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Recent advances in regenerated cellulose materials

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ABSTRACT

The dual threats of the depletion of nonrenewable energy and environmental pollution caused by petroleum-based polymers motivate utilization of naturally occurring polymers to create new materials. Cellulose, as the most abundant natural polymer on earth, has attracted attention due to its renewability, wide availability, low-cost, biocompatibility and biodegradability, etc. Regenerated cellulose may be constructed simply *via* physical dissolution and regeneration, an environmentally friendly process avoiding the consuming of chemicals since most of the reagents (solvents, coagulant, *etc.*) may be recycled and reused. "Green" solvents and techniques for the preparation of the environmentally friendly regenerated cellulose materials have been developed successfully, showing great potentials in the fields of polymer science and technology.

In this article, the widely used non-derivatizing cellulose solvents are summarized, including their dissolution mechanisms. Regenerated cellulose materials with different functions and properties have been designed and fabricated in different forms, such as filaments, films/membranes, microspheres/beads, hydrogels/aerogels and bioplastics, *etc.*, to meet various demands. The concept of regeneration through a physical process is illustrated, and a number of novel regenerated cellulose materials are introduced for wide applications in textiles, packaging, biomedicine, water treatment, optical/electrical devices, agriculture and food, *etc.* The methodology of material processing and the resultant properties and functions are also covered in this review, with emphasis on the neat regenerated cellulose materials and the composite materials. The 277 references cited concerning the direct preparation of cellulose materials *via* physical dissolution and regeneration are representative of the wide impact and benefits of the regenerated cellulose materials to society.

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1. Introduction

In the 21st century, the trend of science and technology is tending towards environmentally friendly materials, renewable resources and energy, as well as sustainable techniques and processes. The depletion of non-renewable resources (petroleum, coal and gas) in the future and the environmental pollutions caused by the petroleum-based polymers motivate increasing demands from renewable resources, which are biodegradable, non-petroleum based, carbon neutral, and posing low environmental, animal/human health and safety risks [1]. The themes of the 239th (2010), 241st (2011), 243rd (2012), 245th (2013), 247th (2014) and 249th (2015) American Chemistry Society National Meetings were “Chemistry for a Sustainable World”, “Chemistry of Natural Resources”, “Chemistry of Life”, “Chemistry of Energy & Food”, “Chemistry & Materials for Energy” and “Chemistry of Natural Resources” again, respectively. They are regarded as directions and guidance to the advances and developments in chemistry all over the world, suggesting the wide utilization of renewable resources to produce environment-friendly materials *via* physical approaches with no chemical reactions, to avoid using or producing any hazardous substances, a component of the new international frontier of “green” and sustainably developing processes. In that case, the research and development of renewable biomass was highly valued by governments, business communities and academia. The Technology Road Map for Plant/Crop-based Renewable Resources 2020, sponsored by the U.S. Department of Energy, has targeted to achieve 10% of basic chemical building blocks arising from plant-derived renewable sources by 2020, with development concepts in place by then to achieve a further increase to 50% by 2050 [2]. This addresses renewable natural resources to the topics important to life in the 21st century.

In the last several decades, increasing attention turned to natural polymers in the development of environmentally friendly and biocompatible products and fuels [3], among which cellulose constitutes the most abundant renewable polymer resource available today and has gained particular attention, due to its renewability, availability, non-toxicity, low-cost, environmental friendliness, biocompatibility, biodegradability, thermal and chemical stability and derivatizabilty [4,5]. Plants produce over tens of billions of tons of cellulose per year globally, making this polysaccharide the largest organic carbon reservoir [6,7]. Cellulose is a linear chain comprising two anhydroglucose rings ($(C_6H_{10}O_5)_n$), linked together through an oxygen covalently bonded to C1 of one glucose ring and C4 of the adjoining ring (1–4 linkage), with the so called the β 1–4 glucosidic bond giving rise to a flat ribbon-like conformation [1,8,9]. The number n of repeat units per chain depends on the source, *e.g.*, n is approximately 10,000 in wood and 15,000 in native cotton in nature.

The relatively high persistence length of the cellulose molecular chain conformation and their close packing through numerous hydrogen bonds have made the dissolution of cellulose to be a difficult process. Thus, development of environmentally friendly low cost solvents for cellulose is essential for the successful utilization of the cellulose as a component of polymeric materials. Usually, regenerated cellulose materials may be prepared directly from cellulose solution *via* a physical dissolution, shaping and regeneration process. The process is environmentally friendly by avoiding consuming chemicals since most of the agents (solvents, coagulant, *etc.*) may be recycled and reused, with no accompanying chemical reaction. By changing the regeneration parameters, the regenerated cellulose vary in different shapes, such as powder, fibers, films, hydrogels, spheres, *etc.* Especially, the dissolution and regeneration is a “green”, clean and physical process when “green” cellulose solvents are applied, leading to sustainable development, environmental preservation and energy conservations. Thus, regenerated celluloses have drawn attention, since they are easy to fabricate, biocompatible, biodegradable, thermal and chemical stable, *etc.* However, the difficulty in dissolving cellulose has hindered the advancement and development of regenerated cellulose. Therefore, there is a growing urgency to develop novel and green techniques to physically prepare regenerated cellulose. “Green” solvents for the preparation