Dissolving of cellulose in PEG/NaOH aqueous solution

Lifeng Yan · Zhijuan Gao

Abstract Here, a new solvent system for cellulose is reported. The solvent is a mixed aqueous solution of 1.0 wt.% poly(ethylene glycol) (PEG) and 9.0 wt.% of NaOH. Cellulose powder was added into the mixture at room temperature at first, and freezing it at −15 °C for 12 h following a thaw of the mixture at room temperature under strong stirring. There formed a clean solution of cellulose, and the optical microscopy was used to record the dissolving process. ^{13}C-NMR, FT-IR, XRD, and intrinsic viscosity measurements revealed that there forms a homogeneous solution of cellulose in the new solvent system. The maximum solubility of cellulose with average molecular weight of 1.32×10^5 g mol^{-1} in the solvent system is 13 wt.%. The cellulose solution in the new solvent system is stable, even for 30 days storage at room temperature.

Keywords Cellulose · Aqueous solution · Dissolving

Introduction

As the affluent biopolymer resource in the world, cellulose has attracted much attention for preparing novel polymers and materials (Rosenau et al. 2006; Nishio 2006; Klemm et al. 2006). However, a bottle-neck question to cumber the application of it is the dissolving of cellulose in a simple solvent system. The existence of the crystalline of cellulose makes it difficult to dissolve. Although some solvent systems had been found in the past century, such as ammonium thiocyanate (Degroot et al. 1986), calcium and sodium thiocyanate (Hattori et al. 1998), lithium chloride/ *N,N*-dimethylacetamide (LiCl/DMAc) (McCormick et al. 1985; Ramos et al. 2005), and NH$_3$/NH$_4$SCN (Cuculo et al. 1994) etc. Most of them are limited in a laboratory scale or result in serious environmental problems. Recently, a little green solvent systems have been developed by different groups which include *N*-methylmorpholine-*N*-oxide (NMMO) (Schrempf et al. 1995), ionic liquid (Swatloski et al. 2002), and water-based solvent systems (Isogai and Atalla 1998). Since the discovery of cellulose can be dissolved in a NaOH aqueous solution by freezing the suspension into an ice-state following a thawing process at room temperature, it opens new chance to dissolve cellulose in aqueous solution. Recently, efforts have also been done on understanding why the dissolving of cellulose in the alkali aqueous solution needs a precooling process. Solid-state ^{13}C-NMR (Porro et al. 2007), low temperature DSC (Roy et al. 2001), small-angle X-ray scattering (Egal et al. 2007), and synchrotron radiation microdiffraction (Schoeck et al. 2007) studies revealed that the Na-cellulose complex and the hydration of alkali ions formation are the key factors to the

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dissolving mechanism. The results also showed that the solubilization of cellulose is limited into a very narrow region of 8–9 wt.% NaOH and at temperature of 4 °C and below is quit remarkable. In additional, the solubility of cellulose in NaOH aqueous solution is low, typically only 5–6% for wood pulp, which limits the application of the solution. The other problem for the solvent system is the stability of the solution, and it usually result in the formation of gel in a short period of storage at room temperature. So, a number of additives have been tested to increase the solubility and stability of cellulose in the NaOH aqueous solution.

Lately, Zhang et al (2002; Cai and Zhang 2005) have found that cellulose can be easily and quickly dissolved in any of the pre-cooled aqueous solution of LiOH/urea, NaOH/urea or NaOH/thiourea, and produce stable cellulose solution. The role of urea and thiourea are believed the acceptor of hydrogen-bonding, which connect to the hydroxyl groups in cellulose and prevent the regeneration of cellulose through the inter- and intra-chains association. Our recent studies revealed that there exists a synergic interaction of NaOH and thiourea during the dissolving process of cellulose (Yan et al. 2007). In theory, the molecules with hydrogen-bonding acceptor are a possible candidate to stable the cellulose solution.

Poly(ethylene glycol) (PEG) is a typical environmental benign molecule, and its aqueous solution, especially the PEG-base aqueous biphasic systems (ABSs), such as the mixture of PEG with NaOH, Na_2S, Na_2CO_3 etc., are regarded recently as a potential green solvent system (Chen et al. 2005), which had been applied in both separation lignin from wood and organic reactions.

The repeat unit of PEG is –(CH_2–CH_2–O)–, and the oxygen atoms in the PEG chain are the hydrogen-bonding acceptor, which maybe an alternative regent to urea or thiourea to stable the cellulose solution. In this study, the mixture aqueous solution of NaOH and PEG was employed to work as a new solvent system for cellulose.

Experimental section

Materials

Cellulose powder ($M_\eta = 1.32 \times 10^5$ g mol^{-1}, Shanghai Hengxin Chemical Reagent Co., Ltd).

Sodium hydroxide and PEG-2000 were purchased from the Sinopharm Chemical Reagent Co., Ltd, and were used without further treatments. Ultrapure water with resistivity of 18 MΩ cm was produced by a Milli-Q (Millipore, USA) and was used for solution preparation.

Dissolution of cellulose in PEG/NaOH aqueous solution

Cellulose was dried in vacuum at 35 °C overnight before use. One gram of PEG-2000 and 9.0 g of NaOH were added into 90 ml of ultrapure water to prepare the mixture aqueous solution of PEG/NaOH. Then 1.0–13.0 g of cellulose was added to the mixture and swell for 3 h at room temperature. Then the suspension was cooled down to −15 °C and held at that temperature overnight (12 h) until it became a solid frozen mass. The frozen solid was then allowed to thaw out at room temperature under strong stirring, and at the end a homogeneous cellulose solution was obtained.

Characterization

The regeneration of cellulose was carried out by adding 1 N HCl into the cellulose solution, after washing by ultrapure water and it was dried in vacuum. The FT-IR spectra of the cellulose powder and regenerated cellulose were measured by using a Bruker spectrometer (KBr). ^{13}C-NMR spectrum of the cellulose solution was measured on a Bruker spectrometer (Avance 300, 300 MHz). D_2O was used instead of H_2O to dissolve the cellulose and to make the NMR measurement directly.

Wide-angle X-ray diffraction (XRD) analysis of the cellulose samples was carried out on an X-ray diffractometer (D/MAX-1200, Rigaku Denki Co. Ltd., Japan) by a reflection method using a Cu Kα target at 40 kV and 30 mA. The diffraction angle ranged from 10° to 40°. All samples were ground into particle-like size to erase the influence of the crystalline orientation of each sample.

The viscosity of the cellulose in 9.0 wt.% NaOH/1 wt.% PEG aqueous solution was measured at 25 ± 0.1 °C with an Ubbelohde viscometer. The intrinsic viscosity ([η]) and Huggins constant (k') were estimated by Huggins and Kraemer plots. In addition, the viscosity of the cellulose samples in LiCl/DMAc at 25 °C were also measured, and their

M_η were calculated by the following equation (McCormick et al. 1985):

$$[\eta] = 1.278 \times 10^{-4} M_\eta^{1.19} \ (\text{ml g}^{-1})$$

The optical images of the cellulose solution were determined by pipetting 50 μl of the solution onto a clean glass following covered by another glass slide to form a middle liquid layer of cellulose solution between two glass slides. Then the samples were measured by a polarized optical microscopy (POM) (LW200-PC, Cewei, Shanghai) at room temperature.

A Shimadzu SEM (Superscan SSX-550, Japan) was used for the space resolved analysis. The apparatus is equipped with a low vacuum system which allows direct measurement of sample without gold coating. The backscattered electron images were recorded at low vacuum. The sample was prepared by depositing 50 μl of cellulose solution onto freshly cleaved mica and spin coated at 3,000 rpm for 60 s.

Results and discussion

Figure 1 shows the photo of the dissolved cellulose in PEG/NaOH aqueous solution (a) and the regeneration


Fig. 1 The photos of cellulose aqueous solutions in 1.0 wt.% PEG/9.0 wt% NaOH (**a**) and the regeneration of cellulose by adding dilute HCl acid (**b**)

of cellulose (b) by adding dilute HCl aqueous solution into it. Clearly, the cellulose solution is transparent at the beginning and some white cellulose aggregates appear after adding acid, indicating the regeneration of cellulose.

The dissolving process of cellulose in the new solvent system can be detected by polarized optical microscopy (POM). As shown in Fig. 2, before dissolving the cellulose exists in aggregative state, and the size of the aggregates is about several micrometers in diameter and tens micrometers in length. However, the big aggregates disappear (Fig. 2b) after a cooling-thaw treatment of the cellulose in the 1.0 wt.% PEG/9.0 wt.% NaOH aqueous solution, and at the end there forms clean solution with some air bubbles under the strong stirring (Fig. 2c), indicates the completely dissolving of cellulose. If the solution was dried in air, cellulose should be regenerated and there forms many small aggregates as shown in Fig. 2d. The size of the new formed aggregates is much smaller than the original ones, and the fractal aggregates also indicates the well dissolving of cellulose in the solution before drying.

To investigate the state of cellulose molecules in the solvent system, D_2O was used instead of H_2O to dissolve cellulose directly and the concentration of cellulose is 4.0 wt.%. Figure 3 shows the ^{13}C-NMR spectrum of the cellulose solution at room temperature. Table 1 shows the summaries the chemical shifts of the cellulose solution in the aqueous PEG/NaOH solution and other solvent systems (McCormick et al. 1985; Zhang et al. 2001; Sun et al. 2001). Comparing with the ^{13}C-NMR of cellulose I, the chemical shifts of cellulose in PEG/NaOH aqueous solution obviously shift to a higher magnetic field. The peaks locate at 103.9 ppm, 79.2 ppm, the double peaks at 75.5, 74.2, and 60.9 ppm are assigned to the C1, C4, C3,5, C2, and C6 carbon in cellulose, respectively (Zhang, et al. 2002). The shift of C4 indicates that the intramolecular hydrogen bonds in cellulose were destroyed, and it is similar to that of wood pulp dissolved in LiCl/DMAc (McCormick et al. 1985). The peak locates at 69.6 ppm is assigned to the carbon in PEG chain. So it can be concluded that the added cellulose was dissolved in the solution. The results reveal that the 1.0 wt.% PEG-2000/ 9.0 wt.% NaOH aqueous solution is a direct cellulose solvent rather than a derivative aqueous solution system.

Fig. 2 Polarized optical microscopy (POM) images of cellulose before dissolving (**a**), after a cooling–thaw treatment in 1.0 wt.% PEG/9.0 wt.% NaOH aqueous solution (**b**), the as-prepared cellulose solution under strong stir with air bubbles (**c**), and the regenerated cellulose particles after the evaporation of water (**d**)
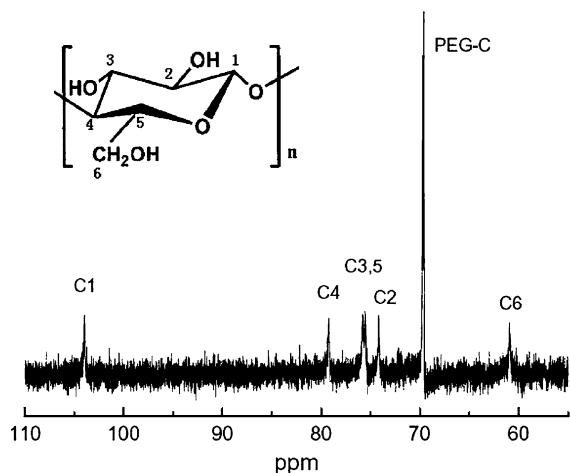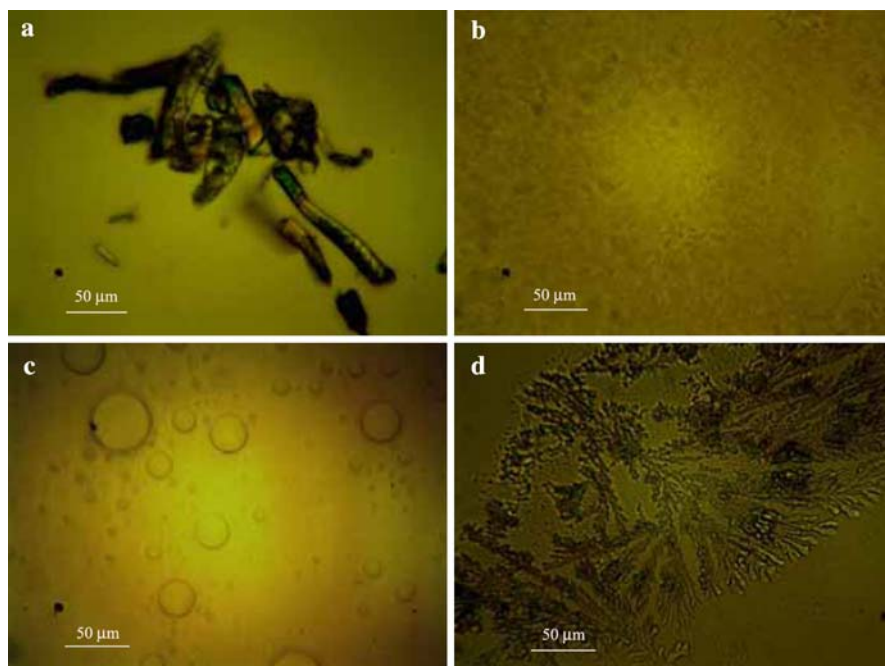

Fig. 3 ^{13}C-NMR spectra of 4.0 wt.% cellulose in 1.0 wt.% PEG/9.0 wt.% NaOH/D$_2$O aqueous solution

Figure 4 shows the WAXD curves of the cellulose (curve 1) and the regenerated cellulose (curve 2) from its PEG/NaOH solution. In curve 1, the diffraction peak at $2\theta = 15.4^{\circ}$ was the superposition of $(1\bar{1}0)$ and (110) planes, the peak at $2\theta = 22.7^{\circ}$ was for (200) plane, these peaks are the characteristics for cellulose I crystal. In curve 2, the peaks at $2\theta = 12.3^{\circ}$, 20.3°, and 22.1° for $(1\bar{1}0)$, (110), and (200) planes are characteristic for cellulose II crystal (Zhou et al. 2004). Both the WAXD curves and the IR spectra indicate a typical regeneration of the cellulose from its solution, transition of cellulose I to II has occurred during the dissolution process.

The dissolved cellulose can be regenerated by adding dilute HCl. After washing and dried, the regenerated cellulose powder was obtained. Figure 5 shows the FT-IR spectra of the cellulose (curve 1),

Table 1 ^{13}C-Chemical shifts of C1, C4, C3,5, C2, and C6 for the cellulose in 1.0 wt.% PEG-2000/9.0 wt.% NaOH and other solvent systems

| Samples	Chemical shifts (ppm)				
	C1	C4	C3, C5, C2	C6	Source
Cotton linters dissolved in 6 wt.% NaOH/4 wt.% urea	103.9	79.2	75.7, 74.0	60.7	Zhang et al. (2001)
Cellulose dissolved in LiCl/DMAc	103.0	79.6	76.6, 74.4	60.7	McCormick et al. (1985)
Cellulose dissolved in 9 wt.% NaOH/1 wt.% PEG	103.9	79.5	75.5, 74.2	60.9	This work
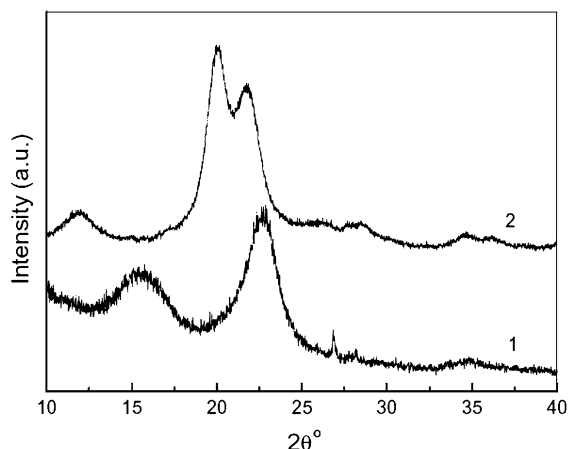
Fig. 4 XRD patterns of the cellulose (curve 1) and regenerated cellulose (curve 2) from its PEG/NaOH aqueous solution
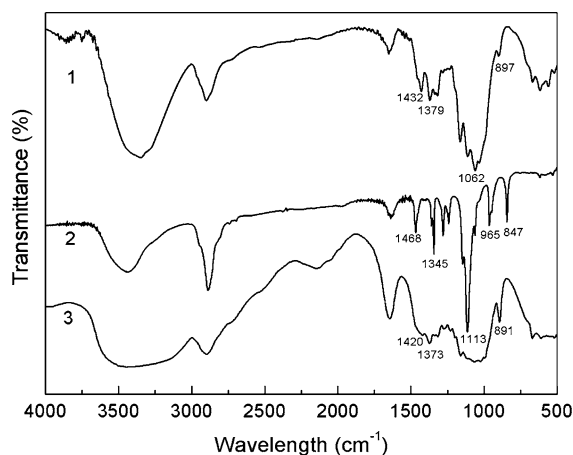
Fig. 5 FT-IR spectra of the cellulose (curve 1), PEG-2000 (curve 2), and regenerated cellulose (curve 3) from its PEG/NaOH aqueous solution

PEG-2000 (curve 2) and the regenerated cellulose from its PEG/NaOH solution (curve 3). Comparing curve 1 to curve 3, it can be found that the two curves owns near the same shape, but the characteristic band at 1432 cm^{-1} (curve 1) for cellulose I shifts to 1420 cm^{-1} (curve 3) for regenerated cellulose, indicating the formation of cellulose II. The shift is attributed to the change in the form of rotamers of the hydroxyls in positions "3" and "6" (corotations around bonds C3–O3 and C6–O6) (Sun et al. 2001). In addition, the band at 897 cm^{-1} also increases, which corresponds to the vibration band of C5 and C6. The results reveal that after regeneration the
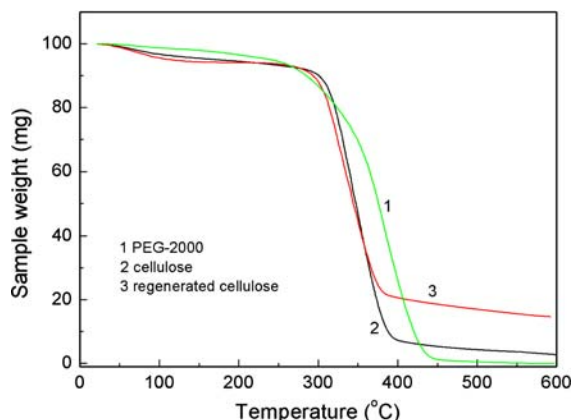

Fig. 6 Thermal analysis of PEG-2000, the original cellulose and regenerated cellulose

crystalline of cellulose take place a change from cellulose I to cellulose II (Zhang et al. 2002), and it also indicates that cellulose dissolved well in the aqueous PEG-2000/NaOH solvent system. However, comparing the curve 3 and curve 2, it also can be found that there are trace of PEG residue in the regenerated cellulose.

Figure 6 shows the thermal analysis of the PEG-2000, cellulose and regenerated cellulose. The degradation of PEG-2000 takes place between 250 and 450 °C, while cellulose takes place degradation between 298 and 397 °C. For the regenerated cellulose the TGA curve is near the same to the original cellulose but gives a higher char yield on pyrolysis, indicates a high residual masses after the decomposition. The result also the reveals that the regenerated cellulose are relative pure, and most of PEG was removed.

Here, three aqueous solvent systems for cellulose were studied for comparison, and they are the 9.0 wt.% NaOH aqueous solution, 6.0 wt.% NaOH/4.0 wt.% urea aqueous solution, and 1.0 wt.% PEG-2000/9.0 wt.% NaOH aqueous solution. Figure 7 shows the photos of them at different periods of storage. The 9.0 wt.% NaOH aqueous solution and 1.0 wt.% PEG/9.0 wt.% NaOH aqueous solution without cellulose are also shown in Fig. 7a. Figure 7b–d are the fresh 4 wt.% cellulose solutions in PEG/NaOH, NaOH and NaOH/urea systems, respectively. All the three solutions are flowing. However, after 4 days of storage at room temperature, there forms gel from the cellulose solution in 9.0 wt.% NaOH, while the solutions of cellulose are still flowing
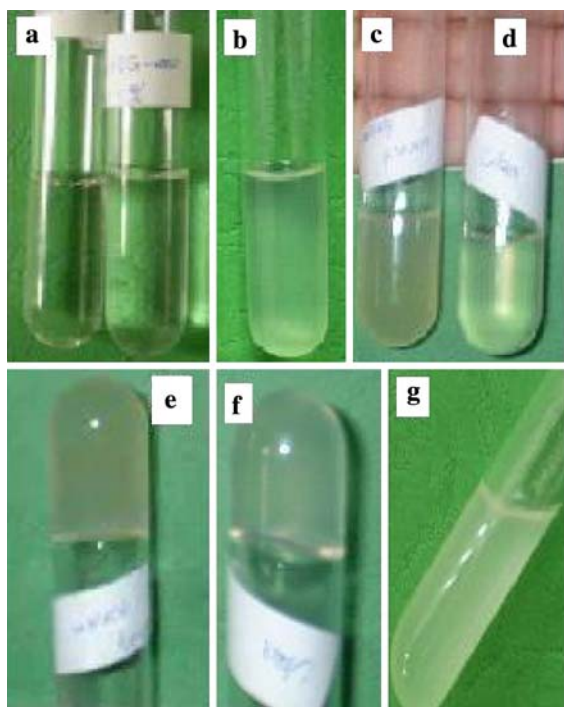
Fig. 7 Photographs of: (**a**) 9.0 wt.% NaOH aqueous solution (left) and 1.0 wt.% PEG/9.0 wt.% NaOH aqueous solution (right); (**b**) fresh 4.0 wt.% cellulose aqueous solution in 1.0 wt.% PEG/9.0 wt.% NaOH; (**c**) fresh 4.0 wt.% cellulose aqueous solution in 9.0 wt.% NaOH; (**d**) fresh 4.0 wt.% cellulose aqueous solution in 6.0 wt.% NaOH/4.0 wt.% urea; (**e**) gel formed after 4 days storage of the cellulose aqueous solution in 9.0 wt.% NaOH; (**f**) gel formed after 11 days storage of the cellulose aqueous solution in 6.0 wt% NaOH/4.0 wt.% urea; (**g**) the cellulose aqueous solution in 1.0 wt.% PEG/9.0 wt.% NaOH after 11 days of storage at room temperature

and homogeneous in both aqueous solutions of 6.0 wt.% NaOH/4.0 wt.% urea and 1.0 wt.% PEG/9.0 wt.% NaOH. It indicates that both urea and PEG-2000 have ability to stable the cellulose solution. Continually, after storage at room temperature for 11 days the cellulose solution in aqueous NaOH/urea forms gel (Fig. 7f) while the cellulose solution in PEG/NaOH is still flowing (Fig. 7g), indicates PEG-2000 is a much better stable reagent than urea for cellulose solution. The experimental result shows that the cellulose solution with PEG-2000 is stable at least for 30 days, which is attractive for its potential application. The reason maybe that PEG-2000 is a polymer with flexible chain and the motility of its basic units are limited in the chain. After cellulose dissolving, the PEG molecules maybe form new complex by

entanglement with cellulose which prevent the association of cellulose molecules, and it is also difficult to extrude them out again from the entangling complex dues to the chain limit and make the cellulose solution stable. However, urea and thiourea are small molecules, which are easily extruded out than PEG-2000 by the self-association of cellulose. The mechanism is still under investigation.

The stability of cellulose solution is another key index to evaluate the solvent system. Generally, the cellulose solution is unstable, and the self-association of cellulose chain always results in the gelation. For example, the 4.0 wt.% cellulose solution in NaOH/urea forms hydrogel after storing at 8 °C for 4 days (Cai and Zhang 2006). However, in our new solvent system, the cellulose solution is much stable. Figure 8 shows the 4.0 wt.% cellulose solution in 1.0 wt.% PEG-2000/9.0 wt.% NaOH after storage at room temperature in air for 30 days. Clearly, the solution is still flowing. Figure 8b shows the POM image of the solution between two glass slides, and there are no obvious aggregates appear. After deposited the cellulose solution onto surface of freshly cleaved mica, the SEM image (Fig. 8c) shows many small aggregates and they are the regenerated cellulose particles after the evaporation of solvent.
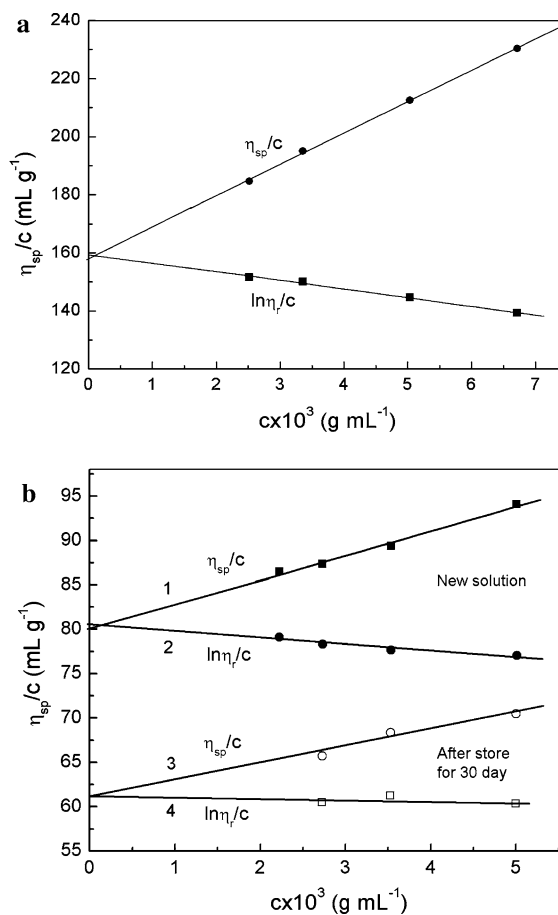
The PEG/NaOH aqueous solution system owns powerful dissolving ability for cellulose. In this study, the maximum solubility of the 1.0 wt.% PEG-2000/9.0 wt.% NaOH aqueous solution for the cellulose with average molecular weight of 1.32×10^5 g mol^{-1} is 13 wt.%.

Figure 9 displays the Huggins and Kraemer plots for the cellulose in 9% LiOH/DMAc solution (Fig. 9a) and 1.0 wt.% PEG/9.0 wt.% NaOH aqueous solution at 25 °C, respectively. The Huggins plots and the Kraemer plots had good intersections at $(0, \eta)$ for both systems, and it also indicates that the PEG/NaOH system is a good solvent for cellulose. From Fig. 9a, the average molecular weight of the cellulose can be calculated and the value is 1.32×10^5 (g mol^{-1}). Compared to the intrinsic viscosity for the two solvent systems, it can be concluded that the cellulose molecules in PEG/NaOH aqueous solution are less expanded than in DMAc/LiCl. As stated before, the cellulose solution in PEG/NaOH is still flowing after 30 days of storage at room temperature, and the Huggins and Kraemer plots were also measured. As shown in Fig. 9b, there are still good
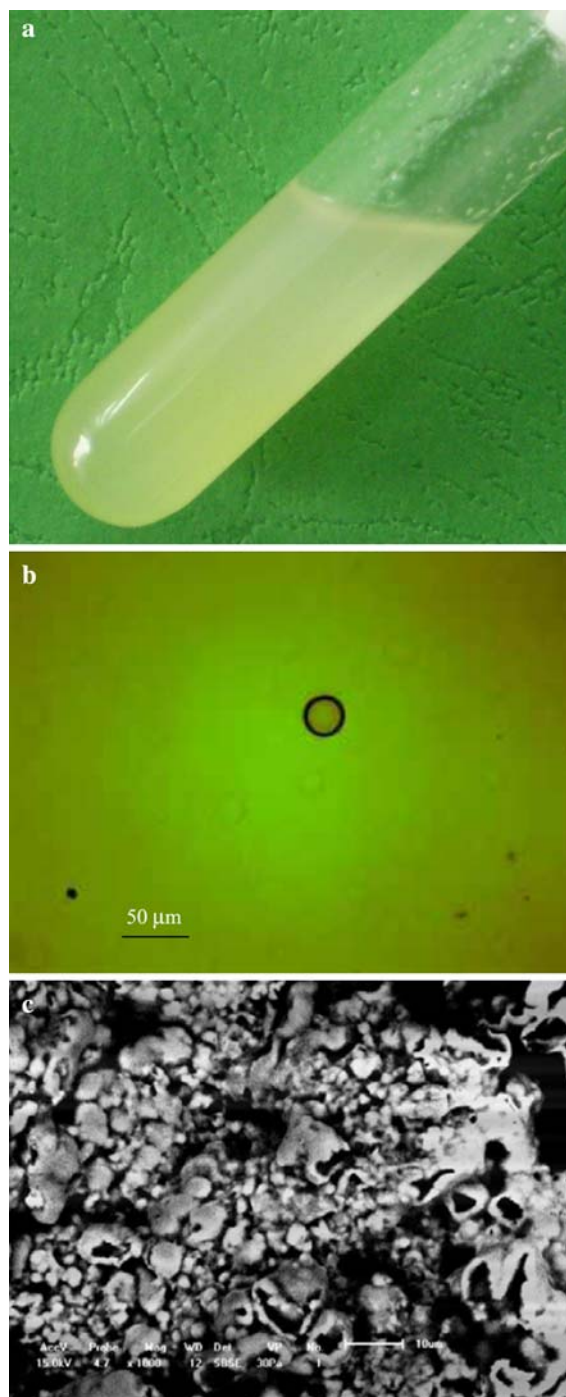
Fig. 8 Photo (a), POM (b) and SEM images (c) of the 4.0 wt.% cellulose solution in PEG-2000/NaOH after storing at room temperature for 30 days

Fig. 9 Intrinsic viscosity ([η]) dependence on concentration (c) of the cellulose in 9 wt.% DMAc/LiCl solution (a) and 1 wt.% PEG/9 wt.% NaOH aqueous solution (b) at 25 °C. The curves 1 and 2 are for cellulose solution as-prepared, and the curves 3 and 4 are for cellulose solution after 30 days store at room temperature

linear relation between [η] and the concentration (c), indicating the good dissolving of cellulose in the solution. However, the values of [η] become smaller comparing to the fresh solution. A slight degradation on the molecular weight took place and the M_η for the regenerated cellulose is 1.26×10^5. In additional, the dynamic rheological experiments should be done in near future to understand its solution behavior.

Conclusion

In conclusion, here we report a new solvent system for cellulose, the aqueous solution of 1.0 wt.% PEG/9.0 wt.% NaOH, in which cellulose can be well dissolved and forms a homogeneous solution with a long period of stability. The role of PEG molecules is believed the hydrogen-bonding acceptor that prevent

the re-association of hydroxyl groups of cellulose to form gel. It is also believed that the chain of PEG make its repeat units difficult to be extruded out from the solution than small molecules such as urea or thiourea by the self-association of cellulose molecules, which results in the stable of the cellulose solution. Furthermore investigation include dynamic rheological experiments and laser light scattering will be done to study the new solvent system.

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