Influence of Soft Segment Molecular Structure on Physicochemical Properties of Cellulose Nanocrystals based Polyurethane

Maolan Zhang, Jiale Wang, Yan Li, Xiujuan Lu, Xiaoling Liao, Guoming Zeng

1Chongqing Engineering Laboratory of Nano/Micro Biological Medicine Detection Technology, Chongqing University of Science and Technology, Chongqing, 401331, China
2School of Pharmacy, Taizhou polytechnic college, Taizhou 225300, China
3School of Civil Engineering and Architecture, Chongqing University of Science and Technology, Chongqing 401331, China

Abstract—SPUs are commonly used in clinic due to their good biocompatibility and can respond to different external stimuli. Among them, introducing CNCs into PUs to prepare water-driven PUs had attracted increasing attention. Herein, we report two new types of CNCs based PU nanocomposites by chemically cross-linking CNCs and PDLLA soft segment with flexible PEG chain or rigid piperazine ring structures. Specifically, the prepared nanocomposites were characterized by their morphology, chemical structure, thermal property, hydrophilicity as well as crystallinity, and the results showed that regardless of the molecular structure of the PDLLA, chemically cross-linking CNCs and PDLLA could significantly improve their compatibility. In addition, when the soft segment contains hydrophilic flexible sections, ie, PEG 200, the compatibility of CNCs with PU and crystallinity of obtained materials were better, and when the PDLLA contains a rigid cyclic structure, the thermal stability of obtained CNCs based PU would be more excellent. These results suggest that we can design the soft segment molecular structure of CNCs based PU to meet the performance requirements of different biomedical applications.

1. Introduction
Polyurethane (PU) is a class of polymers containing a carbamate group (-NHCOO-) in its main chain structure. Since it was first successfully synthesized by Dr. Bayer in 1937, it has been widely used in various fields due to their excellent mechanical strength, high elasticity, as well as good processability [1-3]. In addition, various performance products can be prepared by controlling different process conditions and parameters, ie, biodegradable PU, choosing biodegradable macromolecular alcohol, such as polyactic acid (PLA), polycaprolactone (PCL) or polyether as soft segment, disocyanate and small molecule with multi hydroxyl or multi amino as hard segment [4-6]. What's more interesting is that by designing the type, content and relative molecular weight of hard segment and soft segment, crosslinking agent and filler doping method, the mechanical parameters such as shape, position and...
The elongation rate of PU can be restored to the original state before the parameters change under different environment (temperature, light, electromagnetic, magnetic and solvent) [7-12]. Therefore, PU has great potential with its development and applications.

Cellulose nanocrystals (CNCs) have attracted much attention in the field of biomimetic stimulation sensitive mechanical adaptive composites in recent years due to their excellent intrinsic properties, including unique morphology, nano size, low specific gravity, high specific surface area, high crystallinity, excellent mechanical strength as well as the advantages of renewable, degradable and wide sources [13-15]. However, to the best of our knowledge, most of these composites were obtained by physical incorporation of CNCs into the polymeric matrix [16,17]. Consequently, the weak bonding force between CNCs and polymer molecular chains, as well as the dispersion and interfacial compatibility of CNCs in polymer were always the most important factors affecting the properties of the nanocomposites [18]. Therefore, some researchers have turned their research stress to introduce CNCs into the polymer matrix by chemical cross-linking to prepare water-sensitive PU materials [19]. However, when the soft segment contains fragments of different molecular structures (or properties), there is a lack of research about its impact on the properties of obtained materials.

In this work, we also use the strategy of chemical cross-linking to introduce CNCs into the molecular structure of PU. Moreover, in order to study the influence of different molecular structures of soft segment on the physical and chemical properties of CNCs based PU, we first took PDLLA as the matrix, introduced a rigid piperazine (PA) ring or flexible PEG segment into it, and then used this two kinds of PDLLA macromolecular alcohol as soft segment, CNCs as hard segment to prepare a series of CNCs based PUs. Finally, the dispersion of CNCs in obtained PU material, the thermal stability, hydrophobicity and crystallinity have been carefully investigated in order to provide a reference for further improving the properties of water-sensitive PU materials.

2. Methods

2.1 Preparation of CNCs

CNCs were prepared from microcrystalline cellulose (MCC) by hydrolysis treatment according to a previously published method of few modifications [20]. More specifically, MCC was first added into the 64 wt % sulfuric acid (H$_2$SO$_4$) in water to hydrolysis at 45 ℃ for 1.5 h, then the obtained mixture was transferred to the ultrasonic device and continued ultrasonic (~350 W) at room temperature for 0.5 h to further isolation of CNCs. Finally, the CNCs were obtained after repeated centrifugation, water washing and freeze-drying.

2.2 Preparation of CNCs based PUs

PU nanocomposites composed of HDI, PDLLA with different molecular structures (PDLLA-PA, PDLLA-PEG), and CNCs as chain extender were synthesized by a two-step process. First, the PDLLA diols with different molecular structure were synthesized by ring-opening polymerization of D,L-lactide in the presence of Sn(Oct)$_2$ as an initiator and PA or PEG 200 as a co-initiator according to our previously study [21]. Subsequently, A set proportion of CNCs was dissolved in the right amount of DMF, and a stable solution was obtained through a 10 min ultrasonic treatment. Later, the solution was dried over activated 4 Å molecular sieves for about 1 week. Finally, predetermined amounts of PDLLA diol (PDLLA-PA or PDLLA-PEG), HDI, Sn(Oct)$_2$ and anhydrous toluene were added into a 100 mL three-necked round flask equipped with a magnetic stirrer, and this device was placed in an oil bath at 75 ℃ for 3 h under flowing nitrogen atmosphere to remove the moisture. Subsequently, the stable CNCs solution in DMF was added into the reaction system slowly for chain extension at 80 ℃ for another 4 h. The PUs were successively purified by distilled water, absolute ethanol and then dried under vacuum at room temperature for at least 48 h. Another PUs prepared as controls were synthesized using a directly comparable methodology, however, in this case the chain extender was PA in place of CNCs.
2.3 Structural Characterization

Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and transmission electron microscopy (TEM, JEM 1200) were selected to characterize the structure of CNC.

2.4 Dispersion property

Series of PUs were first dissolved thoroughly in the mixture of chloroform and DMF ($V_{CHCl3}:V_{DMF} = 9:1$), and then cast as films. After drying at room temperature, the dispersion of CNCs in different types of CNCs based PUs was finally observed by optical microscope.

2.5 Physicochemical properties

Contact angle equipment (DSA 100, KRUSS), STA449C thermal analysis system (NETZSCH) and differential scanning calorimetry (DSC) were used to measure the hydrophilic properties and thermal stability of PU series materials. Polarized optical microscopy (POM) was conducted to characterize the crystallization behaviour of the CNCs based PUs using Nikon Eclipse Ci-POL (Japan).

3. Results and discussion

3.1 Structure and morphology analysis CNCs

![Fig. 1](image)

Fig. 1 (A) XRD and (B) FTIR spectra of CNCs. (C) and (D) TEM images at different magnification of CNCs.

CNCs prepared in this study were characterized by FTIR, XRD and TEM, respectively, and the results were shown in Fig. 1. The FTIR and XRD results were consistent with those reported in the literature[21]. Fig. 2 C and Fig. 2 D were the TEM images of the prepared CNCs. As shown in the figures, the CNCs presented a bright long rod-like structure, and their size is between 100 - 200 nm in length and 10 - 20 nm in width, which is consistent with the reported. Meanwhile, agglomeration was observed in the TEM images, and this is mainly due to the formation of hydrogen bonds on the surface of nano cellulose.
3.2 FTIR analysis of PUs

Aiming at studying the effect of different soft segment molecular structures on the chemically cross-linking of CNCs with PUs, four types of PU (PU$_{PA}$, NPU$_{PA}$, PU$_{PEG}$, NPU$_{PEG}$) were synthesized. The structure of PUs was investigated by FTIR, and the resulting curves were presented in Fig. 2. Specifically, the characteristic peak at 3509 cm$^{-1}$ in PDLLA diol spectrum was replaced by a wide peak at around 3200 cm$^{-1}$ to 3500 cm$^{-1}$ of PU$_{PA}$ and PU$_{PEG}$ curves, which is assigned to the stretching vibration of -NH and -OH groups in PUs. Moreover, the intensity of those peaks increases obviously in NPU$_{PA}$ and NPU$_{PEG}$ curves due to the large amount of -OH in the surface of CNCs. Additionally, a sharp characteristic peak at around 1755 cm$^{-1}$ represents the typical C=O stretching vibration, the characteristic peak at 1668 cm$^{-1}$ is attributed to the amide I stretching vibration in urethane amide and urea amide, which is coincide with the N-C=O stretching vibration of PDLLA diol. Moreover, a new absorption band appeared at 1525 cm$^{-1}$, which can be assigned to -NH bending deformation combined with C-N asymmetric stretching, respectively. Thus, it can be inferred that four types of PU have been successfully synthesized in this study.

3.3 Dispersion and hydrophilicity analysis of PUs

The surface morphology of PUs was observed by optical microscope, and the results were shown in Fig. 3A. Compared with PU$_{PA}$ and PU$_{PEG}$ films, white dots could be clearly identified in the matrix of NPU$_{PA}$ and NPU$_{PEG}$ nanocomposites, which corresponded to the CNCs in the surface of the CNCs based PU nanocomposite films. When it was magnified 100 times, it could be clearly observed that these CNC fillers were well dispersed in the PU matrix, implying that a good compatibility between the CNC fillers and PU matrix was achieved, which may be ascribed to the covalent bonding between CNCs and the molecular chains of PUs [22]. In addition, Compared with NPU$_{PA}$ group, the dispersion of CNCs in NPU$_{PEG}$ group was more uniform, which indicated that CNCs and PU have better compatibility when the PDLLA soft segment contains hydrophilic chain structures such as PEG 200. In addition, another interesting phenomenon was observed on the PU$_{PA}$ film. Specifically, there were many regular shuttle-shaped structures on the surface of PU$_{PA}$ film under the 100× field of vision, which may be due to the symmetrical rigid ring structure of PA in the soft segment not only acted as...
nucleating agents, but also limited the movement of PDLLA soft segment. With that in mind, this phenomenon may affect the crystalline property of the CNCs based PU nanocomposites. Hydrophilic and hydrophobic properties have great influence on the water sensitivity of PU, and Fig. 3B showed the water contact angle analysis of PUs. From the figure, it can be observed that all four kinds of PU held a contact angle less than 90°, indicating that they were hydrophilic, which could be useful for biomaterials to favor cell attachment [23]. Compare with control PU groups (PU-PA: 80.1±1.6°, PU-PEG: 73.3±0.8°), after chemically cross-linking of CNCs with PUs, the obtained CNCs based PUs showed better hydrophilic property (NPU-PA: 70.0±1.3°, NPU-PEG: 67.7±2.2°), which was consistent with previous reports [19]. In addition, the hydrophilic property of CNCs based PU was highly related to the molecular structure of soft segments, when there were hydrophilic chain structures, ie, PEG 200, the obtained nanocomposites usually have better hydrophilic property.

3.4 Thermal properties of the PUs

Thermal degradation behavior of the PUs was investigated by TGA measurement as shown in Fig. 4A. For the PU-PA and NPU-PA materials, an abundance of rigid PA rings could restrict the mobility of soft segments, and compared NPU-PEG with PU-PEG, it can be observed that the thermal stability of material was significantly improved after chemical cross-linking of CNCs with PU, which may be due to the hydrogen bonds form between the large number of -OH groups in CNCs surface, PDLLA doil and the -NH- in urethane groups and urea groups, further hindering soft segment chain rotation. While compared NPU-PA with PU-PA, although their initial thermal decomposition temperature was approaching, the decomposition temperature range of NPU-PA was extended, and two stages were observed in the TGA curve, this may be the result that the HDI/PA hard segments in PU-PA played a role similar to the hydrogen bonds in NPU-PA. In brief, these results suggested that the molecular structure of both hard and soft segments would have a greater impact on the thermal degradation property of materials, and compared with flexible PEG 200 section, the thermal stability of CNCs based PUs could be significantly improved when the PDLLA soft segment contained a rigid ring structure. However, the melt temperature (T_m) of PUs is highly dependent on the crystallization of soft segments, thus DSC was employed to monitor the crystallization behaviors of four kinds of PU. The
testing program was shown in Fig. 4B, where the glass transition temperatures were recorded in the second heating process. As shown in the figure, four different points were measured, 42.0, 48.3, 35.8 and 44.7 °C for PU-PA, NPU-PA, PU-PEG and NPU-PEG, respectively, and there was a complete phase transformation process at these points. This result suggested that after introduction of CNCs into the polymer matrix through chemical cross-linking could increase the crystallinity of composite materials. In addition, when there were rigid ring structures of the soft segments, it would also contribute to the crystallinity of CNCs based PU.

Fig. 4 The TGA curve (A) and DSC curve (B) of PUs.

3.5 Crystallization property of the PUs

When CNCs were added into the polymer as a green reinforcing phase to form nanocomposites, CNCs and polymer could form co-crystallization to improve the crystallization performance of the nanocomposites [24]. Considering this, the POM study was conducted for observing the effect of molecular structure of the soft segment on the crystallization property of CNCs based PUs in this study, and the results were shown in Fig. 5. From the figure, it can be seen that when the PDLLA soft segment was chain and contained hydrophilic PEG 200 sections, it could entangle with CNCs to promote its nucleation. Moreover, it also indicated better compatibility between CNCs and PDLLA-PEG doil. However, when the PDLLA soft segment was chain and contained rigid ring sections, restricted chain motion hindered the growth of overlapped spherulites. On the other hand, as shown in Fig. 5A, the symmetrical structure of PA would provide more nucleation sites and ultimately affect the crystallization property of CNCs based PUs, changing its size and crystal form.

Fig. 5. Polarizing microscope images of (A) NPU-PA and (B) NPU-PEG.
4. Conclusion
In conclusion, we successfully prepared two novel types of CNCs based PU nanocomposites with PDLLA-PEG doil or PDLLA-PA doil as soft segments and CNC nanofillers as cross-linkers. Good compatibility between CNCs and PU could be obtained through chemical cross-linking of CNCs with PDLLA doil. Simultaneously, compared with PU-PEG and PU-PA, the NPU-PEG and NPU-PA nanocomposites exhibited an excellent thermal stability, hydrophilicity and crystallinity. What's more, when the soft segment contained hydrophilic flexible sections or rigid ring structures, the above property of CNCs based PUs would be affected greatly. For example, when PDLLA soft segment contained flexible PEG 200, the compatibility of CNCs with PU and crystallinity of CNCs based PUs would be better, and when the PDLLA segment contained a symmetrical rigid cyclic structure, the thermal stability of the CNCs based PUs would be more excellent. Therefore, considering the literature and the results of this study, the CNCs based PUs could be potentially applied in different biomedical field by designing the molecular structure of the soft segments.

Acknowledgments
This work was supported by the National Natural Science Foundation of China [52103156], Youth fund project of Chongqing University of Science and Technology [ckrc2019015], Provincial and Ministerial Co-constructive of Collaborative Innovation Center for MSW Comprehensive Utilization [shljzyh2021-2], Innovation - entrepreneurship Seed Foundation of Chongqing Engineering Laboratory of Nano/Micro Biological Medicine Detection Technology (Chongqing University of Science and Technology) [1155108202005] and Technical innovation training program for College Students (Chongqing University of Science and Technology) [2021198].

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