All-Cellulose Material Prepared by Zinc Chloride Treatment

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Research Article

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Abstract

Vulcanized fiber is an all-cellulose material made from cotton and/or wood cellulose after zinc chloride treatment. This material was invented in the UK in the mid-19th century and is widely used because of its excellent characteristics, such as impact resistance and electrical insulation. Recently the matured vulcanized fiber has been recognized as a renewable and biodegradable material and reevaluated with advanced cellulose nanofiber (CNF) technologies. The microscopic analysis based on the improved freeze-drying method revealed that the vulcanized fiber strength can be attributed to the chemically defibrillated cellulose nanofibers. The architecture is similar to a composite made from the same raw material in which the residual cellulose fibers serve as reinforcement, and the nanofibers serve as adhesives. In this report, we describe the history and structural characteristics of vulcanized fibers and introduce a new aspect in zinc chloride treatment of cellulose.

Keywords

Vulcanized fiber, cellulose, zinc chloride, nanofibers

Introduction

A concentrated aqueous zinc chloride solution dissolves cellulose (Fisher et al. 2003), and this solution has been discreetly used for producing “vulcanized fiber” so far (Brown 1999). The vulcanized fiber is a material in which the surface of cellulose fibers derived from cotton or wood pulp undergoes swelling or semi-dissolution with an aqueous zinc chloride solution to firmly bond the fibers. Since the cellulose fibers adhered to cellulose in the vulcanized fiber, it can be regarded as a composite material made of the same component. Today, the material is called an all-cellulose material, in contrast to materials containing petrochemical-derived components (Nemoto et al. 2018). The all-cellulose material has the same concept as the all-cellulose composite proposed in 2004 (Nishino et al. 2004).

Zinc chloride is used in various fields such as catalysts for synthetic organic chemistry, cleaning agents for plating, and electrolytes for dry batteries. Zinc chloride anhydride is a colorless crystalline powder with the presence of hydrated salts depending on the temperature. The aqueous solution concentration that dissolves cellulose exceeds 70 wt%, which corresponds to zinc chloride trihydrate (zinc chloride concentration 71.6 wt%). Since a solid crystal of zinc chloride trihydrate is obtained at 6 °C or lower, it can be regarded as a molten salt at room temperature. An ionic liquid is also a molten salt at room temperature; thus, the concentrated aqueous zinc chloride solution is similar to ionic liquids. In fact, reports mention the ionic liquid properties of the solution and the structures of the cations and anions in $[Zn(H_2O)_6]$ and $[ZnCl_4]$ (Wilcox et al. 2015; Sen et al. 2016).

Advances in cellulose nanofiber (CNF) technologies have widened the knowledge about cellulose, which prompted us to reevaluate the matured vulcanized fibers. With improved basics of CNF and analytical techniques, the classical zinc chloride treatment of cellulose has been reviewed from a new perspective (Nemoto et al. 2018; Burger et al. 2020). In this report, we briefly describe the history, production process, and structural characteristics of vulcanized fibers and discuss the role of zinc chloride during the production process.

History

A vulcanized fiber or vulcan fiber is a tough cellulose material invented in the UK in the 1850s. It was manufactured by laminating several sheets of base paper made of cotton and/or wood pulp, then impregnating them into an aqueous solution of zinc chloride, followed by washing and drying. Finally, the paper changed into a tough, board-like material. The toughness of the material was attributed to the firmly bonded cellulose fibers caused by swelling or semi-dissolving (also called gelatinization) of the cellulose fiber surface. Originally “Vulcanized” refers to the cross-linking of

natural rubber to improve its physical properties. Therefore, "vulcanized fiber" might have been named with a sense of changing natural paper into an epoch-making industrial material.
Thereafter, the vulcanized fibers were developed in the US (Schmidt 1871; Taylor 1871) and played an important role as an innovative material, as exemplified by Edison's inventions. Thomas A. Edison made many inventions including light bulbs, generators, and motors (Edison 1879). At that time, rubbers and potteries were used as insulating materials, but vulcanized fiber was an innovative material with excellent insulation, high impact resistance, oil resistance, and heat resistance. The most famous application of vulcanized fibers is the travel trunk. The vulcanized fiber trunk is lightweight, impact-resistant, and easy to maintain. In addition, it was able to withstand polar conditions, as symbolized by its use in Antarctica and Everest.
Since the 1950s, with the rise of other materials including plastics, the production of vulcanized fibers in the UK came to an end by the end of the 20th century. Overcoming hard times, some manufacturers in Japan, Germany, and China, who have optimized production costs and quality, still produce vulcanized fibers.
In the 21st century, vulcanized fiber has been recognized as a renewable and biodegradable material. In addition, zinc chloride is inexpensive and has relatively low environmental risks than other solvents that dissolve cellulose. Therefore, both the material and the production process are advantageous.

Production process

A typical base paper sheet consists of cotton pulp and/or softwood bleached pulp and does not include sizing agents for the saturation of zinc chloride solution. The base sheet was impregnated in a zinc chloride solution with a concentration of 65−72 wt% zinc chloride. After impregnation, several sheets were overlapped and nipped. The excess zinc chloride solution attached to the laminated sheets was removed by nipping. Thereafter, the obtained sheet was immersed in successively less concentrated baths of zinc chloride solutions and finally in water to wash away the remaining zinc chloride. Zinc chloride gradually leaches due to osmotic forces in the baths. The water-washed sheet is heat-dried and then sheeted or wound up into rolls, depending on the demand. Currently, the production process is continuous manufacturing, while there used to be a batch process, especially for manufacturing thick products that require several months to remove zinc chloride.
The dimensions of the sheets remained almost unchanged during the zinc chloride treatment and water washing. However, substantial shrinkage of the sheets (~10% in the machine direction and ~20% in the cross direction) occurred during the heat-drying, especially at higher zinc chloride concentrations.

Microstructures

Since shrinkage during drying is crucial for analyzing the cellulose microstructure, freeze-drying is used to preserve the microstructure. By adding tert-butyl alcohol to the aqueous dispersion of cellulose nanofibers (CNFs) before freeze-drying, the microstructure is preserved and favorable for microscopic analysis without structural deformation derived from ice crystal growth during freezing (Nemoto et al. 2015).
Using this method, the microstructure of cellulose before and after zinc chloride treatment and washing was observed (Nemoto et al. 2018). Fig. 1 shows SEM images of the surface of the heat-dried sheet (upper) at low magnification, surface of the freeze-dried sheet (middle) at high magnification, and cross-section of the freeze-dried sheet (lower). First, from the comparison in the upper images, it seems that the surface of the cellulose fibers is partially dissolved after the zinc chloride treatment. Looking at the microstructure on a magnified scale (middle images), fine fibers (nanofibers) emerge on the surface of the cellulose fibers. This is comprehensible from the cross-sectional images (lower images). By treating cellulose with zinc chloride, white areas in the lower right of Fig. 1 can be seen between the cellulose fibers (acceleration voltage and contrast in SEM are optimized). These areas consisted of cellulose nanofibers. After zinc chloride treatment, the nanofiber network region can be seen between the cellulose microfibers. As the zinc chloride concentration increases, the micro-sized cellulose fiber region decreases and the nanofiber network region increases (Nemoto et al. 2018).
From the structure in the lower images of Fig. 1, the nanofiber network generated from the surface of the cellulose fibers appears to be an adhesive, strengthening the remaining cellulose fibers. Therefore, it is similar to a composite made from the same raw material in which the residual

cellulose fibers serve as reinforcement, and the nanofibers serve as adhesives.

Although it is uncertain whether the nanofibers are so-called CNFs with the same crystalline structure as natural cellulose, the X-ray diffraction of the vulcanized fiber (Fig. 2) indicated that the crystalline structure was unchanged, even after zinc chloride treatment (Modi et al. 1963; Hamed et al. 1995; Nemoto et al. 2018; Tian and Li 2018). If the swelling of cellulose by zinc chloride solution progresses from inter-crystallites to intra-crystallites, the cellulose phase may change continuously from natural cellulose, which is hardly affected by zinc chloride, to chemically disintegrate CNFs and finally to regenerated cellulose nanofibers. Although there are reports that the swelling of cellulose by zinc chloride solution is intercrystalline (Modi et al. 1963), the swelling or dissolution is affected by the concentration and temperature of the zinc chloride solution, time of impregnation, and the origin of the cellulose (Pandey and Nair 1976). Therefore, it is difficult to clarify the phase of the nanofibers during the vulcanized fiber production. However, it would be interesting if the phase of the nanofibers continuously changed from cellulose I to amorphous or cellulose II crystalline structure.

Physical properties

The strength, elongation, and Young's modulus of the sheets increased significantly after zinc chloride treatment. Compared to ordinary paper, vulcanized fiber has higher strength and breaking elongation, which gives the material toughness against a strong impact (Table 1). With increasing zinc chloride concentration, both the tensile strength and elongation tended to increase; however, in the sheet treated with high concentrations of zinc chloride (>70 wt%), the values decreased slightly (Hamed et al. 1995; Nemoto et al. 2018). Typical stress–strain curves (SS curves) of the vulcanized fibers in the machine direction treated with different concentrations of zinc chloride are presented in Fig. 3, which clearly shows that the yield point occurred after the zinc chloride treatment and that strain hardening occurred from approximately 2% elongation. Slips between cellulose fibers by the load led to an alignment of the fibers, which appeared to have hardened the sheet. The yield strength obtained from these SS curves increased in both MD and CD with increasing zinc chloride concentration.

Table 1. Tensile properties of the base and $ZnCl_2$-treated sheets. Zn-1, Zn-2, and Zn-3 were prepared with different $ZnCl_2$ concentrations shown in Fig. 2.

	dry tensile strength		dry tensile elongation		wet tensile strength	wet tensile elongation
	MD	CD	MD	CD	MD	MD
	MPa	MPa	%	%	MPa	%
Base sheet	20 ± 0.4	11 ± 0.2	2.3 ± 0.1	3.5 ± 0.3	0.7 ± 0.0	2.1 ± 0.2
Zn-1	68 ± 1.1	37 ± 0.6	13.7 ± 1.1	11.5 ± 2.9	31.8 ± 1.1	19.6 ± 0.2
Zn-2	106 ± 5.0	65 ± 0.7	16.0 ± 2.1	19.5 ± 0.5	33.8 ± 0.3	29.9 ± 0.6
Zn-3	100 ± 2.8	56 ± 1.9	15.7 ± 0.8	13.3 ± 1.7	45.1 ± 2.4	20.3 ± 0.4

The wet tensile strength was greatly increased by zinc chloride treatment (Table 1). In the base sheet, the wet tensile strength decreased to as low as 3.5% of the original strength; by contrast, 30% or more of the original strength was maintained for the zinc-chloride-treated sheet. Since the wet tensile strength increased with the zinc chloride treatment, it is thought that the firmly bonded nanofiber network forms a semi-crystalline structure that does not completely detach, even in water. Moreover, the extended elongation of the zinc-chloride-treated wet sheets indicates that the presence of water molecules between the cellulose fibers enhances the slip between them. Therefore, water can be used as a plasticizer for vulcanized fibers.

Processing and Application

Among the various forming or shaping methods for this material, bending and press forming are common methods. In particular, under high moisture conditions, water acts as a plasticizer in vulcanized fibers, which expands the range of forming processes. When heat is applied in the shaped state, hydrogen bonds are formed, resulting in shape preservation. Although it is not as flexible as plastics in molding, shallow 3D drawn molding is acceptable. Polishing the surface of the vulcanized fiber makes it glossy, and a marble-like surface appears. There are various applications such as electric insulators, abrasive discs, travel cases, containers, and stationery. An electric insulator has been a major application. While vulcanized fiber is a durable material, it is biodegradable, which makes it unique compared to plastics.

Summary

Researchers and engineers have empirically determined the optimum conditions such as zinc chloride concentration and treatment time for producing tough all-cellulose material "vulcanized fiber" for more than 150 years. With the increasing attention of CNFs, the knowledge about cellulose is being widened even after zinc chloride treatment. The swelling or semi-dissolution of cellulose by zinc chloride solution during the production of vulcanized fiber is a technology that takes advantage of the intermediate region between the swelling and dissolution of cellulose. Zinc chloride is cost-effective and safer than other cellulose solvents, and recovery and regeneration technologies have been established. Therefore, it has the potential to progress further toward the next century, following a spiral development.

Declarations

Conflicts of interest

This work was supported by Hokuetsu Corporation and Hokuetsu Toyo Fibre Co., Ltd. The authors are employees of Hokuetsu Corporation.

Human and Animal rights

Not applicable.

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Figures and figure Legends

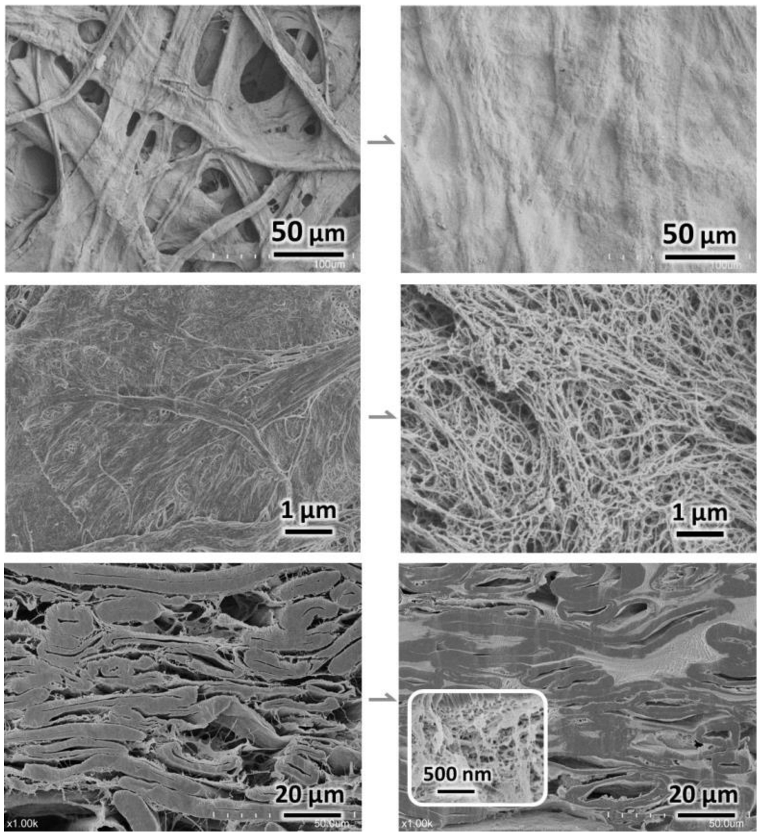

Fig. 1 SEM images of surfaces and cross sections of the base and $ZnCl_2$-treated cellulose sheets. Upper images are surfaces of the sheets after heat-drying. Middle images are surfaces of the sheets after freeze-drying. Lower images are cross sections of the sheets after freeze-drying (Inset is a magnified image of a nanofiber region)

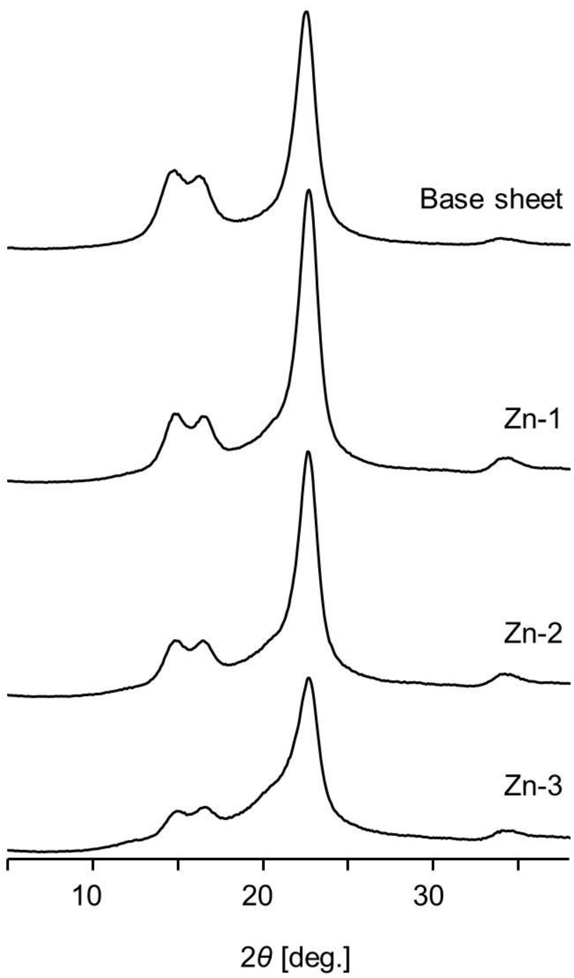

Fig. 2 XRD patterns of the base and $ZnCl_2$-treated sheets after heat-drying. Zn-1, Zn-2, and Zn-3 were prepared with different $ZnCl_2$ concentrations, corresponding to 63.9 wt%, 67.9 wt% and 70.8 wt%, respectively (Nemoto et al. 2018)

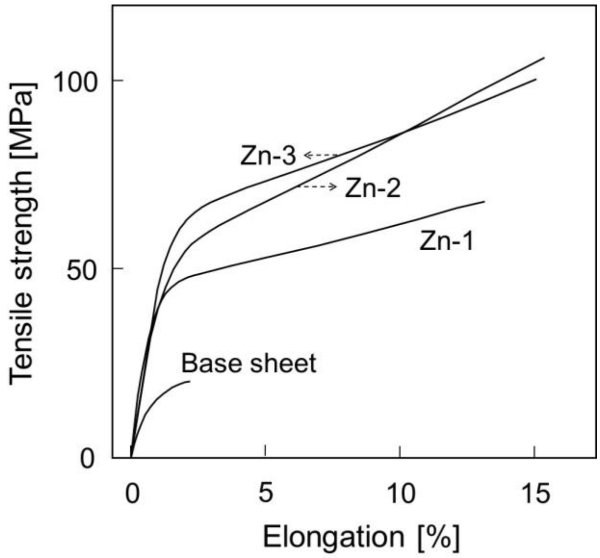

Fig. 3 Typical stress–strain curves (MD) of the base and $ZnCl_2$-treated sheets after heat-drying. Zn-1, Zn-2, and Zn-3 were prepared with different $ZnCl_2$ concentrations shown in Fig. 2 (Nemoto et al. 2018)