Intermediate Physical State of Gel And LC In Cellulose Solution And Its Synergetic Effects

Taeho Kim

Konkuk University

Younghan Song

Konkuk University

Jungbin Ahn

Konkuk University

Minhyung Kim

Konkuk University

Hyungsup Kim (✉ iconclast@konkuk.ac.kr)

Konkuk University <https://orcid.org/0000-0002-9326-9943>

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Abstract

In this study, the physical state of cellulose in solution was analyzed via rheological observations under three different conditions, i.e. steady state, small amplitude oscillatory shear, and large amplitude oscillatory shear conditions. The physical states of the solution were changed from isotropic phase to gel structure via liquid crystalline (LC) phase as the concentration increased. The rheological analysis showed that the solution of 16 wt% was physically gelled at the anisotropic phase. This instantaneous gelation at the LC phase dramatically enhanced the mechanical performance of the film obtained from the solution. The study provides a fundamental strategy for the huge improvement of the mechanical properties of the cellulose fibers or films.

Introduction

For sustainable development, researchers put a huge amount of effort to find alternatives to petroleum-based polymers. Among eco-friendly and bio-comparable polymers, cellulose gains more attention due to its abundancy, high mechanical strength, and biocompatibility (Ahn et al. 2012; Ahn et al 2016; Chiellini and Solaro 1996; El-Sakhawy and Hassan 2007; Siró and Plackett 2010). It has been used for thousands of years in various areas such as textile and paper (Sayyed et al 2019; Huber et al. 2012). Recently, its applications have expanded into advanced technology-based industries including filters, batteries, membranes, and drug delivery systems (Kim et al 2018; Ko et al 2019; Rohrbach et al. 2014; Song et al 2019; Zhang et al. 2013).

Due to the abundant hydroxyl groups in glucose units, cellulose can have various physical states in solution. When the intramolecular hydrogen bonds are dominant, cellulose chain became rigid and finally forms liquid crystal (LC) over the critical concentration (Ahn et al. 2016; Canejo et al 2017; Luo et al. 2014; Song et al 2011; Zhang et al. 2010). Cellulose chains can also be physically networked by the intermolecular hydrogen bonds (Lee et al. 2015; Lu and Hsieh 2010; Maréchal and Chanzy 2000; Nishiyama et al 2002; Parthasarathi et al. 2011). Especially, the powerful solubility of ionic liquid (IL) provides a chance for cellulose to form an organic gel in highly concentrated solution (Carotenuto and Grizzuti 2006; Hauru et al 2016; Kadokawa et al 2008; Song et al. 2013). Cellulose gel can be used to prepare the high-performance fiber or film with outstanding mechanical performance. Gel spinning has been widely applied to manufacture high-strength fibers using various polymeric gels of polyethylene (PE), polyvinyl alcohol (PVA), polyacrylonitrile (PAN) and so on (Barham and Keller 1985; Chang et al. 2015; Zhang et al. 2004). Especially, the gel spinning of ultra-high molecular weight polyethylene (UHMWPE) has been successfully commercialized to produce ultra-high strength polyethylene (UHSPE) (Cha et al 1994; Fang et al 2016; Yufeng et al 1999). The gel process can be applied to cellulose gel for the improvement of its mechanical performance.

For the optimization of cellulose gel process, it is important to understand the viscoelastic behavior of the cellulose chain in the solution. The viscoelastic characteristics are sensitively affected by the changes in the relaxation behavior of main chain or secondary bonds between chains (Graessley 1974; Lee et al

2015; Lee et al. 2017; Salehiyan and Hyun 2013). The changes in the relaxation behavior or the secondary bonds of polymer chains induce the phase transition such as gelation or LC formation (Haq et al 2019; Song et al. 2011; Song et al 2010). However, the rheological approach on the phase transition is limited because of a large number of influencing parameters such as hydrogen bonds, chain rigidity and functional groups. In that point, the rheological study on cellulose phase transition is extremely hard to conceive. Recently, the rheological analysis in LAOS (large amplitude oscillatory shear) region is expected to give intuitive information about the physical state of the polymer solution (Hyun et al. 2011). The physical states of polymer are dramatically changed in LAOS region, which would give amplified information on the interaction and the behavior of chains. According to Hyun et al, the LAOS behaviors can be categorized into 4 groups based on conformational changes of the polymer solutions (Hyun et al 2002). The grouping of the behavior provides the fundamental understanding for chain-to-chain interactions. Unlike conventional rheological analysis in a small amplitude region, the yield stress can be obtained in LAOS test (Lu and Hsieh 2010). As well known, the structures of material were changed at yield stress. The analysis of yield stress affords an in-depth understanding for the physical states of polymer chains.

We studied the physical state changes of cellulose/IL solution by the phase transition via rheological analyses. For the study, cellulose was dissolved in IL with different concentrations. The rheological behaviors of the solutions were measured in the steady shear state, SAOS (small amplitude oscillatory shear), and LAOS conditions. Each test showed the unique behaviors of LC transition and gelation. Finally, the film was prepared from the solution with different physical states and studied via tensile test and X-ray diffraction. The study gives a strategy to produce the high-performance film via controlling the molecular conformation.

Experimental

2.1 Preparation of the cellulose/AmimCl solutions

Microcrystalline cellulose (MCC, DP 200) and 1-Allyl-3-methylimidazolium chloride (AmimCl, purity $\geq 97\%$) were purchased from Sigma Aldrich. Before use, AmimCl and MCC were kept at 5 °C and 70 °C, respectively. Cellulose was dissolved in AmimCl with various concentrations. After the dissolution, the solutions were kept in a vacuum oven to remove the trapped air for 30 minutes. The prepared solutions were kept at 5 °C to prevent the depolymerization by AmimCl (Su et al. 2011).

2.2 Fabrication of the regenerated cellulose film

The regenerated cellulose films were fabricated using the cellulose/AmimCl solutions. The solutions were heated to 80 °C before the fabrication to reduce the viscosity. 2 mL of the heated solution was poured into a flat glass substrate. The solution on the glass substrate was heated again at 80 °C for 5 minutes to remove the extra bubble in the solution. The heated solution was casted into a film by a glass bar. The film on the glass substrate was washed three times using the distilled water. The regenerated film was immersed in a distilled water bath for 12 hours for the complete removal of the solvent. The coagulated

film was dried at room temperature for 48 hours. The average thickness of the regenerated films was about 50 μm . All films showed high transparency regardless of the cellulose concentration (See Figure S2).

2.3 Characterization

Polarized optical microscopy (POM, BX-41, OLYMPUS) was used to confirm the anisotropy of the solutions. The POM images of the solutions were taken at room temperature by a digital camera with a 530 nm sensitive tint plate (U-TP530, OLYMPUS). The rheological behavior of the solutions was characterized using a stress-controlled rheometer (RS-1, HAAKE) with a parallel plate ($\phi = 20\text{ mm}$) and a 1 mm gap between the plates at 30 $^{\circ}\text{C}$. The open side of the solution sandwiched between the plates was covered with a thin layer of silicone oil (Shin-Etsu Chemical Co.) to prevent water absorption during the measurement. The steady shear test was carried in the range of shear rate from 0.01 to 100 s^{-1} and the dynamic test was measured in the range of angular frequency from 0.1 to 100 $\text{rad}\cdot\text{s}^{-1}$. Time-dependent stress sweep was tested at fixed shear rate of 0.1 s^{-1} . The rheological behavior of the solutions under the large shear strain was studied by stress amplitude sweep in the strain amplitude range from 0.1 to 10 at the fixed angular frequencies of 1 $\text{rad}\cdot\text{s}^{-1}$. To confirm the microstructure of regenerated films, a wide-angle X-ray scattering system was used in the 2 theta range from 5 to 75 degrees using $\text{Cu K}\alpha 1$ (D8 Discover, Bruker). The tensile properties of regenerated films were tested using a universal testing machine (UTM5900, INSTRON) with test rate of 5 mm/min. The specimens for the tensile tests had rectangular shapes of 5 X 40 mm^2 (width X length).

Results And Discussion

By the steady shear test, the zero shear viscosities of the solutions were characterized and shown in Fig. 1(a). The inserted images show the polarized optical micrographs of the solutions. The concentration range of the solutions can be divided into four regions; non-contact region (3 ~ 9 wt%), entanglement region (9 ~ 14 wt%), anisotropic region (14 ~ 16 wt%), and gel region (16 ~ 18 wt%). The zero-shear viscosities changed significantly with the region.

In the non-contact region, the zero-shear viscosities slowly increased as the concentration increased. The cellulose chains with low concentration have little chance to contact with each other due to the small number of molecules in unit volume. In the entanglement region, the zero-shear viscosities rapidly increased with the concentration increase. The cellulose chains started to contact and entangle each other, resulting in large viscosity increase. As the concentration increased from 14 to 16 wt% (anisotropic region), the zero-shear viscosities decreased mainly because of the phase transition to LC. It is well-known that cellulose forms LC phase over the critical concentration. The cellulose chains become rigid by the intramolecular hydrogen bonds. The rigid chains were easily aligned and showed the cholesteric LC transition (Luo et al. 2014; Song et al. 2011; Song et al. 2010). In turns, the interchain contacts decreased in aligned chain conformation. It resulted in the viscosity drop at 16 wt%. With the further increase of the concentration, the zero-shear viscosity rapidly increased again in the gel region. In the highly

concentrated solution, cellulose chains were physically networked by the intermolecular hydrogen bonds and gave in the organic gel. The 3-D physical network structure needed more intensive shear to deform. As a result, the viscosity rapidly increased in the gel region.

The polarized optical micrographs confirm the phase transition of the solution along the concentration. (See Fig. 1(a) and Figure S1). In the non-contact and the entanglement regions (≤ 14 wt%), the solution showed the fully isotropic phase regardless of the concentration. In those regions, the cellulose concentrations were too low to form an anisotropic phase. As the concentration increased, the anisotropic phase was observed in the concentration range from 14 to 16 wt%. As described above, cellulose chains were aligned in the anisotropic region. The aligned chains formed the LC phase and showed anisotropy in the polarized optical micrographs. With the further increase of concentration (the gel region), the solution showed a fully isotropic phase again. The cellulose chains formed a strong 3-D physical network by the gelation. Due to the 3-D chain network, the chain movements were seriously restricted and lost a chance to be aligned. In other words, the chains were randomly oriented by the strong intermolecular hydrogen bonds.

Figure 1(b) shows the dynamic viscoelastic behavior of the solutions in the frequency range of 10^{-1} to 10^2 rad/s at 30 °C. As well known, the crossover (ω_c) of the storage (G') and loss (G'') moduli have strong dependency on the physical states such as the LC and gel (FitzGerald et al 2013; Huang et al. 2018). In the non-contact region (3 ~ 9 wt%), ω_c was not observed in the measured range because of the low chain-to-chain interaction as explained in Fig. 1(a). Above the entanglement region (9 wt% $\leq$), ω_c began to appear. The appearance of ω_c in the measured range means that the interaction between the chains was drastically increased (Ahn et al. 2016; Kim et al. 2018). As the concentration increased up to 14 wt%, the cellulose chains can have more chance to entangle by the close intermolecular distances. In the anisotropic region (LC phase) from 14 to 16 wt%, ω_c was shifted to higher frequency (See Fig. 1(c)). The increase of ω_c at 16 wt% was originated from the LC formation. In the LC phase, the aligned cellulose chains had less chance to contact each other, resulting in fast relaxation under the dynamic test. Although the zero-shear viscosity of 16 wt% solution was similar to the isotropic solution, G' and G'' were crossed in the measured range. It indicates that the chains were physically networked and gelled even in the LC phase. In other words, it can be said that the intermediate physical state of gel and LC existed in 16 wt% solution. In the gel region (16 ~ 18 wt%), ω_c rapidly decreased again. The solution was fully gelled and then the relaxation was significantly hindered.

The entanglement molecular weight (M_e) was calculated using Eq. (1) and shown in Fig. 1(c). The measured values are summarized in Table 1. For the calculation, the plateau modulus (G_N^0) was obtained as the storage modulus having the lowest tangent delta in the rubbery plateau region (See Figure S3) (Liu et al 2006). As similar to ω_c , the entanglement molecular weight decreased as the concentration increased up to 14 wt%. In general, polymers in concentrated solution have many entanglements due to the increase of chain-to-chain contacts. It results in a lower entanglement molecular weight. In other words, the degree of entanglement is inversely proportional to the

entanglement molecular weight (Huang et al. 2013; Wool 1993). As the concentration of cellulose increased up to 14 wt%, the entanglements increased which led to an increase of the contacts between neighboring chains. Whereas M_e was decreased in the anisotropic region (14 ~ 16 wt%). Cellulose chains in the anisotropic region maintained the aligned state during the dynamic test. It led to the increase of M_e . M_e decreased again by the gelation with the concentration increase (18 wt%). As the cellulose chains were gelled, the contact distance between the chains drastically decreased by the formation of physical network.

$$M_e = \frac{\rho RT}{G_N^0} \quad (1)$$

Table 1
The plateau modulus and entanglement molecular weight of solutions for the different concentrations

Concentration (wt%)	G_N^0 (10^3 Pa)	M_e (10^3 g mol^{-1})
3	-	-
5	-	-
7	-	-
9	15.27	115.14
12	21.34	70.86
14	39.32	38.46
15	38.27	39.51
16	33.22	45.52
17	34.53	43.79
18	45.67	33.11

The fluidity and gelation of the solution were confirmed by the classical “vial upside-down” method (See Fig. 2 (a)). The solution with low concentration (9 wt%) flowed down immediately after the upside-down of the vial, while the solutions with 12 and 14 wt% flowed down very slowly. After 12 hours, most parts of the solutions moved to the bottom. However, the solutions with high concentrations (16 and 18 wt%) did not flow and remained on the top side of the bottle even after 12 hours. It indicates that the solutions with high concentration were gelled by the strong physical network between the chains. In the high concentrations, the intermolecular hydrogen bonds and the chain entanglements were dramatically increased, resulting in the gelation of the solutions. It can be a solid evidence that the intermediate state of gel and LC was formed in 16 wt% solution.

Figure 2(b) shows the time-dependent stress sweep results. The test results of each solution were shown in Figure S4(a). The time-dependent stress sweep was performed to study the change of the physical states and the interaction of the chains along time. During the test, the stress was recorded for 300 s at the fixed shear rate of 0.1 s^{-1} . After that, the shear deformation was stopped, and the solution was kept for the designated rest time (0, 60, and 360 s). The '60 s' means that the shear was re-applied after a temporal pause for 60 s. After the rest time, the shear stress was recorded again under the same condition of the initial run. The shear stress was normalized by the relaxed stress (τ_{∞}). τ_{∞} means the shear stress when the solution was fully relaxed (See Figure S4(b)). In the initial run, the solutions with the concentration under 14 wt% reached steady state right after a small stress overshoot around 60 s. The stress overshoot was originated from the chain disentanglement by the applied shear. When the concentration was higher than 16 wt%, the overshoot dramatically increased. It means that large stress was required to break the strong gel network. Comparing with another anisotropic solution of 14 wt%, the solution of 16 wt% showed more intensive overshoot. It is again resulted from the anisotropic gel. The concentration of 14 wt% was not high enough for physical networking. The second sweep run started right after the first pause without resting. As shown in Figure 2(b), the overshoot was not observed for the solutions with the concentrations from 5 to 16 wt%. It is because the chain had no time to recover the intermolecular interaction destructed during the initial run. However, the stress overshoot was still observed at 18 wt% solution in the second run. This overshoot was originated from the unbroken chain network rather than the spontaneous recovery of the network. It showed that the chain network in the gel state was not completely destroyed by the applied shear due to the strong hydrogen bonds and the entanglement. The third run was carried out after 6 minutes of resting following the second run. The overshoot was also strongly dependent on the concentration. When the solution concentration was lower than 12 wt%, the size of each overshoot was similar to that of the initial run. It indicates that the intermolecular entanglement was almost recovered by the chain relaxation. In 14 and 16 wt% solutions, the overshoot during the third run did not appear due to the stable chain alignment of the LC phase. The cholesteric phases of the anisotropic solutions (14 and 16 wt%) were changed to the nematic structure by the shear deformation in the first and second runs. In the nematic structure, 3-D chain network formation is limited by the lack of physical interaction between the chains. As a result, the complete recovery of the stress overshoot was not observed at the third run. It means that the nematic structure derived by shear deformation can remain stable in the resting time. This behavior is a key point to produce regenerated films with high chain orientation. Especially, 16 wt% solution showed a strong stress overshoot at the initial run and the slow recovery which were originated from the intermediate state of gel and LC. In 18 wt% solution, the overshoot was recovered completely. The randomly oriented chains in 18 wt% solution can form the 3-D network again. The network structure spontaneously recovered by the chain relaxation resulting in complete recovery of the stress overshoot in the third run.

Figure 3(a) shows the strain amplitude sweep results of the cellulose solution under large dynamic strain conditions. The test results of all solutions are shown in Figure S5. Hyun et al grouped the LAOS (large amplitude oscillatory shear) behavior of polymer solution or melts into four types; type I (strain thinning), type II (strain hardening), type III (weak strain overshoot), and type IV (strong strain overshoot) (Hyun et

al. 2002). The prepared solutions in this study belong to the type I LAOS behavior (Hyun et al. 2011). Type I behavior refers to the strain thinning behavior of typical linear polymer solution or melt. As clearly seen in the Fig. 3(a), all the curves can be divided into two regions; one is steady state region in low amplitude, and the other is strain thinning region in high amplitude. In the steady state region, both G' and G'' were independent of the amplitude, indicating that the physical state of cellulose in the solution was not changed by the deformation. In the strain thinning region, the solution became more fluid-like with the amplitude increase due to the disentanglement and the alignment of cellulose chains. The entanglements and gel network of cellulose chains were destroyed due to the large deformation. The moduli were also relied on the concentration. As similar to the zero-shear viscosity, the solution of 16 wt% showed the smallest values in both moduli (G' and G'') among the concentrated solutions (14 ~ 18 wt%), mainly because of the phase transition from isotropic to anisotropic phase. The increases in G' and G'' were originated from the interchain contacts and entanglements. As the concentration increased, the physical interaction between the chains increased which led to the increase in the moduli. In the anisotropic solutions (14 and 16 wt%), the aligned chains could easily slip between them. The slippage between the chains resulted in the decrease in the moduli of the solutions.

Figure 3(b) shows the tangent delta ($\tan \delta$) of the solution under the LAOS condition (presented as a black dotted line). The $\tan \delta$ decreased as the concentration increased up to 14 wt%. It is because the solution became more elastic with the concentration increase. As the concentration increased, the physical interaction between the chains made the solution more solid-likely. The further increase to 16 wt% resulted in the decrease of $\tan \delta$. It also indicates the alignment of the cellulose chain. The gelation at 18 wt% decreased the $\tan \delta$ again.

The yield stress (τ_y) was calculated and displayed in Fig. 3(b) as a red dotted line. The yield stress was calculated using Eq. (2). G'_0 means the storage modulus at zero strain and γ_c (critical strain) means the strain to break the chain network of the solution (See Figure S6).

$$\tau_y = G'_0 \gamma_c \quad (2)$$

The yield stress increased monotonously with the concentration. The initial increase was resulted from the entanglement and the later increase was resulted from the gel networking. In the low concentration, the chain entanglement increased the elastic properties of the solution. As the solutions were gelled, the yield stress of the solutions was increased. The yield stress of a polymer solution refers to the strength of the chain network (Chejara et al 2013; Lu and Hsieh 2010). As illustrated in Fig. 3(a), the moduli (especially G'_0) at 16 wt% decreased as the liquid crystal was formed. Likewise, γ_c was expected to decrease by LC transition at 16 wt%. However, the chains were strongly networked in the gel at 16 wt%, which led the increase in γ_c . The chain network was not destructed by the large shear deformation. As a result, the yield stress increased as the solution was gelled at 16 wt%. With the rheological observation under the LAOS condition, it was clearly revealed that the presence of the intermediate state of the gel and LC.

Figure 4(a) shows the digital image of the film regenerated from the 16 wt% cellulose/AmimCl solution. The transparent films were successfully prepared using the solutions with the concentration range of 9 to 18 wt% (See Figure S2). However, the film was not fabricated from the dilute solution (≤ 7 wt%) due to the low chain entanglement. In the film process, the prepared cellulose solution was unidirectionally spread on a glass substrate. The chain orientation in the film was estimated using 2D-WAXS. The in-plane orientation was strongly developed from the anisotropic solution (See Figs. 4 (b) and (c), and Figure S7.). Figures 4(d), (e), and (f) show the polarized microscope images of the film along the polarized angle. The magenta-color was obtained by tint plate insertion. The images of 0° and 90° tilted against the polarizing direction show a similar magenta color, indicating that the polarized lights did not pass through the film. Whereas the 45° image shows the fully strong bright green color. It reveals that the film was uniaxial chain orientation in the film originated from the LC phase in the solution.

Figure 4 (g) shows the stress-strain curves of the films, of which important parameters were summarized in Table 2. The initial modulus and the tensile strength of the film were increased with the increase of the concentration up to 16 wt% and then decreased with the further increase in concentration. The tensile strength depends on both chain orientation and the interactions, while the initial modulus mainly on the orientation. In the low concentration (≤ 12 wt%), both modulus and strength were increased with the concentration by the chain-to-chain entanglement. The phase transition to LC increased the initial modulus dramatically. The cholesteric phase in the solution was changed into the nematic phase during the film casting, resulting in uniaxial chain orientation. The uniaxially aligned structure was not easily deformed by the applied stress comparing the randomly oriented structure. The tensile strength was drastically improved when the concentration increased from 14 to 16 wt%. The solution of 16 wt% had a robustly networked structure in aligned chains as described above. This intermediate phase gave a better chance to redistribute the applied stress effectively. The aligned network can maintain the structure without significant destruction even under the large deformation. At 18 wt%, both the tensile strength and initial modulus decreased rapidly. Meanwhile, the toughness was continuously increased in the concentration range in this study. The increase of toughness up to 16 wt% was originated from the entanglement, the chain orientation, and the robust network, respectively. Although the chain in 18 wt% solution did not have preferred alignment, it showed the highest toughness among the prepared films. It was mainly resulted from the large increase of the strain at breakage. During the deformation, the networked structure was partially destroyed and gave partial freedom for the chain. By the applied strain, the randomly oriented chain can be reoriented and extended along the strain direction. It can be confirmed from several yield points in the stress-strain curve (denoted as green arrows line in Fig. 4(g)). At the yield points, the stress was used for reorientation and extension of the chain rather than elongation. By the process, the film can have the aligned and robustly networked structure as similar to the film from 16 wt% solution.

Table 2
The mechanical properties of the regenerated cellulose films

Cellulose content (wt%)	9	12	14	16	18
Tensile strength ^a (± SD) (MPa)	133.0 (± 19.4)	170.5 (± 15.2)	259.2 (± 22.1)	420.2 (± 28.7)	228.4 (± 20.1)
Initial modulus ^a (± SD) (GPa)	4.21 (± 1.12)	3.69 (± 1.71)	9.03 (± 2.09)	9.44 (± 1.55)	3.25 (± 0.91)
Toughness (MJ/m ³)	3.32	8.81	9.05	18.6	20.3
^a Data presented are the mean of triplicate measurements (± SD)					

Conclusions

Based on various rheological observations, we confirmed and analyzed the physical states of the cellulose solution along with the concentration. The concentration increase changed the solution from isotropic phase to anisotropic phase due to the intramolecular hydrogen bonds. The further increase resulted in the gelation of the solution by the intermolecular hydrogen bonds. In the concentrated solution, the intermediate state of gel and liquid crystal was observed. The abundant hydroxyl groups led the alignment and physical network of the chains simultaneously. Using the solution of the intermediate phase, high strength film with aligned gel structure was obtained.

Declarations

Author contributions

Taeho Kim: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft, Writing - review & editing, Visualization. **Younghan Song:** Conceptualization, Writing - review & editing, Visualization. **Jungbin Ahn:** Conceptualization, Visualization, Formal analysis, Investigation. **Minhyung Kim:** Formal analysis, Methodology, Visualization. **Hyungsup Kim:** Conceptualization, Methodology, Supervision, Writing - review & editing, Funding acquisition, Project administration.

Conflicts of interest There are no conflicts to declare.

Ethical approval This manuscript does not contain any studies with human participants or animals performed by any of the authors.

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References

1. Ahn Y, Hu DH, Hong JH, Lee SH, Kim HJ, Kim H (2012) Effect of co-solvent on the spinnability and properties of electrospun cellulose nanofiber. *Carbohydr Polym* 89(2):340–345. <https://doi.org/10.1016/j.carbpol.2012.03.006>
2. Ahn Y, Kwak SY, Song Y, Kim H (2016) Physical state of cellulose in BmimCl: dependence of molar mass on viscoelasticity and sol-gel transition. *Phys Chem Chem Phys* 18(3):1460–1469. <https://doi.org/10.1039/c5cp06616f>
3. Barham PJ, Keller A (1985) High-strength polyethylene fibres from solution and gel spinning. *J Mater Sci* 20(7):2281–2302. <https://doi.org/10.1007/BF00556059>
4. Canejo JP, Monge N, Echeverria C, Fernandes S, Godinho M (2017) Cellulosic liquid crystals for films and fibers. *Liq Cryst Rev* 5(2):86–110. <https://doi.org/10.1080/21680396.2017.1394923>
5. Carotenuto C, Grizzuti N (2006) Thermoreversible gelation of hydroxypropylcellulose aqueous solutions. *Rheol Acta* 45(4):468–473. <https://doi.org/10.1007/s00397-005-0075-x>
6. Cha WI, Hyon SH, Ikada Y (1994) Gel spinning of poly (vinyl alcohol) from dimethyl sulfoxide/water mixture. *J Polym Sci B Polym Phys* 32(2):297–304. <https://doi.org/10.1002/polb.1994.090320211>
7. Chang H, Chien AT, Liu HC, Wang PH, Newcomb BA, Kumar S (2015) Gel spinning of polyacrylonitrile/cellulose nanocrystal composite fibers. *ACS Biomater Sci Eng* 1(7):610–616. <https://doi.org/10.1021/acsbiomaterials.5b00161>
8. Chejara DR, Kondaveeti S, Prasad K, Siddhanta A (2013) Studies on the structure–property relationship of sodium alginate based thixotropic hydrogels. *RSC Adv* 3(36):15744–15751. <https://doi.org/10.1039/C3RA43070G>
9. Chiellini E, Solaro R (1996) Biodegradable polymeric materials. *Adv Mater* 8(4):305–313. <https://doi.org/10.1002/adma.19960080406>
10. El-Sakhawy M, Hassan ML (2007) Physical and mechanical properties of microcrystalline cellulose prepared from agricultural residues. *Carbohydr Polym* 67(1):1–10. <https://doi.org/10.1016/j.carbpol.2006.04.009>
11. Fang X, Wyatt T, Hong Y, Yao D (2016) Gel spinning of UHMWPE fibers with polybutene as a new spin solvent. *Polym Eng Sci* 56(6):697–706. <https://doi.org/10.1002/pen.24296>
12. FitzGerald PA, McDonald DM, Warr GG (2013) The effect of degree of polymerization on intra-and interchain micellization of a tail-type cationic polysoap. *Soft Matter* 9(9):2711–2716. <https://doi.org/10.1039/C3SM27573F>

13. Graessley WW (1974) The entanglement concept in polymer rheology. In *The entanglement concept in polymer rheology*. Springer:1-179. <https://doi.org/10.1007/BFb0031037>
14. Haq MA, Habu Y, Yamamoto K, Takada A, Kadokawa J (2019) Ionic liquid induces flexibility and thermoplasticity in cellulose film. *Carbohydr Polym* 223:115058. <https://doi.org/10.1016/j.carbpol.2019.115058>
15. Hauru LK, Hummel M, Nieminen K, Michud A, Sixta H (2016) Cellulose regeneration and spinnability from ionic liquids. *Soft Matter* 12(5):1487–1495. <https://doi.org/10.1039/C5SM02618K>
16. Huang Q, Mednova O, Rasmussen HK, Alvarez NJ, Skov AL, Almdal K, Hassager O (2013) Concentrated polymer solutions are different from melts: Role of entanglement molecular weight. *Macromolecules* 46(12):5026–5035. <https://doi.org/10.1021/ma4008434>
17. Huang Z, Delparastan P, Burch P, Cheng J, Cao Y, Messersmith PB (2018) Injectable dynamic covalent hydrogels of boronic acid polymers cross-linked by bioactive plant-derived polyphenols. *Biomater Sci* 6(9):2487–2495. <https://doi.org/10.1039/C8BM00453F>
18. Huber T, Müssig J, Curnow O, Pang S, Bickerton S, Staiger MP (2012) A critical review of all-cellulose composites. *J Mater Sci* 47(3):1171–1186. <https://doi.org/10.1007/s10853-011-5774-3>
19. Hyun K, Kim SH, Ahn KH, Lee SJ (2002) Large amplitude oscillatory shear as a way to classify the complex fluids. *J Non-Newton Fluid* 107(1–3):51–65. [https://doi.org/10.1016/S0377-0257\(02\)00141-6](https://doi.org/10.1016/S0377-0257(02)00141-6)
20. Hyun K, Wilhelm M, Klein CO, Cho KS, Nam JG, Ahn KH, McKinley GH (2011) A review of nonlinear oscillatory shear tests: Analysis and application of large amplitude oscillatory shear (LAOS). *Prog Polym Sci* 36(12):1697–1753. <https://doi.org/10.1016/j.progpolymsci.2011.02.002>
21. Kadokawa J, Murakami M, Kaneko Y (2008) A facile preparation of gel materials from a solution of cellulose in ionic liquid. *Carbohydr Res* 343(4):769–772. <https://doi.org/10.1016/j.carres.2008.01.017>
22. Kim Y, Song Y, Kim H (2018) Preparation of transparent cellulose film with controlled haze using halloysite nanotubes. *Cellulose* 25(2):1239–1248. <https://doi.org/10.1007/s10570-017-1625-y>
23. Ko E, Park KS, Kim S, Kim T, Kim H (2019) Morphological study of cellulosic hydrogel nanofiber for biomedical application. *Cellulose* 26(17):9107–9118. <https://doi.org/10.1007/s10570-019-02725-1>
24. Lee CM, Kubicki JD, Fan B, Zhong L, Jarvis MC, Kim SH (2015) Hydrogen-bonding network and OH stretch vibration of cellulose: comparison of computational modeling with polarized IR and SFG spectra. *J Phys Chem B* 119(49):15138–15149. <https://doi.org/10.1021/acs.jpcc.5b08015>
25. Lee SH, Yong Song H, Hyun K, Hyup Lee J (2015) Nonlinearity from FT-rheology for liquid crystal 8CB under large amplitude oscillatory shear (LAOS) flow. *J Rheol* 59(1):1–19. <https://doi.org/10.1122/1.4901288>
26. Lee YJ, Kwon MK, Lee SJ, Jeong SW, Kim HC, Oh TH, Lee SG (2017) Influence of water on phase transition and rheological behavior of cellulose/ionic liquid/water ternary systems. *J Appl Polym Sci* 134(22). <https://doi.org/10.1002/app.44658>

27. Liu C, He J, Van Ruymbeke E, Keunings R, Bailly C (2006) Evaluation of different methods for the determination of the plateau modulus and the entanglement molecular weight. *Polymer* 47(13):4461–4479. <https://doi.org/10.1016/j.polymer.2006.04.054>
28. Lu P, Hsieh YL (2010) Preparation and properties of cellulose nanocrystals: rods, spheres, and network. *Carbohydr Polym* 82(2):329–336. <https://doi.org/10.1016/j.carbpol.2010.04.073>
29. Luo Z, Wang A, Wang C, Qin W, Zhao N, Song H, Gao J (2014) Liquid crystalline phase behavior and fiber spinning of cellulose/ionic liquid/halloysite nanotubes dispersions. *J Mater Chem A* 2(20):7327–7336. <https://doi.org/10.1039/C4TA00225C>
30. Maréchal Y, Chanzy H (2000) The hydrogen bond network in I β cellulose as observed by infrared spectrometry. *J Mol Struct* 523(1–3):183–196. [https://doi.org/10.1016/S0022-2860\(99\)00389-0](https://doi.org/10.1016/S0022-2860(99)00389-0)
31. Nishiyama Y, Langan P, Chanzy H (2002) Crystal structure and hydrogen-bonding system in cellulose I β from synchrotron X-ray and neutron fiber diffraction. *J Am Chem Soc* 124(31):9074–9082. <https://doi.org/10.1021/ja0257319>
32. Parthasarathi R, Bellesia G, Chundawat S, Dale B, Langan P, Gnanakaran S (2011) Insights into hydrogen bonding and stacking interactions in cellulose. *Journal Phys Chem A* 115(49):14191–14202. <https://doi.org/10.1021/jp203620x>
33. Rohrbach K, Li Y, Zhu H, Liu Z, Dai J, Andreasen J, Hu L (2014) A cellulose based hydrophilic, oleophobic hydrated filter for water/oil separation. *Chem Commun* 50(87):13296–13299. <https://doi.org/10.1039/C4CC04817B>
34. Salehiyan R, Hyun K (2013) Effect of organoclay on non-linear rheological properties of poly (lactic acid)/poly (caprolactone) blends. *Korean J Chem Eng* 30(5):1013–1022. <https://doi.org/10.1007/s11814-013-0035-6>
35. Sayyed AJ, Deshmukh NA, Pinjari DV (2019) A critical review of manufacturing processes used in regenerated cellulosic fibres: viscose, cellulose acetate, cuprammonium, LiCl/DMAc, ionic liquids, and NMMO based lyocell. *Cellulose* 26(5):2913–2940. <https://doi.org/10.1007/s10570-019-02318-y>
36. Siró I, Plackett D (2010) Microfibrillated cellulose and new nanocomposite materials: a review. *Cellulose* 17(3):459–494. <https://doi.org/10.1007/s10570-010-9405-y>
37. Song H, Luo Z, Zhao H, Luo S, Wu X, Gao J, Wang Z (2013) High tensile strength and high ionic conductivity bionanocomposite ionogels prepared by gelation of cellulose/ionic liquid solutions with nano-silica. *RSC Adv* 3(29):11665–11675. <https://doi.org/10.1039/C3RA40387D>
38. Song H, Niu Y, Wang Z, Zhang J (2011) Liquid Crystalline Phase and Gel – Sol Transitions for Concentrated Microcrystalline Cellulose (MCC)/1-Ethyl-3-methylimidazolium Acetate (EMIMAc) Solutions. *Biomacromol* 12(4):1087–1096. <https://doi.org/10.1021/bm101426p>
39. Song H, Zhang J, Niu Y, Wang Z (2010) Phase transition and rheological behaviors of concentrated cellulose/ionic liquid solutions. *J Phys Chem B* 114(18):6006–6013. <https://doi.org/10.1021/jp1013863>
40. Song Y, Seo JY, Kim H, Beak KY (2019) Structural control of cellulose nanofibrous composite membrane with metal organic framework (ZIF-8) for highly selective removal of cationic dye.

Carbohydr Polym 222:115018. <https://doi.org/10.1016/j.carbpol.2019.115018>

41. Su Y, Brown HM, Li G, Zhou X, Amonette JE, Fulton JL, Zhang ZC (2011) Accelerated cellulose depolymerization catalyzed by paired metal chlorides in ionic liquid solvent. *Appl Catal A-Gen* 391(1–2):436–442. <https://doi.org/10.1016/j.apcata.2010.09.021>
42. Wool RP (1993) Polymer entanglements. *Macromolecules* 26(7):1564–1569. <https://doi.org/10.1021/ma00059a012>
43. Yufeng Z, Changfa X, Guangxia J, Shulin A (1999) Study on gel-spinning process of ultra-high molecular weight polyethylene. *J Appl Polym Sci* 74(3):670–675. [https://doi.org/10.1002/\(SICI\)1097-4628\(19991017\)74:3<670::AID-APP21>3.0.CO;2-8](https://doi.org/10.1002/(SICI)1097-4628(19991017)74:3<670::AID-APP21>3.0.CO;2-8)
44. Zhang J, Liu Z, Kong Q, Zhang C, Pang S, Yue L, Cui G (2013) Renewable and superior thermal-resistant cellulose-based composite nonwoven as lithium-ion battery separator. *ACS Appl Mater Inter* 5(1):128–134. <https://doi.org/10.1021/am302290n>
45. Zhang X, Liu T, Sreekumar T, Kumar S, Hu X, Smith K (2004) Gel spinning of PVA/SWNT composite fiber. *Polymer* 45(26):8801–8807. <https://doi.org/10.1016/j.polymer.2004.10.048>
46. Zhang Z, Zhang Q, Wang J, Song H, Zhang H, Niu X (2010) Chemical modification and influence of function groups on the in vitro-antioxidant activities of porphyrin from *Porphyrin haitanensis*. *Carbohydr Polym* 79(2):290–295. <https://doi.org/10.1016/j.carbpol.2009.08.004>

Figures

Figure 1

(a) The zero-shear viscosity as a function of concentration. The inserted image shows the polarized optical micrograph of each solution. The dynamic viscoelastic behavior of the prepared solution at 30 oC: (b) The changes of storage (G' , solid symbol) and loss (G'' , open symbol) moduli as a function of angular frequency. Each data was multiplied by 10^n and shifted vertically to prevent overlapping of data. (c) The frequency at the crossover point (ω_c) and the entanglement molecular weight (M_e) along the concentration.

Figure 2

(a) The vial upside-down images of the solutions with different concentrations. (b) The effect of rest time on the shear stress overshoot with the different concentrations at shear rate of 0.1 s⁻¹ at 30°C.

Figure 3

(a) The change of storage (G') and loss (G'') moduli as a function of strain at 1 rad/s. (b) The $\tan \delta$ and the yield stress of cellulose solutions along the concentration.

Figure 4

(a) The image of the regenerated cellulose film fabricated from 16 wt% solution. The 2D-WAXS patterns of the films made of (b) 5 wt% and (c) 16 wt% solutions, respectively. The polarized optical micrographs of the film from 16 wt% solution tilted by; (d) 0°, (e) 45°, and (f) 90° against the fabricating direction. The arrows of A and P denote the directions of the analyzer and the polarizer, respectively. (g) The strain-stress curves of the regenerated films.

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