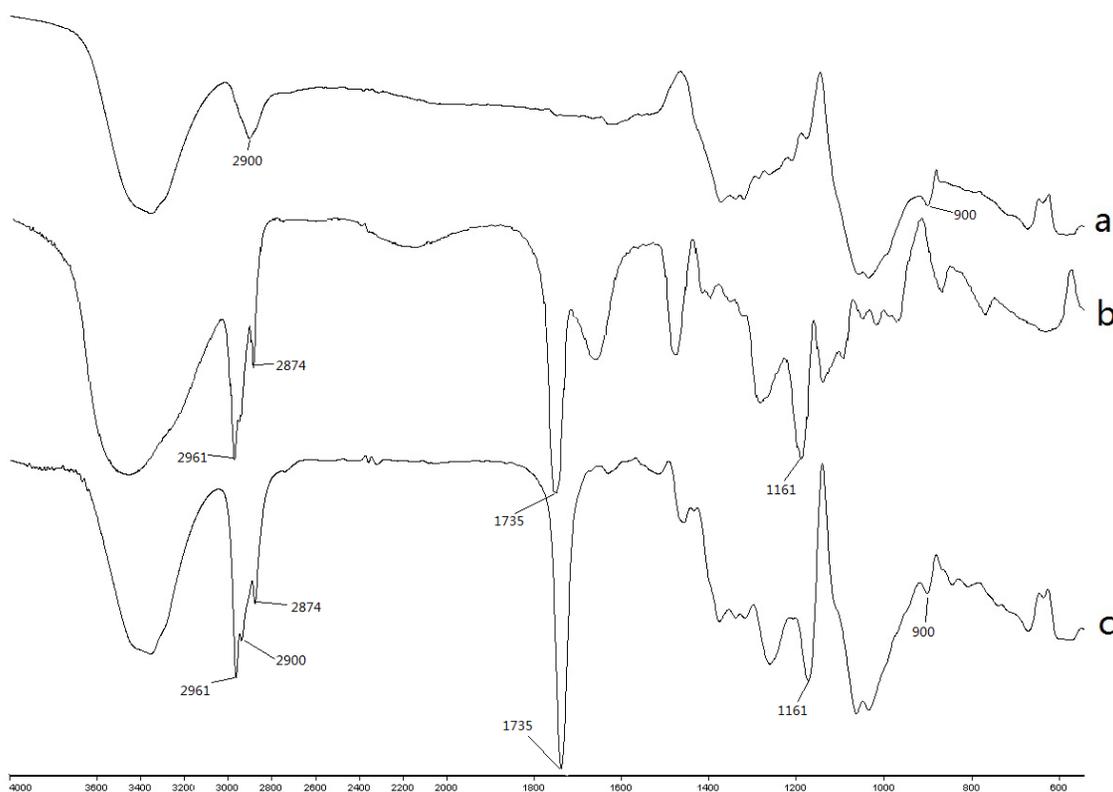


**Fig. 2.** SEM micrographs of surfaces of cellulose fiber (a); BuAc-cellulose graft copolymer without ultrasonic processing (b); BuAc-cellulose graft copolymer with 20 min ultrasonic processing (c); and grafting copolymerization with 5h ultrasonic processing (d)

surface structure. In Fig. 2b the fibroid morphology of cellulose and the polymerization reaction on the surface of cellulose are preserved by grafting copolymerization. Fig. 2c shows the images of BuAc-cellulose graft copolymer with 20 min ultrasonic processing. In Fig. 2c, there is a small difference in the surface morphology compared to Fig. 2b. It can be seen that the surface of the ultrasonic processed material was more regular. Comparing Fig. 2c with Fig. 2d, with the increase of the ultrasonic treatment time, the depolymerization due to the ultrasonic waves was evident. In Fig. 2c, the surface of the cellulose fiber is covered by grafted poly(BuAc) heterogeneously, and some fibers were crosslinked together, just like a block. After a 5 h ultrasonic process the graft copolymer became more homogeneously distributed on the surface of the cellulose, and the material was transformed into a homogeneous network polymer having a good structure for an adsorbing material.

### Fourier Transform Infra-Red Analysis (FT-IR)

Figure 3 shows the FT-IR spectra of cellulose fiber (a), poly(BuAc) (b), and BuAc-cellulose graft copolymer (c). From the spectrum of cellulose fiber (a), it can be seen that the hydrogen bonded -OH stretching is located at 3400 to 3600  $\text{cm}^{-1}$ , the C-H stretching is at 2900  $\text{cm}^{-1}$ , and the C-H bending is at 1370  $\text{cm}^{-1}$ , which represents characteristic peaks of cellulose. The peak at 1058  $\text{cm}^{-1}$  is related to the C-O stretching. The C-H bending and -CH<sub>2</sub> stretching at 900  $\text{cm}^{-1}$  indicate the amorphous structure of cellulose.



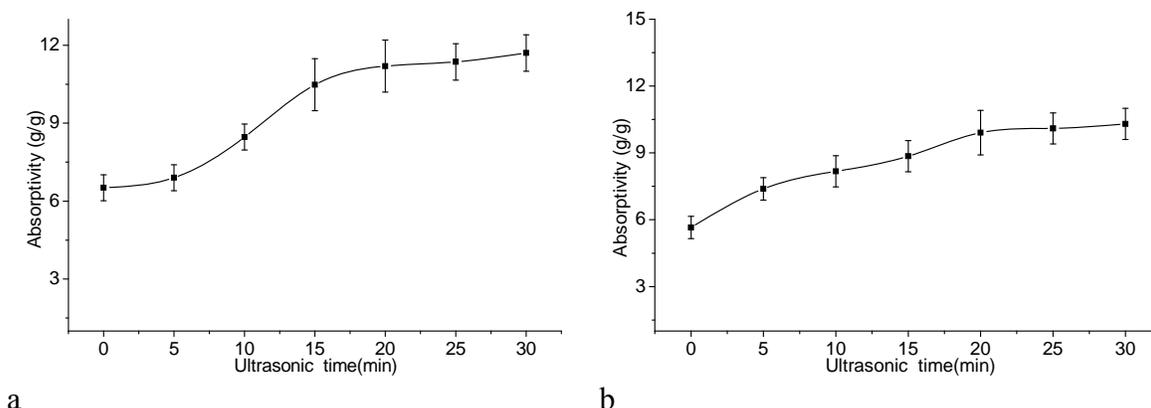
**Fig. 3.** FT-IR of cellulose fiber (a); poly(BuAc) (b) and BuAc-cellulose graft copolymer (c)

Spectrum b shows characteristic peaks of poly(BuAc) molecular structure. The presence of two new peaks at  $2961\text{ cm}^{-1}$  and  $2874\text{ cm}^{-1}$  indicates the presence of the aliphatic chain. A new sharp peak around  $1735\text{ cm}^{-1}$  is due to C=O stretching of an ester. The C-C(=O)-O band of a saturated ester appears at  $1161\text{ cm}^{-1}$ . From spectra of cellulose (a) and BuAc-cellulose graft copolymer (c), besides of the peaks attributed to the stretching of cellulose functionalities, the additional dominant peaks at  $2961\text{ cm}^{-1}$  and  $2874\text{ cm}^{-1}$  indicates the presence of the aliphatic chain,  $1161\text{ cm}^{-1}$  indicates the C-C(=O)-O band of a saturated ester, and  $1735\text{ cm}^{-1}$  is due to the C=O stretching of the ester groups providing evidence of grafting (Ibrahim et al. 2003). From the FT-IR data it can be inferred that the resulting material is a copolymer that is functionalized on the cellulose backbone.

## Oil Absorbency

### *Effects of the Ultrasonic Processing Time*

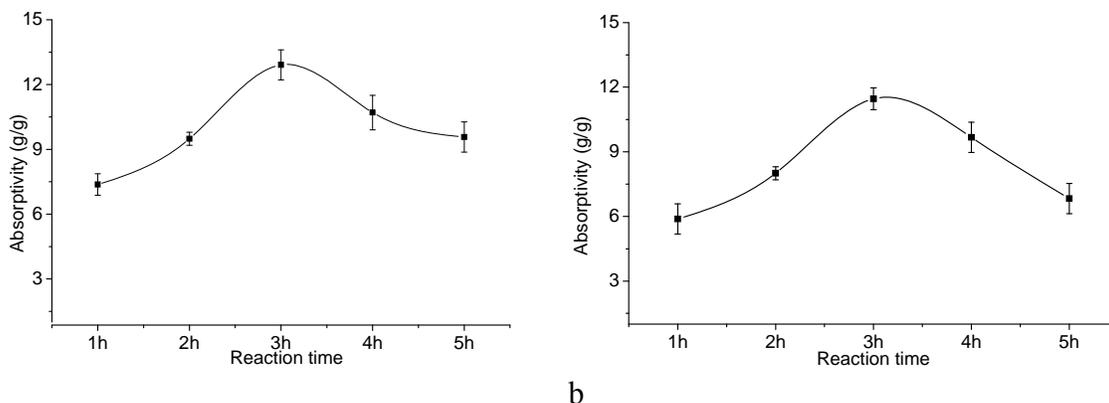
The oil absorbing capabilities of the BuAc-cellulose graft copolymer obtained after 5 h chemical reaction under different ultrasonic processing time are shown in Fig. 4. Clearly, the graft copolymer was more efficient at absorbing oil when the total ultrasonic time increased from 0 min to 20 min. With a further increase of the ultrasonic time after 20 min, the oil absorption rate increased slowly. The increased oil uptake with increasing treatment may be because the grafted poly(BuAc) is hydrophobic and its incorporation onto cellulose renders the product lipophilic. The limited amount of butyl acrylate monomer after 20 min ultrasonic processing makes the oil absorption rate increase only slowly with further ultrasonication.



**Fig. 4.** Oil absorption of BuAc-cellulose graft copolymer under different ultrasonic processing time (a) benzene (b) edible oil

Further insight into the oil absorption capacity of BuAc-cellulose graft copolymer under ultrasonic processing for different total reaction time can be developed from Fig. 5. It is clear that the oil absorptivity increased in first 3 h and then decreased as reaction time increased beyond that point. The reason why the oil absorbing capability increased along with reaction time (below 3 h) is presumed to be the longer reaction time, during which both polymerization and depolymerization occur. The net effect is to facilitate formation of the material into a network polymer structure. The expanding grafted poly(BuAc) and network polymer structure in the graft copolymer lead to an increasing

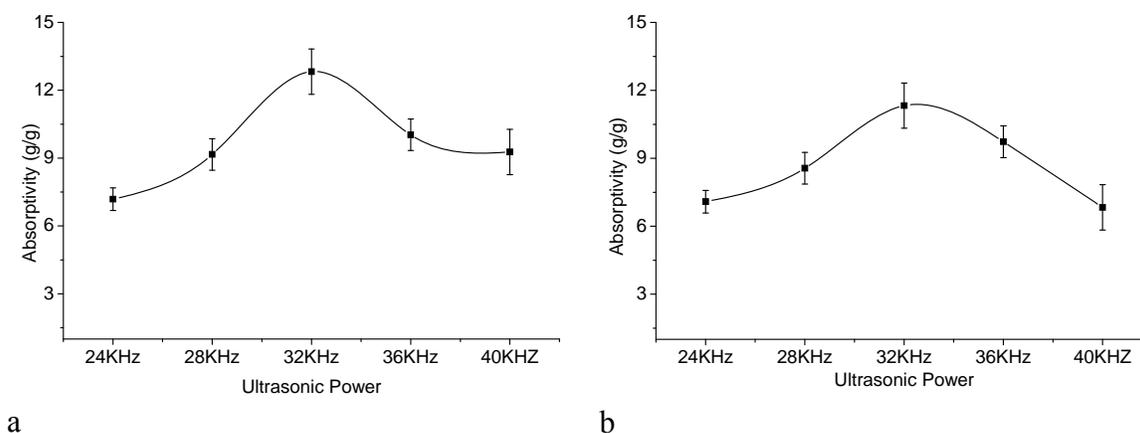
oil absorption rate. However, the polymerization became lower as the extent of reaction increased, and the ultrasonic waves caused depolymerization. Along with the decreasing extent of grafting with poly (BuAc), the extent of oil uptake also decreased.



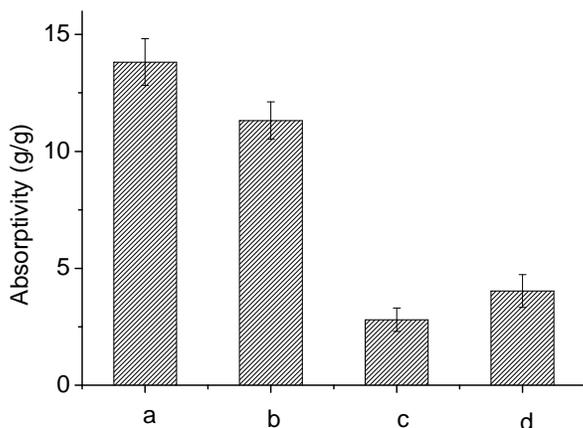
**Fig. 5.** Oil absorption of BuAc-cellulose graft copolymer produced for different reaction time under ultrasonic processing (a) benzene (b) edible oil

#### *Effects of the Ultrasonic Power*

Figure 6 shows the effect of the graft copolymer material produced after 5 h chemical reaction under different ultrasonic powers. The oil absorption rate increased slightly along with the increase of reaction temperature (below 28 KHz). However, after the ultrasonic power reached 32 KHz the oil absorption rate began to decrease. The reason is that under lower ultrasonic power the chemical initiator obtained from broken water molecules stays at a depressed level, and so does the depolymerizing capacity of the ultrasonic waves. As the ultrasonic power is strengthened, the concentration of chemical initiator and the effects of ultrasonic depolymerization are both enhanced at the same time. The change in the depolymerizing capacity of the ultrasonic wave is not significant when the ultrasonic power stays at a lower level. So, oil absorption rate increases at first. When the ultrasonic power reaches a higher level, oil absorption rate begins to drop due to limited monomer and increased ultrasonic depolymerization.



**Fig. 6.** Oil absorption of BuAc-cellulose graft copolymer produced after 5h chemical reaction under different ultrasonic powers (a) benzene (b) edible oil

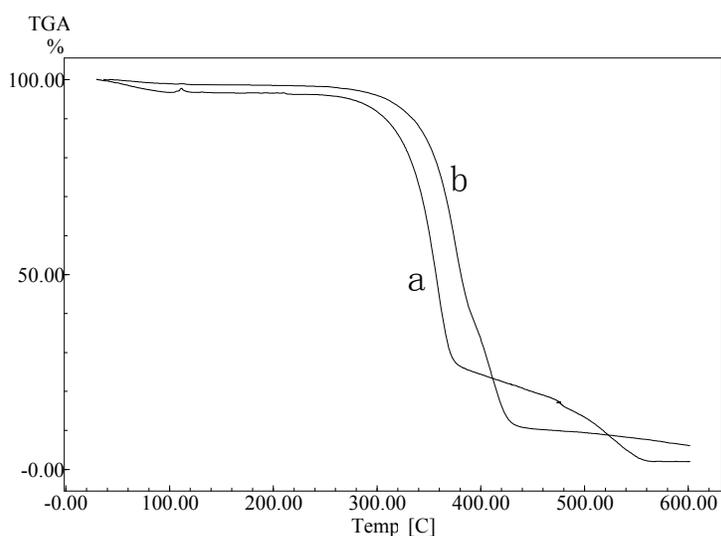


**Fig. 7.** Oil absorption of BuAc-cellulose graft copolymer in (a) benzene (b) edible oil; and of cellulose in (c) benzene (d) edible oil

#### *Effects of the modification*

Figure 7 shows the oil absorption of BuAc-cellulose graft copolymer under the best experimental conditions as well as unmodified cellulose. Obviously, the oil absorptive increases dramatically after the modification. Grafted poly(BuAc) is oleophilic resin, and its incorporation onto cellulose makes BuAc-cellulose graft copolymer lipophilic. Meanwhile the network polymer structure makes copolymer more efficient in oil absorption. The results suggest that the BuAc-cellulose graft copolymer is possibly a good material to be used in oil spill cleanup.

#### **TGA of Cellulose and Graft Copolymer**



**Fig. 8.** TGA curves of cellulose (a) and BuAc-cellulose graft copolymer (b)

The thermogravimetric curves of cellulose fiber and BuAc-cellulose graft copolymer are shown in Fig. 8. Due to the differences in the chemical structures, cellulose fibrils and grafted poly(BuAc) decompose at different temperatures. From curve a, the weight loss started at 275 °C and continued until 375 °C, showing a solid residue at 600 °C. This stage is attributed to the decomposition of cellulose fibrils. From curve b, the weight loss started at 255 °C and continued until 450 °C. The curve indicates that cellulose fibrils were decomposed first. The range from 375 °C to 450 °C represents a weight loss process of grafted poly(BuAc). Comparing curve a and curve b, the decomposition temperature of cellulose fibrils in the copolymer was lower than that of pure cellulose fibrils materials. These results demonstrate that there are interactions between cellulose fibrils and butyl acrylate. The thermogravimetric curve of the graft copolymer does not indicate significant weight loss until the temperature reaches 250 °C. This implies that composite materials can fully satisfy the demands of various applications.

## CONCLUSIONS

A BuAc-cellulose graft copolymer having potential to be used for oil absorption was successfully prepared using an ultrasonic processing method. According to the results of ultrasonic dose tests, a low dose of ultrasonic processing can affect the chemical reaction rate. On increasing the ultrasonic processing time from 0 min to 20 min during a 5 h reaction, the weight of the copolymer increased from 3.65 g to 4.30 g, which was attributed to the in-situ formation of a higher dose of chemical initiator. Simultaneously, according to the oil absorbency tests, with the ultrasonic power being 32 KHz during a 5 h chemical reaction, the oil absorption reached 13.83 g/g (for benzene) and 11.32 g/g (for edible oil), about 3 to 4 times compared with the raw cellulose. Both FT-IR analysis and TGA analysis showed the resulting material is a copolymer of the functionalized on the cellulose backbone. In addition the TGA analysis also showed that composite material is sufficiently thermo-stable to satisfy the demands of various applications. Based on SEM images, a high dose of ultrasonic processing can affect the surface structure of the grafting copolymerization. The surface of the ultrasonic processed material became more regular. The copolymer is more likely to be transformed into a similarity network polymer after ultrasonic processing, and it is more efficient in oil absorption.

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