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Review

Recently developed applications for natural hydrophilic polymers

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ABSTRACT

Natural hydrophilic polymers have been utilized for a variety of applications, ranging from the food industry to the coatings industry. However, recent social needs have demanded rapid progress with regard to medical and environmental applications. Natural hydrophilic polymers have attracted considerable interest due to their physicochemical properties and useful functions. This report explores recent findings made in medical, environmental, and food applications of natural hydrophilic polymers and their modified polymers. Applications of these materials are based on their intrinsic biocompatibility, biodegradability, and non-toxicity. Advances in the chemical modification of natural polymers as well as new source developments are overcoming the physicochemical property limits and high costs of these materials, opening up new opportunities for the development of future applications.

Contents

Introduction

Natural polymers are a class of polymeric materials that have natural (animal, plant, and algal) origins, consisting primarily of glycosidic linkages [1–6]. Natural polymeric raw materials hold a special importance to both industry and our daily life [7–15]. A global revival with regard to the utilization and interdisciplinary research of natural polymers has been spurred on due to the importance of renewable resources, the development of innovative products for science and technology through functional modifications, and an abundant availability of natural polymers [9,16–47]. The excellent biological and chemical properties of natural polymers make them potentially useful in areas including: chemical engineering, environmental engineering, agriculture, nutrition, pharmaceuticals, biomedical, membranes, coatings, food, and horticulture [16,48–106]. Among these, medical, environmental, and food applications are likely to be the fastest growing areas for natural hydrophilic polymers. In this report, we review recent progress that has been made in these areas to highlight the common aspects of natural hydrophilic polymers.

Recent fast growth in the application of natural hydrophilic polymers has also triggered efforts to develop new sources of natural polymers, particularly those that are safe and environmentally friendly. In the case of animal collagens, potential risks

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related to mad cow and foot-and-mouth disease have been increasing [107–117]. As a result, interest in marine-derived collagens has increased. Typical gelatin production processes are based on acid or liming processes. In the acid process, an acidic solution is used to hydrolyze collagen, yielding type-A gelatin. In the liming process, alkaline materials are used for hydrolysis, yielding type-B gelatin. However, both processes possess several disadvantages, including the generation of large amounts of waste and limitations due to a lack of raw materials. On the other hand, enzymatic hydrolysis processes possess several advantages over conventional processes due to their short processing times and a reduced generation of waste [118].

Damrongsakkul et al. proposed the enzymatic hydrolysis of rawhide using two separate enzymes, papain and neutrase [119,120]. Protein recovery rates increased sharply during the initial 10 min of enzymatic hydrolysis prior to a slowing down of the rate. The optimum working conditions of papain and neutrase for the highest protein recoveries were 70 °C at pH 6–7, and 40–50 °C at pH 6–7, respectively. Due to the different hydrolysis mechanisms of papain and neutrase, the obtained gelatins yielded different properties. Long peptide chains obtained from papain hydrolysis exhibited a solution sol–gel transition. On the other hand, neutrase severely attacked collagen molecules, resulting in short peptide chains of collagen hydrolysate that could not gel.

Carbohydrates extracted/derived from natural resources have excellent biocompatibility and biodegradability, making them suitable for various medical, cosmetic, environmental, and food applications [7,8,121–134]. The recent green chemistry has focused on natural hydrophilic polymers and developed variety of derived functional materials [135–138]. The publications highlight new methodologies to prepare, characterize and apply materials for specific application needs and the current society's needs such as eco-friendly energy, global warming, and the interest in sustainability [8,119,135–138].

In this review, the recent progress highlights are described with concerning the basic structures, properties, and property modifications through chemical grafting, e.g., phenol-based antioxidant property, corrosion property, enzymatic inhibitions of polyphenols, blending, mixing, etc. [139–142]. These research activities are mainly grouped into three beneficial categories, food, environmental, and medical fields, which provides an opportunity for manipulating physicochemical characteristics. Efforts are particularly made in the research and development areas of polysaccharide derivatives as basic materials for new applications using new and/or improved properties. Recently developed interest in hydrophilic macromolecules is evident from the increased number of research articles that appear each year. This review summarizes the preparation, modification methods, and applications in areas with emphasis on the biomimetic functions of natural polymers.

Medical applications

Chitosan has been widely applied within the biomedical and pharmaceutical fields as drug delivery vehicles, carriers of immobilized enzymes and cells, biosensors, ocular inserts, and artificial organ scaffolds [118,135,136]. Due to its crystallinity, chitosan is soluble only in dilute acids; this drawback has emphasized the importance of its chemical modification. A recent study by Zou et al. [118] indicated that carbohydrates derived from natural resources had an ability to scavenge reactive free radicals and were able to break the oxidative sequence [118]. Je et al. revealed that chitosan and chitosan oligosaccharides with high degrees of substitution were able to scavenge 2,2-diphenyl-1-picrylhydrazyl, hydroxyl, super-oxide, and carbon-centered radicals [137,138].

Chitosan has two reactive groups, hydroxyls and amino functional groups, which can be synthetically modified. Corrole grafted transparent chitosan films demonstrated fluorescence and bacteriostatic effects against *S. aureus*, in addition to good thermomechanical properties [139]. The positively-charged characteristics of chitosan have been investigated for the development of effective adsorption materials as the solution to environmental problems [140]. Liu et al. developed a multilayered lipid based delivery system that involved the electrostatic interactions between the charges of chitosan and alginate at a specific pH. This multilayered polymer coating on the lipid-based delivery system of vitamin C, which was released via enzyme digestion, exhibited better stability to environmental stress than bare liposomes [135,141–144]. Within the field of nanotechnology, Liu et al. reviewed that due to its strong immunostimulatory and low immunogenicity properties, chitosan has been used as a nanoparticle-mediated carrier to deliver pharmaceutical actives (drugs or genes) through biological barriers [145].

It is hard to achieve proper targeting and absorption speed control through the oral administration of hydrophilic drugs [146–149]. In order to solve these problems, acryl-type polymers or pH-sensitive polymers have been developed for extended or delayed release control, respectively [150–154]. However, the use of a single matrix has not been entirely satisfactory. Chitosan and alginate can swell due to pH-sensitivity, which is a sol-gel phase transition. To simultaneously obtain extended and delayed release effects, double-layered microspherical carriers were considered [155–157]. Due to the mucoadhesive and penetration enhancement properties of chitosan, its various formulations, including: solutions, suspensions, gels, microemulsions, and powders were reviewed with regard to the nose-to-brain delivery of drugs [158–160]. Covalently cross-linked chitosan was developed through the chemical oxidation of catechol to form *o*-quinone, resulting in a pH responsive material [161–166]. Chitosan-based electrospun nanofibers have been investigated for various applications in foods, medicines, fibers, filters, films, and biodegradable plastics. Chitosan-based electrospun nanofibers are recommended as suitable functional materials due to their excellent biocompatibility, biodegradability, non-toxicity, and adsorption properties [167].

Seo et al. reported novel visible-light induced photocurable low molecular weight chitosan derivatives for biomedical applications [136]. Common photocurable polymers employ UV radiation for curing, which often results in the denaturation of biomolecules and a subsequent loss of bioactivity [168,169]. To overcome this drawback, Seo et al. switched to the use of visible light by modifying chitosan with photocurable furfuryl moieties and visible light initiator systems [136,170,171].

For the development of a versatile drug delivery matrix, lipoic acid, a powerful antioxidant that plays the role of an active oxygen removing species in mitochondria, was encapsulated in monodispersed particles of poly(ethylene oxide)-chitosan via single-capillary electrospraying [172]. At a certain critical aggregation concentration, the modified polymer formed nanoparticles, whose core and shell were lipoic acid and chitosan, respectively. Nanoparticle sizes decreased with an increase in the amount of conjugated lipoic acid employed. The conjugated polymers possessed an improved long-term cancer-cell killing effect. The grafting/encapsulation of natural polyphenols such as catechin onto chitosan imparted an enhanced antioxidant property against hydroxyl radicals and antidiabatic activities through the inhibition of α-glucosidase and α-amylase [173–175]. Therapeutic benefits have been proven through the injection of hyaluronic acid based products, although it will undergo fast digestion in presence of enzyme. The improved resistance against enzymatic digestion has been achieved through chemical grafting, and significant