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CHEMICAL MODIFICATION OF NATURAL POLYMERS IN CHINA

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Key Words: Chemical modification; Silk; Chinese lacquer; Gutta-percha; Cellulose; Chitin

ABSTRACT

This paper introduces the main Chinese research work on the chemical modification of natural polymers including silk, Chinese lacquer, gutta-percha, cellulose, and chitin. The following aspects of this research work are emphasized: research on the mechanism of graft copolymerization of vinyl monomer onto natural polymers, research on overcoming the defects of natural polymers to allow further application by chemical modification, and research on exploring new applications of natural polymers.

INTRODUCTION

Our ancestors were inspired by nature to develop a long-standing cultural tradition. A number of inventions including silk textile, lacquer, paper, etc. became

important contributions to world civilization. However, for a long period in our country inventions related to natural polymers were developed as an art but not as a science. Although scientific concept about natural polymers started to be accepted in this century and some research work on the modification of natural polymers was conducted, the research in this area was very weak until the 1980s. Recently, because of the development of improved techniques, the pollution by synthetic materials, and the shortage of resources, natural polymers and their derivatives as renewable, degradable materials, as well as some special materials which can meet the demands of advanced techniques, have attracted considerable attention in our country. Research on their modification has achieved remarkable success [1]. This paper will mainly introduce the following aspects of recent Chinese research work in this field: research on the graft copolymerization mechanism of vinyl monomer onto natural polymers, research on overcoming the defects of natural polymers to meet further applications by chemical modification, and research on exploring new applications of natural polymers.

SILK

Silk originated in China and spread to Europe via the "silk road." An archaeological excavation in Hubei province proved that weaving silk fabrics of fine quality was successfully established in China more than 2300 years ago. Although today silk production is only about 0.2% of the total production of world textile fibers, silk production has increased rapidly during the last few years. In 1992 China produced 659,500 tons of raw silk, which was 71.8% of the world raw silk production, and exported 20,000 tons of silk, which was 85–90% of the world silk trade [2, 3].

Silk is the only natural fiber with a length of hundreds of meters. The silk filament is made of two strands of fibroin and a gummy material (sericin) that holds the fibroins together. In most cases the sericin has to be removed to give the silk fabrics luster and a soft handle. Although the fibroin is a relatively simple protein, mainly consisting of 18 kinds of amino acid residues including glycine, sericin, and alanine as well as cysteine, tyrosine, and tryptophan, its primary structure and conformation are still uncertain. It is believed that the fibroin is a block polymer with both crystalline regions and amorphous regions. The crystalline region mainly contains antiparallel β -sheet silk. The mechanism of fiber formation was investigated by Yu and Li [4], and the conformational transition of silk fibroin in different parts of the silk gland was determined by Raman spectroscopy and LAXS (large-angle x-ray scattering). It was discovered that the β -sheet conformation of fibroin appears gradually when the stress is increased by stretching the fresh fibroin directly with an Instron. The denaturing process of silk fibroin under stress was revealed on the microcosmic level, and its relevant model was made as shown in Fig. 1.

Silk has many excellent properties such as noble gloss, soft handle, scrapping feel, good drapability, high water absorption and heat retention, and ultraviolet light screen property, so people like to wear silk clothes. However, silk also has such defects as creasing, yellowing, and unwashability that limit the consumption of silk for clothing. The demand to overcome silk defects promotes research on silk modification. There are two approaches to the modification of silk: physical modifi-

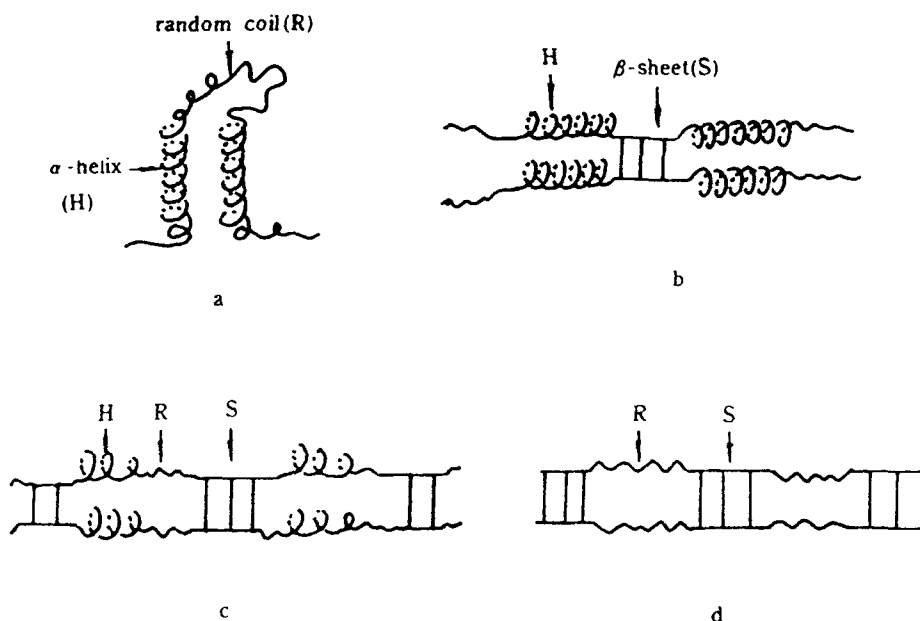


FIG. 1. Model of conformation transition of silk fibroin under stress. Drawing ratio: (a) $R = 0$, (b) $R = 4$, (c) $R = 15$, (d) degummed silk. Drawing rate: 500 mm/min.

cation and chemical modification. Blending is the most important method of physical modification widely used in textile industries; for example, a cotton or linen core wrapped with silk was developed [2]. In this paper we stress chemical modification.

It is believed that the defects of silk originate in the amorphous region of fibroin. Chemical treatment changes the structure of the amorphous region, improving crease resistance and washability as well as providing antiyellowing [5].

Graft copolymerization of silk with vinyl monomers as an important approach to the modification of silk has attracted tremendous attention [6, 7]. It is generally believed that graft copolymerization takes place on the amino acid residues in the amorphous region. Nayak et al. reported that the site of graft copolymerization is on the S atom of methionine when Ce(IV) is used as the initiator [8]. Liu and Yu reexamined these results by using a differential IR technique and showed that the main grafting reaction site is really on the SH group of cysteine rather than that of methionine with aid of the laser Raman spectroscopy. In addition, Liu and Yu confirmed the presence of Cu^{2+} in natural silk fiber by absorption spectra, and they found that graft copolymerization can be carried out without adding initiator. They suggested the real initiator was the Cu^{2+} originally present in the silk fiber. In this research, Yu et al. noticed that part of the β -sheet conformation was converted into an α -helix and random coil, and suggested that control of the graft ratio could moderate the transition of conformation. They also investigated the stereochemistry of the grafted chain of PMMA with NMR, and found that the atactic isomer of the grafted chain was lower than that of ordinary PMMA. This result was ascribed to steric hindrance during the graft copolymerization of monomers [9]. The reaction

mechanism of graft copolymerization in the presence of Cu^{2+} is not very clear, so more works needs to be done.

The graft copolymerization of silk fabrics with methyl methacrylate (MMA), methacrylamide, acrylamide, 2-hydropropyl acrylamide, etc. with potassium persulfate or Ce^{4+} as initiator was investigated by Wang, Xie, and others [10–13]. Radiation graft copolymerization with methacrylamide and MMA was investigated by the Sichuan Institute of Silk Technology [14]. Although graft copolymerization can improve such properties of silk fabrics as crease resistance, elastic recovery, anti-static, moisture absorption, and dyeability, it may cause some characteristics of silk to be lost, especially when hydrophobic monomers such as MMA are used as the grafting monomers. It will worsen the handle and hydrophilic properties, and sometimes the pearl luster. Nowadays research on graft copolymerization is concentrated on hydrophilic grafting monomers such as hydroxyethyl methacrylate, hydroxypropyl methacrylate, and glycerol methacrylate. It was reported that when polyethylene diacrylate was used as the grafting monomer, the silk fabric kept its characteristics [2].

The yellowing of silk has been partly ascribed to the photodegradation of tryptophan and tyrosine residuals, which convert to color substances on exposure to sunlight. Song et al. indicated that the yellowing effect of tryptophan was predominant over tyrosine. The latter in the crystalline region did not affect yellowing [15–17]. An ultraviolet absorber, such as 2-hydroxy, 4-methoxyl benzophenone-5-sulfonic acid (HMBS), has been used to treat silk, and the antiyellowing property is improved markedly, but the washing fastness is very poor. The adhesion of HMBS on silk has been improved by using thiourea-formaldehyde resin to form a cross-linked structure with silk [18]. Graft copolymerization is an important approach to solve the yellowing problem because the monomer may react with tryptophan and tyrosine to block them. Liu and Yu reported that three acrylic esters, 2,4-dihydroxybenzophenone, 1,2-dihydroxyanthraquinone, and 1,2,5,8-tetrahydroxyanthraquinone, which are UV-resistant compounds, and dyes with different color, were grafted on silk in the presence of ceric ion as initiator. The grafted silk showed better thermal stability and UV resistance, but the mechanical properties became worse. Later, they found that if the graft silk was obtained in the absence of initiator, the graft ratio of silk fibers and the graft coefficient of monomers were much higher than when ceric ion was used, and the mechanical properties remained the same. In addition, when MMA was used as a comonomer, the appearance of grafted silk could be improved and the color could be controlled [19, 20].

Resin finishing is another approach to improving the crease resistance and washability, as well as antiyellowing [2], because the finishing resins can isolate the silk from the atmosphere to protect it from direct radiation and can block the active residues. Kitamura and Chen systematically inspected the effect of crease resistance of resins including dihydroxymethyl urea, trihydroxymethyl melamine, and dihydroxymethyl ethylene urea and suggested the ΔT_g (the difference between the glass transition temperatures in dry and in wet) of the finished silk could be the measure of wet crease resistance. A smaller ΔT_g gives better crease resistance [21–23]. Epoxy resin, reactive polysiloxane, and water-soluble polyurethane as finishing resins have been investigated. Now epoxy resin has been widely used to finish silk fabrics, which results in better crease resistance, washability and antiyellowing properties [24–26]. China has produced machine washable silk fabrics which are treated with difunc-

tional hydrophilic epoxy resin and dyed with reactive dyes [2]. Silk also was treated with formaldehyde-bromine and a rare-earth compound. The dyeability of the modified fibroins was improved [27, 28]. A kind of antistatic silk was made by treating silk with a metal salt solution and a crosslinking agent [29].

Because silk is harmless, has no deteriorating effect on biological material, and is compatible with the human body, its use has been expanded to medicine, food, cosmetics, and other uses. Silk polypeptide (3000–6000 MW) was obtained by partial hydrolysis of a dialyzed solution of silk, and its physical and chemical properties were investigated. It has a random coil structure and a natural moisturizing factor for skin. Since it can be absorbed by human skin to bring smoothness and softness, and can restrain the formation of melanin, it can be used in cosmetics [30, 31].

Immobilization of enzymes or biologically active materials with silk fibroin has attracted much attention because it is suitable for use as a support. It was proposed that methanol treatment causes a structure transition of the silk fibroin membrane from random coil to antiparallel β -sheet, and that during this transition the intermolecular hydrogen bonds of the β -sheet molecule creates spaces that enable the enzyme to be immobilized. A sensor of glucose oxidase immobilized in a *Bombyx mori* silk fibroin membrane was made by Sho and Yu, and it showed very good response time, recovery, and thermal and storage stability [32].

The use of silk waste is important because the cost of silk has increased rapidly in recent years. A solution of silk can be cast or coated to form a membrane or film by means of a binding and crosslinking agent. Thus, coating synthetic fibers with a silk solution was proposed many years ago for use as medical and special textile materials. Generally, the silk is first dissolved in a neutral salt solution and then dialyzed with water to eliminate the salt [33]. Yang et al. reported that silk fibroin dissolved in a $\text{CaCl}_2\text{-C}_2\text{H}_5\text{OH-H}_2\text{O}$ mixture was applied to polyester fiber after dialyzing. The properties and morphological structure of such a polyester fiber coated with the regenerated fibroin film were investigated. The results showed that the coated polyester fiber had better dyeability with acid dyes, water absorption and washability, and good resilience [34–36]. Studies on sericin-fixed silk with glutaraldehyde were conducted by Liu [37] and Yang et al. [38, 39]. A sericin-Cu(II) complex was prepared and examined as a catalyst for the oxidation of 3,4-dihydrophenylalanine, and the results showed that the activity and selectivity of sericin-Cu(II) was better than that of cupric chloride [40].

CHINESE LACQUER

Raw lacquer or urushi is a viscous sap of the lacquer tree which grows in 22 provinces of China where the climate and soil present appropriate conditions for its growth. China has abundant resources of lacquer; about 4000 tons of sap is produced per year. Natural urushi has been used as a coating for 7000 years because of its unique properties. It is still widely used in daily supplies, crafts, and industrial equipment.

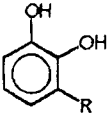




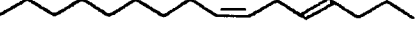






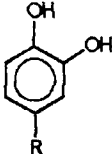


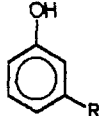



The composition and constituents of the lacquer tree sap have been investigated by Kumanotani et al. [41–43]. The composition of raw urushi depends on the species, the area of plant growth, and the season. The main constituents are urushiol

(60–82%), water (10–30%), plant gum (4–10%), *Rhus laccase* (0.15–0.30%), and water-insoluble glycoproteins (3–5%). Urushiol is a mixture of catechol with a C₁₅ or C₁₇ alkyl or alkenyl group (the catechol nucleus with a long, unsaturated side chain), and is the main film former. Its structure is shown in Table 1. An urushiol constituent, a six-membered unsaturated lactone, is an allergen. *Rhus laccase* is a multicopper oxidase which plays the role of catalyst in the oxidation of urushiol. The main constituent of plant gum is lacquer polysaccharide.

The lacquer film forms via the oxidation of urushiol catalyzed by laccase, which is followed by a coupling reaction as well as an autooxidation reaction on the long, unsaturated side chains. The autooxidation reaction of urushi is similar to the dry reaction of dry oil via the autooxidation of active methylene groups between two double bonds.

As a coating film, the air-dried film of urushi has good anticorrosive and delicate decorative properties, superdurability, water repellency, good wearability,

TABLE 1. Urushiol Constituents of the Chinese Lacquer Tree

R (C ₁₅ –C ₁₇)		%
	1	 57.5
	2	 Trace
	3	 Trace
	4	 9.9
	5	 8.4
	6	 21.2
	7	 Trace
	8	 2.1
	9	 1.4
	10	 1.2
	11	 0.6
	12	 2.5
	13	 2.5
	14	 1.1
	15	 2.3
		 2.3

and supplies good insulation. Urushi also has some deficiencies: slow curing, dark color, poor photostability, and poor alkali resistance. In addition, urushi is considered toxic since it is an allergen, although the dry film has been proven to be nontoxic. Much attention has been paid to the chemical modification of raw urushi to solve those problems [44–47].

The common method of modification is blending. In the traditional process, raw urushi is blended with tung oil or linseed oil. The refined urushi is blended with epoxy resin and other resins. However, the most important approach to modification is via the reaction of isolated urushiol with aldehyde, vinyl monomer, maleic anhydride, epichlorohydrin, isocyanate, chlorosilane, etc. to prepare urushiol phenolic resin, urushiol vinyl resin, urushiol alkyd, urushiol epoxy resin, urushiol polyurethane, and urushiol silicone resin, respectively. This results in some improvement of color, thermostability, cure rate, mechanical properties, and alkali resistance. However, this modification may cause some of the favorable characteristics of urushi to be lost [48]. Gan et al. carried out the modification of urushiol with metals; for example, urushiol reacted with aluminum chloride and copper chloride in the preparation of the corresponding urushiol–metal chelate. The cured film of such a chelate shows excellent mechanical properties, thermal stability, and chemical resistance without character loss [49, 50]. A antimony–urushiol chelate was prepared by the reaction of urushiol with antimony trichloride in alkaline medium, and the cured film of this chelate exhibits very good antflammability as well as excellent alkaline resistance and thermostability [51]. It was found that when urushiol reacted with FeCl_3 , the urushiol–Fe(III) complex was first formed, and this was followed by a redox reaction of urushiol and Fe(III) within the complex molecule that resulted in the formation of quinone and Fe(II). Consequently, a black urushiol quinone–ferrous chelate film was obtained [52].

On the other hand, some Chinese chemists are interested in the use of urushi in noncoating areas. Since the metal enzyme of *Rhus laccase* can selectively catalyze the oxidation reactions of phenol, aniline, and their derivatives, the immobilization of *Rhus laccase* has attracted much attention. It was reported that *Rhus laccase* was immobilized with ZrCl_4 as carrier. Compared with the native *Rhus laccase*, the immobilized laccase had better activity recovery and stability [53–55]. In addition, Huang et al. synthesized a series of saturated urushiol crown ethers, some of which were crosslinked. The saturated urushiol crown ethers have good lipophilicity and show fair potential for such applications as a potassium ion selective electrode, a potassium sensitive field electronic transistor, and a piezoelectric crystal detector used for monitoring benzene, toluene, xylene, and nitric oxides in ambient air in working environments. Because of their better thermal stability and higher decomposition temperature, saturated urushiol crown ether polymers have also been used as the stationary phase in chromatography and ion selective membranes [56–58].

CHINESE GUTTA-PERCHA

Chinese gutta-percha is a natural *trans*-polyisoprene which is contained in the leaves, bark, and seeds of the *Eucommia ulmoides* tree. This tree can be planted in a broad area from the south to the north of China. Gutta-percha was only used as a plastic for a long time because of its crystallization. Many polymer scientists have

spent a lot of time and energy trying to convert it into a high elastomer, but they have not achieved satisfactory results. Nevertheless, gutta-percha can be converted into its elastic isomer, *cis*-polyisoprene, by isomerization. However, because of its low mechanical properties and high expansion it has little practical value. In 1984 Yan discovered that through quantitatively controlling the degree of crosslinking the vulcanization process of gutta-percha can be divided into three stages in which three kinds of materials, a thermoplastic (A), a thermoelastomer (B), and a high elastomer (C) are formed, respectively. The crux of obtaining high elasticity (C) gutta-percha lies in control of the critical degree of crosslinking [1, 59, 60]. It is believed that at the critical degree of crosslinking the crystallization of gutta-percha is suppressed, so that the vulcanized gutta-percha (C) behaves as an elastomer instead of as a plastic. Lightly crosslinked gutta-percha (B) also can convert into a high elastomer at high temperature (Table 2). Yan et al. indicated that because of the excellent processability and compatibility of gutta-percha, it can be mixed not only with plastics but also with rubbers. The blends can be vulcanized or unvulcanized. Therefore, materials with various properties can be prepared (Table 3) [61–63].

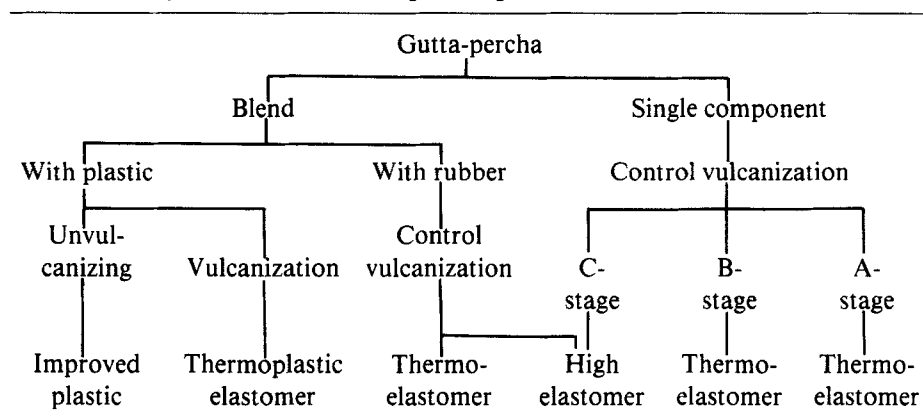
Based on this discovery, a series of new products has been developed, such as a medical orthopedic splint made of A-stage gutta-percha, shape memory materials made of B-stage gutta-percha, tire treads made of a blend of *cis*-PB/ gutta-percha, and the sealing film materials for radar made of improved gutta-percha.

Table 4 shows a series of mechanical properties of high elastic gutta-percha together with those of natural rubber (NR). Even though the tensile strength and elongation at break of elastic gutta-percha are lower than those of NR, its hardness and stress at 300% elongation are higher than those of NR. Its dynamic tensile fatigue is better than NR and much better than *cis*-PB [60–62].

TABLE 2. Characteristics of Vulcanized Gutta-Percha at Three Stages

Stage	Degree of cross-linking	DSC analysis	Tensile deformation		Characteristics	
			At room temperature	At 70°C	Microscopy	Macroscopy
A-stage	Zero	Multiple melting peaks	Yield deformation	Melting flow	Linear crystal polymer	Thermoplastic
B-stage	Low	High-melting peak disappears	Yield deformation	Elastic deformation	Partial crystal network	Thermoelastomer
C-stage	Critical	All peaks disappear	Elastic deformation	Elastic deformation	Amorphous network	High elastomer

TABLE 3. Systematic Material Engineering of Gutta-Percha



CELLULOSE

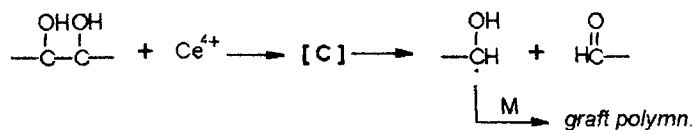
The application of cellulose has a long history in China as the raw material of paper and textiles. Cellulose esters such as cellulose nitrate and cellulose acetate as explosives, lacquers, plastics, and film materials, and regenerated cellulose as a fiber are produced on a large scale in China. Recently the production and application of such cellulose ethers as carboxymethyl cellulose (CMC) and methyl cellulose (MC) have also rapidly developed. However, research work on the chemical modification of cellulose and its derivatives is relatively weak in China. Particular attention has recently been paid to grafting modifications, liquid crystals, and applications.

As a main approach to modifying natural polymers, graft polymerization of vinyl monomer onto cellulose is a key research subject in China [64]. The reaction mechanism of graft copolymerization of vinyl monomer and acrylate on cellulose

TABLE 4. Mechanical Properties of High Elastic Gutta-Percha at C-Stage

	Gutta-percha	NR
Tensile strength, MPa	20	> 22
Breaking elongation, %	500	> 600
Permanent elongation, %	15	20
Stress at 300% elongation MPa	12	< 10
Hardness (Shore A)	> 120 min	~ 90 min (< 20 min ^a)
Dynamic tensile fatigue 170 times/min at 200% elongation brittle point	- 54°C	- 60°C

^aThe value of *cis*-PB.

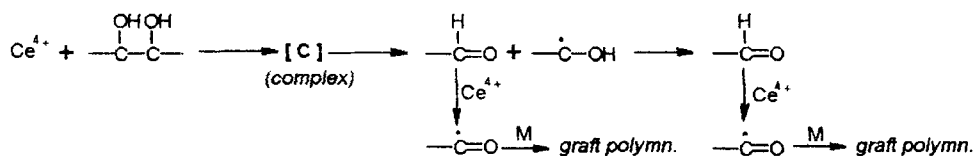


SCHEME 1.

has been investigated with 1,2-diols as the model compound by many researchers. With Ce^{4+} as the initiator for graft copolymerization, a reaction mechanism was proposed as shown in Scheme 1 and the presence of complex [C] was proved by various researchers.

But Feng et al. noticed that simple aldehyde could form an effective initiation system with ceric ion for vinyl monomer polymerization and showed high activity. So they doubted the mechanism of Scheme 1 was correct, i.e., where was the real site of grafting and how could the high activity $-\text{CHO}$ remain there and not react with the ceric salt [65]. Doba and Ranby studied the oxidation of model compounds with Mn(III), Ce(IV), and V(V) ions, and the acyl radical was detected with the ESR spin trapping technique [66]. Based on these results, Feng et al. further examined this mechanism by means of kinetic measurement and polymer chain structure studies, and a more detailed mechanism was proposed. They demonstrated that the initiation reaction could be divided into two steps. In the first step, the 1,2-diol is oxidized to dial, and in the second step aldehyde is further oxidized to generate the initial radical. The proposed process is shown in Scheme 2 [67, 68].

In order to modify the cellulose of various plants, the graft copolymerization of MMA, EA, AN, etc. onto flax and allied fibers with potassium persulfate-thiourea (KPS-TU), KPS- NaHSO_3 redox initiators, and Ce^{4+} as initiator were examined by Wu and others [69–73]. The results showed that the grafted products with EA and AN had higher flexibility, higher breaking elongation, and lower Young's modules than grafted products with MMA. This was ascribed to the rather rigid MMA grafting chain and the flexible EA chain. The chemical and physical properties of microcrystalline cellulose, including cellulose gel, were investigated by Chen [74, 75]. The graft polymerization of acrylamide onto microcrystalline cellulose with permanganate as the initiator was studied by Pan and Zhu [76]. A superior water absorbing resin was made by grafting CMC with acrylic acid, which has a high capability for absorbing water (1200–2000 g/g) and exhibited good stability [77]. Lu et al. investigated the process of ultrasonic copolymerization of hydroxyethylcellulose (HEC) with poly(ethylene oxide) (PEO) in aqueous solution, the effect of various factors on the grafting copolymerization, and the properties of the grafting polymer. The results showed that the grafting copolymer was an effective



SCHEME 2.

compatibilizer for the incompatible HEC/PEO system. The properties of HEC/PEO in the presence of HEC-*block*-PEO was much better than that without HEC-*block*-PEO. This new grafting copolymer was expected to be an effective oil field additive for exploitation and exploration of petroleum oil and natural gas fields [78].

Many cellulose derivatives can form both lyotropic and thermotropic liquid crystals because of the semirigid chains, and they show promise for applications in various areas. The mechanism of the cholesteric-nematic phase transition, rheological and mechanical properties, and the formation and processing of liquid crystalline cellulose derivatives attract considerable attention [79]. Research on liquid crystal derivatives including methyl-cyanoethyl cellulose, ethyl-cyanoethyl cellulose, cyanoethylcellulose, and ethyl-acetyl cellulose in different solvents were conducted by Huang et al. [80–88]. Solutions of ethyl-cyanoethylcellulose liquid crystals in monomers such as acrylic acid, acrylate, and methacrylate were examined. This system can be cured via the polymerization of monomers to obtain composite materials with cholesteric order [89–92]. In addition, Huang, Chen, Qian, et al. investigated the texture of various mesophases of cellulose derivatives. The band texture formation mechanism of a cholesteric solution of ethyl cellulose in dichloroacetic acid was studied by using a parallel plates shearing apparatus [87, 93–96]. Huang et al. also investigated the molecular interaction of methyl-cyanoethylcellulose/dichloroacetic acid and hydrogen bonds during the transition between the isotropic and anisotropic phase by FT-IR [97]. The results of such research revealed that the cellulose derivatives of lyotropic liquid crystals show a multitexture behavior, intermolecular reactions play an important role in the formation of the liquid crystal phase, the mesophase is heterogeneous, and the heating rate strongly influences the texture. However, because this research is limited to the lyotropic area, further work is needed for the practical use of cellulose derivatives of liquid crystals.

The poor solubility of cellulose stands in the way of its processing and application. Investigation of the solvent system of cellulose is another key research point [1, 98]. The CH₂O/DMSO system was used to prepare fiber, hollow fiber, and artificial kidneys, and the CH₂O/DMSO and LiCl/DMAC systems were used to prepare fiber blends by Yang et al. [99–101]. A double swelling agents composed of DMSO and NaOH was used to modify flax [102]. A number of solutions of cellulose derivatives with additives for use in casting reverse osmosis membranes were investigated by Yang et al. [103–106]. The formation, structure, and properties of hollow fiber reverse osmotic membranes made from a cyanoethylcellulose were studied by Cen and Chen [107]. The preparation and properties of ethyl cellulose membranes for the separation of O₂ and N₂ were studied by Liu and Xu [108].

As a renewable resource and a degradable material, the application and modification of cellulose has attracted particular attention in China. Studies on cellulose as a substitute for plastic films are in progress. It was reported that nitrocellulose is sensitive to 193 and 157 nm excimer lasers and shows a self-developing behavior. Based on this report, nitrocellulose was investigated as self-developing photoresist with 254 nm UV light. It was found that dinitrophenyl acetate is a good sensitizer and can enhance the sensitivity of nitrocellulose to 254 nm UV light [109].

Carboxymethyl hydroxylpropyl cellulose crosslinked with organic titanium has been prepared and its properties investigated by Xu and Wang. The results indicated that the crosslinked product exhibited good thermostability and that its hydrogel retained a high viscosity at high temperature. It was proved that the active

crosslinking sites were not only on the carboxyl groups but also on the hydroxylpropyl groups [110].

CHITIN AND CHITOSAN

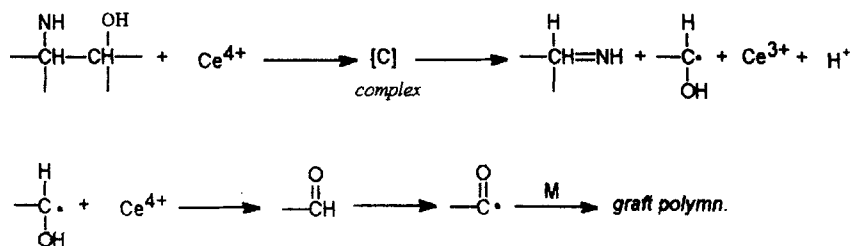
Chitin is the most abundant organic skeletal component of invertebrate and is easily obtained from crab and shrimp shell. It is abundant in China. Chitosan is the most important derivative of chitin and is prepared by deacetylation of chitin. Chitosan has been shown to be a reactive polysaccharide, a functional polymer applicable to various fields. It can be used as a wound-healing accelerator, a blood anticoagulant, a carrier for the controlled release of drugs, for functional membranes, etc. It seems to be able to fulfill a number of demands in our technological world. However, its application was not paid much attention in China until the 1980s, in spite of the fact that its application was first reported in the 1950s and the quaternary ammonium of chitosan was used as a mordant in dyeing movie films in the 1970s.

Grafting copolymer chains onto chitosan can enhance or introduce desired properties. Many papers and patents have been published. The first paper about using Ce(IV) salt as an initiator was by Yang et al. [111]. A study on the mechanism of graft copolymerization with ceric salt was conducted by Feng et al. [112]. They pointed out when Ce^{4+} reacts with the adjacent hydroxyl-amine structure in chitosan, a chelate complex is first formed and then disproportionates to a radical to initiate polymerization. There are two ways for such an initiation to take place, depending upon the reaction temperature. At reaction temperatures higher than $40^{\circ}C$ a $-CHO$ group and a $-C=NH$ group are introduced, and the aldehyde group reacts with Ce^{4+} ions to form an acyl radical which initiates a graft polymer chain in this saccharide unit. At temperatures higher than $90^{\circ}C$ the $-C=NH$ group hydrolyzes to form an amine and an aldehyde group which also reacts with Ce^{4+} ions. In this case there would be two aldehyde groups, i.e., two initiation sites in one adjacent hydroxyl-amine structure, which means the initiation radical in the chitosan/ Ce^{4+} system is similar to that of the cellulose/ Ce^{4+} system, but the former usually has a lower grafting reactivity than the latter due to higher stability of the complex. The proposed mechanism is shown in Scheme 3.

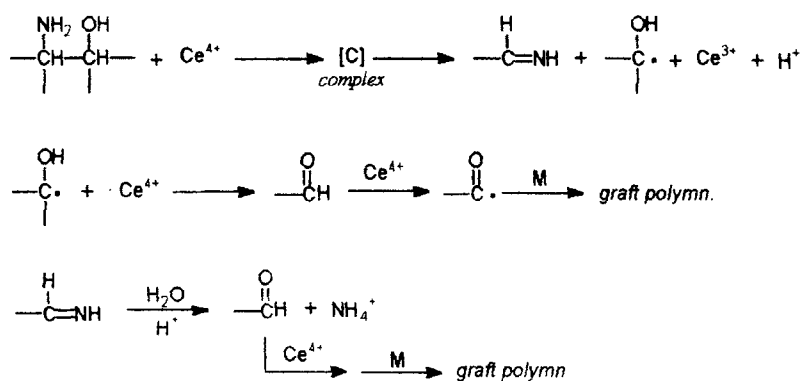
Wang and Qiu investigated the mechanism of graft polymerization of MMA onto chitosan with $K_2S_2O_8$ as the initiator. By comparing the reaction results of different degrees of deacetylated chitosan, it was demonstrated that the amino group of chitosan is involved in the initiation process. The graft ratio of chitosan depends upon the degree of deacetylation, and the optimum deacetylation degree is 38–46%. The mechanism of graft copolymerization is shown in Scheme 4 [113].

Considering the excellent permeability and antithrombogenic properties of acetylchitin with a high degree of acetylation, Yan investigated some new approaches to the acetylation of chitin to prepare acetylchitin with a high degree of acetylation which has good solubility in formic acid [114]. Research on the membranes of chitosan and their derivatives has attracted much attention. An alloy membrane of chitosan with polyvinyl alcohol (PVA) and a composite membrane of chitosan with polyacrylonitrile were prepared and used for the pervaporation separation of an alcohol/water mixture by Li et al. For example, a kind of chitosan composite

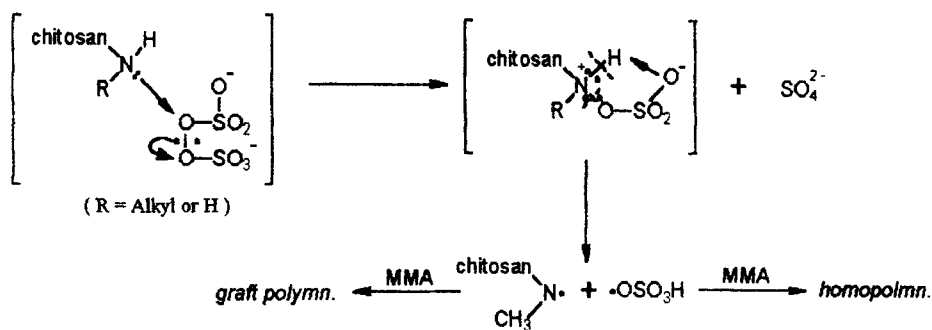
At 40°C:



At 90°C:



SCHEME 3.



SCHEME 4.

membrane was prepared by pouring chitosan-HOAc solution onto a polyacrylonitrile microporous supporting membrane which was used for pervaporation for an azeotropic isopropanol/water mixture. It showed an extremely high flux and separation factor in comparison with a crosslinked chitosan membrane. Li et al. also examined the effect of such factors as temperature, feed concentration, and composition of alloy membranes on separation, and they indicated that the pervaporation behaviors of the membranes were influenced by the molecular and aggregation state structure of the membranes and that the main factor affecting separation was the free volume of the membranes [115–119]. A study on composite chitosan with various degrees of deacetylation on a porous polyacrylonitrile membrane for pervaporation separation of alcohol-water mixtures was carried out by Zhang and Shen. The results revealed that the separation factor depends on the degree of deacetylation [120]. Chitosan membranes filled with Si_3N_4 , SiO_2 and TiH_4 powder have been investigated. The results showed that the filled chitosan membranes had lower swelling, higher strength, and higher separation factors than a normal chitosan membrane [121–123]. Chitosan coated on the inner surface of a polyacrylonitrile ultrafiltration hollow fiber membrane was crosslinked with H_2SO_4 to produce a composite membrane used to separate a water-ethanol mixture by pervaporation. A separation factor of 5000 and a permeation rate of $616 \text{ g/cm}^2 \times \text{h}$ were achieved when using a feed of 56 wt% ethanol at 75°C [124]. In addition, a composite membrane of chitosan with polyvinyl alcohol/polysulfone (PVA-CS/PSF) was crosslinked with polyacid and used as an alcohol dehydration membrane. It had high selectivity and promising permeability, especially in separating ethanol-water near the azeotropic region. It had better mechanical strength, stability, and water resistance compared to a PVA composite membrane [125].

Chitosan acid complex membranes and several chitosan-polymer complex membranes were prepared, and the gas permeabilities of these membranes were examined by Bai et al. [126]. It was found that a chitosan-acetic complex membrane showed high permeation selectivity for oxygen and carbon dioxide. Synthetic water-soluble polymers could modify the permeation of this membrane and increase the $\alpha\text{CO}_2/\text{O}_2$ (except for polyacrylamide membranes). The separation factor $\alpha\text{CO}_2/\text{O}_2$ of these membranes was much smaller than 1, indicating possible applications for the preservation of fruits and vegetables. The permeation behavior of these membranes was markedly influenced by the addition of metal ions which also decreased the $\alpha\text{CO}_2/\text{O}_2$. Ni(II) was the most effective metal ion. The mechanical strengths of these membranes were enhanced by the added metal ions. Composite membranes of chitosan and polysulfone amide with or without cobalt salts were prepared and investigated as oxygen enrichment membranes. The results revealed that damp membranes could enrich oxygen from air while dry membranes could not. The cobalt salt increased the separation factor [127, 128]. It was reported that carboxymethyl chitosan was successfully used as an agent to keep the fresh properties of fruits and vegetables [129]. A series of membranes of various *N*-acylchitosans was prepared, and the permeability of vitamin B_{12} and dissolved oxygen, the tensile strength, and the blood compatibility were examined. The results indicated that *N*-hexanoylchitosan possesses the best blood compatibility. When polyethylene glycol was used as an additive, the permeability, tensile strength, and blood compatibility were improved [130]. A chitosan-polyurethane composite membrane was prepared and used as a biomedical material. The interface adherence was improved by

the reaction of the free isocyanate groups on the polyurethane prepolymer with chitosan [131].

It is well known that 5-fluorouracil (5-FU) has remarkable antitumor activity, but it has strong side effects. In view of its good biological properties, its affinity to tumor cells, and the reduced rate of metabolism of polymer-bound drugs, it is advantageous to incorporate 5-FU into chitosan to decrease the side effects. Yang and Zhou prepared a series of chitosan-bound 5-FU and examined their properties. The results revealed that some of them could slowly release 5-FU or its derivatives in both alkali and neutral buffers and were more effective on tumor cells than were other drugs. In addition, chitosan-bound 5-FU became more effective with a decrease of molecular weight of the chitosan used [132]. Studies on the reaction of chitosan with carrageen in solution and in aqueous solution to form water-insoluble polyelectrolyte were reported by Lin, Jiang, and Zhang. The resulting polyelectrolytes suppressed the coagulation of blood [133].

Wang et al. immobilized glucose oxidase (GOD) and cellulase on a complex of chitosan and sodium carboxymethyl cellulose (SCC) by the entrapment method. The immobilized enzymes show high activity, good storage life, and can be reused many times [134]. Thermolysin was immobilized on chitosan with glutaraldehyde as crosslinking agent by Tao et al. The properties of thermolysin were improved after immobilization. The active recovery of immobilized thermolysin reached 38% when casein was used as the substrate [135].

Sodium salts of carboxymethyl chitin and chitosan acetate were examined as protective polymers for the formation of precious metal colloids. It was found that in the presence of these salts the stable, narrowly dispersed metallic colloids of palladium, rhodium, ruthenium, platinum, silver, and gold of fine particle size were formed in a methanol-water system. The metallic colloids of palladium, rhodium, and platinum were tested as catalysts for the partial hydrogenation of 1,3-cyclooctadiene and showed quite good activity as well as selectivity [136]. A chelating resin was obtained by the reaction of chitosan with chloromethylthirane. The crosslinked chitosan obtained was used to chelate mobile metals. The adsorption capability increased with an increase of the S content [137].

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It is our great pleasure to contribute this paper to this issue of *Journal of Macromolecular Science* honoring Prof. Rånby on his 75th birthday. Prof. Rånby is a respected and sincere friend of Chinese scientists. We are grateful to Prof. Vogl and Prof. Albertsson for organizing this special issue and providing this opportunity for us to express our thanks for his great contribution to polymer science and to the friendship between China and Sweden.

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