

( 続紙 1 )

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論文題目	Optically Transparent Nanocellulose-Reinforced Composites <i>via</i> Pickering Emulsification (ピッカリングエマルジョンによるナノセルロース補強透明材料)		
(論文内容の要旨)			
<p>Cellulose nanofibers (CNFs), ~15–20-nm-wide semi-crystalline long fibers made up of 3–5-nm-wide microfibrils of extended cellulose chains, are one of the marvelous materials produced in the plant cell walls. With their strength seven times stronger than steel and an elastic modulus of 100–130 GPa (of the crystalline part called cellulose nanocrystals, CNCs; 70–90% of the CNF), CNFs not only support the huge body of a tree, but also offer an incredible potential as the reinforcement material for man-made nanocomposites. Also, CNFs have a very high thermal-dimensional stability (coefficient of thermal expansion, CTE: 0.1 ppm K<sup>-1</sup>), and therefore, are expected to reduce the otherwise high thermal expansion of the polymers. However, the processing of CNF-reinforced nanocomposites suffers from the difficulty of dispersing native hydrophilic CNFs in a hydrophobic resin matrix (most resins are hydrophobic). Therefore, many surface modification techniques have been employed to produce hydrophobic CNFs, which made the composite fabrication process long.</p> <p>Aimed to address the above issues, in this study a very simple water-based method was devised by exploiting the idea of emulsification of oil and water. The dual role of the nanocelluloses as the Pickering-stabilizer of the resin-in-water emulsion and the resin reinforcing nano-component was utilized.</p> <p>In Chapter 2, the detailed development of the facile Pickering emulsification method to obtain novel transparent materials reinforced with native CNFs was presented. In this method, an acrylic resin-in-water Pickering emulsion (PE) stabilized solely by CNFs was successfully prepared by vigorously agitating in a blender. Because of the strong encapsulation of the liquid resin micro-droplets by the CNFs network, the emulsion could be easily dehydrated by vacuum-filtration and subsequently hot-pressed with a negligible loss of resin followed by UV-polymerization to obtain CNF-reinforced transparent materials. The optical transparency of the nanocomposites was as high as 89% at 16 wt% CNFs content, which indicated that a good dispersion of the network of hydrophilic CNFs in a hydrophobic resin can be achieved <i>via</i> PE method without any chemical intervention. Interestingly, the nanocomposites had a unique self-assembled two-tier hierarchical architecture resulted from the aggregation of the CNF-encapsulated resin micro-droplets during dehydration of the emulsion. Because of the hierarchical structure of the nanocomposites, they possessed a rare but desirable combination of high strength, toughness, and mechanical flexibility compared to their counterparts having a</p>			

similar CNFs content prepared *via* impregnation (IM) method which has been developed to produce nanocomposite by impregnating hydrophobic resin into a nanopaper of the native (non-modified) CNFs.

Meanwhile, because of the inclusion of liquid resin micro-droplets in the CNF-network, which also reduced the H-bonding among the nanofibrils, the nanocomposites could easily be molded into 3D-shaped transparent materials during the hot-pressing. Such a 3D molded transparent material could not be achieved *via* IM method. The surface of the nanocomposites could even be nano- or micro-molded easily by simple hot-pressing.

The effect of CNFs concentration in the PEs on their stability, morphology of the resin micro-droplets, and the properties of the resulting nanocomposites was reported in Chapter 3. As the CNF-concentration in the emulsion increased, a denser network was formed around the resin micro-droplets, resulting in higher stability of the emulsions. However, the droplet size and polydispersity were increased with increasing viscosity, i.e., with increasing CNFs concentration. Interestingly, the nanocomposites maintained a high mechanical flexibility (the fracture strain of about twice as high as the neat resin), even with a CNFs content as high as 25 wt%. This was attributed to the distinct hierarchical structure of the nanocomposites that provided a synergistic load-bearing, stress-dissipating, crack-deflecting, and crack-delaying mechanism. The PE nanocomposites also possessed a high thermal-dimensional stability (CTE similar to that of glass, 7–8 ppm K<sup>-1</sup>, at 18–25 wt% CNFs reinforcement) compared to the IM nanocomposites owing to their distinctive brick-and-mortar microstructure having a horizontal in-plane orientation of the CNF-network and the platelet-like resin micro-droplets.

In Chapter 4, using nanocelluloses (i.e., CNFs and CNCs) of different lengths (300–4000 nm) and crystallinities (70–80%), a tunable high mechanical and thermal properties of the PE nanocomposites with a high flexibility (elongation-at-break: ~15%) were obtained even at a similar nanocelluloses content of ~10 wt%. This was due to the difference in the hierarchical microstructure resulted from different network structure of the nanocelluloses with different length and crystallinity around the resin micro-droplets/platelets. The short nanocelluloses with high crystallinity produced stiffer and highly thermally stable nanocomposites; a CTE (3.4 ppm K<sup>-1</sup>) as low as that of silicon crystals was obtained only at a 10 wt% CN-content. The nanocomposites were also highly thermomechanically stable even up to 150 °C, compared to the commercial thermally-stable PET film. Furthermore, the optical transparency (~90%) of the nanocomposites was highly stable even at 180 °C for 2 h. The high thermal stability of the micro-lenses on the micro-molded nanocomposite was also demonstrated.

Finally, to demonstrate the great potential of the transparent PE nanocomposites, which

were prepared using short CNCs having an excellent thermal stability, as the substrate for optoelectronic devices, a high-thermal-performing flexible AgNW electrode and a smart optical device were fabricated in Chapter 5. It was successfully demonstrated that the resulting AgNW electrodes and smart optical device can survive repeated heating and cooling conditions at extreme temperatures ( $-196\text{ }^{\circ}\text{C}$ – $150\text{ }^{\circ}\text{C}$ ) compared to those prepared on non-reinforced acrylic resin films. This was because of the high thermal-dimensional-stability of the PE nanocomposite substrates owing to which the thermomechanical stresses induced by the extreme temperature change were incredibly low, and hence, the electrically conducting AgNW-network on the nanocomposite remained unbroken.

In Chapter 6, the whole doctoral research work was summarized. A simple Pickering emulsification method to prepare nanocomposites of immiscible nanocelluloses and resins was devised. The potential of this new method in order to fabricate structurally hierarchical, highly transparent, strong, tough, super thermally-stable, and macro/micro/nano-moldable nanocomposites of hydrophilic ‘native’ nanocelluloses and hydrophobic resins for application in the next-generation optical devices was explored. The successful fabrication of 3D-molded transparent nanocomposites could open new application areas of the nanocellulose reinforced materials.

注) 論文内容の要旨と論文審査の結果の要旨は1頁を38字×36行で作成し、合わせて、3,000字を標準とすること。  
論文内容の要旨を英語で記入する場合は、400～1,100 wordsで作成し  
審査結果の要旨は日本語500～2,000字程度で作成すること。

(論文審査の結果の要旨)

セルロースナノファイバー (CNF) は、パルプをナノオーダーにまで微細化することで得られるナノ繊維である。軽量、高強度、低線熱膨張などの優れた機械的特性を有している。さらにCNFは可視光波長に対して十分に細いことから透明補強が可能なプラスチック補強用ナノ繊維としての期待が大きい。しかしながら、親水性のCNFと疎水性のプラスチックとの複合化は水と油を混ぜる様なものであり、CNFの製造、疎水化、樹脂複合、成形、用途までの過程において、製造や変性処理のコスト、親水性ナノ繊維のハンドリング等で多くの課題がある。この課題を解決するために本論文では親水性のCNFを疎水性樹脂と簡便に複合化する方法として、CNFとモノマーを水中で強く攪拌し、CNFが油滴化したモノマーの表面を覆い合一を妨げることでモノマーを微細な油滴として水中に均一分散できる”ピッカリングエマルジョン法”に着目した。得られた主要な成果は以下の通りである。

(1) CNF、アクリル樹脂モノマー、水からなるピッカリングエマルジョンを作製しメンブレンフィルターを用いたろ過により脱水、シート化し、乾燥後、アクリルモノマーを熱および紫外線照射でポリマー化した。それにより透明性に優れた低線熱膨張のシート材料を得ることに成功している。また、CNFとアクリル樹脂モノマーの比率を変えて検討し、CNF率16%でもシートは高い透明性を保ち、ガラスに匹敵する低線熱膨張を示すことを明らかにしている。

(2) さらに、得られた透明シートの力学特性と微細構造との関係について検討し、CNFに覆われたマイクロレベルのアクリル樹脂粒がCNF高次ネットワークによって結合しており、その様な階層的構造が複合材料にじん性を付与していることを明らかにしている。

(3) 完全硬化前のCNF強化アクリル樹脂は3次元成形が容易であることを示し、さらに、凸型の直径 $2\mu\text{m}$ の半球を表面に並べたサファイアガラス製のテンプレートを未硬化のCNF強化アクリル樹脂シートに押し付け硬化させると、シート表面に凹型のマイクロレンズアレーを転写できることを示した。得られたマイクロレンズアレーは熱的に寸法が安定しており、室温から $140^{\circ}\text{C}$ 付近まで安定したレンズ性能を維持することを認めた。

(4) CNF強化アクリル樹脂シートの太陽電池やディスプレイ用の透明基板への応用に向けて銀ナノワイヤーをシート表面に塗布し、シートの導電性の熱的安定性を評価した。 $-196^{\circ}\text{C}$ から $150^{\circ}\text{C}$ まで繰り返し温度変化を与えてもシートは導電性を示した。一方、ニート樹脂では銀ナノワイヤーの切断により導電性が得られなくなったことから、CNF添加による線熱膨張の低下が透明基板の熱安定性に有効であるといえた。

(5) 上記の結果より、ピッカリングエマルジョン法を用いた親水性CNFと疎水性樹脂の複合化は高性能の機能性材料を簡便に製造でき、CNF材料の用途の拡大に貢献するといえる。

以上のように、本論文はセルロースナノファイバーと樹脂との新規複合化技術および得られた材料の特性ならびに3次元精密加工性について幅広く考察したものであり、木質バイオマス資源の先進的利用に向けた技術を提案するもので、セルロース科学、木質材料学、生物機能材料学の発展に寄与するところが大きい。

よって、本論文は博士（農学）の学位論文として価値あるものと認める。

なお、令和元年7月19日、論文並びにそれに関連した分野にわたり試問した結果、博士（農学）の学位を授与される学力が十分あるものと認めた。

注) 論文内容の要旨、審査の結果の要旨及び学位論文は、本学学術情報リポジトリに掲載し、公表とする。

ただし、特許申請、雑誌掲載等の関係により、要旨を学位授与後即日公表することに支障がある場合は、以下に公表可能とする日付を記入すること。

要旨公開可能日： 年 月 日以降（学位授与日から3ヶ月以内）