

# Properties of Regenerated Cellulose Films Plasticized with $\alpha$ -Monoglycerides

Chaobo Xiao, Zhenjun Zhang, Jinhua Zhang, Yongshang Lu, Lina Zhang

Department of Chemistry, Wuhan University, Wuhan 430072, People's Republic of China

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**ABSTRACT:** Regenerated cellulose (RC) films were plasticized with glycerol, glycerin  $\alpha$ -monobutyrate, glycerin  $\alpha$ -monocaproate, glycerin  $\alpha$ -monocaprylate, and glycerin  $\alpha$ -monocaprate. The structure and properties of the films were investigated by using Fourier transform IR, wide-angle X-ray diffraction, differential scanning calorimetry, scanning electron microscopy, and tensile tests. The experimental results showed that the addition of plasticizer enhanced the elongation at break, thermal stability, and crystallinity and lowered the tensile strength of the films. The formation of hydrogen bonds between the cellulose and plasticizers weakened the inter- and intra-hydrogen bonds among cellulose molecules, leading to reduced tensile strength. These  $\alpha$ -monoglycerides have relatively good plasticizing effects.

Compared with glycerol, the resistance against water washing of the synthesized compounds was significantly enhanced. With the increase of the carbochain length of the  $\alpha$ -monoglycerides, the plasticizing effect decreased but the resistance against water washing was enhanced. When the RC films were immersed in a 10% glycerin  $\alpha$ -monocaproate solution, the elongation at break increased to 15% and stayed at 14.8% after water washing. Glycerin  $\alpha$ -monocaproate might be better for plasticizing RC films than others. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3500–3505, 2003

**Key words:** regenerated cellulose; plasticizer;  $\alpha$ -monoglyceride

## INTRODUCTION

Biopolymers from renewable resources have become increasingly important in the development of advanced materials that exhibit high susceptibility to microbial attack.<sup>1</sup> Cellulose, a linear 1.4  $\beta$ -glucan, is the most abundant polymer found in nature.<sup>2</sup> It is produced in a sustainable way and offers many possible uses, because it is renewable and biodegradable. It is possible to base an entire line of chemistry on cellulose.<sup>3</sup> Now scientists have made cellulose into all kinds of films, such as films for hemodialysis<sup>4</sup> and water resistance.<sup>5</sup> Cellulose also has some undesirable properties, such as low tensile strength when wet, high moisture transmission, and low strength against microbial attack.<sup>6</sup> To improve its chemical or physical properties, many studies have been done on cellulose, such as grafting,<sup>7</sup> blending with other polymers,<sup>8,9</sup> and plasticization. Plasticization is a very simple but useful method to improve the mechanical property of a polymer. Glycerol and glycols have been widely used as plasticizers for cellulosic materials. These

compounds are fairly effective but have two major defects, mobility and volatility, and hence are easily lost by migration or evaporation. They are also excessively hygroscopic; hence, their effectiveness varies with the temperature and humidity of the surroundings.<sup>10</sup> Naimak et al.<sup>11,12</sup> used ethylene glycol, glycerol, and H<sub>2</sub>O as cellulose plasticizers and found good plasticizing effects. However, the problem was that the plasticizing effects disappeared when the plasticized films were soaked in water; thus, the problem was not solved. Kaimins<sup>13</sup> used triethylphenylammonium hydroxide as a cellulose plasticizer. The addition of a plasticizer decreased the temperature of its phase transition and promoted relaxation in the amorphous regions of the cellulose. Derivatives of diethanolamine and diethylenetriamine were investigated in our laboratory as plasticizers of regenerated cellulose (RC) film, and they showed good plasticizing effects.<sup>14,15</sup>

In this study we attempted to use  $\alpha$ -monoglycerides as plasticizers of cellulose because monoglycerides have hydrophilic and hydrophobic groups. The structure and physical properties of the plasticized and unplasticized films were studied with Fourier transform IR (FTIR), wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and tensile tests. The effects of various plasticizers on the physical properties of the films and the properties of the plasticized films soaked in water were discussed.

Correspondence to: C. Xiao (cbxiao@whu.edu.cn).

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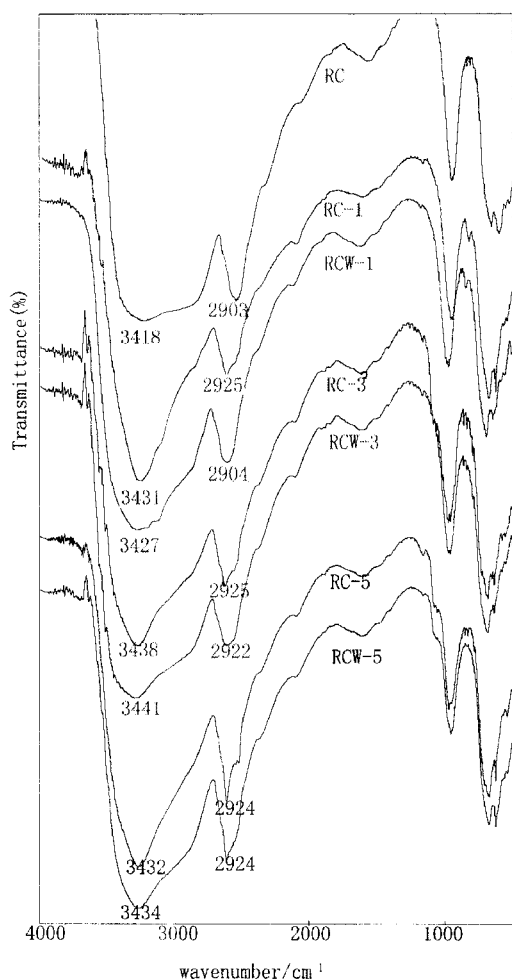


Figure 2 FTIR spectra of the films.

from every solution was dried in air, and another one was soaked in water for 1 h and then dried in air. All films were vacuum dried at room temperature for 12 h. Pure RC films were coded as RC; the RC films plasticized with glycerol, GMBu, GMHexa, GMOcta, and GMDeca were coded as RC-1, RC-2, RC-3, RC-4, and RC-5, respectively. The plasticized films soaked in water were coded as RCW-1, RCW-2, RCW-3, RCW-4, and RCW-5, respectively. The concentration of GMHexa and GMOcta changed from 5 to 10%.

### Characterization

The IR spectra were measured by a Nicolet 170× FTIR spectrometer. The WAXD patterns were recorded with a Rigaku Dmax-II X-ray diffractometer (Japan) using a  $\text{CuK}\alpha$  target at 40 kV and 50 mA. The diffraction angle ranged from  $5^\circ$  to  $40^\circ$ , and the degree of crystallinity ( $X_c$ ) was calculated according to the usual method.<sup>18</sup> The mechanical properties of the films were measured by an electron tensile tester (CMT6202) with a tensile rate of 100 mm/min according to the Chinese standard method (GB4456-84), and we made six mea-

surements for each sample. The surface and cross section of the films were examined with a Hitachi-570 scanning electron microscope (Japan). The films were frozen under liquid nitrogen to fracture and coated with gold under 13.3 Pa vacuum conditions before the SEM experiment. The thermal properties of the samples were measured with a Perkin-Elmer differential scanning calorimeter (DSC-2C) at a heating rate of  $10^\circ\text{C}/\text{min}$  from 50 to  $400^\circ\text{C}$ , and all films were heated to  $200^\circ\text{C}$  to get rid of water before testing.

## RESULTS AND DISCUSSION

### Properties of films

The SEM images of the films are shown in Figure 1. The cross section of the unplasticized RC film was rough, and those of the plasticized films were smooth and compact. After soaking the films in water, those plasticized with glycerol and GMBu became rough. However, the films plasticized with GMHexa, GMOcta, and GMDeca were hardly changed, indicating that the glycerol and GMBu were dissolved in water and lost; but GMHexa, GMOcta, and GMDeca were retained in the films.

FTIR is a useful way to study the molecular structure. The width and intensity of the peaks are sensitive to the environment and conformation of macromolecules at the molecular level.<sup>19</sup> If low weight molecular compounds have a plasticizing effect, intermolecular interaction will occur, resulting in changes in the FTIR spectra of RC. The FTIR spectra of the films are shown in Figure 2. For the unplasticized RC, the characteristic

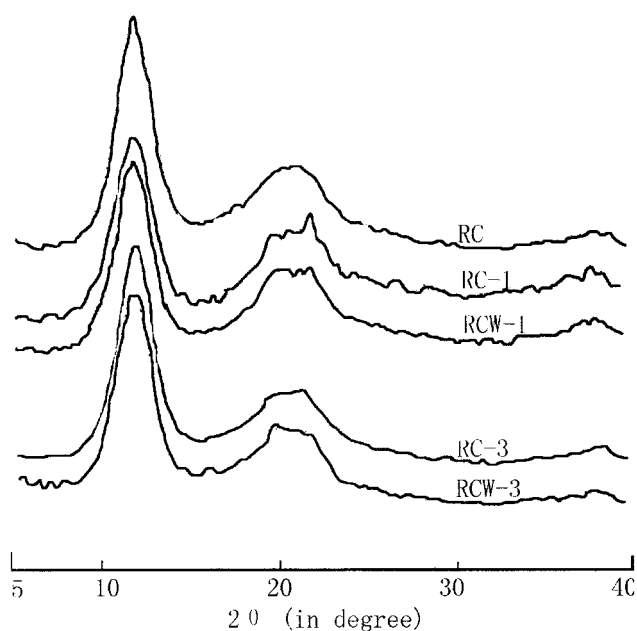


Figure 3 WAXD patterns of RC, RC-1, RCW-1, RC-3, and RCW-3 films.

**TABLE I**  
Crystallinities ( $X_c$ ) of Films

Film No.	$X_c$	Film No.	$X_c$
RC	0.74		
RC-1	0.80	RCW-1	0.74
RC-2	0.75	RCW-2	0.79
RC-3	0.73	RCW-3	0.78
RC-4	0.77	RCW-4	0.78
RC-5	0.78	RCW-5	0.84

absorption appeared at  $1050\text{ cm}^{-1}$  and there were a lot of shoulder peaks. The strong and broad band at  $3418\text{ cm}^{-1}$  and the band at  $2903\text{ cm}^{-1}$  are attributed to  $-\text{OH}$  and  $\text{C}-\text{H}$  stretching vibrations, respectively. Compared with the spectrum of RC, the bands for plasticized films at  $3400\text{ cm}^{-1}$  obviously became sharp and shifted to a higher wavenumber, because of the formation of intermolecular hydrogen bonds between the plasticizer and cellulose and weakened hydrogen bonds among the cellulose molecules. The bands for unplasticized RC at  $2903\text{ cm}^{-1}$  shifted to high wavenumbers at  $2925, 2923, 2925, 2922,$  and  $2924\text{ cm}^{-1}$  for RC-1, RC-2, RC-3, RC-4, and RC-5, respectively; this resulted from the interaction between the plasticizers and  $-\text{CH}_2$  in the cellulose molecules.

If the plasticizer is not retained in the film for some reason, these physical properties of the films will be lost and they will no longer perform their intended functions.<sup>20,21</sup> Plasticizer permanence refers to the ability of a plasticizer to remain stable in a polymer-plasticizer system under different conditions.<sup>22</sup> The IR spectra of the plasticized films soaked in water are shown in Figure 2. After soaking, the  $-\text{OH}$  stretching vibration bands of RCW-1 and RCW-2 shifted to a lower wavenumber compared to RC-1 and RC-2. The spectra of RCW-3, RCW-4, and RCW-5 did not change much compared to the spectra of RC-3, RC-4, and RC-5, respectively, indicating that glycerol and GMBu were dissolved in water and partly lost; but GMHexa, GMOcta, and GMDeca were resistant to water, so they were retained in the RC films.

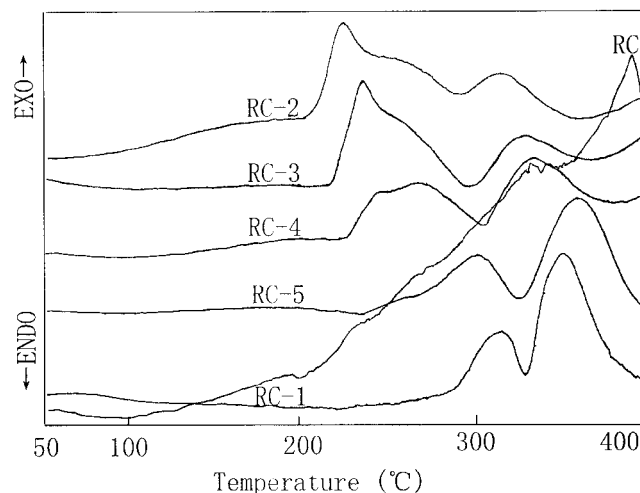
### Crystallinity of films

The X-ray diffraction patterns of plasticized and unplasticized RC films are shown in Figure 3, and the crystallinities of the films were calculated and are shown in Table I. The RC has the crystalline form of cellulose II, showing diffraction peaks at  $2\theta = 12, 20,$  and  $22^\circ$ . The results of the crystallinity calculations showed that the crystallinity of the plasticized RC films is higher than that of the unplasticized one, which may be because the addition of plasticizers made the cellulose molecules more ordered.

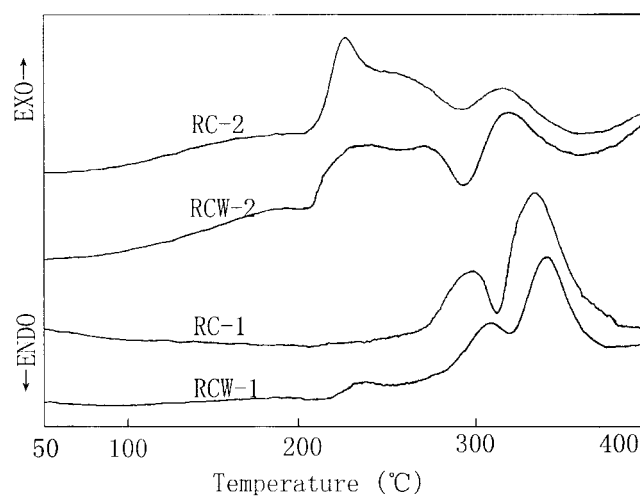
After soaking, the crystallinity of RCW-1 was lower than that of RC-1; but the crystallinities of RCW-2, RCW-3, RCW-4, and RCW-5 were higher than those of RC-2, RC-3, RC-4, and RC-5, respectively, because glycerol dissolved in the water and was lost completely. However, monoglycerides formed strong interactions with cellulose molecules, so they were partly or even completely retained in the films. Moreover, monoglycerides have strong hydrophilic groups to absorb water more easily. Yano and Hatakeyama<sup>23</sup> reported that water was also a good plasticizer for cellulose. The crystallinity of cellulose was increased with the increase of the relative humidity, which is in good agreement with our results.

### Thermal properties of films

The DSC curves of plasticized and unplasticized RC films are shown in Figure 4(a). The onset temperature



(a)



(b)

**Figure 4** DSC curves of the (a) unplasticized and plasticized RC films and (b) plasticized RC films after soaking in water.



of thermal degradation of RC was about 200°C. After plasticization the thermal stability increased, and those plasticized with glycerol were the best. For the four monoglycerides we studied, the onset temperature of thermal degradation of the films was in the order of RC-2 < RC-3 < RC-4 < RC-5. This indicates that the thermal stability of the plasticized RC films was increased with the increase of the carbochain length of the plasticizer, which is attributable to the increased interaction between the plasticizers and RC with the increase of the carbon chain.

The DSC curves of RCW-1, RCW-2, RCW-3, RCW-4, and RCW-5 are shown in Figure 4(b). After the plasticized films were soaked in water, the onset temperature of films plasticized with glycerol decreased remarkably and those plasticized with monoglycerides hardly changed, because glycerol dissolved in the water and was removed from the films. However, the monoglycerides have hydrophobic groups and the interaction between the carbochain of the monoglycerides and the cellulose was strong, so the monoglycerides were retained in the films.

### Mechanical properties

The results of the tensile tests are shown in Table II. The tensile strength and elongation at break of the unplasticized RC films were 68.10 MPa and 6.92%, respectively. The addition of plasticizers lowered the tensile strength and enhanced the elongation at break of the RC films. This can be explained by the fact that the formation of intermolecular hydrogen bonds between the plasticizer and RC weakened the hydrogen bonds among cellulose molecules, and the result was that the micromolecule chains move more easily. Of the five plasticizers we studied, glycerol had the best plasticizing effect. The elongation at break of the films was in the order of RC < RC-5 ≈ RC-4 < RC-3 ≈ RC-2 < RC-1, indicating that, with the increase of carbon chain length of the monoglycerides, the plasticizing effect was decreased. From Table III we can see that the elongation at break values were increased with an increase of the plasticizer contents.

**TABLE II**  
Tensile Strength ( $\sigma_b$ ) and Elongation at Break ( $\epsilon_b$ ) for RC Films

Film No.	$\sigma_b$ (MPa)	$\epsilon_b$ (%)	Film No.	$\sigma_b$ (MPa)	$\epsilon_b$ (%)
RC	68.1	6.9			
RC-1	41.5	25.4	RCW-1	56.6	7.4
RC-2	66.8	13.4	RCW-2	69.6	14.5
RC-3	66.5	12.3	RCW-3	65.1	10.2
RC-4	70.1	9.6	RCW-4	64.3	12.0
RC-5	66.9	8.6	RCW-5	55.9	7.8

**TABLE III**  
Tensile Strength ( $\sigma_b$ ) and Elongation at Break ( $\epsilon_b$ ) for RC Films with Different Contents of Plasticizer

Film No.	Concentration (5%)		Concentration (10%)	
	$\sigma_b$ (MPa)	$\epsilon_b$ (%)	$\sigma_b$ (MPa)	$\epsilon_b$ (%)
RC-3	65.1	10.2	68.0	15.2
RC-4	64.3	12.0	64.5	14.0
RCW-3	66.5	12.3	67.4	14.8
RCW-4	70.1	9.6	68.3	14.2

Table II lists the mechanical properties of the plasticized RC films after soaking in water. The mechanical properties of RCW-1 are almost the same as those of RC, indicating that glycerol dissolved in the water and was removed from the RC film, so the plasticizing effect disappeared. The mechanical properties of the RC films plasticized with monoglycerides hardly changed, suggesting that monoglycerides were retained in these films. Thus, these synthetic plasticizers have better resistance against water washing than glycerol.

### CONCLUSION

The four  $\alpha$ -monoglycerides that we synthesized exhibited relatively good plasticization of RC films and good resistance against water washing. The addition of plasticizers decreased the tensile strength and enhanced the elongation at break of RC films, which was due to the formation of intermolecular hydrogen bonds between the plasticizers and RC, which weakened the hydrogen bonds among the cellulose molecules. The crystallinity and thermal stability increased after the films were plasticized. Compared with glycerol, the plasticizing effect of monoglycerides decreased and was in the order of RC-5 ≈ RC-4 < RC-3 ≈ RC-2 < RC-1. However, the resistance against water washing was enhanced significantly and increased with the increase of the carbochain length. The results indicated that GMHexa might be better than others.

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