論 文 の 内 容 の 要 旨

論文題目　Experimental Investigation of Cellulose-based Nanostructures with Promoted Thermal Conductivity
（熱伝導率促進型のセルロースナノ構造体の実験的研究）

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Abstract

To curb the emission of carbon dioxide and control the global warming, it is pertinent to develop innovative materials and technologies using renewable resources. Cellulose is regarded as a green and renewable resource that has attracted attention in recent years due to its excellent mechanical properties. Cellulose can be obtained from many kinds of plant resources such as wood and stems. Although the mechanical properties of such cellulose materials are well investigated, research on understanding the thermal properties of such materials is at an early stage. The thermal conductivity of cellulose materials has not been fully investigated yet since it strongly depends on the structure, purity content, and morphology, etc. To explore the use of cellulose-based materials in industrial applications, it is important to investigate their thermal properties in detail.
In the first work of this thesis, we obtained cellulose filaments with the diameter ranging from 6-18 um under two kinds of gelled conditions (with hydrochloric acid or

ferric chloride). We setup a flow-focusing channel system to enhance the thermal conductivity of cellulose filaments by controlling the alignment, crystalline nature, and orientation. The cellulose nano-fibrils dispersed in deionized water are processed by the flow focusing channel, where cellulose nano-fibrils get hydrodynamically aligned along the flow due to the contraction. In addition, salt or acid is added into the channel, which makes the cellulose filaments become gelled by forming hydrogen bonding or ionic bonding.

The thermal conductivity of individual filaments is measured using a custom-built T-type measurement technique. Our results show that the highest thermal conductivity of cellulose filament reaches 14.5±0.49 W/m-K. Smaller diameter filaments show higher thermal conductivity due to the formation of high crystallinity regions during the gelation process, which is confirmed by Raman spectroscopy. In addition, we found that residual stress produced during the gelation process lead to a decrease in crystallinity, which in turn decreases thermal conductivity. Furthermore, filaments gelled with hydrochloric acid show higher thermal conductivity than the ones with ferric chloride, mainly due to high crystalline regions are more likely to form with gelled with hydrochloric acid filaments.

In the second part of the thesis, we studied thermal conductivity of cellulose based composite, and find its anisotropy ratio of thermal conductivity. Wood, which is composed of cellulose, is widely used in building systems mainly due to its lightweight and strong mechanical properties. However, cellulose is flammable, which brings hidden danger to the safety of buildings. Most of the flame-retardant materials contain bromine and chlorine that are reported to form toxins. On the other hand, a new green functional flame retardant material, montmorillonite-clay is widely used due to its excellent mechanical properties, gas barrier properties, biodegradability, and flame retardant properties. However, the thermal conductivity of pure montmorillonite clay is low, which is problematic for its application. One possible solution is to improve the thermal conductivity of pure montmorillonite clay by adding high thermal conductivity materials. Nano-cellulose is generally introduced for its high strength and high crystalline stiffness to improve composites' mechanical properties, but it also may have an advantage in thermal conductivity.

With the inspiration based on the high thermal conductivity cellulose filaments, we aimed to expand its application to a larger scale. For this, we performed anisotropic thermal conductivity measurements of films of a layer-by-layer hierarchical structure of Montmorillonite-clay/cellulose nanocomposite with thickness around 90 μm fabricated by vacuum-filtration and drying. Montmorillonite platelets act as ‘brick’ with a

thickness of around 1.1 nm, and nano-cellulose acts as 'mortar' with 3 nm in diameter and several micrometers in length. The aim is to realize a composite with a relatively high anisotropy ratio of thermal conductivity, to decrease the localization of high temperature. We measured the anisotropy ratio of thermal conductivity as a function of montmorillonite-clay/cellulose content using the laser flash technique. Our result shows that the cross-plane thermal conductivity depends on the clay content non-monotonically; as the clay content increases from 0% (pure cellulose), the thermal conductivity decreases until the content reaches 80% and then increases until 100%. The in-plane thermal conductivity also shows a non-monotonic dependence on the content; increasing to 50 % and then decreasing. This gives rise to the largest anisotropy for clay content of 50 %, where in-plane thermal conductivity is 30 times larger than the cross-plane thermal conductivity. Furthermore, Raman spectroscopy was performed to investigate the orientation of cellulose nano-fibrils in the composite, and the analysis reveals that the degree of alignment strongly depends on the clay content with the maximum achieved at 50 % content and the large anisotropy is originated from the alignment of the cellulose nano-fibrils.

KEYWORDS: cellulose filament, montmorillonite, thermal conductivity, anisotropy ratio