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主 論 文 の 要 旨

論文題目　Material Evaluation of Cellulosic Materials by Terahertz Time-domain Spectroscopy
（テラヘルツ時間領域分光法によるセルロース系材料の材質評価）

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論 文 内 容 の 要 旨

With the wild use of fossil resources since the second industrial revolution, global environmental problems such as global warming and climate anomalies have now become significant challenges for human survival. Cellulose, as an important recyclable and abundant resource, the effective using and development of cellulose materials such as wood and bamboo is an essential countermeasure against global warming and other environmental issues, thus, the non-destructive evaluation of material properties is necessary. Terahertz (THz) radiation lies in far-IR radiation between microwaves and IR of the electromagnetic spectrum with a frequency range of 0.1–10 THz, corresponding to wavelengths of 3–0.03 mm, and terahertz time-domain spectroscopy (THz-TDS) has been developed for commercial. THz radiation is non-ionizing, safe for human bodies, and many non-conductive dry materials (wood, ceramic, paper, etc.) are transparent at THz frequency. This transparency allows for transmission imaging of many materials with sub-millimeter spatial resolution. Besides, with one measurement, the refractive index and absorption coefficient can be obtained simultaneously by calculation. Furthermore, THz radiation is responsive to optical phonons in crystalline lattices. This means that THz is very suitable to investigate cellulose crystalline and cellulose-based materials. Therefore, in this study, THz-TDS was used to investigate various porosities of cellulosic materials.

First of all, moisture content (MC) and density influence the mechanical and physicochemical properties of wood, therefore, an accurate prediction of these properties is necessary. In the previous study, the prediction was approached by the effective medium theory (EMT) model combined with the Double Debye model to express the dielectric function of water in the cell wall of wood. However, using the Double Debye model to explain the behavior of water in the cell walls, particularly at a relatively low MC under fiber saturation point (FSP) is inaccurate, because the Double Debye model is applied to the bulk water, and when the MC is relatively low, the behavior of water in the cell wall is closer to the bound water, thus, using the Double Debye model led to a systematic underestimation of MC. In this study, by building an MC-dependent dielectric function of water in the THz region, the accuracy of the prediction model of density and MC of wood was significantly improved compared with the previous model, and the problem of systematic underestimation of MC was solved.

Undertaking the above research, the other important properties of wood, including density, MOE, cellulose crystallinity, and microfibril angle (MFA) was attempted to predict by THz-TDS with a simpler multiple linear regression (MLR) model (compare with the EMT model using dielectric function). The density and MOE can be predicted well. However, the prediction accuracy of MFA and cellulose crystallinity was limited. This result indicated the possibility of using THz-TDS to predict the physical properties of cellulosic materials simultaneously. Thus, in order to improve the prediction accuracy of MFA and cellulose crystallinity, the following study is focused on the optical properties in the THz region of various cellulose crystallines.

It has reported of the absorption coefficient spectra of some polysaccharide crystals, including fructose, glucose, and sucrose. However, the virous crystalline of cellulose has not been studied in detail in the THz region. In this study, native cellulose I_α and I_β allomorphs were investigated by THz-TDS and X-ray diffraction (XRD). In the XRD patterns, the difference between these allomorphs was difficult to identify since there are only slight changes in peak positions that can be observed. On the other hand, cellulose I_α and I_β showed a characteristic absorption at 2.38 THz and 2.11 THz, respectively. Furthermore, different from the relative content cannot be calculated directly in the XRD patterns, the intensity of the absorption peaks in the THz region was directly correlated with the relative content of the component, which makes the evaluation of the cellulose allomorphs in the THz region is easier and simpler.

After this, the amount of cellulose in various materials which is also an important parameter that influences the properties of the cellulosic materials was determined by THz-TDS and XRD with wood, microcrystalline (MCC) cellulose, and pseudo-wood (MCC mixed with lignin). The standard for evaluating the cellulose crystallinity has been used as the cellulose crystallinity index (CrI, related to the relative content of cellulose in materials), which is just a relative parameter calculated from XRD patterns and the calculation was dependent on the experience of the analyst, where the available profile for the peak deconvolution is not unique. On the other hand, cellulose I regardless of I_α or I_β all showed absorption peaks around 3.04 THz, the integrated intensity of the absorption peaks at 3.04 THz was directly correlated with the amount of cellulose I, which showed a more reasonable result of the cellulose crystallinity compared with CrI. This means that the integrated intensity of the THz absorption peaks has the potential to instead of the CrI which is a relative parameter calculated from XRD becoming a new standard for evaluating the amount of cellulose crystalline in materials.

At last, the crystalline lattice structure and the crystallinity changing of cellulose I after chemical treatment. Tracing the transformation of the crystalline structure is essential for a better understanding of the processes of industry and biosynthesis where cellulose is involved, such as viscose rayon manufacturing. In this study, the transformation of the crystalline lattice of cellulose I to cellulose II was traced by using THz-TDS and XRD. Cellulose I and cellulose II was shown a different characteristic absorption profile in the THz region, and the relative content can be expressed by the coefficient calculated from fitting the absorption coefficient spectra in the THz region. And the crystallinity changing of cellulose II after ball-milling was evaluated by the integrated intensity of the characteristic absorption peaks of cellulose II.

In summary, THz-TDS was used for investigating various cellulosic materials. The THz signal can be measured at room temperature and does not require sample pretreatment, the measurement and analysis processes are rapid and simple compared with the XRD patterns. As the results obtained, we believe THz-TDS not only can be used to predict the properties of cellulosic materials but also has the potential to become a useful tool in the research and understanding of cellulose crystallography. Especially when analyzing the cellulose crystallinity, the results are better than XRD, which demonstrates the great potential of THz-TDS in the research of cellulosic materials.