Preparation of high-performance cellulose composite membranes from LiOH/urea solvent system

Yinke Liu, Shuman Xu, Mengfan Jing, Yuan Wei, Hua Deng and Qiang Fu

College of Polymer Science and Engineering, Sichuan University, State Key Laboratory of Polymer Materials Engineering, Sichuan, P.R. China

ABSTRACT
New green solvent system alkali (such as NaOH and LiOH)/urea which could rapidly dissolve cellulose could be potentially used to prepare high-performance regenerated cellulose materials with low cost. Pure regenerated cellulose materials have relatively low strength inherent effects. In this work, we choose TEMPO-oxide cellulose nanofiber (CNF) and graphene oxide (GO) as fillers to prepare isotropic regenerated cellulose membrane (RCM) with significantly enhanced mechanical properties. Dynamic mechanical analyzer (DMA) test shows that RCM with content of 5 wt% CNF has the maximum enhancement value of 32.5% improvement comparing with pure RCM. And RCM with 0.4 wt% GO has the maximum improvement of 17.9%. Mechanical properties decrease with further increasing filler contents. We employ transmission electron microscopy to confirm the structure of fillers in solution and scanning electron microscopy to observe the microstructures of these RCMs. The results are consistent with DMA tests. In addition, XRD results confirm that the crystal structure of RCMs is the same with RCMs without filler. Thermogravimetric analyses results indicate that RCMs keep great thermal stability below 300°C. Transmittance (T) property is carried out by UV-Vis spectroscopy. Pure RCMs and CNF/RCMs keep high transparency at the wavelength of 800 nm. Transparency of RCMs with GO decrease quickly when the content of GO increases. In conclusion, the enhancement mechanism is proposed as the addition of fillers makes up the defects in RCMs. Furthermore, CNF illustrates large aspect ratio which is beneficial for stress transfer. As for GO, polar groups on surface provide strong interaction with the matrix. This is the first time that the enhancement effects of different fillers are systematically analyzed and compared for RCMs system. Our work could benefit the selection of appropriate fillers for such green solvent system and expand its range of applications.

ARTICLE HISTORY
Received 1 February 2019
Accepted 13 May 2019

KEYWORDS
Green solvent; regenerated cellulose membrane; cellulose nanofiber; graphene oxide; reinforcement

CONTACT
Hua Deng huadeng@scu.edu.cn
College of Polymer Science and Engineering, Sichuan University, State Key Laboratory of Polymer Materials Engineering, Sichuan, P.R. China

© 2019 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group.
This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
Introduction

Widely used polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC) are petro-based materials, which is not sustainable. Besides, those polymer materials could not be biodegraded and it will remain in the environment for long time once they were abandoned, causing growing environmental pollution and resource exhaustion problems [1,2]. Obviously, it is important to develop environmentally friendly and renewable materials which could replace traditional polymers in some or even all respects.

As the most abundant natural polymer resource on earth [3], cellulose attracts increasing amount of attention [4,5]. Cellulose exhibits excellent properties such as low density, high strength, highly hydrophilic, easy chemical modification, and biodegradability, which makes it ideal for the preparation of high-performance materials [6]. However, because of the high crystallinity and strong intermolecular hydrogen bonds, cellulose could not be melted or dissolved in common solvents, which limits their applications. Some materials based on nano-sized cellulose and chemically modified cellulose have been prepared [7–9]. However, the production costs needs to be significantly reduced to extend their range of applications.

In recent years, several types of solvents that could successfully dissolve cellulose have been developed [10–12], making it possible to obtain functional regenerated cellulose materials. These solvents could be divided into two categories: derivative solvents and nonderivative solvents [13]. Derivative solvent could achieve dissolution by forming covalent bond with cellulose, such as NaOH/CS₂ and alkali/urea system. They are being widely used in viscose spinning industry, but toxic CS₂ would be generated when cellulose materials were produced via dissolution–regeneration process. Meanwhile, nonderivative solvents such as NMMO (N-methylmorpholine-N-oxide), DMAc/LiCl and ionic liquids, form strong intermolecular forces with cellulose thus destroy hydrogen bonding and ultimately dissolve the cellulose. Some regenerated cellulose materials have been successfully prepared from those solvent. For instance, Sam et al. [14] prepared antimicrobial m-aramid/cellulose blend membranes from DMAc/LiCl for water disinfection. Kim et al. [15] prepared graphene oxide (GO)/cellulose composite with electrical conductivity by regenerating composites from N-methylmorpholine-N-oxide (NMMO).

It should be noticed that the solvents mentioned above are of high cost and the residual solvents are harmful to humans, which limit the applications of those regenerated cellulose materials. Among the solvents above, alkali/urea is a low-cost, green, nontoxic, and environmental friendly solvent system which was first discovered in 2003 [12,16,17] (All the ions contained in this system are harmless to humans and the environment, which is reported in [12,16,17]). Such alkali/urea aqueous solution could quickly (in a few minutes) dissolve cellulose at −12°C. The advantages make the system suitable for producing cellulose materials in bulk scale and researchers have paid much attention to this system.

Zeng et al. [18] prepared cellulose films containing TiO₂ nanoparticles which could photocatalysis degrade phenol under weak UV light irradiation. The cellulose matrix films were regenerated from Na₂SO₄ aqueous solution coagulation bath and worked as backbone. Tian et al. [19] obtained polyaniline (PANI)/cellulose gels deposited with Ag nanoparticles for energy storage. The PANI/cellulose was prepared by in situ polymerizing aniline on the porous structured cellulose which regenerated from anhydrous ethanol. Wang et al. [20] prepared cellulose–phosphor hybrid hydrogels using epichlorohydrin (ECH) as chemical-crosslinking agent. Such materials could emit green fluorescence under UV lamp, as well as keep brightness and long-lasting after glow. These characteristics could be used for bioimaging.

However, the metastability of alkali/urea/cellulose solution system limits the content of cellulose and causes defects during regenerating process. Thus, causing decreased mechanical strength for these cellulose materials [21]. Furthermore, those defects in regenerated cellulose could not be healed by annealing. Those disadvantages limit the application of cellulose materials regenerated from such system. Using fillers to enhance the mechanical performance of those cellulose materials is a viable way to broaden their application. Unfortunately, the strong alkaline and aqueous surrounding makes it challenging to choose suitable fillers. Traditional fillers such as carbon nanotubes (CNT) and glass fiber (GF) are unsuitable for this system. Therefore, the investigation of new fillers is essential.

Recently, regenerated cellulose filaments (RCF) enhanced by cellulose nanofiber (CNF) has been prepared successfully [22]. Inspired by this, we choose cellulose membrane (CM), which could be widely applied in food packaging and medical industry [23], as our research object. And TEMPO-oxide cellulose nanofiber (CNF) and GO are selected as fillers in this work. CNF was prepared from microfibrillated cellulose (MFC), which is made up of nano-sized cellulose fibrils. Thus, CNF has large aspect ratio and high degree of crystallinity, which provide high strength to the final composites [24]. Besides, carboxylate groups on TEMPO-CNFO introduced by oxidation process could interact
well with water as well as cellulose matrix, allowing them to disperse well in aqueous solution and cellulose matrix. Graphene oxide was prepared from graphite by Hummers method, which is monolayer with high sheet strength. Furthermore, polar groups (such as −C=O) on the surface of GO improve the dispersing ability in water and interaction with cellulose matrix. It is worth noting that GO could be reduced to graphene, which is widely used in various functional materials [25]. The properties of CNF and GO make the improvement in the mechanical performance possible. Comparing the two fillers, CNF is cellulose with fibrous shape and the obtained composite regenerated cellulose membrane (RCM) is called self-enhanced RCM. On the other hand, GO illustrates high-sheet strength and a layer shape, which is different from CNF, and could be reduced to graphene. The differences between those two fillers suggest different enhancement mechanism. The effect of these fillers on the mechanical performance of regenerated cellulose will be summarized, which would help the selection of suitable components for the preparation of high-performance functional cellulose composites from such alkali/urea system.

**Experiment section**

**Materials**

Cellulose pulp was obtained from Jilin Chemical Fiber Group Ltd. (China) with more than 95% α-cellulose; microfibrillate cellulose (MFC) with solid content of 25% was purchased from Daciel Chemical Industries, Ltd., Japan (Celish,KY100-S); TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) and NaBr were offered by Sigma-Aldrich; sodium sulfate anhydrous (AR) was purchased from Kelong Industries, Ltd., Chengdu; Graphite intercalation compound (GIC) was purchased from Qingdao Jin Ri Lai Graphite Co. Ltd. (50 mesh); Potassiumpermanganate (KMnO4, AR > 99.5%), sodium nitrate(NaNO3, AR > 99%), concentrated sulfuric acid (H2SO4, AR, 95–98%), hydrogen peroxide (H2O2, AR, 30%) and hydrohalic acid (HI, AR, 45%) were obtained from Kernal Chemical Reagent Plant, China. Phytic acid solution (70% in H2O) was provided by Aladdin, Ltd., Shanghai. All agents were used as received.

**Preparation of pure regenerated cellulose membrane (RCM)**

The solvent was prepared by mixing LiOH-H2O, urea, and deionized water with a proportion of 8:15:77 in weight and precooled to −12°C. Then, a certain amount of cellulose pulp was dispersed into the solvent to form transparent solution by vigorous stirring for about 10 min with 3 wt% cellulose content. The solution was degassed via centrifuging of 2200 r/min for 10 min. Finally, the ultimate solution was casting on a glass plate to form a liquid layer with certain thickness. Then we immersed the glass plate in the aqueous coagulation bath which comprises 7.5 wt% phytic acid and 2.5 wt% sodium sulphate anhydrous. Then, the membranes were thoroughly washed with deionized water and sandwiched between two glass plates. After drying in the air for about 2 days, transparent membranes were obtained. The pure RCM was also prepared for reference.

**Preparation of TEMPO-oxide-cellulose nanofiber (CNF)**

Microfibrillated cellulose was used as resource to prepare CNF via common TEMPO-oxide method [26]. Before oxidation, MFC were emulsified for 15 min to make the oxidation easier and more thorough (5 g MFC/1000 g deionized water). Then, 0.32 g TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) and 2 g NaBr were added into the MFC suspension. After adjusting pH to 10, NaClO was added into above suspension with the ratio of 2.5 mmol per 1 g of cellulose. The PH of the suspension was kept at 10.5 and reacted for 5–7 h. Alcohol was added to stop reaction. TEMPO-oxide-cellulose nanofiber (TCNF) and unreacted MFC were separated and washed by repeated vacuum filtration. After that, unreacted MFC was removed by centrifugation. Finally, the obtained CNF dispersion was stored at 25°C for further fabrication process.

**Preparation of graphene oxide (GO)**

We prepared GO via Hummers method with graphite intercalation compound (GIC) which expanded from multilayer graphite (MLG) at 900°C for 2 min in furnace. One gram expanded GIC, 0.5 g NaNO3, 100 ml H2SO4 were mixed in a beaker under ice bath to keep the temperature below 10°C. Eight grams of KMnO4 was divided into several parts averagely and added in reaction mixture every 10 min to keep the temperature not exceeding 10°C. Reacted for another 10 min after all KMnO4 was added and then temperature of the bath was increased to keep reaction mixture at 35°C for 2 h. Afterwards, 200 ml deionized water was dropped into the beaker to avoid temperature exceeding 40°C. In order to deplete unreacted KMnO4, we added H2O2 aqueous solution until no bubbles appeared. Finally, repeated centrifugations were carried out to remove unreacted GIC and residual acid.
The obtained yellow GO dispersion was kept at 25 °C.

**Preparation of CNF/cellulose regenerated membrane (CNF/RCM) and GO/cellulose regenerated membrane (GO/RCM)**

The preparation of CNF/RCM is described as an example and GO/RCM was prepared through similar process. CNF is added into cellulose dispersion at room temperature to avoid dissolving of CNF (in order to control the variables, GO was also added at room temperature). CNF suspension was concentrated via filtration. Then, 15 g concentrated CNF suspension of different concentration was added into 200 g cellulose solution to form 1 wt% CNF/cellulose solution, 3 wt% CNF/cellulose solution, 5 wt% CNF/cellulose solution, and 7 wt% CNF/cellulose solution, respectively. Then, the mixed solution was casted on a glass plate and the glass plate was immersed into coagulation bath for about 5 min. The regenerated membranes were washed with deionized water thoroughly and dried in air for 2 days. The preparation process is summarized in **Figure 1**. The obtained membranes were labeled as 1CNF-RCM, 3CNF-RCM, 5CNF-RCM, 7CNF-RCM, corresponding to RCM with 1 wt% CNF, 3 wt% CNF, 5 wt% CNF, and 7 wt% CNF, respectively. GO/cellulose regenerated membrane were labeled as 0.2GO-RCM, 0.4GO-RCM, 0.8GO-RCM correspond to RCM contained 0.2wt%GO, 0.4wt%GO, and 0.8wt%GO, respectively.

Mechanical tests were carried out on a dynamic mechanical analyzer (DMA Q800 analyzer TA instruments) in a ramp force mode ranged from 3 N/min to 18 N. Scanning electron microscopy (SEM) images were produced by SEM (JEOL JSM-5900LV) at an accelerating voltage of 10 kV. X-ray-diffraction (XRD) study was carried out on an X-ray diffractometer (PhilipsX’Pert pro MPD, Holland) with a Cu-Kα radiation (λ = 1.5406 Å) with scanning angle of 2θ from 10° to 40° at scanning speed of 2°/min. Transmission electron microscopy (TEM) images were obtained on a Tecnai G2 F20 TEM. Thermogravimetric analyses (TGA) results were obtained on TG 209F1 Iris (Netzsch, Germany) under N₂ atmosphere with heating rate of 5°/min and reached 400 °C. Specimens for TGA test were kept at 100 °C for 5 min to remove the water completely. The optical transmittance (Tᵣ) properties were characterized on UV/VIS Spectrometer Lambda 650 (PerkinElmer).

**Results and discussion**

It should be noted that though both CNF and RCM are cellulose, their degree of polymerization, fiber morphology, degree of crystallinity (χc), and crystalline morphology are different. Also, cellulose from different biological source has significant differences. Those differences cause different mechanical properties between CNF and the matrix cellulose. CNF is prepared by oxidation with less amorphous region and nanosize. The high crystallinity endows CNF higher strength than the matrix and the small size makes it possible to decrease the defects in matrix and improves the ability of stress transfer. On the other hand, though GO sheets are aggregated to some extent in the alkali solution when the content of GO increases, which limits the maximum filler content. The high sheet strength of GO contributes much to the enhancement effect, which could
explain the fact that GO has relatively high enhancement effect even if only small amount of GO is incorporated into the matrix. The aim of our research is to compare the effects of different fillers on the properties of cellulose membrane regenerated from alkali/urea solvent system. Therefore, the relationship between the structures and properties is the key point of the research. Various methods were applied to characterize the structure of membranes containing different fillers with different content and the relationship between morphology of filler and their influence on mechanical reinforcement was investigated.

**Mechanical properties of RCMs**

Figure 2(a) and 2(b) show the suspension of GO and CNF, respectively. Figure 2(c) shows the photo of cellulose LiOH/urea drop. Both GO and CNF are well dispersed in aqueous solution and it is obviously that the suspension of CNF is transparent at 0.16% solid content, while the suspension of GO is dark brown at 0.25% solid content. The great dispersing ability of fillers in aqueous solution is the precondition for the evenly mixing of fillers in matrix cellulose. Figure 3(a) shows the SEM of GO (Spinning GO aqueous dispersion on conductive glass). It shows GO is monolayer with the mean diameter about 45 μm, which is consistent to our previous work [27]. Figure 3(b) shows the TEM image of CNF. The mean length of CNF is 550 nm with the mean width of 15 nm, which has aspect ratio of 36 and appears like curve. Figure 3(c) shows the TEM of cellulose regenerated from extremely dilute LiOH/urea solvent on copper mesh, which presents morphology of fiber [28], suggesting RCM is composed of those filaments (which can be further confirmed by SEM image).

The strain–stress curves of pure RCM and RCM with different fillers are shown as Figure 4. When the filler content reaches 5 wt%, CNF-RCM illustrates the maximum strength of 92.6 MPa, which increases 39.3% comparing with pure RCM. It could be seen that for CNF content above 1 wt%, the enhancement effect increases sharply. This phenomenon could be explained as when filler content is low, CNF have weak interact with each other and the stress transfer is relatively weak, making the enhancement effect mainly depends on the strength of the filler itself. With increasing filler content, CNF with a fibrous shape could form a net-like structure and stress transfer works synergistically with the strength of the filler itself. Meanwhile, GO illustrates weaker mechanical enhancement effect. GO-RCM reaches the maximum strength of 78.39 MPa at 0.4 wt% GO content with 17.9% improvement comparing with pure RCM. It is worth noting that the enhancement effect of GO is
obvious even if only small amount of GO is added into the matrix. It could be explained that the high sheet strength could withstand strong stress and contributes much to the enhancement effect when GO is well dispersed. Moreover, from the content-stress graph, GO could not form the net-like structure which might relate to the relatively weak stress transfer. The mechanical enhancement is shown in Figure 5. Fillers in nanometer size would aggregate when the filler content increases to a certain level. When aggregation occurs, filler aggregates would become the stress concentration points and decrease the strength of these composites. Thus, the determination of optimal filler content is very important. From DMA results, it could be observed that when the content of CNF reaches 7 wt%, the strength of CNF-RCM decreases. This indicates that aggregation may occur. Similarly, when the content of GO reaches 0.8 wt%, the strength of GO-RCM decreases. This could also be caused by aggregation. In order to confirm the micro-structure of RCMs, several methods were employed. As mentioned before, cellulose from different resources demonstrates different mechanical property due to the differences in crystallinity, relative molecular weight, and crystal type. Therefore, comparing the results of this study directly with the results in literatures does not make much sense. Also, the alkali/urea solvent system is a new solvent system for cellulose and research group lead by Prof. Zhang Lina has done much work on such system. Table 1 shows some results comparison. Although the enhancement effect of our work is a slightly lower than that of Prof. Zhang, the filler contents and types are different. The optimal content of CNF and GO are lower than fillers employed in the literatures. Besides, the fillers in RCMs of our work are isotropic comparing with oriented RCMs in literatures. Filler orientation could significantly affect the mechanical enhancement of fibrous fillers. From the table, it could also be observed that BC exhibits extremely high strength, which owes to its high purity and crystallinity (Table 1).

**Transparency property ($T_r$) of RCM**

The transparency property is important for the membrane in electronics devices [31]. Figure 6 shows the photos of RCM with different fillers. RCMs with CNF are transparent even after filler aggregation. On the other hand, the decrease in optical transmittance ($T_r$) is obvious with increasing GO content, since GO is deep colored. Figure 7 shows the $T_r$ of RCMs at the wavelength of 800 nm. With increasing GO content, the transparency of GO-RCM decreases rapidly. It is worth noting that when GO content increases from 0.2 wt% to 0.4 wt%,
$T_r$ decreases significantly, which indicates aggregation would occur in this range. For the same reason, $T_r$ of CNF-RCM decreases much when the content of CNF increases from 5 wt% to 7 wt%, also indicating aggregation. It could be observed that CNF-RCMs keep their transparency above 75% at 800 nm.

Table 1. Comparison with results in literatures.

| Materials      | Filler  | Optimal content (wt%) | $n_b$ (MPa) (no fillers) | $n_b$ (MPa) (with fillers) | Increasing (%) |
|----------------|---------|-----------------------|------------------------|--------------------------|----------------|
| NCC-RCMs [29]  | NCC     | 10                    | 87                     | 124                      | 42.5           |
| BCNC-BC [30]   | BCNC    | /                     | 117                    | 160                      | 36.7           |
| CNF-RCM        | CNF     | 5                     | 66                     | 93                       | 39.1           |
| GO-RCM         | GO      | 0.4                   | 66                     | 78                       | 17.9           |

The content of BCNC is empty because two-layered structure is constructed with BC and BCNC.

Figure 5. Enhancement mechanical of (a) content of CNF below 1 wt%, (b) content of CNF beyond 3 wt%, and (c) GO. The blue cubes stand for cellulose matrix membranes and the big array next to it stand for stretching direction. The small arrays in cubes stand for stress conduction direction. It could be seen that when content increased, CNF form a net-like structure thus is more advantageous for stress conduction. GO sheet could withstand strong stress.

Figure 6. Photos of (a) pure-RCM, (b) 1CNF-RCM, (c) 3CNF-RCM, (d) SCNF-RCM, (e) 7CNF-RCM, (f) 0.2GO-RCM, (g) 0.4GO-RCM, and (h) 0.8GO-RCM. It could be seen that with the increasing of fillers content, $T_r$ of CNF-RCM almost unchanged and $T_r$ of GO-RCM decreases much.
all the time and the addition of CNF only cause a loss of $T_r$ about 5%, which is insignificant comparing to the increasing in mechanical strength.

Thermal stability of RCM

Thermal stability is also an important property for materials. Cellulose could not withstand high temperature so that the determination of the decomposition temperature of these composites is necessary. Figure 8 shows the thermo-gravimetric analysis (TGA) results of RCM. Thermal decomposition temperatures of composite RCMs keep stable with minor changes when the fillers contents are low and decrease slightly when aggregation occurred. The TGA results further support DMA and UV–vis results. Table 2 shows the temperature at weight loss 5% ($WL_{5\%}$) of all RCMs. Even when aggregation occurs, the decomposition temperature at weight loss of 5% decreases not much, which indicates that RCMs keep rather good thermal stability at all filler content. Furthermore, GO-RCMs have higher thermal stability than CNF-RCM, which might be related to the rather good thermal stability of GO.

Morphology structure of composite membranes

To confirm the microstructure of RCM and explore factors that cause the changes in various properties, scanning electron microscope (SEM) is used to observe the cross section of RCM. Based on DMA results, CNF has greater enhancement effect than GO due to its relative high content and fibrous shape. On the other hand, because of the rather ordinary dispersion of GO in LiOH/urea solution, GO illustrates a limited enhancement effect. Such ordinary dispersion status could be explained as the charged groups on the surface of GO accelerates the
aggregation of GO in alkali solution due to their strong ionic strength. Figure 9 shows the SEM cross section of RCM (both RCM and RCM with different fillers). Images of pure RCM further confirms that RCM is composed of cellulose filaments. For filler content of 7wt%, CNF are aggregated to some extent (as shown in red circle in Figure 9(d)) while GO illustrates aggregation at 0.8wt% (as shown in the red circle in Figure 9(h)). Those results are consistent with the DMA results that the strength of composite RCM decreases when the content of CNF reaches 7 wt% and content of GO reaches 0.8wt%. The results indicate that the addition of the selected fillers, CNF and GO, would not change the crystal morphology of cellulose matrix with all contents. CNF comes from MFC and surface groups are similar to that on cellulose filaments which made up cellulose matrix RCM. This indicates that the formation of new crystal types is not induced. Besides, the diffraction peaks of CNF overlap with regenerated cellulose matrix [26]. As for GO, it should be noticed that the diffraction peaks of GO overlap with that of celluloseIcrystal [27]. In addition, new peaks are not observed, which could be explained as the similar reason as CNF. Besides, the degree of

Crystal morphology of matrix cellulose
The crystal morphology of cellulose is diverse and would affect the strength of cellulose [32]. Figure 10 shows the X-ray diffraction patterns of RCM (both pure and RCM with fillers). As shown in blue and red imaginary lines, diffraction peaks at 2θ = 14.8°, 17.0°, and 22.7° are (110) (110) (200) planes for celluloseIcrystal [32], respectively. As shown in black and red imaginary lines, diffraction peaks at 2θ = 11.8°, 19.8°, 22.7° are (110) (110) (200) planes for celluloseIcrystal [32], respectively. Although the peaks of celluloseIcrystal RCM are twisted compared to native cellulose [29], peaks of pure RCM and RCM with different fillers are identical. The results indicate that the addition of the selected fillers, CNF and GO, would not change the crystal morphology of cellulose matrix with all contents. CNF comes from MFC and surface groups are similar to that on cellulose filaments which made up cellulose matrix RCM. This indicates that the formation of new crystal types is not induced. Besides, the diffraction peaks of CNF overlap with regenerated cellulose matrix [26]. As for GO, it should be noticed that the diffraction peaks of GO overlap with that of celluloseIcrystal [27]. In addition, new peaks are not observed, which could be explained as the similar reason as CNF. Besides, the degree of
crystallinity ($\chi_p$) do not change much (varying from 45 to 48%, which is within the measurement error). With no significant changes in the matrix crystal morphology, it could be inferred that the increase in strength is mainly attributed by the properties of CNF and GO.

**Raman 2D band shift**

Raman spectroscopy could be employed to characterize the stress transfer effect from the matrix to fillers which is based on carbon [33–36]. Thus, the stress transfer effect of GO was characterized by Raman spectroscopy. GO-RCMs were strained under the Raman spectrometer and the shifts of the Raman bands were recorded with shifty strain, as shown in Figure 11. It could be seen that 2D band shift increases when content of GO increases from 0.2 wt% to 0.4 wt%, while 2D band shift decreases when content of GO increases from 0.4 wt% to 0.8 wt%. The value of 2D band shift indicates the stress transfer effect from polymer to filler, meaning

![Figure 11](image-url)
that when content of GO increases from 0.2 wt% to 0.4 wt%, stress transfer effect increases. Then, stress transfer effect fall when filler content increases from 0.4 wt% to 0.8 wt%. Raman result further confirms that when content of GO reaches 0.8 wt%, aggregation occurs and stress transfer effect decreases.

**Conclusion**

In our experiments, RCMs with two different fillers have been successfully prepared. The mechanical properties of RCM were characterized with DMA and CNF-RCM with 5 wt% of CNF illustrates the highest tensile strength. GO-RCM has the maximum enhancement effect at 0.4 wt% GO content. According to our results, those nanosize fillers would aggregate at certain filler content levels in matrix. CNF has a relatively high content while the content of GO is limited because of the strong ionic matrix. SEM and T₆ results are in accordance with DMA test. X-ray diffraction test shows that the crystal types of matrix cellulose do not change when fillers are added. TGA result shows that RCMs keep great thermal stability even if the aggregation of fillers occurs. It could be concluded that fillers with great strength is the basis of great mechanical enhancement under the premise of good dispersion. Furthermore, fillers which obtain fibrous shape with large aspect are advantageous for enhancement with great ability for stress transfer. The strong alkaline of solvent means strong ionic strength, which could lead to the aggregation of some fillers with large surface area and charged groups, even if they are well dispersed in aqueous system. Those kinds of fillers should exhibit extraordinary strength to ensure their enhancement effect at low contents. On the other hand, the addition of GO introduces the possibility of functionalization because GO could be reduced to graphite, which is widely used in conductive materials, thermal material, and electromagnetic shielding material areas [25], and would greatly expand the application of composite RCM. Our research not only successfully prepared composite RCM with improved strength, proving that the new alkali/urea solvent is a potential system for preparing high performance cellulose composite materials, but also compared the enhancement effect of fillers with different properties, which could benefit the selection of suitable fillers for our green solvent system and prepare more functional regenerated cellulose materials [30,37].

**Notes on contributors**

**Yinke Liu** received her Bachelor of Science degree in 2016 from Sun Yat-Sen University and studying for a master degree at College of polymer science and engineering, Sichuan University. She joined Prof. Q Fu’s research group in 2016 and her main research direction is preparation of regenerated cellulose membrane.

**Shuman Xu** received her Bachelor degree in 2014. She is currently pursuing the Ph.D. at School of Polymer Science and Engineering, Sichuan University. Her current research is construction and functional application of cellulose and its nanocomposites.

**Mengfan Jing** received his Bachelor degree in 2014. She is currently pursuing the Ph.D. at School of Polymer Science and Engineering, Sichuan University. Her current research is preparation of high-performance poly(lactic acid)/glass fiber composites.

**Yuan Wei** received his Bachelor of Engineering degree from Sichuan University in 2016. He is current studying for a master degree at Prof. Qiang Fu’s research group in College of Polymer Science and Engineering, Sichuan University. His majority is the design and preparations of shape memory polymers.

**Hua Deng** obtained his bachelor degree in Harbin Institute of Technology, China in 2003. In 2004 and 2008, he received his MEng and Ph.D. degree from Queen Mary, University of London. From June 2008 to July 2009, he worked for carbon nanotube producer Nanocyl S.A. (Belgium). He joined Sichuan University, China in 2009 as lecturer. He was promoted to Associate Professor and Professor in 2011 and 2015, respectively. His research interests include: polymer nanocomposites, conductive polymer composites, strain/pressure sensing polymer composites, dielectric polymer composites.

**Qiang Fu** obtained his Ph.D. degree from Sichuan University in 1993. He worked as Post Doctor fellow at The University of Akron from 1995 to 1997, and Humboldt fellow at University of Freiburg from 1999 to 2000. He became Professor in the College of Polymer Science and Engineering at Sichuan University since 1998. Since 2011, he is the Dean of College of Polymer Science and Engineering. His research interests include polymer composites and blends, polymer processing and physics.

**References**

1. Peterson BS, Rauh VA, Bansal R, et al. Effects of prenatal exposure to air pollutants (polycyclic aromatic hydrocarbons) on the development of brain white matter, cognition, and behavior in later childhood. JAMA Psychiatry. 2015;72:531–540.
2. Sharma VK, Fortuna F, Mincarini M, et al. Disposal of waste tyres for energy recovery and safe environment. Appl Energy. 2000;65:381–394.
3. Schurz J. Trends In PS. A bright future for cellulose. Prog Polym Sci. 1999;24:481–483.
4. Lu Y, Huang J, Ge L, et al. Selective localization of cellulose nanocrystals in the biodegradable poly (vinyl alcohol)/poly(epsilon-caprolactone) blend composites prepared by pickering emulsions. Polymer. 2018;156:136–147.
5. Pandey N, Shukla SK, Singh NB. Water purification by polymer nanocomposites: an overview. Nanocomposites. 2017; 3:47–66.
6. Hiroaki I, Mibuki S, Chizuru H, et al. Cellulose nanofiber nanocomposites with aligned silver nanoparticles. Nanocomposites. 2019;4:167–177.
7. Rehman N, de Miranda M, Rosa S, et al. Reinforcement of hydroxypropyl-cellulose films by cellulose nanocrystals in the presence of surfactants. Chin J Polym Sci. 2016;34:1301–1310.

8. Lee K-Y, Bismarck A. Single step functionalization of celluloses with differing degrees of reactivity as a route for in situ production of all-cellulose nanocomposites. Nanocomposites. 2015;1:214–222.

9. Hou M, Xu M, Li B. Enhanced electrical conductivity of cellulose nanofiber/graphene composite paper with a sandwich structure. ACS Sustainable Chem Eng. 2018;6:2983–2990.

10. Dogan H, Hilmioglu ND. Dissolution of cellulose in NMMO monohydrate. Carbohydr Polym. 2009;75:90–94.

11. Zhang H, Wu J, Zhang J, et al. 1-Allyl-3-methylimidazolium chloride room temperature ionic liquid: a new and powerful nonderivatizing solvent for cellulose. Macromolecules. 2005;38:8272–8277.

12. Cai J, Zhang L. Rapid dissolution of cellulose in LiOH/urea and NaOH/urea aqueous solutions. Macromol Biosci. 2005;5:539–548.

13. Heinze T, Liebert T. Unconventional methods in cellulose functionalization. Progress Polym Sci. 2001;26:1689–1762.

14. Kim SS, Jeong J, Lee J. Antimicrobial m-aramid/cellulose blend membranes for water disinfection. Ind Eng Chem Res. 2014;53:1638–1644.

15. Kim CJ, Khan W, Kim DH, et al. Graphene oxide/cellulose composite using NMNO monohydrate. Carbohydr Polym. 2011;86:903–909.

16. Cai J, Zhang L, Zhou J, et al. Multifilament fibers based on dissolution of cellulose in NaOH/urea aqueous solution: structure and properties. Adv Mater. 2007;19:821–825.

17. Lia J, Zhang J, Zhang S, et al. Alkali lignin depolymerization under eco-friendly and cost-effective NaOH/urea aqueous solution for fast curing bio-based phenolic resin. Ind Crops Prod. 2018;120:25–33.

18. Zeng J, Liu S, Cai J, et al. TiO2 immobilized in cellulose matrix for photocatalytic degradation of phenol under weak UV light irradiation. J Phys Chem C. 2010;114:7806–7811.

19. Tian J, Peng D, Wu X, et al. Electrodeposition of Ag nanoparticles on conductive polyaniline/cellulose aerogels with increased synergistic effect for energy storage. Carbohydr Polym. 2017;156:19–25.

20. Wang Z, Fan X, He M, et al. Construction of cellulose-phosphor hybrid hydrogels and their application for bioimaging. J Mater Chem B. 2014;2:7559–7566.

21. Laity PR, Glover PM, Hay JN. Composition and phase changes observed by magnetic resonance imaging during non-solvent induced coagulation of cellulose. Polymer. 2002;43:5827–5837.

22. Qiu C, Zhu K, Yang W, et al. Super strong all-cellulose composite filaments by combination of inducing nanofiber formation and adding nanofibrillated cellulose. Biomacromolecules. 2018;19:4386–4395.

23. Yang Q, Fukuzumi H, Saito T, et al. Transparent cellulose films with high gas barrier properties fabricated from aqueous alkali/urea solutions. Biomacromolecules. 2011;12:2766–2771.

24. Klemm D, Kramer F, Moritz S, et al. Nanocelluloses: a new family of nature-based materials. Angew Chem Int Ed Engl. 2011;50:5438–5466.

25. De.Marchi L, Pretti C, Gabriel B, et al. An overview of graphene materials: properties, applications and toxicity on aquatic environments. Sci Total Environ. 2018;631:1440–1456.

26. Isogai A, Saito T, Fukuzumi H. TEMPO-oxidized cellulose nanofibers. Nanoscale. 2011;3:71–85.

27. Liu Y, Zeng J, Han D, et al. New insight of high temperature oxidation on self-exfoliation capability of graphene oxide. Nanotechnology. 2018;29:185601.

28. Qiu C, Zhu K, Zhou X, et al. Influences of coagulation conditions on the structure and properties of regenerated cellulose filaments via wet-spinning in LiOH/urea solvent. ACS Sustainable Chem Eng. 2018;6:4056–4067.

29. Qi H, Cai J, Zhang L, et al. Properties of films composed of cellulose nanowhiskers and a cellulose matrix regenerated from alkali/urea solution. Biomacromolecules. 2009;10:1597–1602.

30. Urbina L, Corcuera MA, Eceiza A, et al. Stiff all-bacterial cellulose nanopaper with enhanced mechanical and barrier properties. Mater Lett. 2019;246:67–70.

31. Nogi M, Yano H. Transparent nanocomposites based on cellulose produced by bacteria offer potential innovation in the electronics device industry. Adv Mater. 2008;20:1849–1852.

32. Newman RH. Simulation of X-ray diffractograms relevant to the purported polymorphs cellulose IV$_{1}$ and IV$_{3}$. Cellulose. 2008;15:769.

33. Gong L, Kinloch IA, Young RJ, et al. Interfacial stress transfer in a graphene monolayer nanocomposite. Adv Mater. 2010;22:2694–2697.

34. Ahmad SR, Xue C, Young RJ. The mechanisms of reinforcement of propylene bygraphene nanoplatelets. Mater Sci Eng B. 2017;216:2–9.

35. Ferrari AC, Meyer J, Scardaci V, et al. Raman spectrum of graphene and graphene layers. Phys Rev Lett. 2006;97:187401.

36. Liu M, Papageorgiou D, Li S, et al. Micromechanics of reinforcement of a graphene-based thermoplastic elastomer nanocomposite. Compos Part A. 2018;110:84–92.

37. Morgenstern, BA, Kammer, HW. Solvation in cellulose-LiCl-DMAC solutions. Trends Polym Sci. 1996;3:87–91.