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2020 February　JAPAN TAPPI JOURNAL
Vol.75,　No.2　Abstracts

Commercialization and application development of nanoforest

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The cellulose nanofiber (CNF) which is produced by the Aqueous Counter Collision (ACC) method and named as "nanoforest" is suggested to have an amphiphilic fiber surface expressing high affinities for not only water but also oils in addition to general characteristics of CNFs such as light weight, high strength, and low linear thermal expansion. "

This article explains the manufacturing methods and characteristics of nanoforest and the commercialization of nanoforest.

As for the activities of the commercialization, the sample provision is carried out, and the examination is advanced in various fields.

On CNF composite material, the problem became clear in carrying out the sample work, and countermeasures and new development are advanced.

Moreover, this article introduces an outline of the construction of pilot plants for a production of high-functioning CNFs, which was released in May 2019, and the products of those new plants.

Development of Xanthated Cellulose Nanofiber
-Approach for practical application-

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Cellulose nanofiber (CNF) is produced by fibrillating pulp to the nano-sized fibrils either through chemical or mechanical processes. It possesses interesting properties, such as high strength, high elastic modules, low thermal expansion, and thixotropy of the suspension. For these properties, it can be used for various applications, and is drawing great attention in recent years as a promising next-generation material.

Our company, Rengo, has been manufacturing cellophane from pulp for many years. Since cellulose xanthate, an intermediate product in the production process, is an anionic cellulose derivative, we tried to make CNF using this intermediate. We found that xanthated cellulose nanofiber (XCNF) with a diameter of about 3-10 nm can be generated efficiently. Such obtained XCNF can be easily converted (regenerated) to a non-substituted cellulose nanofiber (RCNF) form by treating XCNF with either heat or acid[(1)].

In this presentation, we reports the physical properties of RCNF for practical application.

First, viscosity characteristics of RCNF was investigated. The viscosity of RCNF slurries with different concentrations (0.02～1.0%) was measured and it was confirmed that the viscosity of RCNF slurry was higher than that of hydroxyethyl cellulose in the high concentration region. Further, it was confirmed that the high viscosity was maintained even in the presence of salt and the temperature dependence was low. This suggests that RCNF is useful as a thickener.

Next, emulsifying ability of RCNF was examined. RCNF slurry was mixed with some oily substances and the emulsification performance of RCNF was investigated. RCNF exhibited emulsification performance for many oily substances. Furthermore, it was found that the emulsifying performance was sufficiently exhibited at a low concentration such as 0.5%. This means that RCNF is also useful as an emulsifier.

As the other features, RCNF shows the dispersion stability of the fine powder such as calcium carbonate, and can be dispersed in organic solvents.

From the above results, RCNF is expected to be used in a wide range of applications.

Cellulose Material Fused with Nano/Micro Fiber

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Vulcanized fiber is an all-cellulose material made from cotton and wood pulp. This material was invented in the United Kingdom in the middle of the 19th century, and was used in Edison's numerous inventions due to its excellent characteristics such as impact resistance and electrical insulation. Recent research revealed the reason for the strength of the vulcanized fiber. Cellulose fibers are chemically defibrillated to form a network of cellulose nanofibers (CNF) with a diameter of several nm to several tens of nm, and this CNF network shrinks and binds tightly. when water is removed during the drying process. The vulcanized fiber has revived in the present age when cellulose nanomaterials are drawing much attention, leading to new developments that combine with carbon fibers.

Cellulose Nanofiber Prepared by Phosphorylation and its Utilization

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Cellulose nanofibers (CNFs) are obtained from wood pulp by isolating crystalline microfibrils in which molecular chains of cellulose are regularly arranged. Since CNF is not only a sustainable natural resource but also has unique features, its multifaceted utilization is expected. By subjecting softwood bleached kraft pulp to phosphorylation and then mechanical treatment, the CNFs with phosphate groups on their crystal surface could individually be dispersed in water. The dispersion had unique rheological properties, and the phosphate groups provided stability in a wide pH range to the dispersion. The aqueous dispersion of phosphorylated CNF was commercialized as a thickening and dispersing agent for cosmetics, taking advantage of its high transparency, high viscosity and high dispersant ability. In addition, phosphorylated CNF was adopted for the pump primer to prevent concrete blockage in pumping pipe by forming a thin and uniform lubricating layer on the inner surface of the pipe at construction sites. Due to the rheological properties of the CNF, lubricating layer can be stably formed, and components in pump primer can be stably dispersed and the pump primer can adapt to pumping speed. We can manufacture CNF sheet from aqueous dispersion in which phosphorylated CNFs are individually dispersed. The CNF sheet was adopted for materials used in table tennis rackets. By combining the CNF sheet and the base material wood, a table tennis racket with a new hit feeling has been realized. On the other hand, phosphorylated CNF with further modification can be dispersed in organic solvents. The CNF is provided in powder form and is dispersible in various organic solvents, and the dispersion has characteristics common to CNF aqueous dispersion. This CNF powder made it possible to study applications for use in non-aqueous solvents. Furthermore, we have succeeded in development of the composite material with much more excellent properties (high elastic modulus, and low thermal expansion) than those of conventional materials by combining polycarbonate (PC) with CNF. We will further promote the utilization of phosphorylated CNF.

Contribution to Environmental Issues by Structural Materials Utilizing CNF
-A Report of NEDO Project and Our Effort to CNF Reinforced Resin Composites-

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Nippon Paper Industries Co., LTD.

Cellulose is a most abundant, renewable and environmentally friendly bio-based polymer, which is available from non-edible biomass sources such as woods, grasses and agricultural residues. Cellulose nanofibers (CNFs), including cellulose microfibrils and their bundles, have received much industry attention for use in film, rheology control such as in paints and coatings, paper and paper packaging, cosmetic and medical materials and composites. In particular, reinforcement of polymers to improve their mechanical properties is one of the most promising applications of CNFs.

Nippon Paper Industries Co., Ltd. had taken part in the Kyoto University leading NEDO Project entitled "Development of the technology for the continuous production process "Kyoto Process®" of ligno cellulose nanofibers and their applications for the structural members" between 2013 and 2020.

In this NEDO project, we developed a chemically modified pulp with an improved heat resistance and would be easy to fibrillate to nano order but would not be chopped under melt compounding, and obtained many new knowledge using this modified pulp. The chemically modified CNF, at 10wt% loaded as a filler, increased the Young's modulus and bending strength of PA6, PLA, POM, HDPE and PP by 1.5～2.5 times. We found that Fir (Todomatsu in Japanese) was an ideal biomass for this process by

screening of several biomass. The ligno CNF reinforced resin composites maintained its strength after several times recycling unlike GFRP.

Nippon Paper Industries Co., Ltd. then built a demonstration facility for high strength CNF composite resin materials by implementing this technology, and started to operate at 2017.

The details of the NEDO project and the current situation of the demonstration facility will be described in this paper.

Next-Generation Quality Control With the Latest Finnish Measuring Equipment

Yohei Suzuki
Shin-Nihon Corporation

In recent years, attention has been paid to plastic-free worldwide, and the paper industry has an opportunity. Introducing Finland's latest measurement equipment for new products such as barrier coatings.

Permi Online Porosity Analyzer is a revolutionary system that it measures porosity online in real time. By stabilizing the porosity of the base paper, the coating quality can be maintained. Porosity measurement can also detect web breaks beforehand.

The AX-100 High shear rate viscometer can measure viscosity at high shear rates, which was previously impossible. The viscosity of the coating color actually used in the coater machine can be measured. Prevents troubles due to coating color. You can also reduce costs by optimizing materials.

The RoQ roll hardness tester can profile the winding hardness of the roll in the width direction. It is also possible to detect wrinkle detection inside the roll that could not be detected by the Schmidt hammer.

Effective management for seal water in Pulp and Paper mills
—Stable operation and Environmental load reduction—

Daisuke Tsuchiya
Enginnering Dept.,John Crane Japan,Inc.

Mechanical Seal Engineering Dept., John Crane Japan, Inc.

It is one of main issues at the paper mill plant, where there are many rotating equipment are installed, to maintain those equipment stably in the operation by reducing the troubles from the mechanical seal area.John Crane, the world leading company in the mechanical seal, has found from analyzing the past trouble data, that the most cause of those troubles is due to a lack of control of quenching water.

In order to eliminate this most cause of troubles, Safeunit, Smartflow, Safejet and Safeclean were developed to supply the quenching water with the correct flow rate, pressure and quality.

John Crane hopes to draw an attention to the importance of quenching water by our presentation this time, and assures you that they will help to maintain your equipment stably in the operation and save the water at your plant, by supplying the correct flow rate, pressure and quality of water.

Maintenance about Continuous Digester Vessel (Pressure Vessel)

Fumio Takayasu
Valmet K. K.

In recent years, KP facilities in Japan have been worn out and corroded by long time use for 30 to 40 years after installation. In particular, it is necessary to inspect and repair the first-class pressure vessels, which are required to be inspected by law. Repair methods for pressure vessels include complete renewal, partial renewal, lining, and overlay. Peripheral equipment such as the steaming vessel can be repaired by lining, partial renewal, or in some cases, complete renewal, depending on the state of wear and corrosion. On the other hand, it is not easy to completely or partially replace the continuous digester due to its size. Since the base material of domestic continuous digester is made of carbon steel when they are installed, most repairs are done with lining repairs. Lining repairs can be made partially and inexpensively within the construction period to repair only the areas of wear and corrosion. However, cracks may occur at the welded point because the welding is between different materials that attach a stainless steel plate to a carbon steel base metal. Also, the chemical solution can penetrate between the base metal and the stainless steel plate from the cracks, and corrosion of the base metal can progress. Therefore, if a crack occurs, the stainless steel plate must be temporarily removed and the soundness of the base material must be checked before the stainless steel plate is re-installed. On the other hand, the overlay (Uddcomb method) described in the main paper is a method to form a new duplex stainless steel layer on the surface of the base metal by directly welding the stainless steel onto the base metal. It is an effective and permanent repair method for extending the service life of the base metal of continuous digester and batch digester without the risk of corrosion of the base metal and separation of thermal spraying, which are common in the repair of linings.

Revolutions in the history of civilization induced by paper
Part 1: The arrival of paper to Japan

Kiyoaki iida

How the paper has induced revolutions in the history of civilization will be studied.
Shoso-in documents recorded how paper was used in the 700's in Japan. One category was administrative documents. The government filed family registers in paper all over its control territory, and administrated tax collection. The instruction of the government on paper was delivered to one country, which copied the document and passed it to a neighboring one. At the same time, each country replied back to the government by paper. It also reported tax collection status. The population at that time was estimated to be about several millions, and the government controlled them by delivering documents.
The second category was copying sutras. It was a cultural project nationwide, and more than one hundred thousand volumes were copied. Many scribes were engaged, and greatly improved literacy.
The volume of paper demanded was supplied from governmental paper factory, copying stations of sutras and local paper factories. Most of paper was made of paper mulberry. Some sheets of paper were already made of recycled fibers.
Then, when did the paper arrive at Japan? There is not an accepted theory yet. According to the recent study on wooden slips found in Japan, it would be shortly after characters became in use in Japan.

Kraft Cooking with Teak Wood Extract and Determining Residual 2-Methylanthraquinone in Eucalyptus Pulp

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Anthraquinone (AQ) is used in the pulp and paper industries as a cooking catalyst. However, because AQ is "possibly carcinogenic", it is no longer approved in Germany for the manufacture of paper and paperboard that contact food. To address this problem, we examined 2-methylanthraquinone (2-MAQ), a natural anthraquinone from teak (*Tectona grandis*) wood. *Eucalyptus globulus* wood was subjected to kraft cooking at 145 °C for 3 h with 0.03% 2-MAQ and 15–19% active alkali to provide pulp in 55.5–58.1% yield. Kraft cooking with the acetone extract of Myanmar teak wood increased pulp yield by 1.6% but decreased kappa number by two points compared to that with only 2-MAQ. Ames testing suggests that 2-MAQ is not mutagenic. Unbleached and oxygen-bleached pulp contained 0.40–2.90 ppm and 0.21–0.39 ppm residual 2-MAQ, respectively, while 2-MAQ was not detected in fully bleached pulp; therefore, this pulp should be safe for food-packaging use.